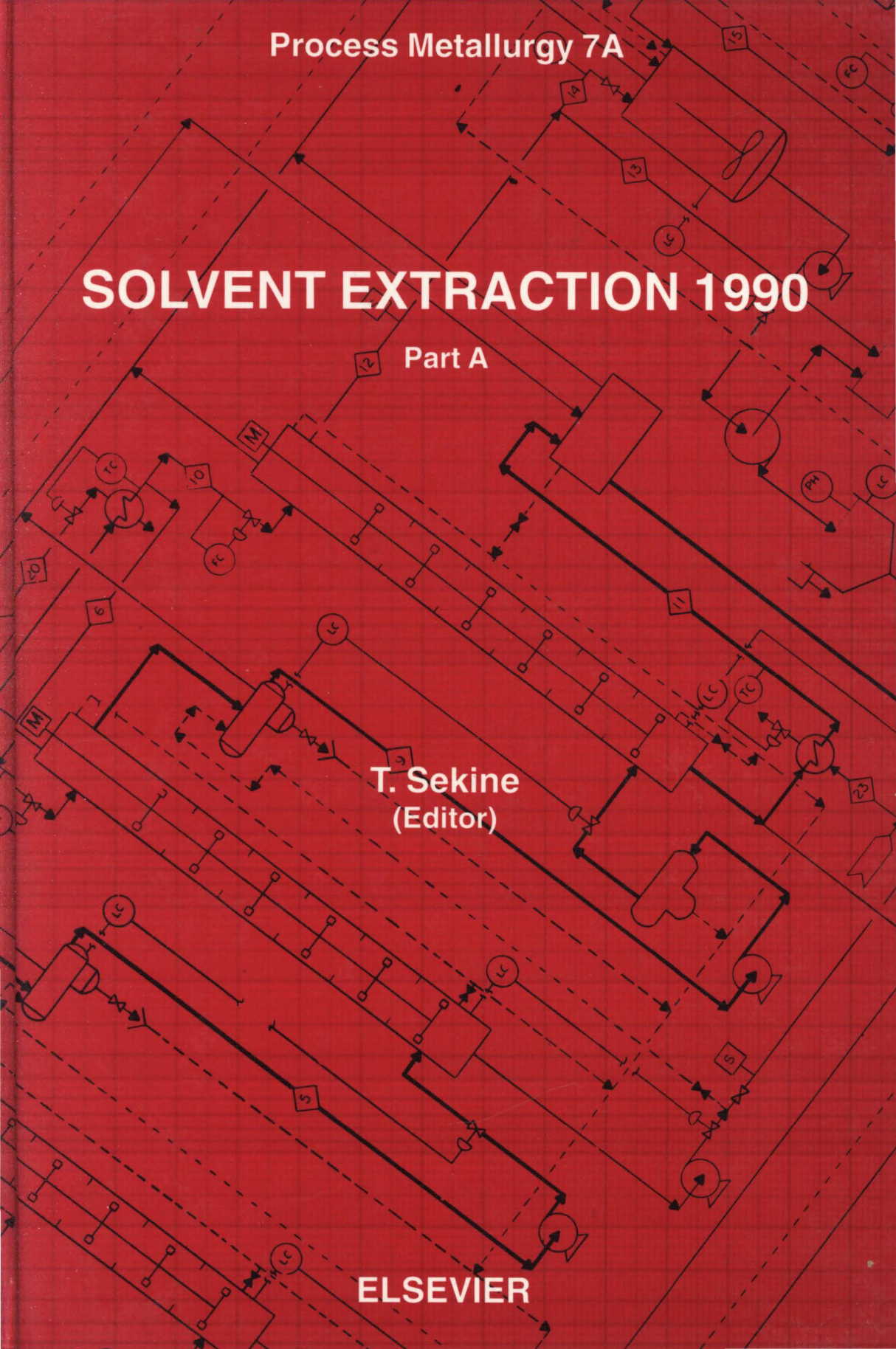
Process Metallurgy 7A

SOLVENT EXTRACTION 1990

Part A



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SOLVENT EXTRACTION 1990

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Process Metallurgy 7A

SOLVENT EXTRACTION 1990

PROCEEDINGS OF THE INTERNATIONAL SOLVENT EXTRACTION CONFERENCE (ISEC '90)

PART A

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PREFACE

Solvent extraction is employed very widely in both fundamental research and technology because of the remarkable features of this simple but very effective technique for the separation of different materials.

The meeting "International Solvent Extraction Conference 1990" was held in Kyoto, in Japan, between 18th and 21st of July 1990 and it was a source of great pleasure that many outstanding scientists and engineers were interested in the topics and came from around the world to attend the meeting, to present papers containing up to date research and to partake in intensive and fruitful discussion.

The papers collected in these volumes were given not only in the plenary and keynote lectures but also in the oral and poster sessions. The manuscripts were submitted by the last day of the conference and each was reviewed by two independent referees. Several papers were recommended for publication as they were but some were accepted in revised form. The result is that we now believe that these volumes contain an excellent essence of the present state of solvent extraction chemistry and technology.

Furthermore, because information on solvent extraction is very often scattered in various journals and proceedings owing to the great variety of the work that is carried out, thus making the following of developments rather difficult, we believe that the collection of papers in these volumes covering the entire field of solvent extraction in one book will be very valuable.

We are very grateful to all the authors and to those who have worked very hard for the conference and towards the appearance of these proceedings volumes. The conference and the publication of the proceedings were supported financially by many societies and companies, all of whom understand and recognize the importance of the conference. We are very grateful to these sponsors.

The Organizing Committee of ISEC'90

Honorable chairman: Professor Taichi SATO
Co-chairman : Professor Sanji NISHIMURA
: Professor Tatsuya SEKINE

INTERNATIONAL SOLVENT EXTRACTION CONFERENCE 1990 IN KYOTO, JAPAN

International meetings on solvent extraction have been held several times. According to the literature, three were held before the early 1960s, one in Gatlinburg, Tennessee, in 1962, and one, referred to in Howell and Windscale, in 1965. However, these were somewhat different from the conferences we now know as International Solvent Extraction Conferences (ISEC) because the papers were mainly invited and the attention was focused on the nuclear energy industry. Thus the conference held in 1966 (August 27-September 2) in Göteborg which was organized by the Swedish group should be considered the first ISEC, even though it was named an International Conference on Solvent Extraction Chemistry". Since then eight ISECs have been held: in 1968 (September 16-18) in Jerusalem, in 1971 (August 19-23) in The Hague, in 1974 (September 8-14) in Lyon, in 1977 (September 9-16) in Toronto, in 1980 (September 6-12) in Liége, in 1983 (August 26-September 2) in Denver, in 1986 (September 11-16) in München, and in 1988 (June 27-July 2) in Moscow. Therefore, the meeting in Kyoto is the tenth International Solvent Extraction Conference. In the first two of these conferences the main attention focused on the chemistry of solvent extraction but since then the application in technology has become the most important subject. At the Kyoto conference, more than two thirds of the papers were concerned with the technical uses.

The decision to hold ISEC'90 in Japan was taken at the ISEC committee meeting in September 1986 in München. The organizing committee for this conference was formed in December 1986 by the members of Japanese Association of Solvent Extraction which was the representative research group of this field in Japan. The first circular was mailed towards the end of November 1988 to 2200 addresses which were collected from the lists of participants of the last five ISECs and other sources. Up to the end of June 1989 the ISEC'90 secretariat had received 742 preliminary applications. By the end of January 1990 it had also received 637 half-page abstracts from authors in 37 countries. The Science Committee was selected in April 1989 from specialists which covered the whole area of solvent extraction: "Fundamentals (physical chemistry) of solvent extraction (Area 1)", "Extractants and diluents (Area 2)", "Analytical chemistry and environmental science (Area 3)", "Nuclear fuel cycles (Area 4)", "Kinetics and interfacial phenomena (Area 5)", "Metal extraction (precious and rare metals) (Area 6)", "Hydrometallurgy (Area 7)", "Simulation, modelling and control (Area 8)", "Equipment and equipment design (Area 9)", "Liquid membranes (Area 10)", "Supercritical and new extraction systems (Area 11)", "Special applications; petrochemicals, biotechnology (Area 12)". The Science Committee started the preparation of the ISEC'90 program with the received abstracts in November 1989. The abstracts were reviewed by the Committee and after some were withdrawn and a few were

rejected, mainly because the subjects treated fell outside the field of solvent extraction, 599 papers were accepted and the abstracts printed. The conference program, containing four plenary lectures, twelve keynote lectures and 96 oral and 487 poster presentations was prepared. The program and the second circular were mailed to the authors in the middle of February 1990.

The conference was held at Kyoto Shigaku Kaikan which is a clubhouse of the Union of Private Schools. It is located in front of a gate of the previous Royal Palace, situated in the center of this historical and yet modern Japanese city. Shigaku Kaikan has four conference halls and several small meeting rooms as well as a hotel section on the upper floors. The whole building was used for the ISEC'90 during the conference and the registration office of ISEC'90 was opened here in the afternoon of July 16th.

On the morning of July 17th, many participants of ISEC'90 enjoyed the procession of 32 colorful floats of the "Gion Festival" which is one of the three biggest festivals in Japan.

The number of participants who registered in the ISEC'90 office numbered 431 representing 32 countries: Australia (6), Austria (5), Belgium (4), Canada (5), China Taiwan (6), Czechoslovakia (1), Egypt (1), Finland (2), France (24), FRG (21), GDR (1), Hungary (2), India (4), Iran (2), Iraq (1), Israel (7), Japan (210), Korea (8), Norway (1), Poland (1), Portugal (1), P.R. China (16), Singapore (1), South Africa (6), Spain (6), Sweden (5), Switzerland (3), The Netherlands (1), UK (21), USA (33), USSR (23), and Yugoslavia (3); there were also 38 student members, and some 50 accompanied members. Furthermore, 235 research scientists were invited by the Organizing Committee from the societies and companies which sponsored the ISEC'90.

The welcoming reception took place on the evening of July 17th in So-Un Hall of Shigaku Kaikan. It was a buffet-style party to which all the participants were invited. Some five hundred participants including the accompanied members, attended.

The scientific sessions started with the opening ceremony at 8.30 on July 18th in So-Un Hall. Professor T. Sekine, the co-chairman, officially opened ISEC'90. Then Professor Yu.A.Zolotov, who was the chairman of the ISEC'88 in Moscow, made a congratulatory speech and Mr. G. Ritcey, the General Secretary of the ISEC Committee, awarded the Hanson Medal, instituted in memory of the late Professor Carl Hanson, who was the first General Secretary of ISEC Committee, to Dr. P. Danesi.

Each morning a plenary lecture was delivered in So-Un Hall, followed by three parallel keynote lectures in the three conference halls, Fuji Hall, Aso Hall, and Daisetsu Hall. The total number of papers to be presented in the oral sessions was 96: on July 18th ten papers were read in each of the sessions of Areas 1, 6 and 10; on July 19th again ten papers in each of the sessions covering Areas 4, 5 and 12; while 6 papers were read on both July 20th in each of the sessions of Areas 2, 7 and 8, and on July 21 in each of the sessions of Areas 3, 9 and 11. Four papers were withdrawn because the authors were unable to attend.

The number of papers presented in the poster sessions was 264: 97 on July 18th when the sessions covering Areas 4, 5, 9, 11 and 12 were held, 108 on July 19th when the sessions dealt with Areas 1, 3, 6 and 10, and 56 on July 20th when Areas 2, 7 and 8 were covered.

The ISEC'90 banquet was held on the evening of July 20th in the banquet hall of Kyoto International Hotel. After the speeches and dinner, 290 guests enjoyed age-old traditional folklore and dances of the Kyoto district, as well as several melodies from the countries of origin of the participants which were performed by a students' brass band.

The closing ceremony was held on July 21st in So-Un Hall at 13.00, when Professor S. Nishimura, the co-chairman declared ISEC'90 closed. This was followed by a congratulatory speech for ISEC'90 by Mr. G. Ritcey, the General Secretary of the ISEC Committee, while a welcoming address to the next ISEC'93 in York, UK, was delivered by Professor M. Cox. All the official business of ISEC'90 had been brought to a successful close by 13.30.

All those who presented papers were requested to submit their manuscripts for the ISEC'90 Proceedings by the last day of the conference. However, the final number of manuscripts received was 311 because some authors chose not to publish their paper in the Proceedings. The manuscripts were reviewed by the Science Committee after which some authors were asked to revise the text, while a few manuscripts were withdrawn or rejected. All of the editorial work for the Proceedings had been completed at the end of March 1991.

April 1991

Professor Tatsuya SEKINE
Editor of ISEC'90 Proceedings

Dr. Satoshi KUSAKABE
Assistant Editor

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ORGANIZED BY

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Japanese Association of Solvent Extraction

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PLENARY LECTURES

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SOLVENT EXTRACTION AND MEMBRANE PROCESSES IN THE TREATMENT OF METALLIFEROUS EFFLUENTS AND WASTES

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INTRODUCTION

In recent years interest in environmental matters has grown rapidly and it nowadays even occupies an important place on political agendas. In the field of minerals and metals, concern with the environment arises at every stage as shown by the "cradle to the grave" type diagram given in fig. 1 wherein various process effluents, wastes and/or off-gases can arise at all stages of the material flow cycle. It is clearly not only a matter for good housekeeping that such wastes and residues should be treated but also in order to minimise as much as possible the environmental impact of metal and minerals extraction and processing. The secondary processing industry is seen to operate alongside the primary industry. In secondary processing the feed material is scrap which is usually treated pyrometallurgically.

The growing use of hydrometallurgy for primary ore processing and metal extraction together with a large and still growing metal finishing industry has led to a wide variety of effluent streams and waste materials that need treatment prior to safe and legal disposal. Originally the global approach to the treatment of metalliferous effluents was precipitation usually by lime addition and subsequent dumping of the sludges so produced in landfill sites. Even where this practice is still permitted it is fast ceasing to be a cheap cost option and there can be little doubt that such practises will have to cease in the near future.

With the development of hydrometallurgy came the development of modern separation science and technology. Although some separation processes are by no means new, new operating techniques, equipment etc have been developed thus providing a high degree of sophistication in today's applications. It was only natural therefore that opportunities to apply such separation processes to the treatment of secondary materials and wastes should be sought in order to provide improved waste treatment processes to meet increasingly strict environmental standards and to achieve cost offsets in effluent treatment by recovery and recycling of valuable components where before they would be lost via direct effluent discharge or through the practise of liming and dumping. Such applications also offered opportunities to develop new markets for reagents and

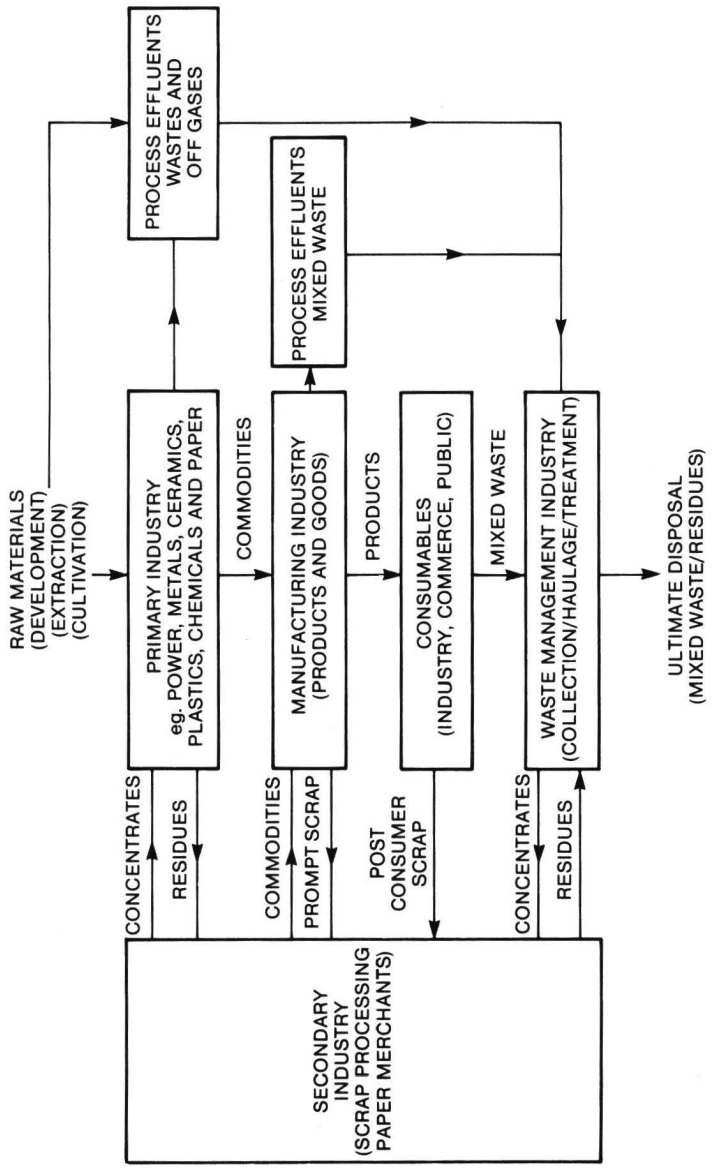


Fig. 1. Material Flow

equipment in this increasingly important metalliferous effluent and waste treatment sector.

Of the processes available to separation science and technology in hydrometallurgy, solvent extraction has been a star performer in the past three decades (although membrane processes are now being hailed as the technology of the future). In 1979 the role of solvent extraction in scrap and waste processing was reviewed (Flett, 1979). Two further authoritative accounts of the application of solvent extraction in the processing of liquid effluents, (Andersson and Reinhardt 1983), and solid wastes, (Flett 1983) appeared in the Handbook of Solvent Extraction. In 1979 it seemed as though solvent extraction would play a very important role in scrap and waste processing. However by the time the Handbook of Solvent Extraction was published in 1983 it was noted that for solid scrap and waste, few commercial processes were in operation and that solvent extraction tended to be used as a sophisticated separation process for production of fairly high purity metals commanding premium prices. For low-value materials it was regarded as a capital intensive process thus requiring a certain level of arisings to ensure profitability and certainty of supply to ensure satisfactory returns on investment. Similarly, on the liquid effluent side, while a large number of processes involving solvent extraction for the recovery of metals from liquid effluents had been proposed, very few had been carried through to commercial operation. This may not be too surprising as application of solvent extraction to the treatment of metalliferous effluents and wastes requires rather different properties from, and constraints on, the process compared with its application in primary extractive metallurgy. Metal combinations in scrap and wastes are different from those occurring in ore bodies and therefore may call for different selectivities from reagents. Demands on recovery levels from effluents will be greater than for leach liquors when production of a final effluent meeting discharge limits may be required rather than recycling raffinate within a process flowsheet. Furthermore replacement of unacceptable levels of metal concentration in effluents by similar levels of organic contamination is equally undesirable. Finally solvent extraction is not the only tool available for waste and effluent treatment and must compete with other processes such as ion exchange, membrane processes, direct electrolytic recovery etc. While a qualitative comparison of these processes can be made for effluent treatment as given in table 1, strict selection criteria for specific cases do not exist and choice of process can only be made on a case by case basis.

As relatively little has changed in the application of solvent extraction to the treatment of solid scrap and waste since the early 1980's, although an area

TABLE 1

Methods of Effluent Treatment Compared

Methods	Quality of treated Effluent	Cost of Effluent Treatment (a)	Selectivity for Individual Metals	Feasibility of Metals Recovery	Cost of Metals Recovery (b)	Other Factrors
Precipitation e.g. as hydroxide	Very good	low/moderate (depends on solid liquid separation)	None	Poor	High	Additional treatment to destroy complexing anions
Ion exchange	Very good	High	High or moderate (Depends on pH etc)	Good	Moderate	Resin may be affected by oxidising agents
Electrolysis	Usually suitable for closed loop operation only	High	High (with control of potential)		Low (included in a)	
Reverse osmosis	Low-high	Depends on desired effluent quality	None	Good for in-plant solution recycle	Low (included in a)	Restriction on pH and Eh of effluents
Evaporation	No effluent	High	None	"	"	
Liquid-Liquid Extraction	Low-high (Organic as well as residual metals in raffinate)	Moderate to high (depends on solvent loss)	High or moderate (depends on pH and extractant)	Good	Low for in-plant recycle otherwise moderate	Truly continuous countercurrent operation

to watch is re-processing of spent catalysts, it is more appropriate to concentrate on liquid effluents, of which the most important must surely arise from metal finishing operations such as plating, pickling, anodising and etching of printed circuit boards. Here waste liquors arise from the spent plating and pickling baths and from dragouts and rinse liquors from cleaning the work pieces themselves. They can contain a whole variety of metal ions e.g. Cu, Ni, Zn, Cd, Fe, Ag, Cr (III) and (VI), precious metals and acids i.e. HCl, H_2SO_4 and HNO_3 and cyanide. The minimisation of waste and the attainment of ever more stringent discharge limits for waste waters presents a great challenge to separation science and technology. The objective must surely be not only to minimise on-cost of effluent treatment by reducing raw materials costs through recycle of feed components (including water!) but to make, if possible, a virtue out of a necessity by actually improving overall process economics by effective use of today's technology.

2 GENERAL CONSIDERATION

The potential for cost saving through effluent treatment and recycling can be seen from the production of electroplated articles where from 10-90% of the plating metals can be discharged in the form of effluents rather than being deposited on the work pieces. There are also significant losses of non-ferrous metals from the other surface finishing operations already mentioned above. For example the value of materials lost from metal finishing in the UK has been estimated (Pearson and Melling 1985) to be of the order of £5×10^6 but the failure to reuse water represents an even greater loss. Bentley (1978) estimated that 1.2×10^8 m^3 of water used by the plating industry cost £22×10^6 for abstraction and disposal. Today that cost figure could be at least doubled if not tripled.

Currently in the UK the most common of all effluent treatment processes is still precipitation. This produces a metal-bearing sludge which is rarely suitable for metals recovery and is therefore dumped. As already noted this is a practice which is unlikely to be permitted much longer. Ion exchange on the other hand while technically excellent for effluent treatment and production of good quality water for recycle can be an expensive process and in the past has tended to be used only for high value metals in waste streams such as precious or platinum group metals. New selective chelating resins may prove attractive however while new process technology using conventional cation and anion exchangers such as the Recoflo process (Brown, 1987) is showing great promise for treatment of a variety of waste liquors such as nickel recovery from plating wastes and acids recovery for recycle from metal finishing applications such as sulphuric acid aluminium anodizing, sulphuric and hydrochloric steel pickling,

sulphuric-peroxidase brass etchants and various aluminium, brass, copper and nickel etchants employing nitric acid, thus reducing costly neutralisation charges prior to discharge. By 1987 over 100 such systems had been installed and were in commercial operation.

Direct electrochemical metal deposition processes for effluent treatment are in commercial operation but such developments have also required new technology through the development of cells of special design (Fleet, 1989) examples of which are Chemelec, the Eco cell, both UK developments, cells with reticulated mesh electrodes (RETEC), the Envirocell and the like. Such cells seldom achieve discharge limits in effluent treatment and thus tend to be used in regulatory applications wherein the spent electrolyte from the recovery cell can be recycled back to the process giving rise to the waste stream e.g. plating bath dragouts etc. The solid metal products whether plate or powder may be less readily recycled within the process plant and may be sold on the open market.

Solvent extraction and membrane processes therefore need to compete on a technical and economic basis with such ion exchange and direct electrolytic processes if they are to achieve commercial acceptance in this growing market sector.

3 SOLVENT EXTRACTION

Solvent extraction for treatment of aqueous effluents is still not widely practised. It has its attractions however as noted by Brooks (1987, a&b) who has discussed the role of solvent extraction in the treatment of metal finishing wastes. Brooks reports testwork using a variety of reagents in the extraction of Cd, Cr, Co, Cu, Fe, Ni and Zn in order to devise sequential solvent extraction schemes for metal removal and recovery from multimetallic mixed metal finishing wastes. He finds that, while technically feasible, the economics may not be wholly favourable. However the economics of metal recovery from waste effluents should not be governed solely by the market value of recovered products and the cost of waste disposal should be taken into account. He concludes that although solvent extraction has received little attention for metal recovery from waste systems, there are technical and economic considerations that merit further evaluation. Other specific commercial applications have been a) treatment of steel pickling liquors b) treatment of rayon manufacturing wastes c) treatment of zinc galvanising pickles and d) treatment of printed circuit board etchants.

3.1 Treatment of Steel Pickling Liquors

The first and probably best known process for recovery of HNO_3 and HF from pickling liquors is the AX Process (Andersson and Reinhardt, 1983). Developed in Sweden and originally run at Storakopparberg the process utilises the capacity of the undissociated acids to form complexes with TBP. The metals in the spent pickle liquor are recovered as a hydroxide sludge. A similar process has been developed in Japan (Nishimura and Watanabe, 1982) but this not only recovers the HNO_3 and HF but also produces a high purity iron oxide. Because the iron is removed by DEHPA extraction the recovery of HF is much enhanced over the AX Process. Similar processes exist for H_2SO_4 and HCl pickles.

A more general approach to the recovery of pure free acids from process waste streams by solvent extraction has been proposed by Mizrahi (1987) who recommends the use of acid-base couple solvents. Basically this idea uses mixtures of strong organic acids such as chloro- or bromo-substituted carboxylic acids or sulphonic acids such as the Synex line from King Industries Inc. and akylamines of appropriate base strength, on a one to one mole ratio basis. Acid recovery after extraction with this mixed solvent is by water stripping. Because of salting out effects in the extraction cycle, higher concentrations of acids are possible in the strip liquor. Acid wastes from TiO_2 production, waste steel pickles, spent electrolytes in copper, zinc etc electrowinning, other acidic bleed liquors etc are suggested as potential feeds for this process. Development however is not believed to have gone beyond the laboratory scale.

3.2 Zinc from Rayon Manufacturing Effluents

In the manufacture of rayon, rinse waters and other zinc containing effluents are produced. The total liquid effluent can amount to several metres^3/min and the zinc content can vary from 0.1-1.0 gl^{-1}. The effluent also contains sodium sulphate and surfactants and the pH of the effluent is normally aprox. 1.5-2. The Valberg process (Andersson and Reinhardt, 1983) developed in Sweden uses DEHPA to extract and the zinc rich strip liquor can be reycled to the spinning bath. The raffinate is lime neutralised and discharged. A full scale plant was constructed and began operation at Svenska Rayon AB in Valberg, Sweden in 1975. A better reagent nowadays would be the di-thiophosphinic acid Cyanex 301 which completely and selectively extracts Zn in the pH range 1-2 from Ca, (Rickelton and Boyle, 1988).

3.3 Zinc Galvanising Pickles

Developed by the National Institute for Metallurgy (now MINTEK) in Johannesburg, the METSEP Process was operated in South Africa by Woodall Duckham in the 1970's for the treatment of spent chloride based zinc galvanising

pickles. The zinc was first of all separated from the iron by extraction as its chlorocomplex by resin ion exchange and thereafter converted to the sulphate by solvent extaction with DEHPA. The chloride bearing effluent from ion exchange was pyrohydrolysed to produce iron oxide and HCl which, combined with the SX raffinate was recovered in an absorber. The zinc sulphate solution was sold to an electrolytic zinc refinery. Changes in market forces caused this original plant to close some years ago.

Today Babcock Metsep operate a centralised hydrochloric acid regeneration service in South Africa capable of processing 80 tonnes of spent pickle liquor. The flowsheet is shown in fig. 2. The plant provides a central processing service, via a fleet of tankers, in the Johannesburg area.

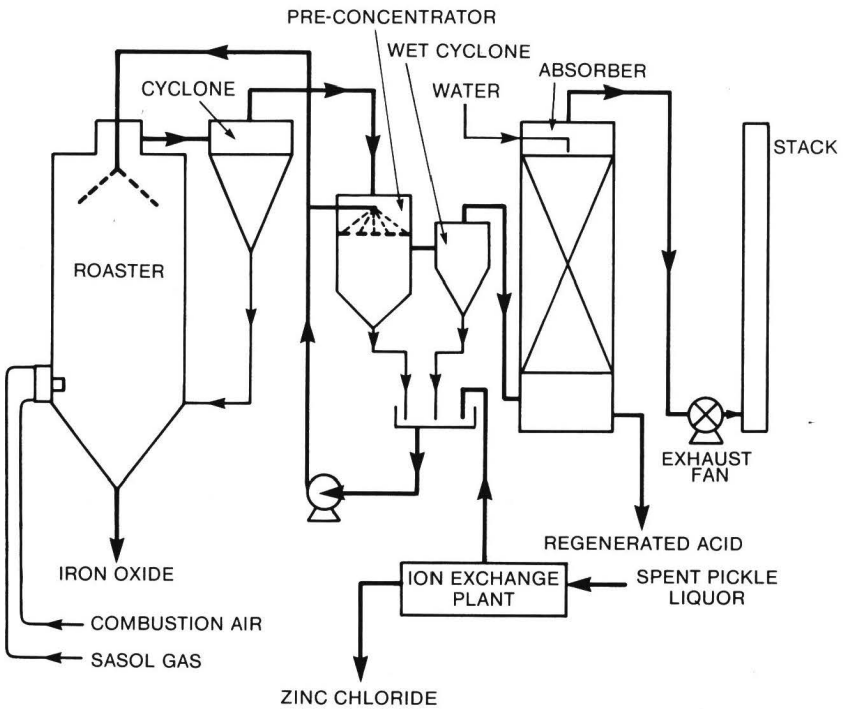


Fig. 2. The Babcock Metsep Acid Regeneration Process

3.4 Printed Circuit Board Etchants

Etching of copper with the use of an ammoniacal solution is a common procedure in the manufacture of printed circuit boards for the electronics industry. The ammoniacal etching solution contains free ammonia, one or more ammoniacal salts and oxidants. During etching the copper concentration of the solution increases and etching efficiency becomes unacceptable when the copper

concentration reaches 150-170 g^{-1}. To maintain a high etching efficiency the etching solution must be continuously removed and regenerated or replaced with fresh solution.

By withdrawing etchant directly from the printed circuit board etching line and recirculating it through a solvent extraction circuit, the copper concentration in the etchant can be maintained within the optimal range of 110-130 gl^{-1}. This is practised in the MECER process (Andersson and Reinhardt, 1983) (fig. 3). Treatment of the rinse water obtained from rinsing the circuit boards after etching can also be integrated into the process. The extractant used is the Henkel β-diketone reagent LIX 54. The regenerated etchant is returned to the etching line after careful removal of the entrained organic solvent and copper is recovered from the acid strip liquor by electrowinning. Forty plants in Europe now use this technology including one in the UK. Etchant makeup can be reduced by 95% and no negative influence has been found on quality.

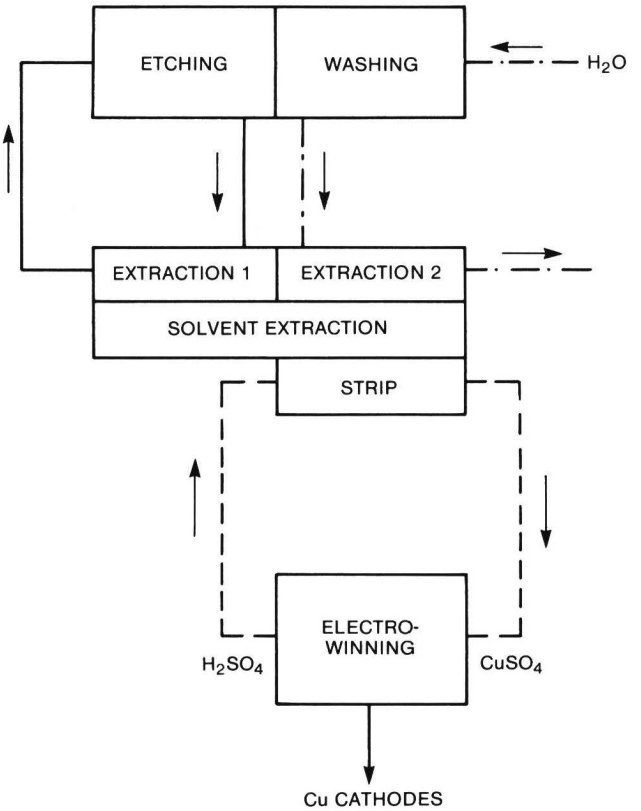


Fig. 3. The Mecer Process for On-line Regeneration and Copper Recovery from Ammoniacal Etchant.

3.5 Other

Japan Solex Corporation has developed a process for treatment of waste sulphuric acid arising from TiO_2 production via the sulphate process, wherein the waste acid is neutralised with $Ca(OH)_2$ and rock salt addition. The process can also be adapted to treat the iron containing H_2SO_4 liquors generated in the production of synthetic rutile. Here HNO_3 is added to oxidise Fe^{2+} to Fe^{3+}, rock salt added and the ferric iron and HNO_3 extracted with their proprietary extractant Soltex 268. HNO_3 is recovered from the organic phase by selective stripping with $FeCl_3$/rock salt and finally iron chloride suitable for high purity iron oxide production is recovered by water stripping. The current state of development of this process is unknown.

Thus while there have been some notable successes for solvent extraction in

the effluent treatment field no really major breakthroughs seem to have taken place.

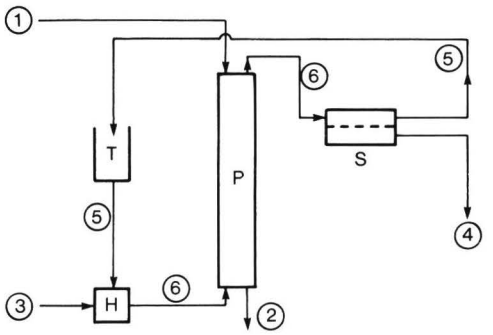
4 MEMBRANE PROCESSES

Membrane technology is well suited to waste water and effluent treatment applications and there would appear to be considerable development potential for this class of technology. Passive membrane processes such as microfiltration, ultrafiltration and reverse osmosis although already in commercial operation are beyond the scope of this paper and subsequent discussion will be focused on liquid membranes and dialysis systems using ion exchange membranes.

4.1 Liquid Membranes

The concept of liquid membranes is now well understood as is the distinction between surfactant liquid membranes and supported liquid membranes, and a very large amount of work has been published (Draxler and Marr, 1986; Noble and Way, 1987; Gu et al, 1988) on the chemistry, mechanisms and modelling of liquid membrane behaviour. Rather less work has been carried out on developing the technology commercially. Liquid membranes however do appear to have advantages over conventional solvent extraction in that the costs of solvent loss should be significantly reduced and there should also be a large saving on the cost of solvent inventory thus rendering this technology more attractive for application in effluent treatment. One potential disadvantage is the inability to provide solvent scrubbing although this may be overcome by using highly selective extractants in the membranes. In supported liquid membrane systems low mass transfer rates may require provision of relatively large areas of expensive polymeric support which has in the past negated the cost advantage of reduced solvent inventory.

Work at Graz University (Draxler et al, 1986) on surfactant liquid membranes led to the installation of a prototype commercial column contactor at Lenzing AG in Austria for zinc extraction from their rayon spinning bath effluent. The outline flowsheet is shown in outline in fig 4. The plant uses an agitated column contactor operating at 30°C as the primary contacting device. The primary stable emulsion between the sulphuric acid strip liquor and the organic phase which consists of bis (2-ethylhexyl) di-thiophosphoric acid (45 gl^{-1}) in Shellsol T plus 2 v/o polyamine as surfactant is produced by two rotor-stator high speed homogenisers operating in parallel. One third (45 m^3h^{-1}) of the waste water flow is treated in this plant. The column diameter is 1.6 m and its active height is 10 m. The feed zinc concentration is 500 mg Zn l^{-1} and a final Zn concentration of 5 mg l^{-1} is achieved



① WASTE WATER, 75 m^3/h, 500 mg/l Zn
② WASTE WATER, 75 m^3/h, 1-3 mg/l Zn
③ RECEIVING PHASE, 0.5 m^3/h, 250 g/l H_2SO_4
④ RECEIVING PHASE, 0.5 m^3/h, 60 g/l Zn
⑤ ORGANIC PHASE, 5 m^3/h
⑥ EMULSION, 5.5 m^3/h
P PERMEATION COLUMN
H HOMOGENISER
S ELECTROSTATIC SPLITTER
T TANK FOR ORGANIC PHASE

Fig. 4. Flow Sheet of a Plant for An-Recovery (From Draxler et al 1986)

against a discharge limit of 20 mg l^{-1}. The Zn loaded emulsion is split electrostatically in three parallel splitters operating at 20-25 kV and 50 Hz. The recovered zinc is recycled to the spinning baths. Adjustment of the feed pH is necessary to achieve satisfactory Zn extraction and there is a degradation problem with the reagent. The economic advantages claimed for the process are the quantity of zinc recovered and the opportunity costs of precipitation and sludge disposal.

This process may be compared with the Valberg Process described earlier in this paper, which is the traditional solvent extraction alternative to the liquid membrane process. As noted for the Valberg Process the Lenzing process could also benefit from use of Cyanex 301 not least in relation to the much greater stability of the dithiophosphinic acid.

Supported liquid membranes on the other hand have no reported commercial application as yet. There are perceived barriers to commercialisation in relation to solute transfer rate per unit membrane surface area, membrane lifetime, degradation of support etc and these have been discussed by Cox et al (1987). Work at Warren Spring Laboratory, (Flett and Pearson, 1985), while noting that the immediate potential for this technology is in effluent treatment, has identified two potential applications namely recovery of nickel

sulphate and chromic acid from their respective plating bath dragouts.

For nickel sulphate recovery Accurel fibres impregnated with DEHPA in 90% MSB 210/10% isodecanol were used. A nickel flux of 3 g m^{-2} hr^{-1} was achieved. Assuming that the hollow fibre supported liquid membrane unit maintains a nickel concentration of 1 gl^{-1} in the dragout tank, and a throughput of 4 t y^{-1} Ni, 167 m^2 of fibre would be required for 8000 hy^{-1} operation. Cost calculation showed that a payback time of three years was possible at the then nickel price of £4000 t^{-1}.

For chromic acid, 20 v/o Primene JMT in MSB 210/10% isodecanol gave a very satisfactory performance as the liquid phase supported by Accurel fibres. Here the strip phase was sodium hydroxide. A flux of 17 g m^{-2} h^{-1} was achieved with this system. A typical plating operation would discharge 0.5 kg h^{-1} Cr to dragout. Thus 30 m^2 of fibre would be required. Ion exchange is also necessary to convert the sodium chromate so produced to chromic acid for recycle. Taking the cost of this ion exchange step into account and assuming a 500 h operating lifetime for the membrane phase shows that, at £3500 t^{-1} for plating grade CrO_3 the installation and operation of such a liquid membrane unit would have a payback time of less than 2 years.

Thus the potential application of supported liquid membranes for treatment of dilute solution such as metal containing effluents from electroplating and pickling operations would seem to be encouraging. As indicated above however, it would seem that industry remains to be convinced about lifetime, support degradation etc and that definitive data on such operating parameters are required before any widespread commercial application will take place.

4.2 Ion Exchange Membranes

The application of ion exchange membranes clearly offers a challenge to solvent extraction and liquid membrane processes. One major advantage of ion exchange membranes is of course their electrical conductivity. Thus electrodialysis is of interest for application in the treatment of waste liquors from metal finishing operations.

The major difference between liquid membranes and ion exchange membranes is that the former relies on selective extraction of the metal species of interest and transport of the neutral organic complex across the membrane by diffusion while ion exchange membranes, while relying on perm- selectivity between anions and cations, also rely on mobility of the ionic species of interest within the membrane. Thus too great an affinity between the fixed charged site in the

membrane and the ionic species of interest is likely to lead to reduced transport numbers which may give rise to the opposite effect to that desired namely selective transport of the species of interest.

Typical areas for application of electrodialysis are the recovery of nickel from Watts plating operations, (Eisenmann, 1981; Tison and Paluck, 1982; Marquardt and Schmid 1989) copper from electroless copper plating processes (Horn, 1983) and chromium from electroplating rinse waters, (Gussack 1983). This last application will of course compete with the proposed use of supported liquid membranes for this purpose. Recovery of precious metals from electroplating rinse waters is also another area of clear interest. Thus circuits have been devised for recovery of gold from gold plating rinse waters (Linstedt and Millman, 1982) and for silver from silver plating plant rinse waters, (Millman and Heller, 1982). A useful review of this whole sector has been given recently by Sata (1989) together with commercial applications.

The recovery of acids and alkalis from waste liquors produced in the metal finishing industry, particularly from pickling processes is also of considerable interest. While electrodialysis theoretically can achieve such an objective (Millington 1983) (fig. 5), in practice it is quite difficult to produce both pure acid and alkali because of performnce limitations with conventional monopolar membranes, although recently Tokuyama Soda in Japan have developed special anion exchange membranes for acid recovery. (Noma, 1989). Currently however acid recovery from spent pickle liquors is practised commercially using diffusion dialysis as shown schematically in fig. 6. This process uses anion exchange membranes which are tailored to allow the passage of hydrogen ions and anions but to prevent the passage of other cations (fig. 7). Typical performance figures for acid recovery from various pickling baths are shown in table 2. Acid recoveries in excess of 80% can be expected and it is claimed that, coupled with the very low running cost of such systems, plants should show a return on capital of under 12 months. Diffusion dialysis is therefore a serious competitor for the ion exchange based Recoflo process mentioned earlier.

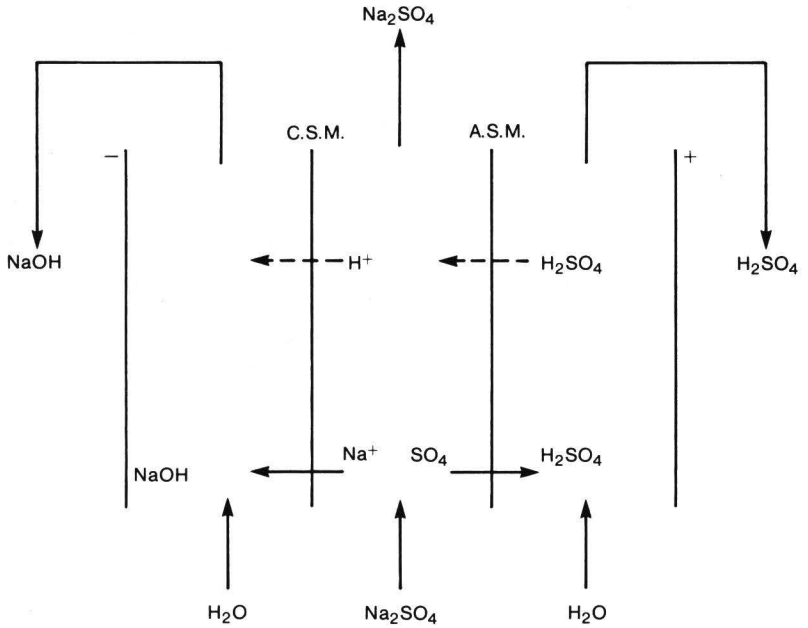


Fig. 5. Three Compartment Cell for the Recovery of Sulphuric Acid and Sodium Hydroxide from Pure Sodium Sulphate.

TABLE 2 Example of Acid Recovery by Diffusion dialysis (Tokuyama Soda Brochure)

Waste Acid (Free Effective Acid and Concomitant Metal)		H_2SO_4-Fe	HCl-Fe	HNO_3-Al
Temperature (°C)		22	27	27
Capacity ($L/Hr\ m^2$)	Water	0.59	1.10	1.02
	Waste Acid	0.60	1.04	1.02
Concentration of Waste Acid (g/100 ml)	Acid	19.16	8.47	9.32
	Metal	4.41	5.89	1.31
Concentration of Recovery Acid (g/100 ml)	Acid	16.56	9.93	10.77
	Metal	0.14	0.89	0.06
Concentration of Waste Solution (g/100 ml)	Acid	3.92	0.37	0.38
	Metal	4.16	4.44	1.13
Recovery Ratio of Free Acid (%)		82.1	95.0	95.0
Leak Ratio of Metal (%)		2.8	13.1	4.3

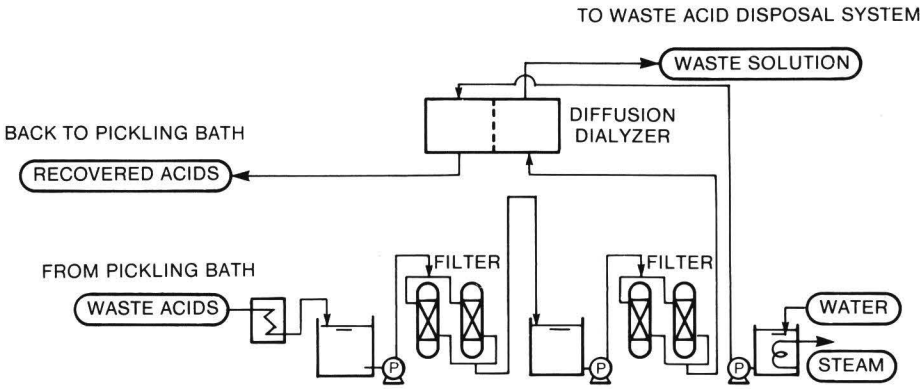


Fig. 6 Flow Diagram of Diffusion Dialysis Process (From Noma 1985)

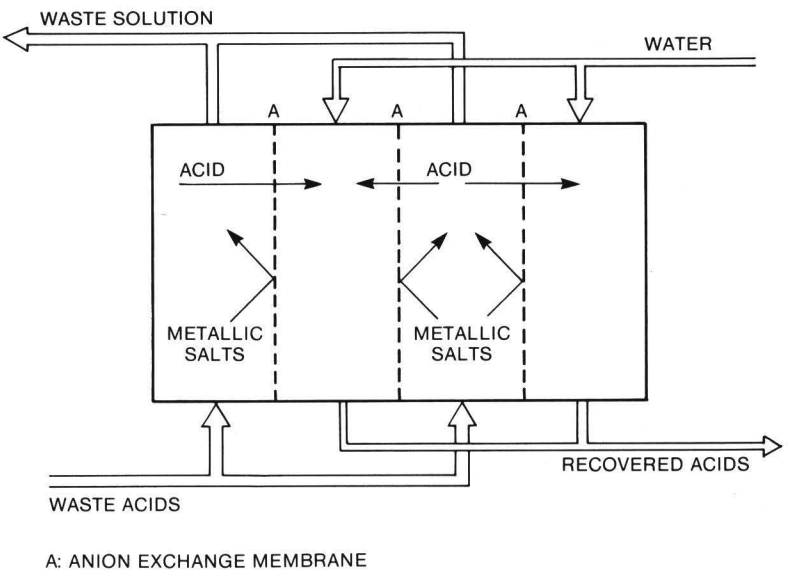


Fig. 7. Principle of Diffusion Dialysis.

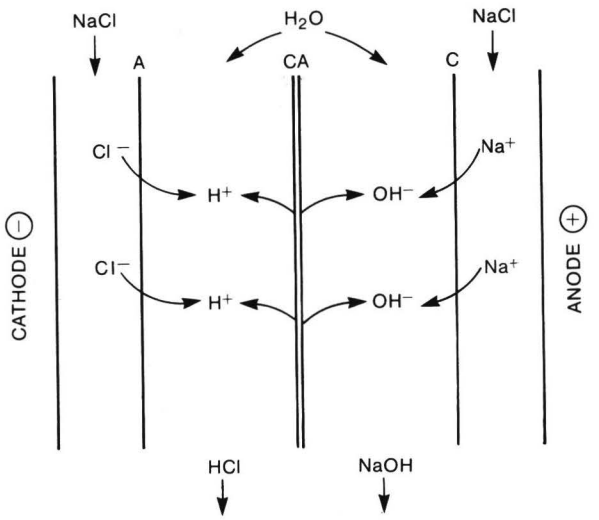


Fig. 8. Acid/Caustic Production with a Bipolar Membrane.

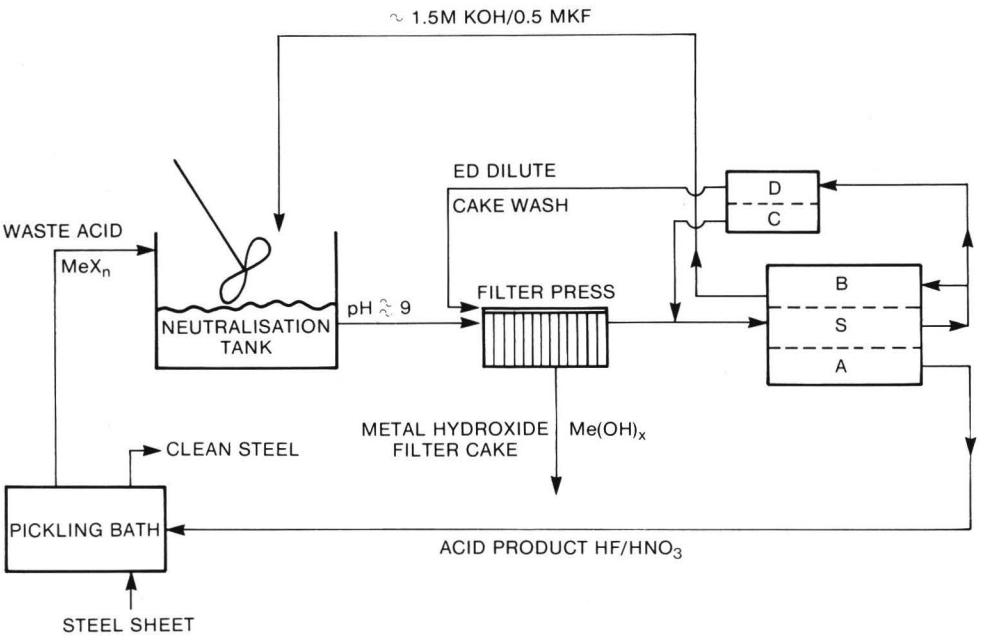


Fig. 9. Aquatech Pickle Liquor Recovery Process.

Bipolar membranes on the other hand can achieve ready recovery of both acids and alkalis (Mani et al, 1986; Byszewski, 1987). These are composite membranes consisting of a cation exchange region, an anion exchange region and the interface between them. On passage of an electric current in the presence of a salt solution, water splitting takes place at the interface region thus producing acids and alkalis (fig. 8). The first known commercial plant to use this technology started treating stainless steel pickle liquors for recovery of HNO_3 and HF at the Washington Steel Plant, Washington PA in the USA in January 1988 (Taffe, 1989). The plant, whose flowsheet is shown in fig. 9, regenerates 1.5×10^6 gals of spent pickle acid per year. Successful operation and satisfactory lifetime of the bipolar membranes will make this process a serious competitor against the AX and Japan Solex solvent extraction based processes.

5 FUTURE DEVELOPMENTS

With ever increasing pressure on discharge limits for effluents and the ever increasing restrictions on dumping of metalliferous wastes there can be little doubt that processing of effluents and wastes for recovery of contained metals, regeneration and recycle of acids and, where appropriate, recycle of water will become mandatory in the future. Separation science and technology offers a variety of process for these purposes as shown above. While these options really relate to add-on technology to treat effluents at the point of arising, there is also the option of centralised plants for treating combined metalliferous sludges produced by liming effluents from a series of metal finishing shops in a locality. The sludges would be trucked to the treatment plant and custom treated for metal recovery. In Roseville, Minnesota a centralized waste treatment facility was opened in 1988 in the Twin Cities area, (Norgaard 1988) conveniently sited to more than 200 surface finishing and electronics manufacturing operations in central Minnesota and Western Wisconsin. This centralized plant concept aims to avoid escalating cost of operation of individual in-plant systems and minimise sludge production by recovery of metals and chemicals for sale. Ion exchange features highly in this plant and metals such as copper, nickel and zinc can be recovered electrolytically. There seems to be no mention of solvent extraction or membrane processes.

On the other hand work at Warren Spring Laboratory (Pearson and Melling, 1985) also examined the concept of a centralized metal recovery plant for treating metalliferous sludges from metal finishing wastes. Based on potential arisings in the West Midlands region of England two potential feedstocks were identified namely a high zinc and a low zinc sludge. Treatment of both these materials is incorporated in the process flowsheet developed in the course of this work (fig. 10). The quantities on the diagram indicate hourly flows. In

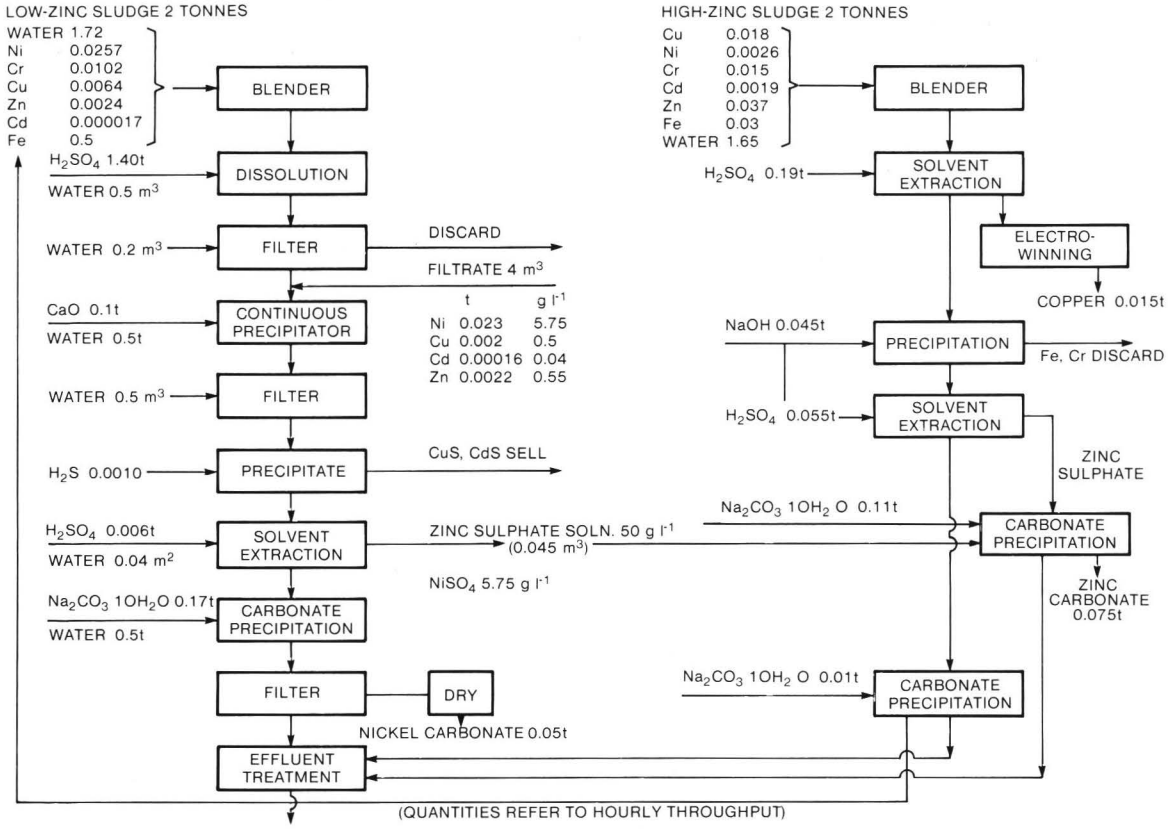


Fig. 10. Warren Spring Laboratory Flow Diagram for Centralised Sludge Treatment

treatment of the high zinc sludge solvent extraction was selected for copper recovery and for zinc recovery both in the high and low zinc feed arms of the flowsheet. At 1985 prices the cost of the plants were calculated to be £2.1 x 10^6 for the low zinc treatment and £1.2 x 10^6 for high zinc. Expected revenues (rounded figures) were estimated to be nickel carbonate £1.5 x 10^6; zinc carbonate £0.5 x 10^6; Cu-Cd sulphides £5 x 10^3; Cu £150 x 10^3 giving a total revenue of £2.2 x 10^6 which would show a loss of £2.5 x 10^3 for an annual throughput of 24,000 tonnes of sludge i.e. approx £10.5/tonne. Thus it was concluded that this process was unlikely to attract commercial interest unless some form of subsidy was provided.

Thus it would seem that the centralised treatment plant will only be cost effective if the throughput is large enough to provide positive net revenue. In other situations, treatment at point of arising seems to be the only effective option. From what has been discussed above traditional solvent extraction processes would seem to have a rather limited role in future waste and effluent treatment. Ion exchange membrane processes on the other hand are already proliferating commercially, particularly for acid recovery and recycle, and would seem to offer considerable scope for future development.

Whether liquid membranes, either surfactant or supported will find wide application is, as yet, difficult to tell but it seems clear that suported liquid membranes could provide useful cost effective technology for effluent treatment particularly where selective recovery of metal ions is required.

Ion exchange membranes therefore seem to have the greatest potential currently and it is confidently believed that considerable expansion of their use in the effluent and waste treatment will take place during the decade of the 90's.

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LIQUID-LIQUID EXTRACTION FOR PROTEIN SEPARATIONS

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ABSTRACT
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Liquid-liquid extraction can be used for the initial bulk concentration and purification of proteins. Suitable non-denaturing solvent systems are two-phase aqueous polymer mixtures and reversed micellar organic solutions. Selective partitioning of proteins in the two-phase polymer systems is affected by whether the polymer solution is dilute, with interaction length scales on the order of the polymer coil size, or semi-dilute, where the extensively-overlapping coils have correlation length scales on the order of a characteristic mesh size. An apparent interphase electrical potential difference, which depends on the type of salt used, gives rise to a pH-, or protein-charge dependent partitioning. Selectivity can be enhanced by derivatising one of the phase-forming polymers with a protein-specific ligand. Protein solubilisation in reversed micellar solutions is mediated by electrostatic interactions between the protein and the surfactant layer stabilising the reversed micellar water droplets, by size exclusion phenomena, and by the addition of ligand-modified cosurfactants. The current understanding of the physico-chemical interactions responsible for the specificity of the protein extraction operations is emphasised, and points of deficiency noted.

1 INTRODUCTION

Proteins are high molecular weight polymers of amino acids. In their native form they have specific configurations which are maintained by a delicate balance of electrostatic, hydrogen bonding and hydrophobic forces, and by some cross-linking through the formation of disulfide bonds between cysteine residues. It is this three-dimensional, or tertiary, structure that imparts to proteins their very specific functions in the body, in plants and animals, and in industrial enzyme processing. Recent advances in genetic engineering and recombinant DNA technology, coupled with improved yields and productivity of fermentation processes, have led to a burgeoning array of possible protein products, ranging from diagnostic and therapeutic enzymes through to industrial enzymes. Solvent extraction can play an important role in the initial bulk concentration and purification of these proteins, providing suitable solvents having the desired capacity and selectivity for the targetted protein product can be identified.

Proteins can be very sensitive to changes in the solvent polarity, pH and ionic strength, which can lead to a disruption of their three-dimensional structures, and hence to loss of protein function. Thus, in establishing a

separations scheme for protein recovery and purification, it is imperative that the system provide not only good capacity and selectivity for the protein product, but also a non-denaturing environment for the labile proteins. These stringent requirements are met by at least two different solvent systems that can be used for the liquid-liquid extraction of proteins, *viz.*, aqueous two-phase polymer systems and organic reversed micellar solutions. Extensive experimental studies have shed much light on the factors affecting protein partitioning in these solvent systems, but the molecular origins of most of these effects are still unclear. The purpose of this paper is to provide a brief overview of the current understanding of these phenomena, and to point out areas where more fundamental research could be profitably undertaken.

2 TWO-PHASE POLYMER SYSTEMS

It is well-known that when two or more polymers are mixed in a common solvent a phase separation can occur in which each of the resulting phases is rich in only one of the two polymer species. The example phase diagram given in Figure 1, that of the polyethylene oxide (PEO)/dextran/water system, shows that such phase separation can occur at fairly low polymer concentrations. Similar phase behaviour is observed with single polymers and high concentrations of salts, such as potassium sulphate or phosphate. The high water content of each phase ensures that it provides a benign, non-denaturing environment for proteins, while the selective partitioning of proteins between the phases can be exploited effectively for their separation and purification. These factors outweigh the disadvantages associated with two-phase polymer systems that would normally disqualify them from consideration in most conventional extraction schemes, *viz.*, their characteristically small density differentials (2 - 4 percent), high viscosities (10 - 1000 cp) and extremely low interfacial tensions (0.001 - 0.1 dyne/cm). While the partitioning behaviour of proteins and other biological materials in these polymer systems has been studied extensively since the mid-fifties (Albertsson, 1985; Walter et al., 1985; Abbott et al., 1990a),

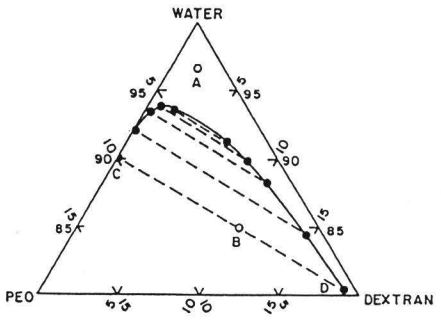


Figure 1 Phase diagram for the PEO/dextran/water system (Adapted from Albertsson, 1985)

it is only in the last fifteen years that aqueous two-phase polymer systems have come to be recognised as potentially useful for protein separations on a commercial scale (Hustedt et al., 1978).

2.1 Effects of protein and polymer molecular weights

The effects of both protein size and polymer molecular weight on the

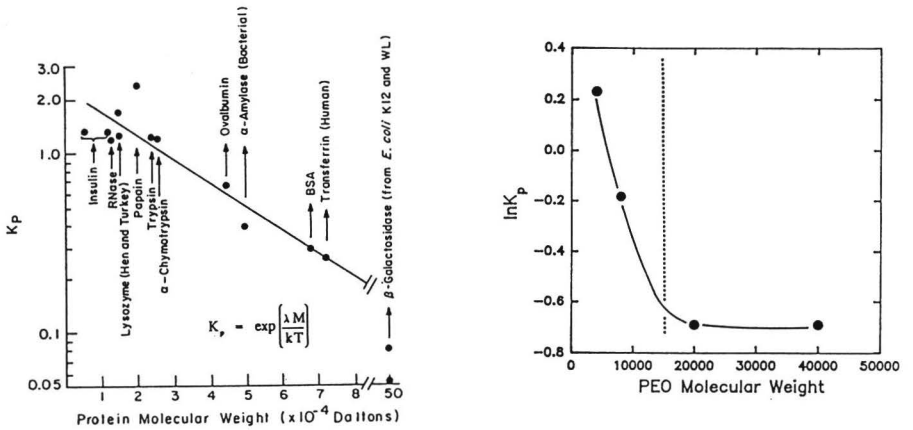


Figure 2 The effect of (a) protein molecular weight (Sasakawa et al., 1972), and (b) polymer molecular weight (Albertsson et al., 1987) on protein partition coefficient

partitioning of proteins are shown in Figure 2. The strong dependence of K_p on the protein molecular weight (Figure 2(a)) is a reflection of the balance between surface, van der Waals and excluded volume interactions of the proteins and polymers in solution, all of which depend on the protein size. The same phenomena are important in determining the effect of the polymer molecular weight on the interphase partitioning of proteins observed in Figure 2(b). A number of theories of protein partitioning have been developed within the framework of Flory-Huggins lattice models, in which the entropic and enthalpic contributions to the free energy of a polymer-protein solution are estimated by modelling the polymer solution as a lattice, the volume of each lattice site being determined by the size of the solvent molecules. These analyses show correct qualitative trends in some instances, but they do suffer from a lack of quantitative predictive capabilities (Brooks et al., 1985; Albertsson et al., 1987; Baskir et al., 1987; Diamond and Hsu, 1989) .

It was recognised recently that these "mean-field" theories, in which the polymer segment concentration is taken to be uniform throughout and long-range correlations are ignored, may not be applicable in the polymer solution regimes

typically encountered in two-phase polymer systems used for protein partitioning (Abbott et al., 1990a,b). This is particularly true at low polymer molecular weights and concentrations, where the individual polymer coils retain their identities, and do not overlap appreciably. In this regime, the excluded volume interactions between the proteins and the polymer coils will depend on the effective hard sphere volumes of the polymer coils, which increase non-linearly with increasing polymer molecular weight. Consequently, at constant polymer molecular weight percent, the excluded volume interactions become more pronounced as the polymer molecular weight increases, influencing the protein partitioning strongly. Excluded volume arguments have been unable to account completely for the observed experimental trends, however, and it has been necessary to invoke some slight attractive interactions between the proteins and the polymers to rationalise the experimental results in terms of these models. It is not clear, though, whether these results simply reflect an inadequate treatment of the entropy of mixing effects, or whether they are genuine surface or van der Waals interactions. If there are true attractive interactions between the protein and the polymer, are they non-specific, or do the nature of the protein surface and its heterogeneity play a role? Such questions have not been addressed to any extent, and yet it would seem crucial that these phenomena be investigated if we are ever to understand protein partitioning in any fundamental way.

At higher molecular weights and/or concentrations (approximately 10,000 Daltons at 10 weight percent PEO), the coils begin to overlap extensively, and the solution resembles a mesh in which the polymer coils are intertwined, and cannot be identified individually. The parameter determining the excluded volume interactions is now the so-called mesh size, which is independent of the polymer molecular weight, and thus we see a diminished dependence of K_p on polymer molecular weight in this range. The fluctuation and correlation length scales of interest are on the order of the protein size, and this then argues against the use of mean field theories of the type discussed above, even in this solution regime. Thus it can be concluded that in treating excluded volume interactions in protein-polymer systems, attention must be paid to the solution regime under consideration, and to developing a clearer picture of the entropy associated with the mixing of a protein in a polymer phase of varying nature. While it is relatively straightforward to analyse the two extremes (although even here the results are not without their ambiguities), no attention has yet been given to the transition zone, or intermediate regime. It would seem that this is an area ripe for study, as it is here that most partitioning studies and practices occur.

Virial expansion models, in which thermodynamic properties of the polymer solution are expanded as a power series in the polymer concentrations, have been used successfully to capture the trends associated with polymer concentration and

salt effects on protein partitioning, with the appropriate interaction parameters being determined experimentally using low-angle light scattering (King et al., 1988). A molecular-level interpretation of these interaction parameters is, however, still lacking, although attempts have been made to rationalise these parameters in terms of excluded-volume arguments (Forciniti and Hall, 1990).

2.2 Salt effects

Perhaps the richest behaviour observed in protein partitioning studies is

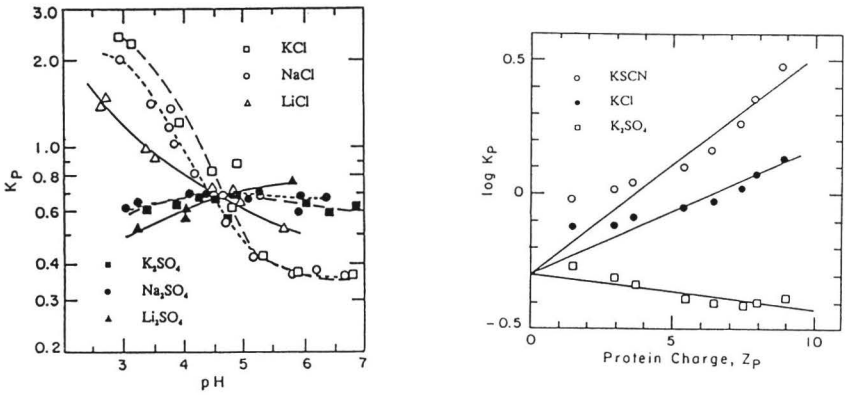


Figure 3 (a) Dependence of ovalbumin partition coefficient on solution pH (Walter et al., 1972), and of (b) ribonuclease-a partitioning on protein net charge (Johansson, 1974) for different added salts.

that related to specific salt effects, as illustrated in Figure 3, where the partition coefficients are shown for ovalbumin as a function of pH and for ribonuclease-a as a function of net charge for a number of different added electrolytes. It is clear from Figure 3(a) that the electrolyte type plays an important role in determining the partitioning behaviour, and that at a certain pH all curves for the different salt types intersect, i.e., there is no salt effect at this one pH, which turns out to be the isoelectric point for the protein. This common intersection of all salt curves argues against there being any specific salt interactions with the protein itself, and the observed behaviour is consistent with there being some charge effect on the protein partitioning. What is the nature of this effect? It can be traced to an observed potential difference between the phases of up to 10 mV, caused by the unequal affinities of different ions for the two phases, and hence the establishment of an interphase potential difference to ensure electrical neutrality (Albertsson et al., 1970; Brooks et al., 1984). The requirement for

equality of the *electro*chemical potential of the protein in the two phases then dictates that

$$\ln K_p = -\left(\frac{\Delta\mu_p^\circ}{kT} + \frac{z_p e\Delta\psi}{kT}\right) \qquad (1)$$

from which we would expect to find a linear relation between log K_p and protein net charge z_p; this is approximately what is observed in Figure 3(b). The interphase potential difference, $\Delta\psi$, which is related to the slope of the curves, can be positive or negative depending on the salt type used. Other terms in this equation are the standard state chemical potential difference, $\Delta\mu_p^\circ$, the Boltzmann constant, k, and the absolute temperature, T; e is the electronic charge.

Clearly, this salt effect is important, and must reflect the nature of the interactions between the salt, polymer and water, which at this point are poorly understood, and have yet to be elucidated. This is a difficult problem as the ion-dipole interactions are of similar strength to the polymer-water interactions, and therefore cannot be treated independently of them. It is evident that, to date, this topic has resisted a full theoretical interpretation, and any advances made in this area will have repercussions far beyond the boundaries of two-phase polymer systems.

2.3 Affinity partitioning

In none of the above mechanisms for protein partitioning are the biospecific molecular recognition capabilities of proteins exploited for separation purposes. It has been demonstrated on many occasions that enhanced partitioning can be attained by derivatising one of the phase polymers with a ligand that will interact specifically with the desired protein. It can be shown by simple thermodynamic arguments that the partition coefficient for the protein in the presence of a ligand having concentration c_L^t in the top phase can be related to the partition coefficient in the absence of the ligand, K_p°, via the equation (Brooks et al., 1985; Cordes et al., 1987)

$$K_p = K_p^\circ\left(\frac{1 + c_L^t K_L / K_a^b}{1 + c_L^t / K_a^t}\right)^n \qquad (2)$$

where K_L is the partition coefficient for the derivatised ligand, K_a^b and K_a^t are the association constants for the protein-ligand complex in the bottom and top

phases respectively, and n is the number of binding sites per protein. The dramatic increase in the partition coefficient in the presence of affinity ligand shown in Figure 4 for five different proteins is in general agreement with the predictions of this model. However, the effects of bulk polymer concentrations and the ligand tail molecular weight on partitioning have not yet been fully explained, neither has the fact that when there are multiple binding sites, the effective number, n, is generally non-integer, indicating there is some interaction beween the first attached ligand and subsequent ones. The lattice model of Baskir et al. (1987) has been partially successful in this regard, but is still subject to the cautionary comments above regarding the applicability of the mean field theories adopted.

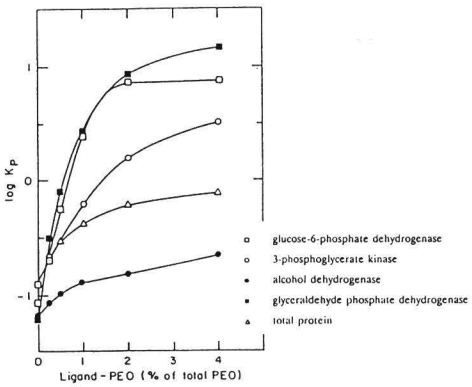


Figure 4 Affinity partitioning of proteins as a function of PEO-ligand concentration (Johansson and Andersson, 1984)

3 REVERSED MICELLAR SOLUTIONS

Reversed micelles are nanometer-scale water droplets dispersed in an organic continuum, stabilised by surfactants. They form spontaneously under

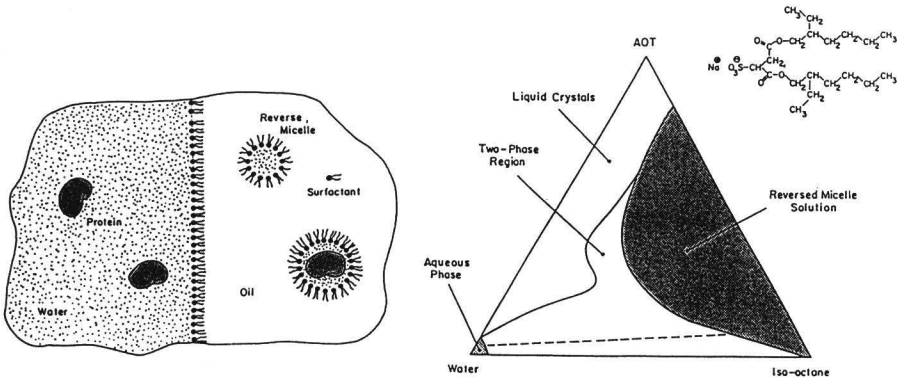


Figure 5 (a) Protein solubilisation in reversed micelles, and (b) Simplified phase diagram for the AOT/isooctane/water system.

appropriate conditions of salt type and concentration, depending on the surfactant and solvent selected. It is now well-established that proteins and other hydrophilic species can be solubilised in organic solvents by being sequestered within the polar cores of these reversed micelles, as shown schematically in Figure 5(a), and that in many instances proteins retain their native conformation and enzymatic activity (Luisi et al., 1979, 1988). The simplified phase diagram for the water-AOT- isooctane system in Figure 5(b) shows that there is a large two-phase region in which a bulk aqueous solution exists in equilibrium with a reversed micellar organic phase. There are many illustrations of the use of such reversed micellar phases as solvents for the selective extraction of proteins, amino acids and other biologicals from aqueous solutions (Pileni, 1989), and it has been shown that these systems are effective even when used to treat directly whole-broth fermentation media (Rahaman et al., 1988).

The physical properties of these systems in some instances are more attractive than those for two-phase polymer systems. Interfacial tensions are generally in the range 0.1 - 2 mN/m, the density differentials are closer to 10-20 percent, and the phase viscosities are more moderate, being on the order of 1 cp. A disadvantage of such systems is that the presence of such large amounts of surfactant can lead to the formation of rather strong macroemulsions, with subsequent phase disengagement problems. Nonetheless, Dekker *et al.* (1986) have operated a continuous mixer-settler extraction/stripping cycle successfully over many residence times with no apparent operational difficulties.

3.1 Interfacial transport characteristics

The solubilisation of proteins in reversed micellar systems is believed to proceed by a cooperative process, whereby the surfactant interface between the two macroscopic phases deforms in response to electrostatic interactions with the approaching protein, and the protein-micelle complex is formed cooperatively (Dungan et al., 1990). For lower molecular weight solutes there appears to be no mechanism for such a cooperative process, and the solubilisation is postulated to proceed via the growth of unstable surface fluctuations, which is significantly slower than the cooperative mechanism postulated for protein transfer. The reverse process, that of transfer out of the micellar phase back to the aqueous solution, is dominated by the rate of coalescence of micelles with the interface, that for protein-filled micelles being two to three orders of magnitude slower than for the empty micelles (Dekker et al., 1990; Dungan et al., 1990).

Results for the transfer of the proteins α-chymotrypsin and cytochrome-c in both directions are shown in Figure 6. It is evident that both pH and ionic

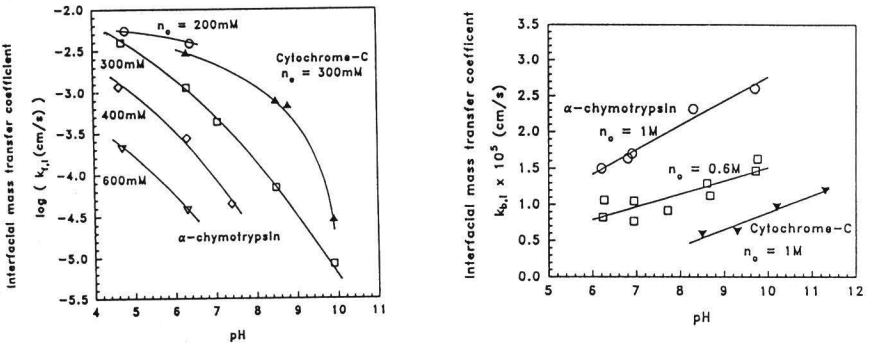


Figure 6 Interfacial transport coefficients for (a) forward and (b) backward protein transfer in AOT reversed micellar systems (Dungan et al., 1990)

strength have an important effect on the forward transfer, pointing to strong electrostatic interactions during the cooperative formation of the protein-micelle complex. The back transfer is less sensitive to pH because the proteins sequestered within the micelles are not exposed to the bulk phase pH until *after* they have been released from these micelles following their rate-limiting coalescence at the interface; the effect of ionic strength probably reflects changes in the interfacial tension and interfacial rigidity, which will affect the ease of coalescence of the micelles with the interface. Little is known about these phenomena, and there is considerable scope for fundamental work on the theoretical and experimental characterisation of surfactant monolayers at planar and curved interfaces, and their interactions with a range of macrosolutes.

3.2 Effects of pH and ionic strength

The solubilisation of proteins in reversed micellar solutions is affected primarily by electrostatic interactions between the hosted protein and the surfactant headgroups, although in some cases hydrophobic effects can also play a role. An indirect consequence of the electrostatic interactions is a volume exclusion effect, whereby if the equilibrium empty micelle size is sufficiently small, there is no energetic gain to placing the protein within the micelle.

Shown in Figure 7 are the degree of solubilisation of α-chymotrypsin in AOT reversed micelles and the sizes of the empty and protein-filled micelles as a function of salt concentration for three different pH's. At the low pH the protein bears a strong positive charge, and the interactions with the anionic

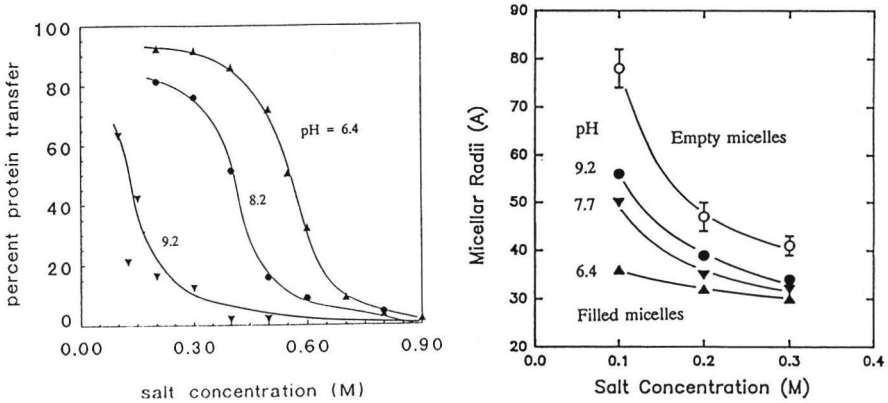


Figure 7 (a) Transfer efficiency of α-chymotrypsin to an AOT reversed micellar phase, and (b) the sizes of empty and protein-filled micelles, as functions of ionic strength and pH (data of Rahaman and Hatton, 1990).

surfactant are sufficiently strong that solubilisation is strongly favoured at the lower ionic strengths. In addition, the presence of the protein effectively screens across-micelle surfactant-surfactant interactions, reducing the total system energy. Thus it is favourable for the protein to be taken up by the reversed micelles under these conditions. With increasing ionic strength, the electrostatic interactions are screened more effectively, with the result that the empty micelles are reduced in size, and the advantages associated with placing the protein within a micelle are reduced. This is also entropically-driven; at low ionic strength, the protein-micelle complex formed is substantially smaller than the equilibrium empty micelle size, and therefore protein solubilisation results in a redistribution of surfactant over a larger number of smaller micelles, giving rise to a higher enropy of mixing of micelles into the solvent. At higher ionic strengths, where the empty micelles are smaller and more numerous, this driving force for protein solubilisation is significantly reduced.

With increasing pH the net charge on the protein becomes less positive, and the electrostatic interactions between the protein and the anionic surfactant shell are reduced, again leading to a lower solubilisation of protein in the reversed micellar phase. Although these effects have been described in terms of electrostatic models of the protein-surfactant interactions (Bruno et al.,1990; Woll and Hatton, 1989; Bratko et al., 1988), the models themselves are still not completely satisfactory, and there is tremendous scope for the development of improved theoretical pictures of protein solubilisation in reversed micelles. Topics to be considered are the location of the protein within the micelles

(Pileni et al., 1985), protein surface charge distributions (Wolbert et al., 1989), electric field and polarisation phenomena (Leodidis and Hatton, 1989b), and the important role the surfactant tail crowding and entropy of mixing the micelles into the organic continuum play as the micelles become larger (Rahaman and Hatton, 1990).

3.3 Specific salt effects

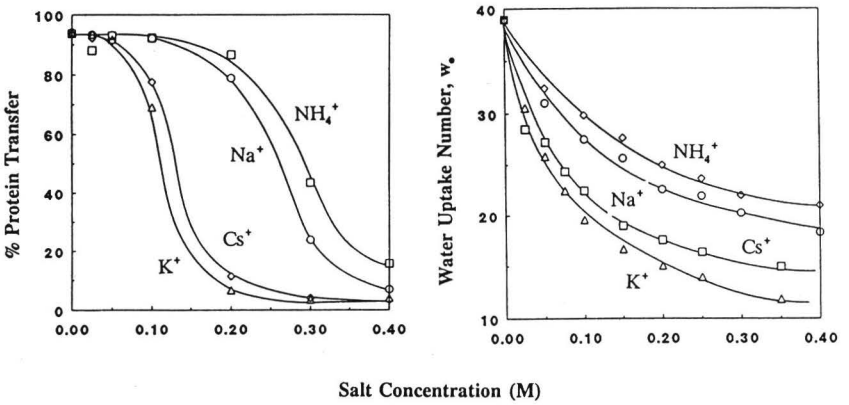


Figure 8 The effect of salt type and concentration on (a) the partitioning of α-chymotrypsin, and (b) the transfer of water to an AOT reversed micellar phase. (Kelley et al., 1990)

Another illustration of the importance of electrostatics and size exclusion in determining the protein solubilisation behaviour is the strong effect that electrolyte type can have (Kelley et al., 1990). It is found that the solubilisation curves are very strongly affected by cation type in these systems; for a given salt concentration, significantly higher protein transfers are obtained with sodium and ammonium salts than with potassium or cesium salts. These trends are also reflected in the amount of water taken up by the reversed micellar solution, expressed in Figure 8 as w_o, the molar water-to-surfactant ratio, which is a direct

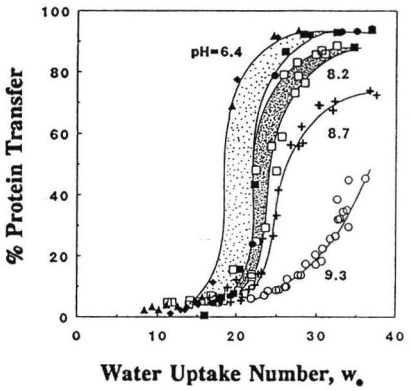


Figure 9 The transfer efficiency of α-chymotrypsin versus water uptake. (Kelley et al., 1990)

indication of micelle size. Models suggest that these results are consistent with the larger hydrated cations being more effectively volume-excluded from the vicinity of the surfactant charged layer, and thereby providing less screening of the across-micelle interactions, resulting in larger equilibrium micelle sizes (Leodidis and Hatton, 1989a,b). When these results are cross-plotted as in Figure 9, the protein extraction curves for any given pH tend to collapse onto a single narrow band for all salt types. This is a strong indication that it is the size of the empty micelles that determines the propensity for the protein to be solubilised, i.e., that an apparent size exclusion phenomenon is operative. These phenomena should be incorporated in any realistic model of protein partitioning in microheterogeneous media.

3.4 Affinity partitioning

There has been one successful report of the use of affinity surfactants in reversed micellar systems for enhancing the selectivity of a protein extraction (Woll et al., 1989). The model developed for two-phase polymer systems was found to be applicable to this system, although it is still necessary to account for the effects of the interface on the location and orientation of the affinity groups and on the binding characteristics of the protein with the affinity surfactants. Again, there is an opportunity to evaluate more closely the physicochemical properties of microstructured fluids and how they can influence interactions with hosted solutes.

4 CONCLUSIONS

Liquid-liquid extraction for protein separations is a viable technique for the biotechnology industries, as it can integrate the initial downstream processing steps of removal of insolubles and partial concentration and purification of the protein product. The requirements for a non-denaturing solvent are satisfied by both the polymer and reversed micellar solutions. This brief overview has concentrated on the factors governing the interphase partitioning of proteins, and what new insights can be gained from further fundamental research into these phenomena. Many other technical challenges need to be addressed as well. These include phase contacting and disengagement, product recovery and recycle of phase-forming materials, development and characterisation of new polymers and surfactants, and the economics of these processes. The technical challenges notwithstanding, however, it is clear that these systems provide intellectual challenges and the successful probing of the fundamental intermolecular interactions responsible for the selectivity of protein partitioning could have consequences in a range of other, related fields, such as protein aggregation and refolding, complex fluids, drug delivery systems,

therapeutic drug formulation, and food processing, to name but a few.

5 ACKNOWLEDGEMENTS

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EMULSION LIQUID MEMBRANES FOR WASTE WATER TREATMENT

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ABSTRACT

A review on the Emulsion Liquid Membrane (ELM) Technique is presented with an emphasis on its application for waste water treatment. The membrane components and the main apparatus such as emulsion preparation, mass transfer apparatus and emulsion splitting are described, then some applications for waste water treatment are suggested and finally an economic consideration is given.

INTRODUCTION

After the Emulsion Liquid Membrane Technique could not be applied for the enrichment of various metal ions, such as Uranium and Copper, due to various reasons (mainly economic due to low price of metals), this technique was tried to be applied for waste water treatment. A very good separation efficiency for the metal ions and a very low solubility of the used organic compounds in the effluent were two features of this technique which were very promising for an application in waste water treatment.

Several pilot plants proved the feasibility of this technique for waste water treatment. In particular, the separation and recovery of Zn in the viscose and rayon industry, of Zn, Cd, Pb and Cu in the mining industry, of Zn, Cd, Pb, Cu and Hg from residues of incineration plants, of Ni and Cr(VI) in the electroplating industry and ammonia and phenols in different industries got some importance.

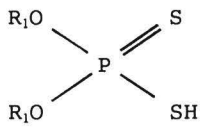
A prior condition for an application of the Emulsion Liquid Membrane Technique in waste water treatment is a low solubility of the organic compounds in the effluent, in order to avoid an additional pollution of the waste water. This is achieved by the use of long-chain aliphatic diluents and high-molecular weight surfactants. Modifiers are not necessary, because the actual concentration of the metals in the organic phase is always very low due to the simultaneous extraction and stripping mechanism. Depending on various parameters such as pH and salt content, the loss of membrane phase by solubility is in the range of 1 - 5 mg/l.

2 MEMBRANE COMPONENTS

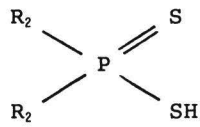
2.1. Extractants

The good separations down in the ppb-range for several metals is made possible by the separation mechanism and by the use of special extractants. Organic thio- and dithio-phosphoric- and phosphinic acids are very strong extractants for most heavy metals, but show very slow stripping kinetics. Therefore they are rarely used for Solvent-Extraction (SX). Due to the high interface area organic/stripping phase (about 10^6 m^2/m^3) the stripping rate is fast enough for an industrial application.

These extractants have following chemical structure:



and



The extraction efficiency is about the same for dithiophosphoric acids (DTPA, e.g. HOE F 3541, R_1 = Di-(2-ethylhexyl)) and dithiophosphinic acids (e.g. Cyanex 301, R_2 = Di-(2,2,4-trimethypentyl)). DTPA is produced in large quantities (motor oil additive, flotation agent) and is therefore very cheap, but in contact with water or mineral acids it is hydrolysed very quickly, especially at higher temperatures. Dithiophosphinic acids, however, are much more expensive, but they are also chemically very stable, so it is a matter of economics, which one is to be preferred.

2.2. surfactants

A lot of surfactants have been tested for the use in ELM and most of them met the requirement of stabilizing the emulsion. Nevertheless, only few are suitable for ELM because there are also other requirements, such as mass transfer resistance, chemical stability and ability for water transport. Especially the last point, the water transport through the membrane is of decisive importance for the choice of a suitable surfactant. This requires long-chain surfactants with low diffusivity. Amines such as ECA 11522 (EXXON) are mostly used, but there are also some new developments (Goto et al., 1989; Zhang et al., 1988).

The surfactants should provide a low interface tension membrane phase/stripping phase in order to stabilize the emulsion, but they

should not affect the interface tension emulsion/waste water. In Solvent-Extraction you have to avoid emulsions, in ELM you have to avoid double emulsions! Interestingly, a too low interface tension emulsion/waste water can be avoided by the addition of higher surfactant concentrations in the membrane phase (fig.1)

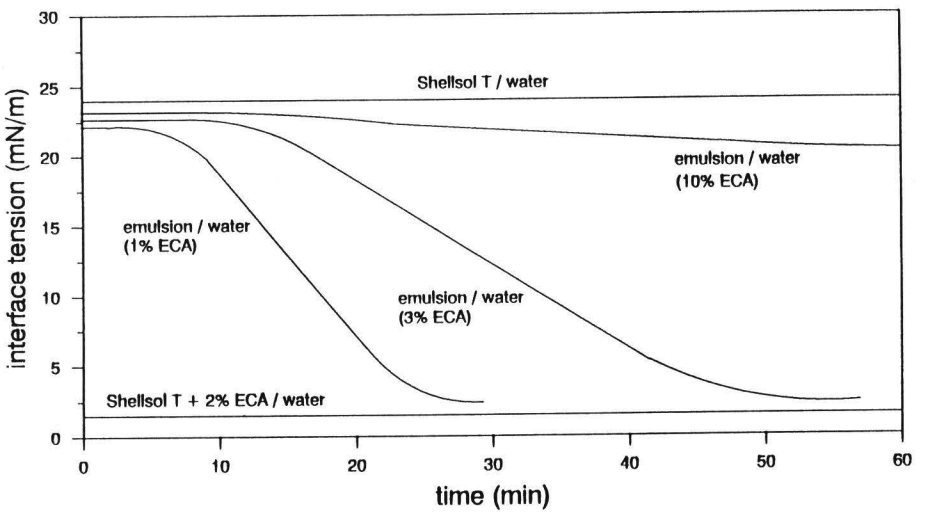


Fig. 1. Interface tensions of pure diluent, diluent + surfactant and emulsion to water.

When preparing the emulsion, the surfactant is completely adhered at the interface membrane/stripping phase. The interface tension emulsion/water is therefore initially nearly the same as the one of pure diluent (without surfactant)/water. By instability of the emulsion, surfactant is released from the inner interface membrane/stripping phase and can diffuse to the outer interface emulsion/water reducing thereby this interface tension. At higher surfactant concentrations, the emulsified stripping acid droplets become smaller and the emulsion more stable. The surfactant is not easily released from the inner interface and cannot diffuse to the outer interface. Therefore the interface tension emulsion/water remains high for a longer time.

2.3. diluents

Due to the simultaneous stripping the concentration of the metal-extractant complex in the membrane phase is always low. Therefore the

are now requirements on the diluents for a good solubilisation of these complexes and no modifiers are needed.

A suitable diluent for ELM should be aliphatic in nature, should have a low viscosity and a high flash point.

3 EQUIPMENT

When the chemical problems are solved and the process has been optimized in pilot tests, scale-up to a full scale plant can be realized. Thereby three main problems have to be faced. These are the scale-up of the mass transfer apparatus, the preparation of the emulsion and the splitting of the emulsion.

3.1. Mass Transfer Apparatus

Although many types of mass transfer apparatus have been used in the past, counter-current extraction columns proved to be most suitable for ELM. Mixer-settlers might also be used, but special types of settlers would have to be devised. The interface emulsion/waste water is continuously renewed in columns, in mixer-settlers, however, it remains nearly quiet. Due to a slow gravitiy settling of the emulsified stripping phase droplets, the emulsion at the interface becomes heavier till the density of this emulsion is higher than the aqueous phase and the emulsion is drained with the waste water phase.

A counter-current mode of operation is to be preferred to a co-current mode, especially when the metal concentrations in the effluent should be very low. In waste water treatment the required levels of the metal concentrations in the effluent are usually very low. This low levels cause many troubles in the scale-up of mass transfer apparatus, because there exists no reliable design basis for such low concentrations. Pilot tests are necessary in any case, but despite of pilot tests the design of a full-scale plant is very problematic, because mass transfer at very low concentrations is very sensitive to hold-up, interface area and many other parameters.

Usually the calculation of columns for ELM is done in a similar way as for SX. A description is given by Bart et al. (1988)

One major economical and technical question in the design of a full plant is, whether one counter-current column is sufficient to achieve the required separation, or whether two serial counter-current columns have to be used. This is very difficult to assess and depends very much on the required concentrations in the effluent and on the results of the pilot plant. Of course, with a high overdesign

one column will always be sufficient and will be cheaper than two smaller columns, but then other problems might arise, e.g. osmosis. Osmosis depends very much on the kind of the extractants and surfactants and will always occur due to the physical solubility of water in the organic phase. At a high overdesign, i.e. long residence time, osmosis might not only dilute the concentrated stripping acid, but also change all physical properties of the emulsion, causing thereby a malfunctioning of the entire plant.

The choice of the type of column seems to be of minor importance. Pilot tests showed no great differences between some commonly used columns, such as RDC, Kühni-, pulsed sieve plate- and Oldshue-Rushton-extractors.

3.2. Emulsion Preparation

There are a number of suitable methods to produce stable emulsions. In ELM-technique one always tried to produce emulsions with narrow drop size distributions. This was important, because too large droplets are prone to break-up, and too small droplets were difficult to split. With improved methods for emulsion splitting one can try now to make more stable emulsions with very small droplets. For this purpose some new devices have been designed, such as a low pressure static homogenizer (Marr et al. 1988), which proved its efficiency in pilot tests. Fig. 2 shows the drop size distribution of a W/O-emulsion produced by this static homogenizer. With this emulsions, break-up of the emulsified stripping phase droplets lies in the range of 0,1%.

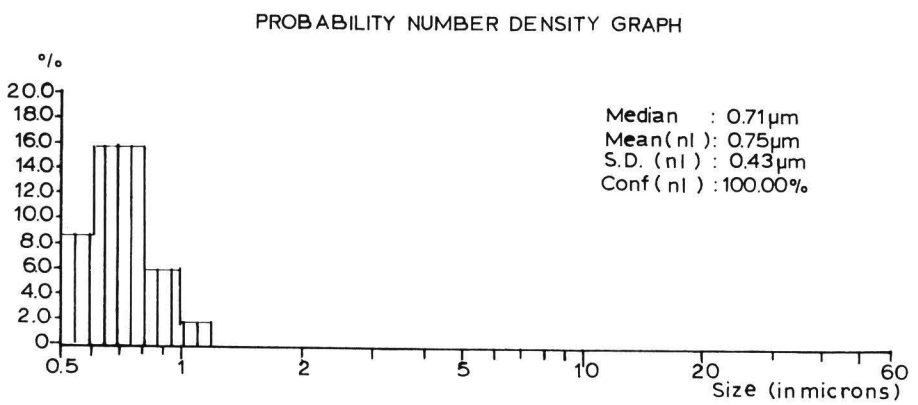


Fig 2. Drop size distribution. Nozzle: 2,0 mm; pressure: 4 bar. 10 parts organic phase (3% ECA 11522, 5% DTPA, 92% Shellsol T), 1 part stripping phase (H_2SO_4, 250 g/l)

3.3. Emulsion Splitting

This is still the most important step in the conception of a full scale plant. Especially for waste water treatment very stable emulsions with a drop size distribution as shown in fig. 2 are required in order to avoid any break-up. The only method applicable for ELM is the electrostatic splitting, but there are a lot of parameters which have to be optimized for each kind of emulsion.

One very important parameter is the frequency of the used A.C.field. It was often proved, that higher frequencies in the range of 3 - 30 kHz can improve splitting essentially, even at lower voltages (1 kV). Also the formation of spongy emulsion is considerably reduced at higher frequencies. The shape of the A.C.field is another important parameter. Compared to all other shapes a rectangular shape improves the splitting efficiency by a factor of about 1,5. Preferably the electrodes are insulated in order to avoid short-circuiting. Suitable insulation material is for instance glass and enamel, respectively.

The shape of the splitting apparatus itself is of minor importance for the splitting efficiency. Fig. 3 shows three types of splitting devices. The choice for one type is mainly made by economic considerations.

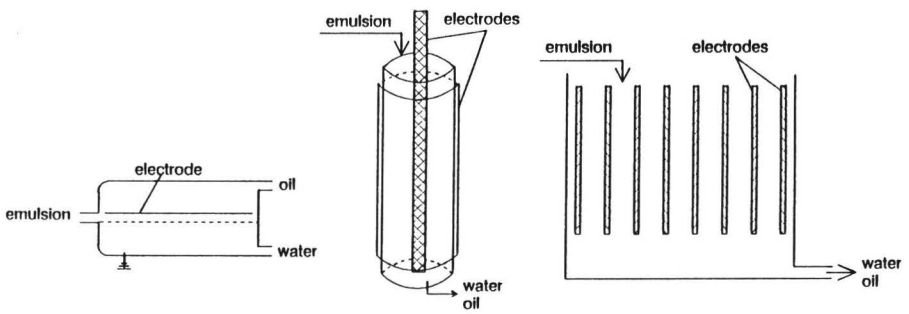


Fig. 3. Types of splitting apparatus

4 APPLICATIONS

4.1. Removal of Zinc in the Viscose Industry

In all viscose and rayon industries zinc ions are used in the spinbaths in order to improve the spinning process and the properties of the fibres. In the subsequent rinsing steps zinc is lost with the waste water. Beside the economic disadvantage the loss of zinc causes

also pollution problems. Therefore most viscose industries have installed plants for zinc-removal. The mere removal of zinc from the wastewater, e.g. by precipitation, represents mostly only a shift from a waste water problem to a landfill problem. Therefore some new processes have been tested and installed recently, which enable a recovery of zinc. For the reuse of zinc in the viscose industry a sufficient selectivity of zinc to calcium is demanded in order to avoid any precipitation of gypsum in the evaporation steps. ELM offer both a sufficient selectivity of Zn to Ca and a reuse of Zn in the spinbaths.

Fig. 4 and 5 show the results of a two-stage pilot plant. 200 l/h of waste water were treated in two counter-current columns (diameter: 0,1m, height: 6m) with an emulsion consisting of 10 l/h organic phase (3% ECA 11522, 5% DTPA, 92% Shellsol T) and 1 l/h H_2SO_4, 250 g/l. Fig. 4 shows the column profiles for Zn. In the first column Zn could be separated from about 120 mg/l to about 10 mg/l, and in the second column to 0,3 mg/l. All Ca-analyses of this two-months pilot run are shown in fig. 5. It can clearly be seen, that both raffinates contained always the same amount of Ca as the feed phase and only traces of Ca could be found in the stripping phases.

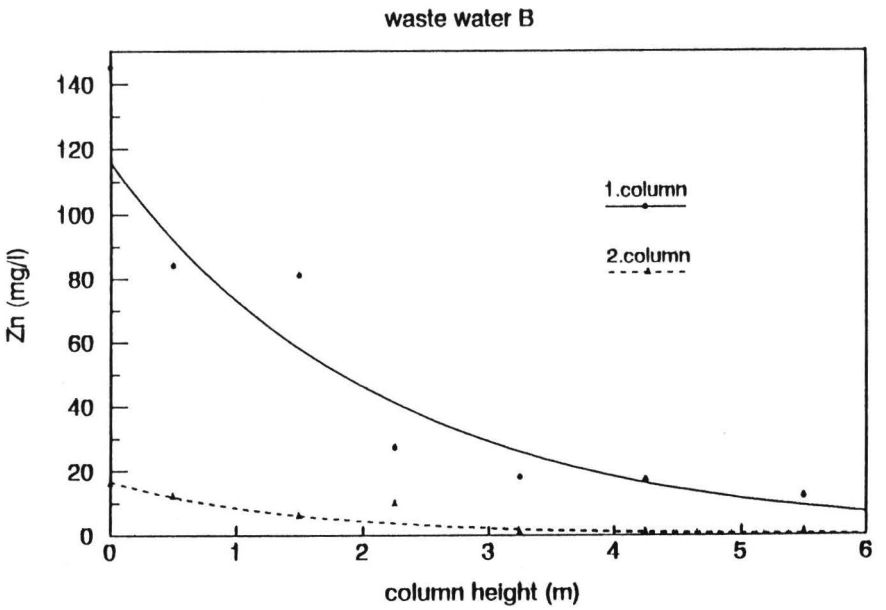


Fig. 4. Zn-results

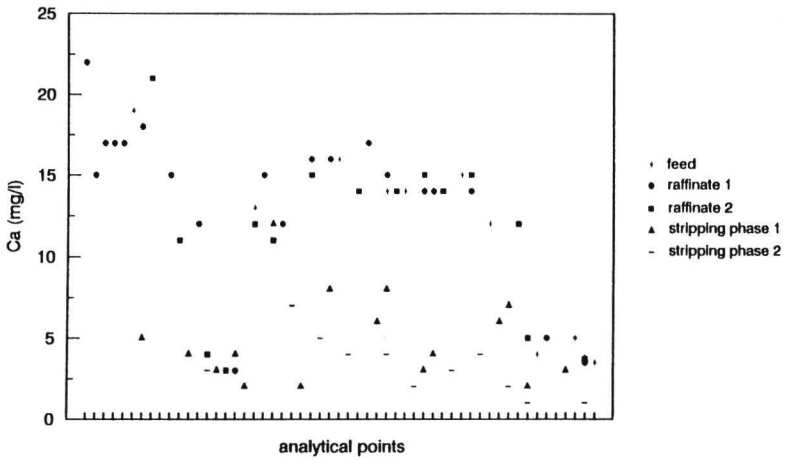


Fig. 5. Ca-results

The viscose waste waters contain different amounts of spin bath additives, mainly polyethylenglycole (PEG) and epoxilized fatty amines. These are surface active agents and have therefore a decisive influence on the feasibility of an ELM-process, respectively. The surface tension between waste water and organic phase is reduced drastically. The influence of the additives on ELM is manifold. They might be partly coextracted (especially the fatty amines), resulting in a higher sulfuric acid consumption; then they might act as an additional mass transfer resistance due to their aggregation at the interface; finally, and most important, they can strenghten or soften the activity of the surfactants, resulting in an increase or decrease of the emulsion stability.

The influence of these additives can't be predicted. Even very similar additives can have a totally different influence. It is therefore always necessary to make pilot tests or intensive laboratory tests prior to a full-scale application.

4.2. Recovery of Nickel from Electroplating Solutions

Nickel is removed from electroplating solutions mostly by precipitation. Also SX using D2EHPA is applied, but the separation is not very efficient. With DTPA the extraction would be very efficient, but stripping is very slow. This led to a new development (Marr et al. 1988), which is shown in fig. 6. This process contains now only the important elements of the ELM-process, but is not a membrane process any more. The advantages of the ELM-process (large interfacial area) could be preserved, whereas the disadvantages of

membrane processes (osmosis) could be avoided.

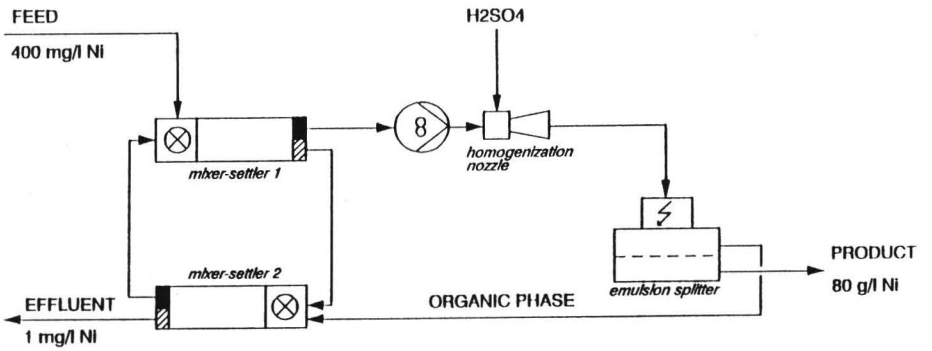


Fig. 6. Combined SX-ELM process for Ni-recovery

The waste water is contacted countercurrently in a two-stage mixer-settler unit with the organic phase containing 5% of a dithiophosphoric acid in an aliphatic diluent and a small amount of surfactant. The surfactant is necessary for the following stripping stage, however, its concentration must remain so low that there is no disadvantageous effect on the extraction step. Due to the strongly acidic extractant DTPA Ni can be removed in the waste water down to less than 1 mg/l, independent of the initial concentration (at least up to about 6 g/l).

Stripping of Ni from the organic phase is done in a homogenizer in order to obtain a large interface area. But despite of very fine droplets and the large specific interface area the residence time must be about 15 min to obtain a sufficient stripping. Therefore a small amount of surfactant is necessary to maintain such small droplets for the required time. Separation of this droplets after the stripping step by gravitiy settling would take too long, therefore an electrostatic splitting device is necessary.

4.3. Removal of heavy Metals in Metallurgical Plants

Waste waters in metallurgical plants usually contain a number of different metals which are to be removed alltogether. As long as there is a use for the stripping phase, ELM is a very efficient technique for this task. In metallurgical plants this is usually the case since the stripping phase can be used for leaching of the metal-ores. Table 1 shows the average results of a six-months pilot run (same conditions as in 4.1.)

TABLE 1: Results of pilot plant

metal	feed mg/l	raffinate 1 mg/l	raffinate 2 mg/l	strip.ph. mg/l
Zn	230	5	0,2	22.000
Cd	2,7	0,1	0,02	270
Cu	1,1	0,1	0,007	90
Pb	0,5	0,02	0,01	6
Fe(II)	90	90	90	20
Fe(III)	20	15	12	700
Co	0,4	0,4	0,38	0,1
Ni	0,3	0,3	0,3	0,1
Mn	25	24	23	20
Mg	37	37	37	4
Ca	220	220	220	44
Na	60	60	60	6
pH	3,4	2,2	2,1	

For these experiments a monothiophosphoric acid was used instead of DTPA. These two extractants have about the same extraction efficiency for all metals (except Ni and to a minor extent Fe(III), Co and Mn). The main difference lies again in the stripping behaviour. Under the conditions used, Cd, Cu and Pb wouldn't be stripped from DTPA by diluted sulfuric acid.

5 ECONOMICS

Contrary to most other membrane processes ELM-technology is not based on modules, but is tailormade for each specific problem. Therefore it doesn't make sense to give prices e.g. in $/m^2$ membrane area. Even figures in $/m^3$ of treated waste water cannot be given in a general way, because it depends on a number of parameters. To give a hint for the costs of an ELM-plant, a complete calculation of a plant for the viscose industry is given. Basis of this calculation was a waste water stream of 75 m^3/h with a Zn-concentration of 300 mg/l. 95% of Zn should be removed in one column.

5.1. Capital Costs

A turn-key plant with new buildings and a separate measuring station was calculated. Prices of all parts are given in table 2.

TABLE 2: Capital costs:

		US $
a)	extraction column including internals	230.000.-
b)	filter for feed stream, oil separator	30.000.-
c)	splitting apparatus (enamel insulated electrodes) plus electronic device	150.000.-
d)	pumps, homogenizer, static mixers	77.000.-
e)	process measuring and control equipment including measuring station	230.000.-
f)	electrotechnical devices	100.000.-
g)	pipes	210.000.-
h)	buildings	420.000.-
i)	steel structure	130.000.-
j)	insulation, paintings	53.000.-
k)	erection, assembling	380.000.-
l)	supervision buildings and erection	130.000.-
m)	setting into operation	70.000.-
n)	Engineering	600.000.-
o)	licenses	80.000.-
		2890.000.-

5.2. Operating costs

For the assessment of the industrial economics following costs were accounted for:

a) direct operating costs of the plant; costs for sulfuric acid and water, organic membrane phase (losses by decomposition and solubility and a total replacement of organic input every second year); included are also costs for the further treatment of the product phase (evaporation); not included are costs for the neutralization of the raffinate. - 70.400.-

b) staff costs, other costs (analysis) - 55.800.-

c) credits for the recycled zinc + 301.400.-

d) credits due to opportunity costs for other treatments to reduce the zinc-concentration + 129.000.-

The total savings are therefore + 304.200.-

5.3. Return on Investment

Fig. 7 shows the payback time for different flowrates and concentrations. It is a rough estimate, an assurance of 0,1% of capital costs, a maintenance of 2% of capital costs and average interests of 5% of capital costs over all years were accounted for.

For the given conditions a payback time of 29 years was calculated.

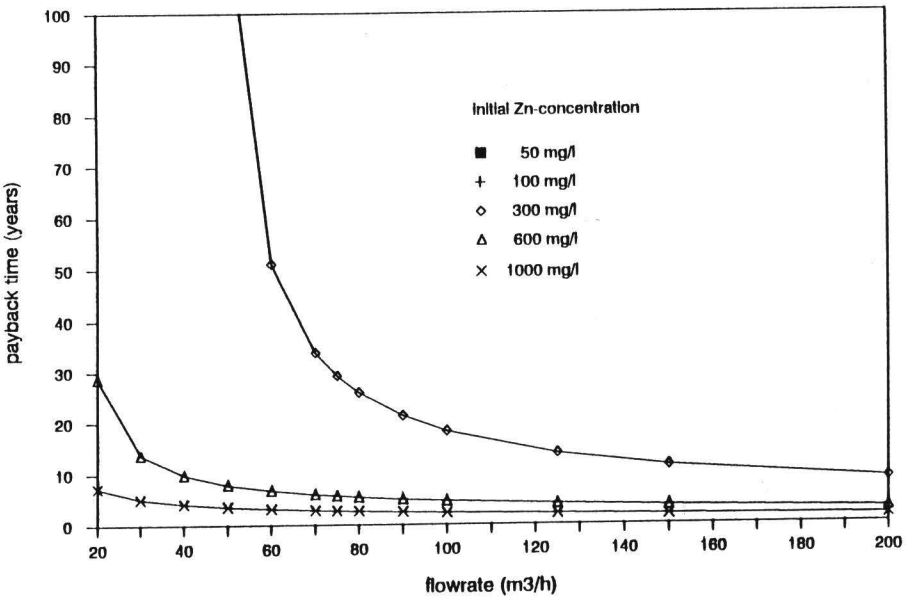


Fig. 7. Dependences on payback time

When calculating a payback time one has to consider that an ELM-plant is an environmental protection plant; it is therefore not convenient to calculate a payback time. The costs for such a plant ought to be integrated in the production plant and accounted for in the calculation of the payback time of the production plant. The shown calculation serves only for comparison to other processes, the absolute figure of the payback time is of no importance. But contrary to many other environmental protection processes there is at least a positive payback time.

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ANALYTICAL SEPARATIONS BASED ON ION-PAIR EXTRACTION PRINCIPLE -DESIGN OF REAGENTS AND SYSTEMS-

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ABSTRACT

Ion-pair or ion-associate formation and their partition between water immiscible two phases provides the one of the most important principle to design the separation methods for ionic species in solution. In this paper, I will make over view of our recent development of these separation systems, including ion-pair solvent extraction of metal chelates.

INTRODUCTION

Methods for analytical separations based on ion-pair formation are summarized in Table 1. Among these, ion-pair solvent extraction and ion-pair partition high performance liquid chromatography (IP-HPLC) are the most popular ones. Ion-pair transparent liquid phase separation phenomena, which are found in the case of quaternaryammonium-perfluorooctanoate ion-pair formation and neutralization of perfluorooctanoic acid derivatives (pH dependent, reversible) has enable us to develop a new type of homogeneous liquid-liquid extraction system. By this method, more than 10000 times concentration for porphyrin complexes can easily be achieved within several minutes (Igarashi et al.,1990). Ion-exchange adsorption followed by ion-pair dissolution method provides a new rapid concentration technique; by the use of 3 g of cotton wool (on which cationic surfactant is coated dynamically) on a grass-filter, feed rate of up to 1000 ml/min was able to apply to adsorption of metal ions as ion-pairs of dithiolene chelates and which was eluted with acetone within several seconds. Concentration ratio of 20000 was attained(Yamazaki et al.,1984). Ion-pair scum can be used for preconcentration and for room temperature phosphorescence media of porphyrin compounds (Endo et al, 1986). Ion-pair film concentration method is an ion-pair extraction with solidified solvent (dioctylphalate, plasticizer of polyvinylchloride), which can be applied for an unique colorimetry of trace metal ions. And ion-pair bubble separation by the use of ionic surfactants can be regarded as an ion-pair partition between aqueous phase and water-air interface. Its partition behavior can also be understood based on ion-pair extraction concept.

As it can seen from these separation methods, ion-pair partition principle has a versatile applicability for many phases of separation problems.

TABLE 1.

Two phase partition systems of ion-pair or ion-associate

[WATER IMMISCIBLE 2ND. PHASE]	[SEPARATION METHOD]
Organic solvent	Ion-pair solvent extraction
Ion-pair liquid phase	Homogeneous liq.-liq. extraction
Hydrophobic stationary phase	Ion-pair HPLC
Gas-liquid interface	Ion-pair bubble separation
Polymer(PVC) film	Ion-pair film colorimetry
	Ion-pair film concentration method
Ion-pair scum(Precipitate)	Adsorbent act as RTP* media
Cellulose matrix	Ion-exchange adsorption followed by ion-pair elution method

*: Room temperature phosphoresecense.

2 ION-PAIR SOLVENT EXTRACTION

2.1 Prediction of extraction constant

Ion-pair partition or extraction process of Q^+ ion with X^- ion is expressed by following equations,

$$Q^+ + X^- = QX = QX_o \quad (1)$$

$$K = [QX]/[Q^+][X^-] \quad (2)$$

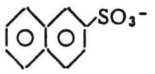
$$k = [QX]_o/[QX] \quad (3)$$

where subscript o denoted the species in organic phase. Among the ion-pair extraction system, the largest extraction constants, Kex, of 10^{22-23} were reported for mareonitrildithiolato chelates, $Q_2[M(mnt)_2]$ for Ni, Cu, Zn, Cd, with Q^+ of tetrahexylammonium ion (Inoue,1978).

In order to design the reagent and system suitable for the separation of metal ions, information about the structure -partition equilibrium constants relationship are essential. Large number of the extraction constants have been reported in the past 15 years. And several proposal have been made by Matsunaga et al.(1983), Motomizu et al.(1983, 1989), Goto et al.(1983), and Kasahara et al.(1990), in which the amount of the constants are divided into the cationic and the anionic contributions, as well as those of solvent. And the functional group contributions of ionic species are also assigned. Some typical data of these assignments are shown in Table 1 and calculated values are in good agreement with experimental ones for $[Ni(dto)_2]^{2-}$, iodide, and perchlorate ions with various kinds of quaternary ammonium cations.

Thus, we can obtained a general image of an equilibrium state of ion-pair extraction systems, even though they are still largely empirical.

Table 2. Extraction constants of ion-pairs ($\log K_{ex}$)

Anion	Cation[c)]	$\log K_{ex}$ Experimental	Calculated	Ref.
$[NiL_2]^{2-}$	DMA^+	8.97	9.01	A
	TBA^+	9.38	9.95	A
	DPY^+	11.37	11.23	A
	CMA^+	12.88	12.77	A
	DBA^+	14.75	14.67	A
	CPY^+	14.82	14.99	A
	Z^+	16.46	16.55	A
	THA^+	18.05	17.47	A
ClO_4^-	TBA^+	3.32[b)]	3.94	B
	DPY^+	4.36	4.55	A
	CMA^+	5.45	5.36	A
	CPY^+	5.67	6.27	A
	Z^+	7.24	7.24	14)[a)]
	THA^+	7.98[b)]	7.70	1)
I^-	TBA^+	3.01[b)]	3.81	B
	DPY^+	4.07	4.45	A
	CMA^+	5.12	5.22	A
	Z^+	7.11	7.11	14)[a)]
	THA^+	7.48	7.56	1)
	CMA^+	6.09	6.05	A
	Z^+	7.94	7.94	14)[a)]
Picrate	TMA^+	0.16[b)]	0.11	B
	TEA^+	2.12[b)]	1.99	B
	TPA^+	4.08[b)]	3.87	B
	TBA^+	5.75[b)]	5.75	B[a)]
	Z^+	9.61	9.05	14)

At 25°C and I=0.3 { b) : corrected for I=0.3 from original data}. a) : Reference ion-pair. A : This work. B : K. Gustavii : *Acta Pharm. Swecica*, **4**, 233 (1967). c) : Q^+ ions——Dodecytlrimethylammonium ion (DMA^+), tetrabutylammonium ion (TBA^+), *N*-dodecylpyridinium ion (DPY^+), hexadecyltrimethylammonium ion (CMA^+), benzyldodecyldimethylammonium ion (DBA^+), *N*-Hexadecylpyridinium ion (CPY^+), benzyldimethyltetradecylammonium ion (Z^+), tetrahexylammonium ion (THA^+).

2.3 Ion-pair extraction from alkaline media

Extraction of gallium(III) from alkaline solution has been a recent topics. In these extraction system, extractant having a long alkyl chain has been used empirically. Obi et al.(1989) demonstrated that in ion-pair system, such long alkyl chain can be placed either on extractant or counter ions. This finding,

which is in accordance with the group contribution concept, provides a useful guideline for designing the reagent system for ion-pair extraction, especially suitable for alkaline media. Unusual behavior was observed in the ion-pair extraction from strongly alkaline solution such as 3 M NaOH aqueous solution. In these conditions, gallium(III) chelate of tetrbutylpyro- cathecolate, $[Ga(pc)_3]^{3-}$, can be extracted with asymmetric counter ions but not with symmetric ones, as shown in Fig. 1. In addition, the extraction ability of tetrahexylammonium ion(Q^+) to the gallium(III) chelate increased as decreasing the length of the one of the hexyl-group on the Q^+ ion, ($C_6H_{13}N^+C_nH_{2n+1}$) extraction efficiency was 4.8 % for n = 6, 50.3 % for n = 4, and 66.2 % for n = 2, respectively. This result seems to argue against the regular solution theory in which molar volume of the species may determine the distribution. But this phenomena can be understood based on the mechanism of ion-pair formation in which a closest approach of cation and anion may play an important role.

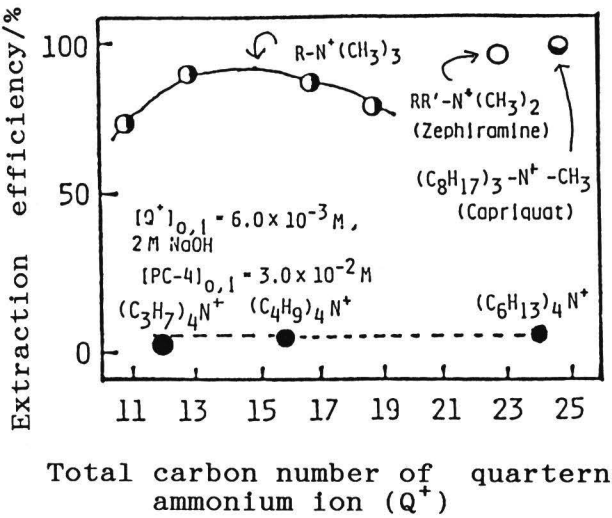


Fig.1 Efect of structure of counter cation

2.4 Kinetic aspects of ion-pair systems

Ion-pair formation is thought to be very fast, because its process is rgely electro-static in nature. But, planer nickel chelate, $[Ni(mnt)_2]^{2-}$ showed unusual ion-pair extraction behavior. By the use of tetrabutylammonium ion, the chelate was extracted quantitatively into chlorofolm phase as shown

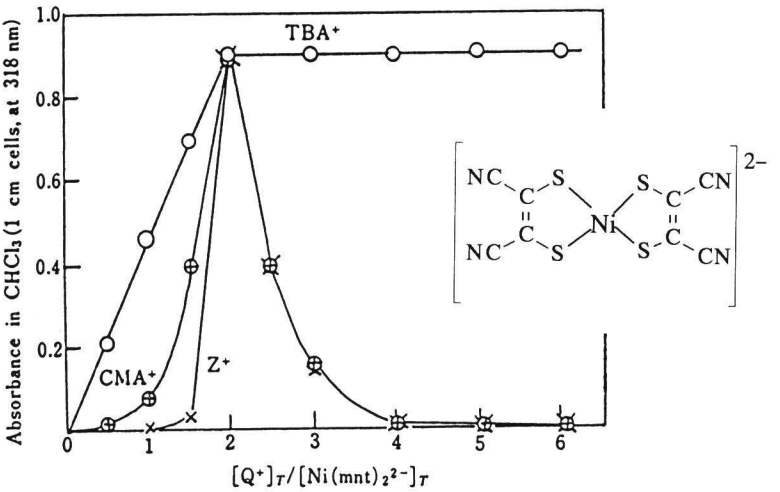


Fig.2 Absorbance-molar ratio plots[26)]

$[Ni(mnt)_2^{2-}]_T = 3.5 \times 10^{-5}$ mol/l; Shaking time : 10 min

in Fig.2. With asymmetric cations of cetyltrimethylammonium(CMA^+) ion and benzyldimetyltetradecylammonium(Z^+) ion, quantitative extraction were observed only at the stoichiometric condition (shaking for 10 minutes). At this time, colloidal suspensions found in aqueous phase have negative charge at molar ratio of $[Q^+]_T/[Ni(mnt)_2^{2-}]_T$ <2, and positive charge at that of >2. After 6 hours shaking, all the data were coincided with those of tetrabutylammonium ones(Yotsuyanagi et al., 1981). Such behavior shuld be attributed to the slow dissociation nature of charged aggregate, and the contribution of association mechanism other than electrostatic interaction, such as hydrophobic and charge transfer ones.

The group contribution concept and its data base are useful for prediction of partition behavior not only for ion-pair solvent extraction, but also for all the method based on ion-pair partition principle, except for above mentioned unusual cases.

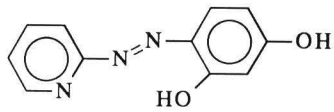
3 ION-PAIR PARTITION HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

3.1 Ion-pair HPLC and solvent extraction

This type of HPLC was first proposed by Eksbork et al.,(1973), and the first application of reversed phase ion-pair mode to charged metal chelates had made by Hoshino et al.,(1978). BY the use of ion-pair HPLC, we have obtained a powerful tool for highly selective and sensitive method for water

soluble charged metal chelates. Its detection limits are easily reached down to sub-ppb level of metal ions. Strong correlation between ion-pair solvent extraction and ion-pair HPLC for 4-(2-pyridylazo)resolsinolato (PAR, R^{2-}) chelates of Fe(III), Co(III), V(V), and HR^{-} has been demonstrated (Hoshino et al., 1984).

PAR:



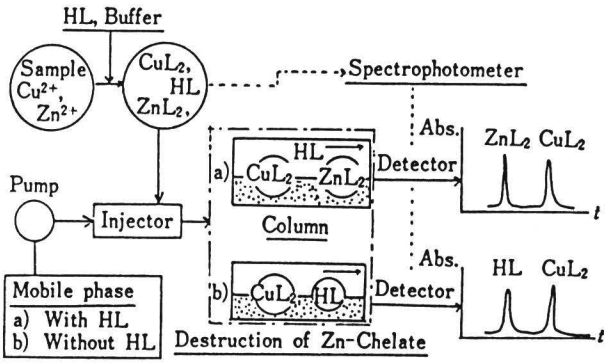
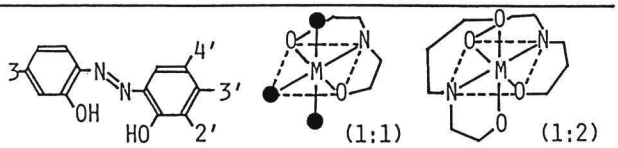


Fig.3 Spectrophotometry and two types of high performance liquid chromatography (reversed phase mode) for metal analysis

3.2 Kinetic differentiation(KD) mode HPLC

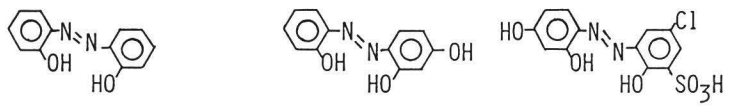
KD-HPLC, which was proposed by Hoshino and Yotsuyanagi(1978, is shown in Fig.3. Metal ion is derivatized to metal chelate(per-column, off-line) and the reaction mixture is injected into eluent stream of reversed phase column system, in which chromogenic chelating reagent is not added. Metal chelate and the reagent are separated on the column, and thus large driving force of dissociation is applied to the metal chelate. Therefore, column acts not only as a conventional separator, but also acts as a selective destroyer to the kinetically labile metal chelates. In addition to such unique kinetic selectivity, it also provides an increase in sensitivity, which is realized by elimination of the background reagent signal from the vicinity of that of metal chelate. Therefore, its detection limit can easily be reached down to

Table 3. Selectivity of 2,2'-dihydroxyazobebzene derivatives



	Reagents	Metal ions detected
1.	Mother compound	(Al) (Co) (Fe) (V)
2.	3-OH	(Cu) Co Fe (V)
3.	3-OH, 4'-SO_3^-	(Cu) (Co) Fe (V)
4.	3-OH, 3'-NO_2	(Al) Cu (Fe) (V)
5.	3-OH, 2'-SO_3^-, 4'-Cl	(Cu) Co Fe (Mo) V (Zr)
6.	3-OH, 4'-CH_3	Cu Co Mo (V)
7.	3-NEt_2, 4'-SO_3^-	(Cu) Co Fe Mo (V)
8.	3-NEt_2, 3'-NO_2	(Al) Cu (Fe) (V)
9.	3-OCH_3, 4'-SO_3^-	(Cu) Mo (V)

Sample : Al,Be,Co,Cu,Cd,Fe(III),Mn,Mo(VI),Ni,Pb,V(V),Zn
○ indicates the metal ion suitable for determination.



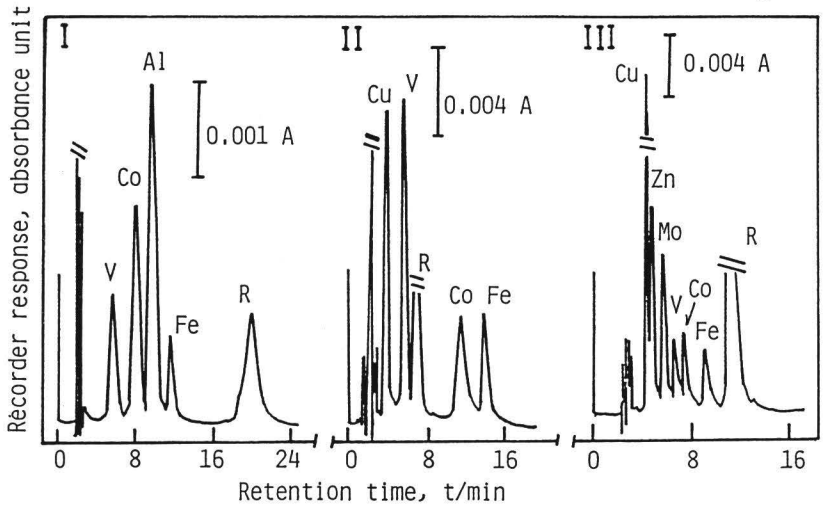


Fig.4 Chromatogram of metal chelates of DHAB derivatives

$[Metal]_{Total}$: $4X10^{-7}$ M in I, $4X10^{-6}$ M in II, and $2X10^{-6}$ M in III.

ppb - sub-ppb level. This mode can also be applied to micellar electro-kinetic capillary chromatography and detection limit was reached to 1.4×10^{-15} mol for chromium(III)-PAR chelate (Saito et al., 1989).

3.3 Design of derivatizing reagent for KD-HPLC system

The reagent for KD-HPLC is requested to form an inert metal chelate as well as to have partition and detection functions. Systematic survey of such reagents revealed that they were found among hydroxyazobebzene-dye (Hoshino et al.,1984, 1985, 1990, Miura et al., 1990), dithiolene (Ebina et al., 1983), polydentate Schiff-base (Kanbayashi et al., 1987), hydorazone (Uehara et al.,1989), and porphyrin (Igarashi et al., 1983).

For example, KD-HPLC properties of 2,2'-dihydroxyazobenzene(DHAB) derivatives are summarized in Table 3 and some of their chromatograms are shown in Fig.4 (Hoshino et al., 1990a). These data clearly show that only very small change in the peripheral parts of reagents produces a drastic change in selectivity toward metal ions. By introduction of -OH group to DHAB at 3-position, aluminum peak disappeared and cobalt gave new peak. And introduction of $-NO_2$ group, aluminum appeared again and cobalt disappeared. Another interesting point is that nickel(II) peak can not be detected, even though nickel chelates were once formed in precolumn derivatization step and they are generally thought to be inert ones. Any derivatives of DHAB can not gave chromatogram peak for nickel. Among such survey of reagent for nickel, specific one for nickel was found (Iki et al., 1991), 2-Pyridylaldehyde-benzoylhydrazone, by which only nickel can be detected among more than 10 kinds of common metal ions including transition metal ions.

The KD-HPLC methods have been successfully applied to the determination of the aluminum in human serum (ppb level; Kaneko et al., 1989) and vanadium (1-30 ng/m^3: urban air level) in air born particulates (Irie et al., 1991).

4 NEW SEPARATION SYSTEMS

4.1 Ion-pair film concentration method

PVC film (dioctylphthalate as plasticizer) acts as a new solid extractant for ion-pair system. This system can extract some neutral metal chelates of 8-quinolinolates, diethyldithio- carbamates, and ion-pair of DHAB chelates, La-alizalin complexone-F^-, but not for PAR ones. These extraction properties seems to indicate some new selectivity to metal chelates.

Simplification of analytical methods is one of the most urgent demand from many laboratories. In addition to such usual needs, it becomes gradually clear that we have to depend more and more simple method due to shortage in any kinds of our resources in near future. From such view point, survey of

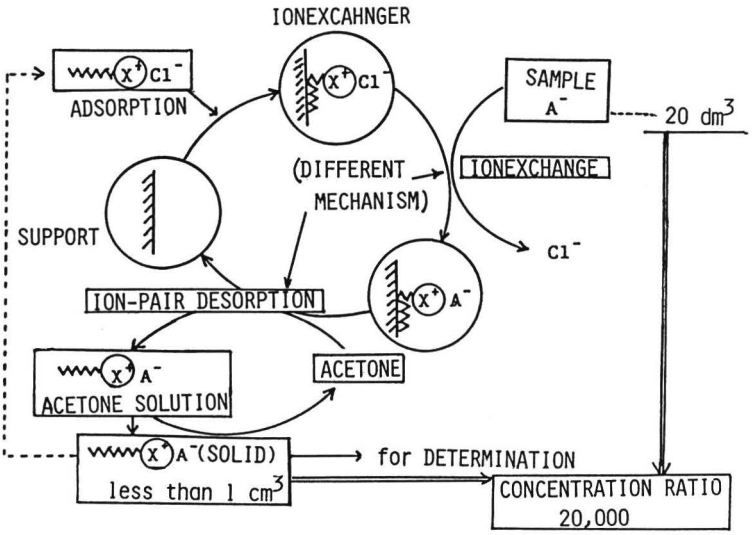


Fig.5. New SEPARATION and CONCENTRATION METHOD
— IONEXCHANGE ADSORPTION - ION-PAIR DESORPTION

Table 4. Recovery of trace amount of Cd with Cellulose Powder and Capriquat.

No.	[Cd] / M	Volume / ml	Recovery / %
1	0	10,000	0
2	2.5×10^{-9}	2,000	96
3	1.25×10^{-9}	4,000	99
4	5.0×10^{-10}	8,000	92
5	5.0×10^{-10}	10,000	93
6	2.0×10^{-10}	20,000	100
7*	5.0×10^{-8}	500	103

Loading condition : Capriquat/Cellulose Powder
=0.05 g / 3.0 g
Flow rate = 600 ml/min , $[mnt^{2-}]_t = 5 \times 10^{-5}$ M ,
pH = 5 , final volume = 10 ml.

* 3.8 % NaCl solution.

visual method, colorimetry, must be promising approach. In order to increase the sensitivity of detection, perconcentration into the transparent film body with 3 primary color system is attractive. Since human eye has high sensitivity towards mixed color system. Combination of 2,2'-dihydroxyazobenzene(Yellow), its Al-chelate (Red), and counter cation (Crystal violet, Blue purple) gave highly sensitive visual colorimetry for aluminum (kaneko et al., in drinking water: detection limit 3 ppb; 1989), and for iron (Kaneko et al., water and serum; 1991).

This system is also useful for protein removal in serum analysis, because such bio-polymers can not penetrate into the film body and solidified solvent is free from troubles of emulsion formation.

4.2 Homogeneous liquid-liquid extraction

Phase separation of perfluoro-octanoic acid (HPF) provides a new type of homogeneous liquid-liquid extraction system; Q^+PF^- ion-pair forms a water immiscible liquid phase (0.1-0.5 ml) from aqueous solution, which can extract various kinds of metal chelates and chlorophyll. High concentration ratio of more than 10^4 can easily be obtained (Igarashi et al., 1989, 1990).

4.3 New type of ion-exchanger

Dynamic coated ion-exchanger is illustrated in Fig. 5, which can be constructed based on the dynamically courted cellulose fiber with hydrophobic Q^+ ion; By the use of 3 g of adsorbent on 3G3 type glass filter, up to 1200 ml/min feed rate was able to apply for the adsorption of anionic dithiolene chelates, which were eluted with acetone within several seconds and concentration ratio of $2x10^4$ was attained (Yamazaki et al., 1981). By this system, 10^{-10} M level of cadmium(II) was recovered quantitatively even in the presence of high concentration of sodium chloride(Table 3, sea water level). This should be attributed to the large ion-pair extraction constant (Kex = $10^{22.4}$ at 25°C, I = 0.3, tetrahexylammonium ion, H_2O-$CHCl_3$ system) as well as its stability (stability constant of $[Cd(mnt)_2]^{2-}$ was $10^{15.9}$).

Versatile applicability of ion-pair partition phenomena of ionic species will provides many kinds of separation methods for ions from industrial scale and to analytical ones.

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1. FUNDAMENTALS OF SOLVENT EXTRACTION

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SOLVATION AND HYDRATION IN SOLVENT EXTRACTION

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ABSTRACT

The effect on inner sphere (i.e., water in the primary coordination sphere of the extracted cation) and outer sphere (i.e., water associated with the complex) hydration on the extraction of metal complexes is reviewed. The thermodynamics of the partition of metal complexes between an aqueous and an organic phase is often "entropy driven" due to the loss of the outer sphere hydration. By contrast, loss of the inner sphere hydration in synergistic extraction systems is often the major factor in the synergistic effect. The salting out effect of inert salts can be explained by the effect of the salt concentration on the outer sphere hydration of the metal complex.

INTRODUCTION

The extent to which a metal ion is extracted from an aqueous into an organic phase is the result of many factors. The relative solvation of the extracting species in the two solvents plays a fundamental role as only if the metal ion forms a species which is more organophilic than hydrophilic is extraction significant.

In the aqueous phase, the first step leading to extraction involves the complexation of the metal ion by one or more ligands which causes the metal to lose some or all of its hydration. This dehydration of the metal ion and that of the complexing ligands (which, generally, is smaller than for metal ions) results in positive contributions to the enthalpy and entropy change for complexation while the combination of the dehydrated cation and the ligands give a negative contribution to these terms. The net enthalpy and entropy changes are the balance of these opposing contributions. The solubility in the aqueous phase of the complex also reflects a balance between the hydration of the complex (favors solubility) and the disruption of the normal hydrogen-bonded structure of the water by the formation of a cavity to accommodate the intrusion of the complex (favors insolubility). The transition metals frequently are coordinately saturated; i.e., all the metal coordination sites are occupied by ligand donor atoms. However, there may be outer-sphere

hydration of these complexes in which water molecules interact with the complex but not directly with the cation (Allard et al., 1979). The lanthanide and actinide cations can have higher coordination number greater than 6 which result in residual inner sphere hydration of the cations. The complexes of the f-elements can also have outer sphere hydration. Figure 1 shows models of inner and outer sphere hydration.

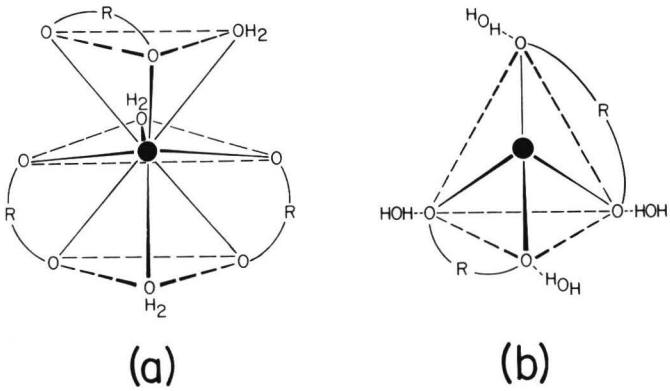


Figure 1. Model structures for (a) inner and (b) outer sphere hydration of extractable complexes.

Organic solvents interact with solutes by dipole and dispersion forces and such solvation is generally weaker than inner sphere hydration. Residual inner sphere hydration of the cation of the extracted complex is disruptive to organic phase solvation and is often removed by reaction with a neutral donor ligand. The resulting increase in the organophilicity is the main basis of synergistic extraction.

In this paper, we consider the role of hydration and solvation in the extraction of several systems.

EXTRACTION OF MAa_n^o

An extracting ligand that has been studied extensively is acetylacetone, Aa, the simplest bidentate ß-diketone. Consider the reaction

$$MAa_{n(a)} = MAa_{n(o)}$$

where Aa = acetylacetonate and n = charge of the metal cation M^{n+}. Table 1 lists the thermodynamic values for this extraction reaction (denoted by the partition constant P) for several metal ions.

The extraction of $BeAa_2$ is entropy driven; i.e., $T\Delta S_P > \Delta H_P$. Also, both ΔH_P and ΔS_P are positive which indicates that dehydration is the dominant factor in the extraction process. Since $BeAa_2$ is coordinately saturated (tetrahedral, CN = 4), the dehydration cannot be due to loss of H_2O from the metal ion. For such systems, it has been proposed by Allard et al. (1979) and by Narbutt (1981) (1,2) that the $MAa_{n(a)}$ is outer sphere hydrated via hydrogen bond interactions with the donor atoms of the acetylacetonate ligand. Extraction occurs with loss of this hydration. Another coordinately saturated complex is $CoAa_3$ (octahedral, CN = 6) and the positive values of ΔH_P and ΔS_P again can be attributed to the dominant role of the loss of outer sphere hydration from the complex upon extraction.

TABLE 1

Thermodynamic Extraction Data

$P = [MAa_{n(o)}]/[MAa_{n(a)}]$

I = 1.0 M ($NaClO_4$); T = 298 K

Species	Solvent	log P	ΔH_P ($kJ \cdot mol^{-1}$)	ΔS_P ($J \cdot K^{-1} \cdot mol^{-1}$)	Ref.
$BeAa_2$	Hexane	0.67	21	85	a
$ZnAa_2$	Benzene	0.48	47	168	b
$CoAa_3$	Heptane	-1.09	53	156	c
$ThAa_4$	Hexane	1.49	68	255	b

[a] Narbutt (1981)
[b] Allard et al. (1979
[c] Narbutt (1990)

$ZnAa_2$ is probably not coordinately saturated but most likely has an octahedral structure with 2 molecules of water bound to the zinc (inner sphere hydration). There may also be some outer sphere hydration. Upon extraction, both the inner and outer sphere hydration is lost and the resultant positive ΔH_P and ΔS_P values are larger than for $BeAa_2$ and comparable to the values for $CoAa_3$ extraction. Th(IV) has CN = 9 or 10 and the thenoyltrifluoroacetone complex $Th(TTA)_4$ was found to have 2 inner sphere waters of hydration by

Caceci, et al. (1985). Therefore, we assume that the analogous $ThAa_4$ also is dihydrated. Like the TTA complex, the $ThAa_4 \cdot (H_2O)_2$ is extracted without loss of the two inner sphere water molecules although the outer sphere hydration is lost. Moreover, since there are 4 ligands about the cation, we expect the outer sphere hydration in the aqueous phase to be greater than for MAa_2 or MAa_3 complexes. This is consistent with the large positive values of ΔH_p and ΔS_p in Table I. It is also reasonable that the extracted $ThAa_4(H_2O)_2$ would not be as solvated by the organic solvent as well as an anhydrous complex such as $CoAa_3$.

TABLE 2

Thermodynamic Data for the Reaction

$ML_{n(o)} + S_{(o)} = ML_n \cdot S_{(o)}$

$\beta = [ML_n \cdot S]/[ML_n][S]$

Metal	log β	ΔH(kJ·mol^{-1})	ΔS(J·mol^{-1}·K^{-1})
	A. L = TTA; S = TBP; Benzene		
UO_2^{2+}	5.10	- 9.3	67
Nd^{3+}	4.37	- 0.1	84
Th^{4+}	4.94	-14.4	46
	B. L = TTA; S = TOPO; Benzene		
UO_2^{2+}	7.05	-19.4	70
Nd^{3+}	7.07	- 2.7	127
Th^{4+}	7.11	-25.2	52
	C. L = PMBP; S = TOPO; Nitrobenzene		
UO_2^{2+}	5.05	- 9.3	66
Nd^{3+}	4.76	+ 6.6	113
Th^{4+}	5.51	-24.1	24
	D. L = TTA; S = 15-C-5; Chloroform		
UO_2^{2+}	4.36	-38	-44
Eu^{3+}	5.78	-30	+ 9
Th^{4+}	5.46	-55	-80

ADDUCT FORMATION

Hydrated complexes such as $ThAa_4 \cdot (H_2O)_2$ are made more soluble in the organic phase by replacing the residual inner sphere water with a neutral organophilic adduct. Our laboratory has studied the thermodynamics of such adduct formation of metal ß-diketonates by

tributylphosphate, TBP, and trioctylphosphine oxide, TOPO, adducts. The metals were UO_2^{2+}, Nd^{3+} and Th^{4+} and the ligands were TTA (studied by Caceci et al., 1985) and 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5, PMBP (studied by Wang et al., 1986). The values obtained by direct calorimetric titration are listed in Table 2. These data are for the reactions:

$$UO_2L_2\cdot(H_2O)_{2(o)} + S_{(o)} = UO_2L_2\cdot S_{(o)} + 2H_2O_{(o)}$$

$$NdL_3\cdot(H_2O)_{3(o)} + S_{(o)} = NdL_3\cdot S\cdot H_2O_{(o)} + 2H_2O_{(o)}$$

$$ThL_4\cdot(H_2O)_{2(o)} + S_{(o)} = ThL_4\cdot S_{(o)} + 2H_2O_{(o)}$$

In all of these reactions, the number of hydrate waters released is the same. For the dehydration, the positive entropy contribution should be similar. The increased solvation of $ML_n\cdot S$ relative to ML_n is associated with a negative entropy contribution. The solvation should parallel the number of organophilic ligands; i.e., ThL_4S > NdL_3S > UO_2L_2S. However, the remaining hydration of $NdL_3\cdot H_2O$ would reduce the solvation. As a result, we see that the order is

$$+\Delta S: \quad ThL_4\cdot S < UO_2L_2\cdot S < NdL_3\cdot S\cdot H_2O$$

The enthalpy change of the solvation effect should follow this same sequence as the greater the solvation, the more negative the contribution to ΔH. Table 2 shows that the sequence is, indeed, the same as for ΔS:

$$+\Delta H: \quad ThL_4\cdot S < UO_2L_2\cdot S < NdL_3\cdot S\cdot H_2O$$

In summary, the thermodynamic parameters support a model of metal ion extraction which is entropy driven as the large, positive ΔS of extraction overcomes the positive ΔH of extraction. Both in the extraction of ML_n^o and in the synergistic reaction to form $ML_n\cdot S$, the positive ΔS and ΔH values reflect the dehydration which accompanies the extraction and which has a greater effect on the ΔS and ΔH values than does the negative contributions from the solvation by the organic solvent.

CROWN ETHER ADDUCT

The effect of solvation can be reflected in the data on the extraction of the TTA complexes of UO_2^{2+}, Eu^{3+}, and Th^{4+} in which the

adduct is a crown ether rather than TBP or TOPO. C-13 and H-1 NMR spectra show that all the oxygens of the 15-C-5 crown ether are equivalently bonded in the $ML_n \cdot CE$ complex as shown by Mathur and Choppin (1990). The thermodynamic data for adduct formation ($ML_{n(o)} + CE_{(o)} = ML_n \cdot CE_{(o)}$) from that study are given in Section D of Table 2.

The 15-C-5 adduct is relatively large and would be expected to interfere with solvation. Addition of 15-C-5 to the ML_n complex, moreover, should provide relatively large negative contributions to the ΔH and ΔS values as there are 5 equivalent metal-oxygen interactions. By independent measurements (Karl Fisher titrations and Eu(III) fluorescent lifetime), we found that the $Th(TTA)_4$ loses 1 (hydrate) water, and the $Nd(TTA)_3$ loses 2 waters upon addition of the crown ether. As seen from Table 2, the net ΔH and ΔS values are quite negative (except ΔS for $Eu(TTA)_3$ for which, however, ΔS is positive but small) in contrast to the more positive values of the TBP reactions. The fact that the crown ether reactions are enthalpy driven reflects the strong effect of the five metal-oxygen interactions of the crown ether complex which overwhelms the opposing contribution from dehydration. These data serve to indicate the relative weakness of the effect of the organic solvent solvation in solvent extraction. The crown ether interaction has a stronger net effect than does the dehydration but dehydration, in turn, has a greater thermodynamic role than does solvation by the organic solvent.

EFFECT OF ELECTROLYTE CONCENTRATION

The preceding discussion reviewed the data supporting a model in which outer sphere dehydration can play a major role in the thermodynamic changes associated with metal ion extraction. Such outer sphere hydration should be sensitive to the concentration of a background electrolyte whose ions would compete for the water molecules. As the salt concentration increases, there would be less water available for hydration of the extractable species and solubility in the aqueous phase can be expected to decrease. This would result in greater extraction.

Such a "salting out" effect was seen in the variation of the distribution coefficient of radon between $NaClO_4$ solution and CCl_4 by Sekine (1969). Figure 2 shows that log D increases regularly as the molality of the $NaClO_4$ increases. Since Rn is neutral, the hydration of Rn would resemble, to some extent, the relatively weak outer sphere hydration of neutral metal species. A second example in

Figure 2 is the curve for $UO_2(TTA)_2$ extraction (Zolotov, 1970). This species extracts as the dihydrate over the range of $NaClO_4$ concentrations so the variation of log D with the concentration of $NaClO_4$ primarily reflects changes in outer sphere hydration. Again, for concentrations up to 9 m $NaClO_4$, the extraction increases regularly.

The curve for the variation of log D for the extraction of $Am(DEHP)_3 \cdot (HDEHP)_3$ was found to be more complex by Rosta (1987). The initial decrease represents the effect of the exchange reaction

$$Am^{3+}_{(a)} + 3(NaHDEHP)_{2(o)} = Am(DEHP)_3(HDEHP)_{3(o)} + 3Na^+_{(a)}$$

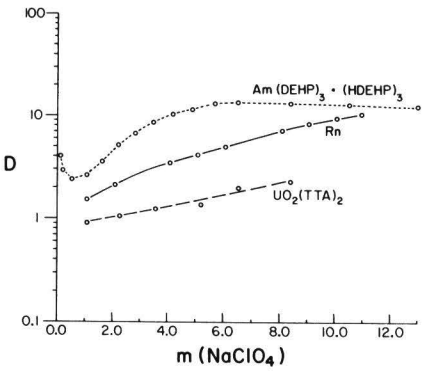


Figure 2. Variation of log D (D = distribution coefficient) as a function of the molality of aqueous $NaClO_4$ solution.

As $[Na^+]$ increases, the equilibrium shifts to the left and log D decreases. At higher concentrations of $NaClO_4$, the salting out effect dominates and log D increases with $NaClO_4$ concentration. As the concentrations further increase, the log D shows a slight decrease. This last trend may reflect the reaction

$$Am^{3+}_{(a)} + 3(NaDEHP)_{3(o)} = Am(DEHP)_3(NaDEHP)_{3(o)} + 3Na^+$$

since the $Am(DEHP)_3(NaDEHP)_3$ species would have a lower solubility in the organic phase than the $Am(DEHP)_3(HDEHP)_3$. Alternately, it could also reflect the increasing competition of complexing by perchlorate in the aqueous phase which was reported by Baisden et al. (1972). Nevertheless, between 1m and 5m $NaClO_4$, the extraction constant does show the effect of salting out as the outer sphere hydration is decreased.

SUMMARY

The extraction of metal ions is affected by many properties of the aqueous and the organic phases. In this paper, the influence of outer sphere hydration on the extracting species is discussed. The thermodynamics (ΔH and ΔS of extraction) of neutral acetylacetonate species, MAa_n^o, are characterized by large positive values which can be attributed to the loss of outer sphere hydration upon extraction contributing more strongly than organic phase solvation. Synergistic reactions involving addition of an adduct to the extracted species in the organic phase which have smaller positive ΔS values positive or slightly negative values of ΔH have been discussed. These reactions have no outer sphere dehydration and the ΔH and ΔS values reflect the effect of replacement of the residual inner sphere hydration by an organophilic adduct. When the crown ether 15-C-5 is the adduct, the ΔH and ΔS values are larger and negative, reflecting the effect of "solvation" by the crown ether. As the concentration of background electrolyte increases, the competition for the water by the salt reduces the outer sphere hydration and increases the extraction.

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ROLE OF THE INTERFACE IN SOLVENT EXTRACTION PROCESSES

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ABSTRACT

This paper reviews our investigation of the role of the interface by means of several new methods developed or extended in our Laboratory during the last decade.

Starting as a somewhat controversial topic mainly of interest to those examining the kinetic aspects of solvent extraction processes involving extractants of hydrometallurgical interest, the role of the interface in such extractions has emerged as a justifiably major concern, not only to extractionists, but to all those concerned with liquid-liquid transfer processes. Over the past decade, prompted by our growing interest in the interface, we have developed a number of interesting new ways to elucidate the role of the interface, some of which will be described here.

An automated solvent extraction apparatus was developed [1], of which a microporous teflon phase separator (MTPS) is a key element. With the MTPS, bulk organic phase is cleanly separated from a fine dispersion of the two phases in the flask, circulated through a spectrophotometric flow cell, and returned. With use of this apparatus, we are able to characterize species possessing interfacial activity by the observation of decrements in absorbances of ligands and chelates which occur on stirring. With such observations, together with the use of interfacial tension measurements, we are now able to interpret the variation of rates of extraction with stirring speed [2].

Using this approach, we have evaluated the role of the interface in the extraction kinetics of nickel with selected 8-quinolinols [3]. Rates of reaction were measured as a function of specific interfacial area (interfacial area per unit volume of the organic phase) over a range of pH values to learn how the ratio of neutral to ligand anion would affect the balance between the two possible pathways (bulk and interfacial). The results are well explained by a scheme which allows for three distinct concurrent reaction

pathways: Path 1: Reaction between metal and neutral ligand in the bulk aqueous phase. Path 2: Reaction of metal with ligand anion in the bulk aqueous phase. Path 3: Reaction of metal and ligand anion in the interface.

FORMATION AND DISTRIBUTION OF CHELATES IN MICELLES

Unfortunately, the high speed extraction apparatus does not give us access to particle sizes significantly below 100 - 200 microns or to specific interfacial areas (area/volume) above 300 cm^{-1}, at which point extraction rates are still rising proportionately with area. The fundamental question of whether further increases in the interfacial area would result in still faster rates could not be resolved. We therefore turned to micelles and microemulsions with particle sizes in the range of 0.001 - 0.1 microns, which should be excellent model systems with which to address this question. Extrapolating the results of the high speed stirred extraction system to micelles and microemulsions where the interface is saturated with the ligand, we might expect huge increases in metal complexation rates, because the latter systems possess much higher interfacial areas.

Our interest in micelles also stems from the existence of two opposite interpretations of metal complexation reaction kinetics in micellar media. These have been interpreted by some in terms of a distribution model based on the analogous solvent extraction system without considering adsorption a noteworthy factor [4], and by others who consider interfacial adsorption to comprise the major influence [5,6]. We initiated this study, therefore, hoping to help resolve this controversy and learn more about the role of the interface in chelate extraction kinetics.

The kinetics of the oxine complexation of Ni^{2+} was studied in the various micelles under pseudo-first order conditions at 25° C in the pH range 6.5 - 9 and ionic strength 0.1 using the stopped-flow technique [7]. All the relevant equilibrium constants were determined independent of kinetic measurements in order to reliably test the distribution model for kinetics in neutral, cationic and anionic micellar media. A number of interesting conclusions result:

1. The distribution constant for the neutral oxine is similar in the neutral, anionic and cationic micelles, as well as its value between water and hydrocarbon solvents,

indicating that the environment of oxine in the three types of micelle is hydrocarbon-like.

2. The protonated oxine ion pairs with cationic micelles and the oxine anion with cationic micelles. This ion pairing explains the differences in the Δ pK values observed between neutral and charged micelles. It also accounts for the difference in the rate constants for the oxine anion in neutral micelles and cationic micelles.

3. The distribution model explains the micellar kinetics while the adsorption model does not. The complexation reaction occurs by concurrent pathways involving both the neutral oxine and its anion in bulk water and the bulk micelle. The rate constants for the neutral oxine show little variation between bulk water and bulk micelle, while the oxine anion reacts faster in the neutral micelles.

Although we have not found any evidence of interfacial involvement with micelle systems to date, probably because the micellar concentrations of extractants are so low, currently we are investigating microemulsion systems which permit much larger concentrations, and hope to be able to report on this work in the near future.

EXAMINATION OF L-L FILMS BY FT/IR-ATR

We have also developed the use of a hydrocarbon film supported on an infrared attenuated total reflection (IR/ATR) internal reflection element (IRE), in contact with aqueous solutions, as a model for hydrocarbon/water interfaces [8]. This technique promises to provide molecular level information for the L-L interface, such as in studies of diffusion, partition, and adsorption in L-L systems.

We been able to obtain surface excess values, Γ, for adsorption of cetylpyridinium chloride (CPC) at the hydrocarbon/aqueous interface as well as to conduct kinetic studies of metal chelation and extraction at the interface. A hydrophobic chelation reagent, dodecylsalicylaldoxime (HDSA), was incorporated into an aliphatic hydrocarbon liquid film (Apiezon M or ApM). Direct observation of the extraction of aqueous Cu^{2+} and Ni^{2+} into the film gave a measure of the diffusion coefficients within the hydrocarbon film and kinetics of the extractions. An estimate (lower limit) of diffusion coefficients in ApM was made from the Cu^{2+} + HDSA/ApM reaction rates, which lie in the regime of diffusion in liquids. If the diffusion coefficient, D, were inversely proportional to

viscosity, and if D in water were 5 x 10^{-6}, estimating the viscosity of ApM at 2.6 x 10^{6} cp, the expected D in ApM would be 2 x 10^{-12}. The time required for a diffusion boundary to progress completely through the film would, thus, be 140 s, with the reaction being essentially complete in perhaps 500 s. Using Cu^{2+}, however, complete reaction of the HDSA within the film occurred in less than 1 m (minimum spectral acquisition time 45s), suggesting that a typical D within the ApM film is closer to 2 x 10^{-11}. Solid-like diffusivity would have required much more time. The aqueous mass transport of Cu^{2+} to the interface was not rate-limiting; the time required for the diffusion from 0.001 M aqueous Cu^{2+} solution to the ApM/HDSA film surface, of sufficient Cu^{2+} to completely react with all the HDSA, was calculated from the Cottrell equation as 2 micro seconds.

The reactions of HDSA in ApM films with Ni^{2+} had half-reaction times of 3-20 minutes. The absorbance vs. time data for HDSA/ApM + Ni^{2+} extraction was analyzed using a pseudo-first order in $[Ni^{2+}]$.

It is interesting that, despite the absence of stirring in the ATR cell, the observed rate for Ni^{2+} extraction could be quantitatively predicted from that found by Akiba and Freiser [9] in a similar extraction system using heptane/water and the high speed stirring apparatus. The small thickness of the ApM phase eliminates diffusion limiting effects, as the high speed stirring does. The ATR technique is thus an improvement over the widely used but flawed Lewis cell, which also features a constant interfacial area.

Previous understanding of the mechanisms of L-L interfacial reactions has lacked details of both interfacial speciation and reactant configuration. This method allows examination of L-L interfaces at the molecular level. We are pursuing additional systems similar to HDSA/ApM/Ni^{2+}, and have obtained preliminary ATR evidence of unusual configuration changes in adsorbed ligand molecules. This type of change is a promising probe of the unique chemical environment existing at liquid-liquid interfaces.

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MODEL INTERFACIAL SYSTEM FOR SOLVENT EXTRACTION STUDIES

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ABSTRACT

As a model interfacial system for the solvent extraction of metal ions, spread monolayers of dihexadecyl phosphate (DHDP) at the heptane/water (aqueous solution of metal salts) interface have been studied experimentally by the Brooks' frame technique. DHDP was observed to form a relatively stable monolayer under certain conditions. Interfacial pressure-area (π-A) isotherms of DHDP monolayers at the interface of heptane/aqueous metal chloride solution of sodium, calcium, or nickel show a general expanded/condensed phase transition. The possibility of surface micelle formation and its role in the solvent extraction of metal ions are briefly discussed.

INTRODUCTION

Adsorbed monomolecular films of di(2-ethylhexyl)phosphoric acid (HDEHP) at the n-hexane/water interface have been investigated extensively (Gaonkar and Neuman, 1987) in conjunction with equilibrium metal distribution and extraction kinetics studies (Gaonkar and Neuman, 1986, 1989). On account of the difficulty of evaluating the interfacial chemical composition, studies of spread films at the nonpolar organic/water interface should be of great value in understanding the interfacial behavior of extractant molecules and their interactions with metal ions. This is so because the quantitatively spread films offer the advantage of a well-defined and well-controlled interfacial system. However, quantitative spreading of HDEHP at the nonpolar organic/water interface is difficult due to its high solubility. Nevertheless, long-chain alkylphosphates which are capable of forming "insoluble" monolayers at the nonpolar organic/water interface can be regarded as model extractants, so that a systematic study should identify to what extent various molecular parameters influence the structure and properties of the interfacial film. A comparison of the adsorbed extractant HDEHP and spread alkylphosphate film at the nonpolar organic/water interface is illustrated in Fig. 1.

Interfacial pressure-area (π-A) isotherm measurements at the liquid/liquid interface are more difficult than those typically performed at the air/water interface in two respects: First, the Brooks' frame and barriers must be made hydrophobic properly to effect a working area without leaks between the barriers and the frame edges. Secondly, a most critical

technique is the preparation of a hydrophobic Wilhelmy plate. Furthermore, in such measurements, the spread film must be relatively stable upon compression. The film stability of alkylphosphates depends on several factors including the molecular structure as well as the pH and metal ions present in the aqueous phase. A longer hydrocarbon chain in the molecule prevents desorption into the aqueous phase, but favors, on the other hand, solubility in the organic phase. Among various alkylphosphates, dihexadecyl phosphate (DHDP) has been screened as a model compound for acidic organophosphorus extractants through a preliminary effort to examine the stability of spread films at the heptane/water interface. The purpose of this communication is to present recent results on the π-A isotherm of DHDP at the heptane/water (aqueous solution of metal salts) interface.

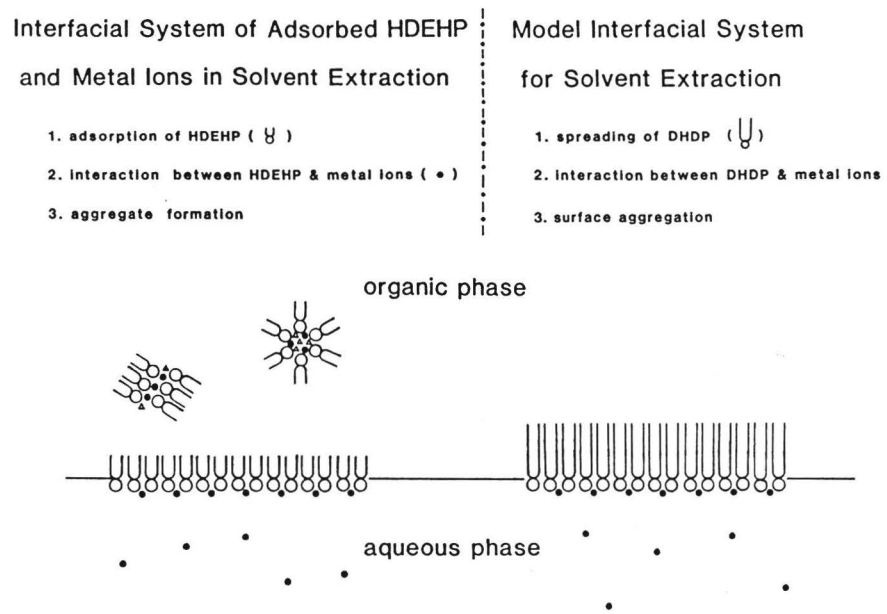


Fig. 1. Schematic illustration comparing adsorbed and spread films at the nonpolar organic/water interface.

2 EXPERIMENTAL MATERIALS AND METHODS

DHDP (Alfa, 99.4%) was used as received for preliminary measurements. The sample of DHDP was also purified by recrystallization five times from chloroform. The heptane (Fisher) was doubly distilled. The water from a

Millipore reverse osmosis/Super Q system was redistilled twice, whereby the first-stage distillation was from alkaline permanganate solution. The inorganic metal salts were ultra-high or high purity grades.

The interfacial pressure of the spread film at the heptane/water interface was measured using the Brooks' frame method (Brooks and Pethica, 1964; Mingins and Taylor, 1974) to vary the film area by compression and a Cahn Model 2000 electrobalance to measure the force acting on a hydrophobic carbon black-coated platinum Wilhelmy plate.

3 RESULTS AND DISCUSSION

The stability of spread DHDP films was first examined. Generally speaking, when DHDP is spread at the interface between heptane and an acidic or alkaline aqueous phase, it is unstable. Desorption into the organic phase apparently takes place as a result of increased solubility of the DHDP molecules. When divalent metal ions are present in the aqueous phase, the interfacial pressure changes in a complicated manner due to the interfacial chemical reaction between metal ions and DHDP, which is strongly dependent on the metal salt concentration and subsolution pH.

The π-A isotherms obtained by continuous compression of the spread DHDP film at the heptane/water (aqueous chloride solution of sodium, calcium, or nickel) interface are shown in Figs. 2-4. The general feature of a phase transition from an expanded state to a condensed state is evident in the π-A isotherms. Also, the purity of DHDP markedly affects the π-A isotherm, e.g., the higher the purity, the less the non-zero slope of the π-A isotherm across the transition region.

In the case of the system heptane/0.01 M NaCl solution, as shown in Fig. 2, the expanded/condensed phase transition does not appear to be a first-order transition but instead it has non-zero slope. When the film was subjected to further compression, the π-A isotherm gave a lower limiting area due to presumed film losses. On the other hand, a relatively stable spread film was formed at the heptane/0.01 M $CaCl_2$ solution interface. As shown in Fig. 3, although the expanded/condensed transition approaches that of a first-order phase transition, there still remains a small but finite slope. On the other hand, the DHDP film spread at the heptane/0.01 M $NiCl_2$ solution interface desorbed to a larger extent after repeated compression. Figure 4 illustrates the π-A isotherm obtained during the first compression. Since the limiting area is very close to that (0.42 nm^2/molecule) of the stable DHDP film, any errors in the measurement of the π-A isotherm due to film losses may not be too serious. Although the expanded/condensed transition appears to be first order, there is the possibility that it may be an artifact due to small film losses during the compression process.

It has been argued in the literature (Mingins et al., 1982) that the first-order-like transition observed for phospholipid monolayers at the heptane/water interface is indeed a second-order transition. One possible explanation advanced for the non-zero slope of the π-A isotherm across the transition region is that the film molecules via surface micelle formation undergo a transition to a close-packed condensed state.

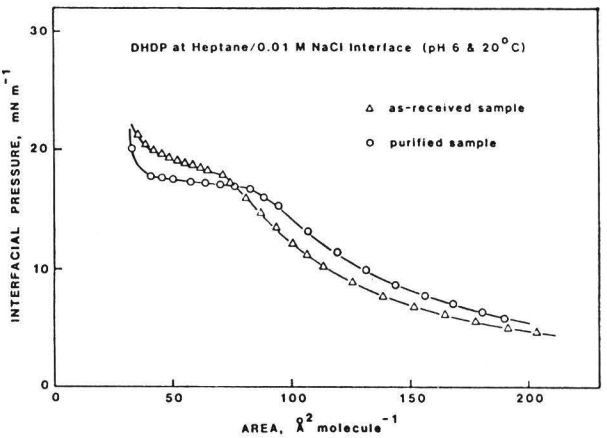


Fig. 2. π-A isotherms of DHDP at the heptane/0.01 M NaCl solution interface at 20°C.

This proposition also seems applicable to our model interfacial system, namely, the spread DHDP film, and may help explain the mechanism of the formation of reversed micelles which promote the mass transfer of metal ions from the aqueous to organic phase in acidic organophosphorus extraction systems (Neuman et al, 1990). Support for this hypothesis comes from recent electron microscopic observations on surface aggregates of the calcium salt of HDEHP (Gaonkar et al., 1986). Furthermore, the observed instability of the DHDP film at the heptane/aqueous $NiCl_2$ solution interface also may be significant to solvent extraction and is under further investigation.

The prerequisite experimental apparatus and techniques to study model extractants which can be spread as "insoluble" monolayers at the liquid/liquid interface have been developed. Thus, the Brooks' frame technique will be used in conjunction with advanced laser techniques (see Table 1) in future work to characterize the structure and dynamics of the liquid/liquid interface in solvent extraction systems (Neuman, 1986).

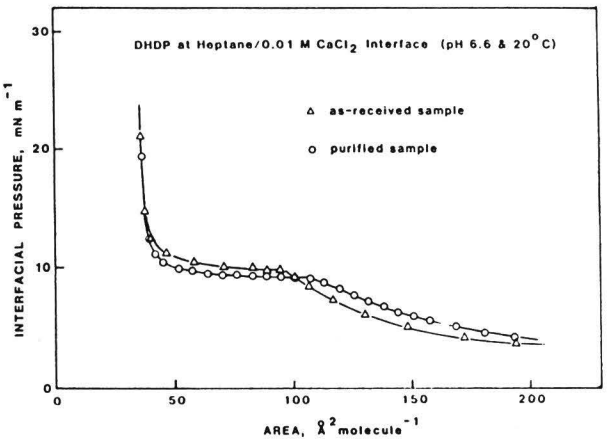


Fig. 3. π-A isotherms of DHDP at the heptane/0.01 M $CaCl_2$ solution interface at 20°C.

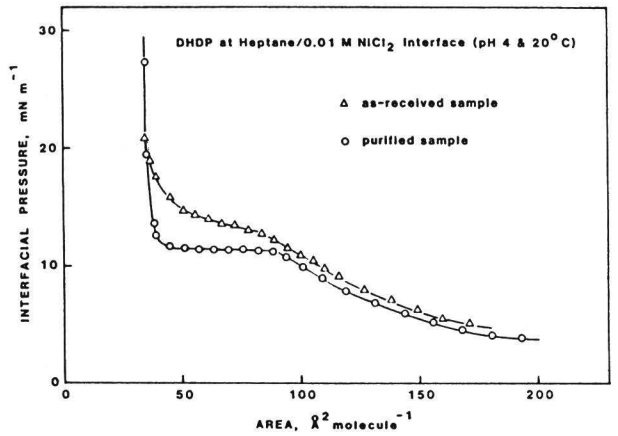


Fig. 4. π-A isotherm of DHDP at the heptane/0.01 M $NiCl_2$ solution interface at 20°C.

Table 1

Advanced laser techniques applicable to liquid/liquid interfaces.

Technique	Information
Laser heterodyne light scattering	Interfacial tension Interfacial viscoelasticity
Laser fluorescence	Surface (lateral) diffusivity Phase behavior (microhomogeneity) Microviscosity/fluidity Aggregation number
Second harmonic generation	Molecular orientation Time-dependent phenomena Interfacial chemical reactions

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EFFECTS OF TEMPERATURE ON THE SOLVENT EXTRACTION OF DIVALENT METAL COMPLEXES WITH 8-QUINOLINOL AND ITS DERIVATIVES

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ABSTRACT

The effects of temperature on the extraction of zinc(II), cadmium(II), cobalt(II) and nickel(II) complexes with 8-quinolinol and its derivatives such as 2-methyl-8-quinolinol and 7-(1-vinyl-3,3,6,6-tetramethylhexyl)-8-quinolinol(Kelex 100) between water and several organic solvents were investigated with regard to the extraction mechanism. The organic solvents used were 1,1,2,2-tetrachloroethane(TCE), 1-octanol and p-xylene. The thermodynamic parameters for the distribution of these complexes were determined. It has been proved that the degree of temperature effects on the distribution ratios of these complexes substantialy depends on those extraction mechanism. Moreover, zinc can be separated from cadmium at high temperatures using 2-methyl-8-quinolinol and TCE.

1 INTRODUCTION

In recent years, a number of studies have been carried out concerning the various factors affecting the solvent extraction of a metal chelate. A few thermodynamic studies have been carried out. In these studies, however, measurements were conducted in the low-temperature region, below 50°C, since volatile organic solvents, such as chloroform and benzene were used. As previously reported,[1-3] we studied the temperature effects on the extraction of 8-quinolinol, itself, and its metal chelates into several organic solvents whose boiling points are relatively high over the temperature range 10 to 90°C.

In this study the effects of temperature on the extraction of zinc(II), cadmium(II), cobalt(II) and nickel(II) complexes with 2-methyl-8-quinolinol[4] and 7-(1-vinyl-3,3,6,6-tetramethylhexyl)-8-quinolinol(Kelex 100) between water and several organic solvents were investigated compared with those obtained with 8-quinolinol. The organic solvents used were 1,1,2,2-tetrachloroethane(TCE), 1-octanol and p-xylene.

2 EXPERIMENTAL

A 30ml of a buffered solution containing metal ion was stirred with a 10ml of 8-quinolinol or its derivative solution of organic solvents standing in a constant-temperature bath for 30min (24hr for nickel with Kelex 100). The pH of the initial aqueous solution was adjusted to the desired value with a small amount of acetic-acetate buffer solution. Also, ionic strength of the aqueous solution was adjusted to 0.1 with sodium salts. After equilibrium, the metal concentration of both phases were determined with a single-channel pulse-height analyzer for zinc, an atomic absorption spectrophotometer for cadmium, and X-ray fluorescence spectrometer for nickel and cobalt, respectively.

3 RESULTS AND DISCUSSION

3.1 Extraction of metal complexes of 8-quinolinol(HQ) or 2-methyl-8-quinolinol(HR) into organic solvents in the presence of inorganic anions.

In the case of TCE, the extraction equilibrium of zinc, cadmium and cobalt can be written as follows(except for that of zinc with 2-methyl-8-quinolinol):

$$2M^{2+} + 6HQ_{(o)} + X^- \rightleftharpoons M_2Q_3(HQ)^+_{3(o)} + X^-_{(o)} + 3H^+ \qquad (1)$$

where X^- refers to inorganic anions such as perchlorate, nitrate, and chloride ions. An ion-pair of the binuclear complex(complex ion pair) dissociates into a complex cation and an inorganic anion in the organic phase. The results of conductivity measurements also endorse the dissociation of complex ion pair in TCE. However, the extraction behavior of zinc-2-methyl-8-quinolinol chelate into TCE is unlike the case of the other metals. In this case, zinc is extracted as an anhydrous complex, such as ZnR_2.

Plots of log D vs. 1/T for zinc and cadmium with 8-quinolinol in the presence of perchlorate and chloride ions are shown in Fig.1. The distribution ratios decrease remarkably with an increase in temperature. Fig.2 shows the plots of log D vs. 1/T for zinc and cadmium with 2-methyl-8-quinolinol. In the case of cadmium, the distribution ratios decrease remarkably with an increase in temperature. The trend is similar to those for zinc and cadmium chelates of 8-quinolinol into TCE. However, in the case of zinc, the distribution ratios increase with an increase in

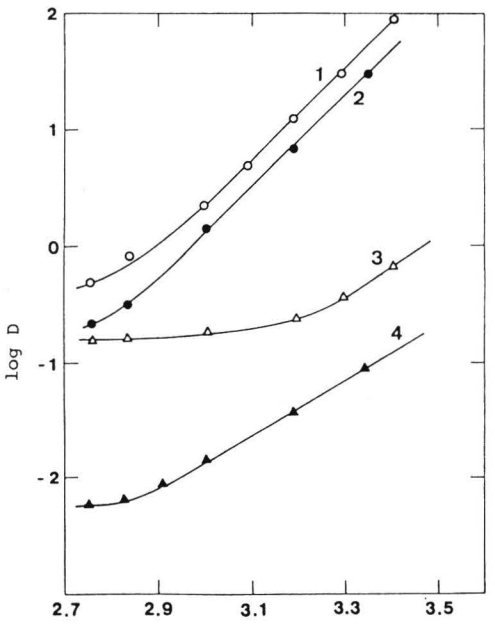


Fig.1

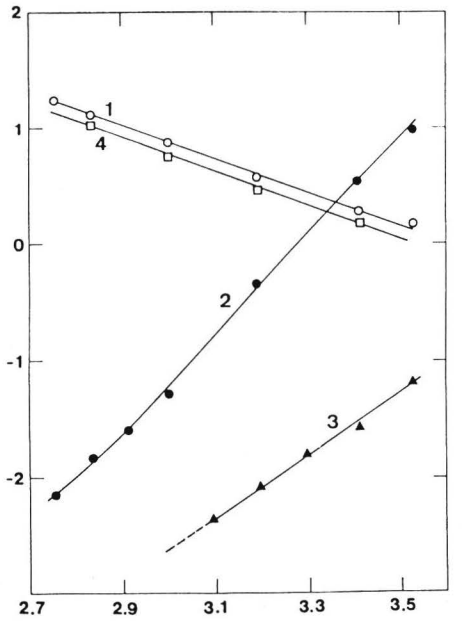


Fig.2

Fig.1 Effects of temperature on the distribution ratio of zinc and cadmium with 8-quinolinol between TCE and water.
pH 5.0, 1;Zn, $NaClO_4$ system, $[HQ]_o=2X10^{-2}M$, 2;Cd, $NaClO_4$ system, $[HQ]_o=10^{-1}M$, 3;Zn, NaCl system, $[HQ]_o=2X10^{-2}M$, 4; Cd, NaCl system, $[HQ]_o=10^{-1}M$.

Fig.2 Effects of temperature on the distribution ratio of zinc and cadmium with 2-methyl-8-quinolinol between TCE (or p-xylene) and water.
pH 5.5, solvent=TCE, 1;Zn, $[HR]_o=5X10^{-2}M$, 2;Cd, $NaClO_4$ system, $[HR]_o=10^{-1}M$, 3;Cd, NaCl system, 4; solvent=p-xylene, Zn, $[HR]_o=2X10^{-1}M$.

temperature. The opposite effect is noted in the cases of cadmium and zinc with 2-methyl-8-quinolinol. These results indicate that the difference in distribution ratios of zinc and cadmium can be enhanced at high temperatures. Hence, solvent extraction with 2-methyl-8-quinolinol at high temperatures can be applied to the separation of zinc and cadmium in aqueous samples.

In the 1-octanol(S) extraction system, zinc and cadmium are extracted as solvent-adducts, such as $MQ_2 \cdot S_2$. The distribution ratios are almost constant with a change in temperature.

In the p-xylene extraction system, a hydrated metal complex, $MQ_2 \cdot 2H_2O$, may precipitate and be deposited at the interface of both phases, except for the extraction of zinc with 2-methyl-8-quinolinol. The zinc complexes of 2-methyl-8-quinolinol are extracted into p-xylene as anhydrous complexes similar to those into TCE.

3.2 Extraction of metal complexes of Kelex 100(HK) into chloroform

The behavior of the extraction of copper, cobalt, nickel and zinc with Kelex 100 into chloroform was studied at various temperatures. The extracted species can be expressed as simple 1:2 chelates, CuK_2 and NiK_2, whereas self-adduct complexes, $CoK_2(HK)_2$ and $ZnK_2 \cdot HK$.

The extraction constants of copper are almost constant with a change in temperature. In the case of cobalt and zinc, those slightly increase with an increase in temperature. While, the nickel complexes of Kelex 100 may be extracted as anhydrous complexes because the extraction constants of nickel increase with an increase in temperature.

3.3 Thermodynamic parameters

The thermodynamic parameters for the distribution of 8-quinolinol and 2-methyl-8-quinolinol between organic solvents and water were determined. In all cases the ΔH values are negative and the ΔS values are positive. Hence, the fact that 8-quinolinol and 2-methyl-8-quinolinol are more soluble in organic solvents such as TCE, p-xylene and 1-octanol than in water is due to the favorable contributions of both enthalpy and entropy.

The thermodynamic parameters for the extraction of zinc, cadmium and cobalt with 8-quinolinol and 2-methyl-8-quinolinol into TCE, p-xylene, and 1-octanol are summarized in Table 1. In a series of the ion-associated complexes of zinc, cadmium, and cobalt, the values of ΔH are largely negative, which shows that the extraction of the complex ion pair is an exothermic reaction. The larger is the size of an inorganic anion or metal ion (Co^{2+} 0.72A, Zn^{2+} 0.74A, Cd^{2+} 0.97A), the larger is the absolute values of ΔH. The values ΔS are also largely negative and proportional to

those of ΔH in the ion-associated complex series of metals and inorganic anions. This is generally the trend observed in the thermodynamics of ion-pair extraction, indicating that the exothermic property is partly compensated with the term of ΔS. On the other hand, the extraction of zinc with 2-methyl-8-quinolinol into TCE and p-xylene is an endothermic reaction. It has been reported that this behavior is characteristic of chelating reactions in which the water molecules of the inner-coordination sphere of the metal ion are displaced by the chelating reagent.

TABLE 1

Thermodynamic values for extraction of Zn(II), Cd(II) and Co(II) with 8-quinolinol and 2-methyl-8-quinolinol into TCE, p-xylene and 1-octanol at 20°C

Ligand	Solvent	Species	$\log K_{ex}$	ΔG	ΔH	ΔS
				$kJmol^{-1}$	$kJmol^{-1}$	$JK^{-1}mol^{-1}$
	TCE	$Zn_2Q_3(HQ)^{+}_{3}ClO_4^{-}$	-0.66	3.70	-153	-535
8-Quinoli-	TCE	$Zn_2Q_3(HQ)^{+}_{3}Cl^{-}$	-4.70	26.4	-95.4	-416
nol	p-Xylene	Precipitated	-	-	-	-
	1-Octanol	$ZnQ_2 \cdot S_2$	-	-	0	-
2-Methyl-	TCE	ZnR_2	-8.10	45.4	33.5	-40.6
8-quinoli-	p-Xylene	ZnR_2	-9.42	52.8	33.5	-65.9
nol	1-Octanol	$ZnR_2 \cdot S_2$	-	-	0	-
	TCE	$Cd_2Q_3(HQ)^{+}_{3}ClO_4^{-}$	-5.57	31.2	-169	-683
8-Quinoli-	TCE	$Cd_2Q_3(HQ)^{+}_{3}Cl^{-}$	-10.33	58.0	-108	-567
nol	p-Xylene	Precipitated	-	-	-	-
	1-Octanol	$CdQ_2 \cdot S_2$	-	-	0	-
2-Methyl-	TCE	$Cd_2R_3(HR)^{+}_{3}ClO_4^{-}$	-8.92	50.0	-163	-727
8-quinoli-	TCE	$Cd_2R_3(HR)^{+}_{3}Cl^{-}$	-13.27	74.4	-106	-606
nol	p-Xylene	Precipitated	-	-	-	-
	1-Octanol	$CdR_2 \cdot S_2$	-	-	0	-
8-Quinoli-	TCE	$Co_2Q_3(HQ)^{+}_{3}ClO_4^{-}$	0.98	-5.59	-137	-441
nol	TCE	$Co_2Q_3(HQ)^{+}_{3}Cl^{-}$	-2.5	14.3	-101	-387

TABLE 2

Thermodynamic values for extraction of Cu(II), Co(II), Ni(II) and Zn(II) with Kelex 100 into chloroform at 25°C

Species	$\log K_{ex}$ (or $\log K'_{ex}\ \beta_{n,o}$)	ΔG	ΔH	ΔS
		$kJmol^{-1}$	$kJmol^{-1}$	$JK^{-1}mol^{-1}$
CuK_2	1.15	-6.56	0	22.0
$CoK_2(HK)_2$	-4.70	26.8	26.5	0
NiK_2	-6.46	36.9	65.9	97.3
$ZnK_2 \cdot HK$	-7.70	43.9	22.0	-73.5

The thermodynamic parameters for the extraction of copper, zinc, cobalt and nickel with Kelex 100 are summarized in Table 2. These results suggest that temperature effects on the divalent metal complexes extracted as simple complexes or self-adduct complexes are smaller compared with those extracted as ion-pair complexes (complex ion pair).

3.4 Separation of zinc and cadmium at high temperatures

Fujinaga et al. have developed a method "Solid-liquid separation after liquid-liquid extraction" in which solid organic compounds are used as molten solvents in the high temperature at 80 to 90°C. Then, separation of zinc and cadmium at high temperatures were examined using molten solvents instead of TCE. As a result, it was found that zinc can be completely separated from cadmium at 80°C using 2-methyl-8-quinolinol and o-phenylphenol as a molten solvent.

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EXTRACTION OF EUROPIUM (III) BY TRIPHENYLARSINE OXIDE MIXED WITH SOME RELATED CHELATING AGENTS IN BENZENE FROM NITRATE MEDIUM

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ABSTRACT

Extraction of Eu(III) by triphenylarsine oxide mixed with the ß-diketones thenoyltrifluoroacetone (HTTA), 1,1,1- trifluoro-5,5-dimethyl - 2,4 - hexanedione (HPVTA) and hexa-fluoro - 2,4 - Pentanedione (HHFA) from aqueous nitrate media was investigated. It is found that europium is generally extracted as Eu $L_2.NO_3$ or Eu L_2. $(Ph_3AsO)_2$. NO_3 by different chelates (L)and their adducts, respectively. The logarithmic extraction constants for europium cationic chelate, K_{21}, the mixed extraction constant K_{212} and equilibrium constant of the adduct $ß_{212}$, were found to decrease linearly with the increase in the pKa values of the chelate ligand used. This is related to the competing action of NO_3^- extracted with europium species.

INTRODUCTION:

Enhancement in the extraction of trivalent actinides and lanthanides is well studied for many systems comprising β-diketones and different neutral oxygen donor ligands, Mathur (1983)and Ramakrishna and Patil (1984).The use of triphenylarsine oxide, Ph_3 AsO, as synergic ligand and the synergic extraction from nitrate medium are rather limited, Laskorin et al (1981).

Introducing a concept relating the extraction constants of the metal chelates or its adducts to each others or to the physochemical properties of the chelate needs more understanding Therefore, this manuscript is directed to investigate the extraction of Eu^{3+} by Ph_3 AsO mixed with selected β - diketones from nitrate medium to evaluate the synergic ability of Ph_3 AsO, the trends in the extraction constants of europium chelates and adducts in terms of the physicochemical properties of the different β- diketones investigated.

EXPERIMENTAL:

The chemicals and reagents employed were of AR grade and used without purification . The experimental extraction procedure was similar to that previously reported by Zakareia et al (1989). Unless otherwise stated, the ionic strength was 0.1 in NO_3^- , the extraction temperature was $25^{\circ}C \pm 2$ and benzene was used as diluent.

RESULTS AND DISCUSSION:

Slope analysis of the extraction of Eu^{3+} by the three β-diketones; 2-thenoyltrifluoroacetone (HTTA), 1,1,1- trifluoro-5,5 -dimethyl - 2,4 - hexanedione (HPVTA) and hexafluoro - 2,4 - pentanedione (HHFA) indicated that the extraction equilibrium from nitrate medium can be presented by

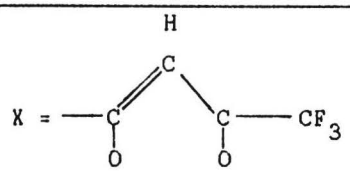
$$Eu^{3+} + NO_3^- + 2\ \overline{HL} \rightleftharpoons \overline{Eu\ L_2 .\ NO_3} + 2\ H^+$$

Where HL stands for the β - diketone.

The extraction constants (K_{21}) obtained for the different β - diketones are given in (Table 1).

TABLE 1: Different constants for the extraction system Eu(III)/β-diketones/triphenylarsine oxide/benzene/0.1 M sodium nitrate.

Different Constants	Chelating Agents *		
	HHFA F_3C-X	HTTA 	HPVTA $(CH_3)_3\ C-X$
pK_a^{**}	4.46	6.33	7.01
log K_{21}	- 1.15	- 3.88	- 4.91
log K_{212}	9.21	5.32	3.36
log β_{212}	10.36	9.20	8.27

X) 

* *) Taken from Stary and Freiser (1975).

The extraction constant sequence as retaled to the β-diketones studied is HHFA ›HTTA ›HPVTA. This sequence violate the general rule for chelate extraction where the stability constant of a metal chelate increases within a family of chelating agents as the proton affinity increases (increase in pKa).

The deviation in this trend observed can be related to the type of extracted species, where a cationic intermediate chelate of the type Eu L_2^+ is formed which is either coordinated or ion - paired with the nitrate ion.

Extraction of Eu^{3+} by Ph_3AsO mixed with the different β - diketones studied showed enhancement in the extraction of Eu^{3+}. Investigating different parameters affecting the synergic extraction followed by slope analysis of the experimental results, shown in Fig (1), indicated the following equilibrium for the extraction by mixed extractants from nitrate medium;

$$Eu^{3+} + NO_3^- + 2\,\overline{HL} + 2\,\overline{Ph_3AsO} \rightleftharpoons \overline{Eu\,L_2.(Ph_3AsO)_2\,NO_3} + 2\,H^+ \quad (1)$$

with extraction constant K_{212}

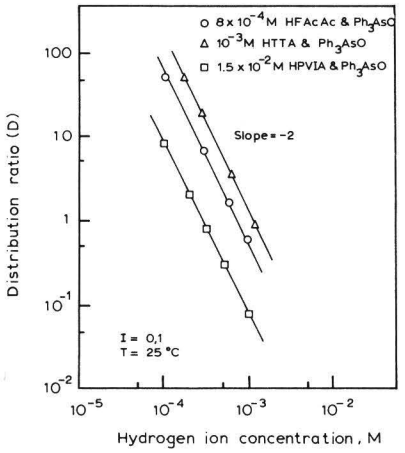
$$K_{212} = \frac{\overline{[Eu\,L_2.\,(Ph_3AsO)_2\,NO_3]}[H^+]^2}{[Eu^{3+}][NO_3^-]\overline{[HL]}^2\,\overline{[Ph_3AsO]}^2}$$

The formation constant, β_{212} ,of the adduct in the organic phase is given by the equilibrium

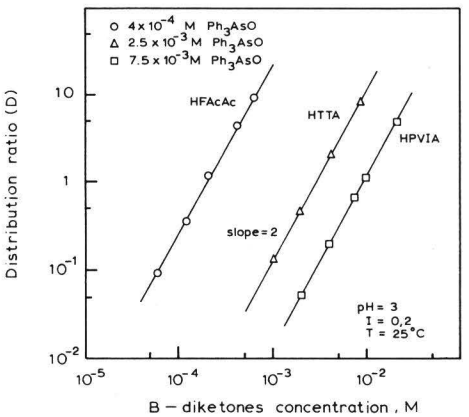
$$\overline{Eu\,L_2.\,NO_3} + 2\,\overline{Ph_3AsO} \rightleftharpoons \overline{Eu\,L_2.\,(Ph_3AsO)_2.\,NO_3} \quad (2)$$

with $B_{212} = K_{212}\ K_{21}^{-1}$

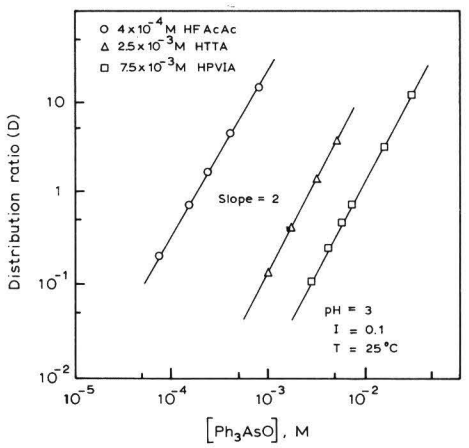
It is clear from table (1) that the values of K_{212} or β_{212} as related to the ß-diketones studied decrease in the order HFAcAc› HTTA› HPVTA. Extraction of nitrate anion with the extracted species was observed when Davis et al (1977) extracted some lanthanides by HTTA-TBP from nitrate medium. To disscuss this variations, previous concepts are consulted. In this concern, a general concept proposed by Irving (1967) and modified by Zolotov



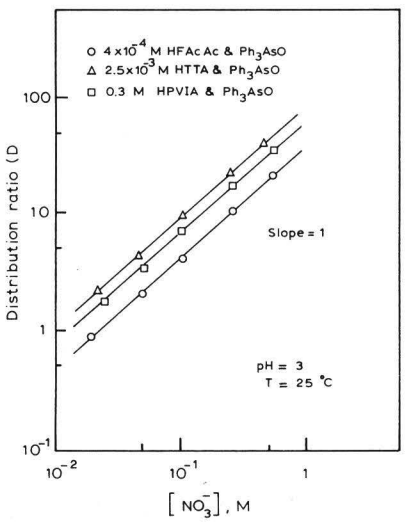
Effect of $[H^+]$ on the extraction of Eu^{3+} from nitrate medium



Extraction of Eu^{3+} by different B-diketones at constant $[ph_3AsO]$



Extraction of Eu^{3+} by constant $[HFAcAg]$ or $[HPVIA]$ and different $[Ph_3AsO]$



Effect of $[NO_3^-]$ on the extraction of Eu^{3+} by B-diketone and Ph_3AsO mixture in bezene

and Gavrilova (1969) is that the stronger the metal chelate formed, the weaker the adduct extracted. This was not obeyed in the present work, Table 1, and the reverse sequence was observed. Such trend can be related to the type of the chelate extracted, where europium cationic intermediate chelate is adducted by the neutral ligand and either coordinated or ion paired with the nitrate ion. Plotting log K and log ß values against pK_a of the different ß-diketones used gave a linear decrease with increasing pK_a, Fig.2. This can be related to the participation of the nitrate anion in the extracted species. In this respect, when the chelate ligand anion has a high tendency to associate with proton, formation of extracted species containing No_3^- is expected to be lower. However, further work is needed to extend this work to other β - diketones and to elucidate the contribution of the nitrate ion in the extracted species.

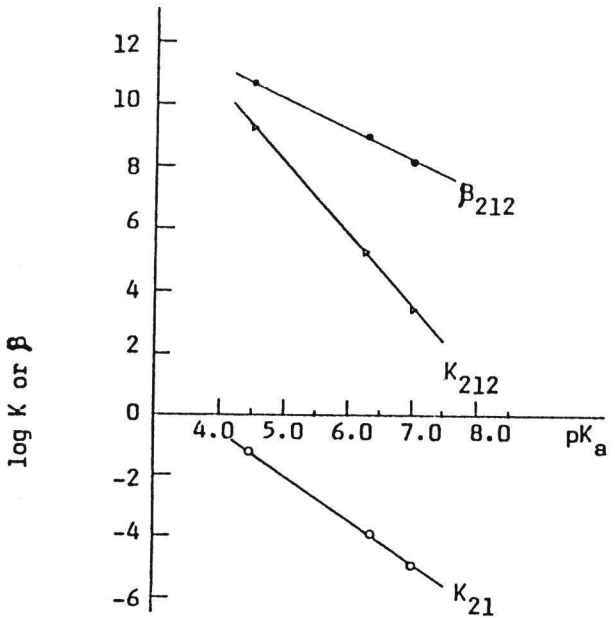


Fig.2 : Relation between pK_a of the chelating agents used and the respective extraction and equilibrium constants.

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CARBOXYLIC ACIDS AS SYNERGISTS IN LANTHANOID(III) EXTRACTION WITH β-DIKETONES

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ABSTRACT

Adduct formation of 2-thenoyltrifluoroacetonato(tta) lanthanum(III), europium(III), and ytterbium(III) with benzoic and phenylacetic acids having hydroxyl or methoxyl group at the ortho and the alpha positions has been studied by solvent extraction technique using radioactive tracers. It has been found that lanthanoid(III) chelates form more stable adducts with these carboxylic acids in the sequence : $La(tta)_3 > Eu(tta)_3 > Yb(tta)_3$, and also the difference of the extraction between a pair of metals as well as the extraction enhancement at a given acid concentration is the largest on using α-hydroxy carboxylic acid among these acids. The adduct formation of $Eu(tta)_3$ with several α-hydroxy carboxylic acids suggests that the formation constants are roughly proportional to pKa of the carboxylic acids.

INTRODUCTION

It has been reported(Hasegawa, et al. 1989a) that the stability constants of all lanthanoid(III) complexes with the carboxylate anions substituted with methoxyl or hydroxyl group at the ortho and the alpha positions as well as with benzoate and phenylacetate anions themselves are all similar except for α-hydroxy carboxylate anions. On the other hand, it has been reported (Hasegawa, et al. 1989b) that the formation constants of adducts of 2-thenoyltrifluoroacetonato(hereafter it is abbreviated as tta) lanthanoid(III) with benzoic and phenylacetic acids decrease with increase of the atomic number. The extraction equilibria of lanthanoids(III) with carboxylic acids and tta shown in Fig. 1 were analyzed in the present paper, to examine the effects of the position and the size of the side groups on the adduct formation in organic solvents.

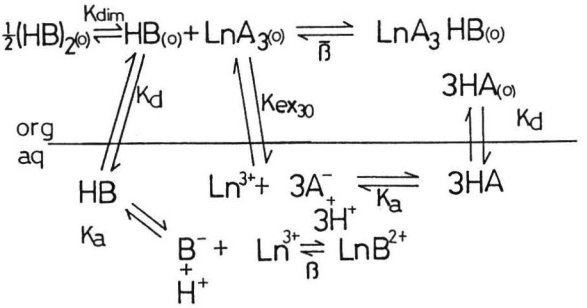


Fig. 1. Extraction equilibria of lanthanoid(III) with 2-thenoyltrifluoroacetone(HA) and carboxylic acids(HB).

EXPERIMENTAL

All the procedures were carried out in a similar way as described elsewhere (Hasegawa, et al. 1989b). The total anion concentration in aqueous solution was adjusted to 0.1M (1M = 1mol/dm^3) by adding sodium perchlorate. The solution containing 0.010M $HClO_4$ + 0.09M $NaClO_4$ was employed as the standard of $-\log[H^+] = 2.00$ (hereafter $-\log[H^+]$ is abbreviated as pC_H). The pKa of the carboxylic acids and the stability constants of the lanthanoid(III) complexes were determined by potentiometry, and the distribution constants and the dimerization constants of the carboxylic acids by spectrometry. The adduct formation constants were determined as follows: a given volume of chloroform containing tta and/or a carboxylic acid and an equal volume of aqueous solution containing a lanthanoid(III) at various pC_H were placed in stoppered glass tubes. The tubes were placed on a rotating frame work set in a thermostated water bath at 25°C and the two phases were shaken mechanically (20rpm) for an hour and then centrifuged. An aliquot of each phase was pipetted and the γ-radioactivity of each solution was measured with a well-type(NaI) scintillation counter. The distribution ratio of the lanthanoid(III) was calculated as the ratio of the γ-activity of the two phases. The hydrogen ion concentration at equilibrium was measured potentiometrically.

RESULTS AND DISCUSSION

The equilibrium constants of carboxylic acids are listed in TABLE1.

TABLE 1.
Equilibrium constants of carboxylic acids

ACID		pKa	$\log K_d$	$\log K_{dim}$
phenyl acetic		4.00	0.43	1.81
α-phenyl lactic		3.30	-0.62	1.48
α-hydroxy phenyl acetic		3.18	-1.47	1.50
α-methoxy phenyl acetic		2.97	0.40	1.40
Benzoic		3.99	0.44	2.22
salicylic		2.72	0.48	1.64
o-methoxy benzoic		3.92	1.58	—

The data in TABLE 1 show that phenylacetic and benzoic acids are of very similar nature. o-Methoxy benzoic acid has a very large distribution constant

and a very small dimerization constant compared to the other acids probably due to the internal complexation through hydrogen bonding. The distribution constant of α-phenyllactic acid, in which the hydrogen from mandelic acid has been replaced with a methyl group, is 7 times larger than mandelic acid, although the other equilibrium constants are very similar.

An example of the effect of side groups on the extraction enhancement is given in Fig. 2.

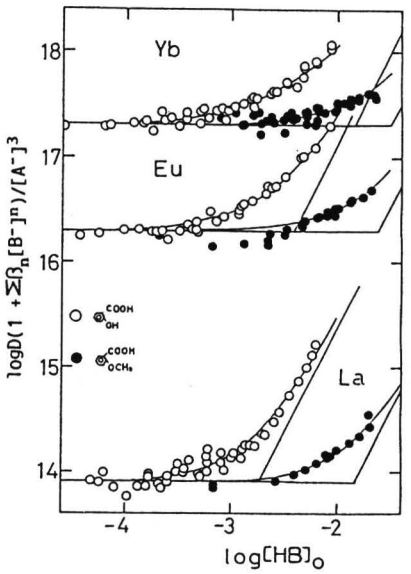


Fig. 2. Extraction of Ln(III) with tta and salicylic acid(○) or o-methoxy benzoic acid(●) as a function of the acid monomer concentration in chloroform.

As seen in Fig. 2, the distribution ratio increases with the increase in acid concentration. The plot has two asymptotes : a flat line and a straight line having slope of +2. This shows that the lanthanoid(III)-tta chelate forms adducts with two molecules of these acids at most. It should be noted that the difference in the extraction with these two acids is smaller for ytterbium, while for lanthanum it is larger. A similar trend was also observed in the extraction with α-phenyllactic acid and α-methoxy phenylacetic acid.

Figure 3 shows the difference of the extraction enhancement among lanthanum, europium, and ytterbium chelates when α-phenyllacetic acid is employed as adduct forming ligand. Similar to the observations with phenylacetic acid or benzoic acid(Hasegawa, et al. 1989b), the enhancement follows the sequence of lanthanum > europoium > ytterbium. All other carboxylic acids studied in the present work show the same order.

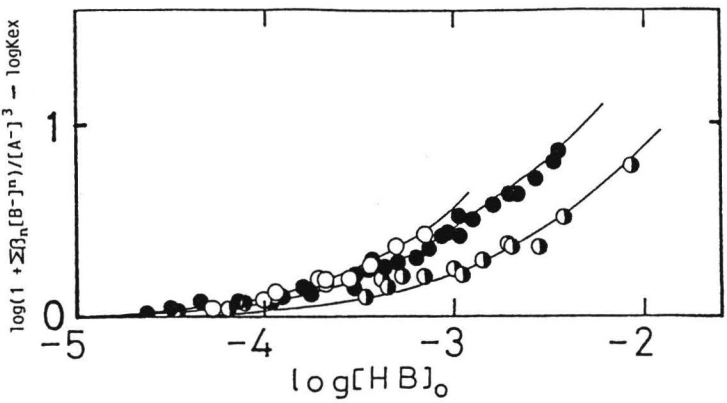


Fig. 3. Enhancement of extraction of lanthanum(III)(○), europium(III)(●), and ytterbium(III)(◑) due to adduct formation between the tta-chelates and α-phenyllactic acid as a function of the carboxylic acid monomer concentration in chloroform.

The solid curves are calculated by $Y = \log(1 + \Sigma\bar{\beta}_n[HB]_o^n)$ using the adduct formation constants obtained.

In Fig. 4, the adduct formation constants obtained are summarized as a function of atomic number. The plots in Fig. 4a show the first adduct formation constants while those in Fig. 4b show the second adduct formation constants. For the first adduct formation constants, the trend is not so clear, but the second adduct formation constants are clearly larger for the lighter lanthanoid chelates than for the heavier ones. The trend is similar to the adduct formation with organophosphorus compounds for which such a trend has been known for a long time. The larger adduct formation constants for lighter lanthanoid(III) chelate would be explained in terms of the difference in coordination number between lighter and heavier lanthanoids. In addition, as already pointed out (Sekine, et al. 1967, 1969) it may be related that heavier lanthanoid(III) with higher charge density tends to form stronger chelate with tta than lighter one does, so that the residual coordination power of the metal ion in the chelate could be weaker than that of the lighter ones. As seen in Fig. 2, the difference in the extraction with two acids having similar structure becomes smaller with the decrease in size of lanthanoid. This may also be explained as follows; since ytterbium(III) does not effectively leave the coordination power after chelation with tta, the adduct formation would not be much different between the two acids having -OH and $-OCH_3$ groups of which basicity is not much different, while the small difference in the basicity would be amplified by increasing ability to adduct formation with increasing size.

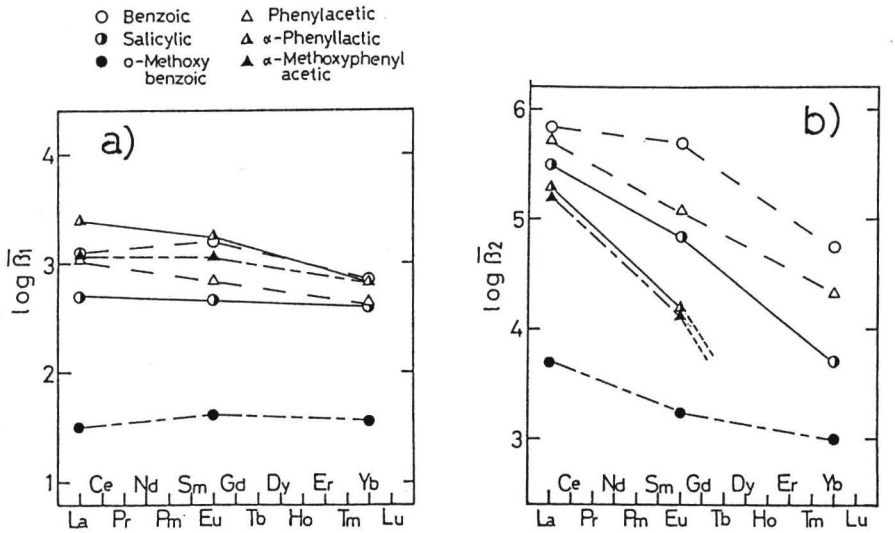


Fig. 4. Adduct formation constants of Ln^{III}-tta chelates with carboxylic acids as a function of atomic number.

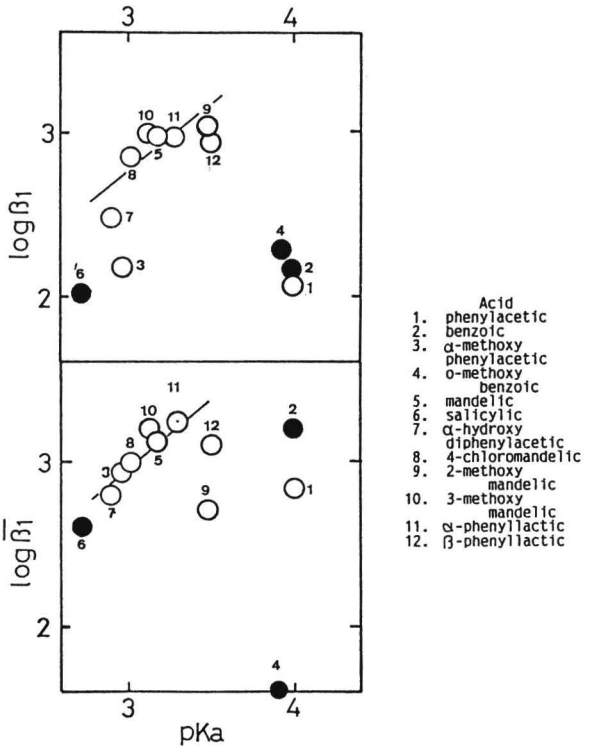


Fig. 5. Formation constants of adducts of Ln(III)-tta chelates with carboxylic acids in chloroform and stability constants of Ln(III) carboxylates in 0.1M sodium perchlorate media as a function of pKa of the carboxylic acids.

The observation that ytterbium(III) does not form the second adducts with α-phenyllactic and α-methoxy phenylacetic acids and furthermore the difference in the adduct formation constants between a pair of metals is larger in phenylacetic acids than in benzoic acids may be accounted for the difference in action between bidentate phenylacetic acid substituents and monodentate benzoic acid substituents, that is, bidentate phenyllactic and α-methoxy phenylacetic acids can not form a second adduct with the heavier lanthanoid with smaller coordination number. Since o-methoxy benzoic and salicylic acids form internal complex through hydrogen bonding as described before, they will not behave as bidentate ligands. The difference in adduct formation between α-phenyllactic and α-methoxy phenylacetic acids may be due to the different basicity.

Figure 5 shows the adduct formation constants with carboxylic acids as a function of pKa. For comparison, the first stability constants in aqueous complexes are given in upper plot. The values of pKa are employed as a measure of the basicity of carboxylic acids. As seen from Fig. 5, phenylacetic acid and benzoic acid form weak complexes in aqueous solutions but form stronger adducts in organic solvents. On the other hand, α-hydroxy carboxylic acids (except for 2-methoxy mandelic acid) form stable complexes either in aqueous or in organic solvents. The presence of methoxyl group in the proximity of carboxyl group seems to be unfavorable for adduct formation (see o-methoxybenzoic acid and 2-methoxy mandelic acid). In addition, the adduct formation constants are roughly in proportion to pKa. Hence, in these carboxylic acids, pKa can be utilized as a measure of strength of Lewis acids.

Besides the basic solution chemistry, the present study will find practical application for the possibility of good mutual separation of lanthanoids with α-hydroxycarboxylic acids, because α-phenyllactic acid forms more stable adduct with lighter lanthanoid-tta chelates in organic solvents, while it forms more stable complexes with heavier lanthanoid ions in aqueous solutions.

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NEW APPROACH TO DESCRIPTION OF COMPLEX FORMATION IN SOLVENT EXTRACTION SYSTEMS; SOLVATION AND HYDRATION CONTRIBUTIONS INTO EXTRACTION CONSTANT

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ABSTRACT

Rozen A.M., 1990. New approach to description of complex formation in solvent extraction systems; solvation and hydration contributions into extraction constant.

Does the extraction constant K_{ex} characterize the strength of metal-extractant complexes? With the traditional approach considering complexing in an aqueous phase it does not and with the suggested one it does as complexing (with the constant β_{org}) in an organic phase is considered. Since the free energy of extraction is the difference in solvation ($\Delta G_{solv} = -RT\ln\beta_{org}$) and hydration ($\Delta G_{hydr}$) energies, $RT\ln\beta_{org}/K_{ex} = -\Delta G_{hydr}$. Using the standard state "pure substance" (e.g., a crystalline salt) one can find ΔG_{hydr} and from the data on K_{ex} determine β_{org}, identify the phase responsible for a stronger or weaker extraction. It is shown that the dependences of β_{org} and K_{ex} on the site of an element in Mendeleev Periodic Table can differ significantly.

Does the extraction constant characterize the strength of resultant metal-extractant complexes? The author of the paper has repeatedly disputed this with experts in analytical chemistry (prof. O.M.Petrukhin and oth.) In their opinion based on the traditional approach to the complexing description (Zolotov, 1973; Sekine, 1988) the extraction constant does not characterize directly the complex stability and hence, the dependence of extraction constants on organic ligand structures found by the author (Rozen et al., 1964, 1966, 1976; Rozen 1967, 1968, 1984, 1988) does not characterise the influence of structure on complex strength. The author holds the opposite viewpoint. The discussion of this problem is of a general interest; the reply is related to the approach to an extraction process description. As it is shown below the difference in the viewpoints is due to the fact that by the traditional approach the constant of a complex stability in an aqueous phase is determined while in the approach below complexing in an organic phase is considered.

The traditional approach to the complexation description developed by analysts considering metal chelates extraction consists of the process divided into the following stages (see, e.g. Sekine 1988): 1. Transition of an organic ligand (HR) into aqueous phase (distribution constant K_d); 2. HR dissociation in aqueous phase (dissociation constant K_a); 3. Complexation with metal ion in aqueous phase ($Me^{z+}_{aq} + zR^-_{aq} = (MeR_z)_{aq}$; complex stability constant $\beta_{aq} = [MeR_z] / [Me][R^-]^z_{aq}$; 4. Distribution of MeR_z complex between the phases (distribution constant K_{dc}). On the other hand, if the extraction is considered as a whole $Me^{z+}_{aq} + zHR_{org} = (MeR_z)_{org} + zH^+$, then by comparing with stage reactions we find

$$K_{ex} = \beta_{aq} K_{dc} (K_a / K_d)^z \qquad (1)$$

A similar division into stages can be also made on extraction with neutral compound ($Me^{z+}_{aq} + zA^-_{aq} + qL_{org} = (MeA_zL_q)_{org}$), which gives

$$K_{ex} = \beta_{aq} K_{dc} K_{ass} / K_d^q \qquad (2)$$

where K_{ass} is an ion association constant ($K_{ass} = 1/K_{diss}$).

In both the cases the extraction constant is proportional not only to the complex stability constant $_{aq}$ but also to the complex distribution constant K_{dc}; on the ligand replacement the K_{ex} changes do not describe the complex strength variation as K_{dc} will also change.

But why is complexing with an organic ligand in aqueous phase considered? Historically it is clear: the traditional approach has been developed by analysts who used water-soluble reagents. But the modern extraction processes are based on reagents very poorly soluble in water. In most cases extraction does not processed in aqueous phase, but at the interphase surface or even in the subsurface organic layer.

Therefore, it is not only natural, but also beneficial to some extent to consider complexing in organic phase.

Consider the following stages of the process: (for simplicity, as in the traditional approach, for the simplest case of only one complex formed).

1. Ion association in aqueous phase

$Me^{z+}_{aq} + zA^-_{aq} \rightleftharpoons (MeA_z)_{aq}$; $K_{ass} = 1/K_{diss}$

2. Ion pair or molecule distribution between aqueous phase and diluent or extractant:

$(MeA_z)_{aq} \rightleftharpoons (MeA_z)_{org}$; k'_d

3. Salt-ligand complexing in diluent

$(MeA_z)_{org} + qL_{org} = (MeA_zL_q)_{org}$

with the complexing constant

$$\beta_{org} = [MeA_zL_q]_{org} / [MeA_z]_{org} L^q_{org} \quad (3)$$

It is not difficult to see that the salt extraction constant will be

$$K_{ex} = \beta_{org} K'_d / K_{diss} \quad (4)$$

The K'_d and K_{diss} values describe the properties of a salt being extracted (K_{diss}) and a diluent (K'_d). With a change of a ligand L they remain unchanged, only the constant of a complex stability in organic phase β_{org} alters. Thus, indeed, the extraction constant directly characterizes the strength or stability of a complex not in aqueous but organic phase. So, the dependence of the extraction constants, on the ligand structure (Rozen 1964–1988) describes a variation in the complex strength.

So, the constants of complexing β_{org} and extraction K_{ex} are interrelated. The question is: we have a bulk of data on extraction constants, is it possible to use it to determine β_{org}? Particularly, if β values are very high and the concentration of an uncomplexed metal $[MeA_z]$ is low and is practically undeterminable. The answer to this question is positive. Indeed, let's consider the relation between complexing and extraction from the general point of view. As is known (e.g. Rozen 1984, 1988) the free (Gibbs) energy of extraction is the difference between solvation and hydration energies:

$$\Delta G_{ex} = \Delta G_{solv} - \Delta G_{hydr} \quad (5)$$

Since in the first approximation $\Delta G_{solv} = -RT\ln\beta_{org}$ and $\Delta G_{ex} = -RT\ln K_{ex}$, we find

$$\beta_{org} = K_{ex} \delta_f(0)^{-\nu} = K_{ex}\, e^{-\Delta G_{hydr}/RT} \quad (6)$$

Since $-\Delta G_{hydr}$ can be several tens of kcal/mole it can be seen that the complexing constant β_{org} can be many orders of magnitude higher than K_{ex}; it can be also seen from eq. (4) - the strong electrolyte dissociation constant is very high.

So, the calculation of the complex stability constant from extraction data is reduced to the determination of hydration energy. The magnitude of this energy is sometimes counted from the standard state "ions in vacuum", which includes the dissociation energy and results in enormous amounts (hundreds of kcal/mole) exceeding the energy of the strongest chemical compounds binding. It is more expedient to use the standart state "pure substance" (SSPS), i.e. liquid acids, molten or crystalline salts (see Rozen et al. 1971; Rozen 1979, 1984, where the transition to this standard state is considered). The found values of hydration Gibbs energy and enthal-

py are listed in table 1.

Table 1

Hydration Free Energies and Enthalpies (kcal/mole)

a. acids

Feature	HCl	HBr	HI	HNO_3	H_2SO_4	$HClO_4$
$-\Delta G$ hydr.l.	10.7	13.8	14.0	7.3	13.03	22.2
$-\Delta H$ hydr.l.	14.8	16.8	15.4	7.95	22.77	21.2
$-\Delta G$ hydr.ions	331	326	317	322	755	303
$f_{\pm}$ (0)	3.2×10^{-3}	2.25×10^{-4}	1.44×10^{-4}	0.0575	1.18×10^{-2}	-

b. Elements of first group

Energy	LiCl	NaCl	KCl	$LiNO_3$	$NaNO_3$	KNO_3
$-\Delta G$ hydr.l.	14.1	10.6	8.7	10.9	7.2	5.1
$-\Delta G$ hydr.cr.	-	2.1	1.3	4.0	1.5	-0.1
$-\Delta H$ hydr.cr.	8.9	-0.9	-4.2	0.6	-4.9	-8.3
$-\Delta G$ hydr. (ions in vacuum)	200	176	158	190	160	148

c. Elements of second group

Energy	$Mg(NO_3)_2$	$MgCl_2$	$MgBr_2$	MgI_2	$Ca(NO_3)_2$	$CaCl_2$	$CaBr_2$	CaI_2
$-\Delta G$ hydr.cr.	20.2	30.3	38.8	47.0	7.7	15.5	26.5	30.2
$-\Delta H$ hydr.cr.	20.7	37.2	44.5	51.0	4.5	19.8	26.2	28.7

d. Lanthanides ($Ln\ Cl_3$)

Energy	La	Pr	Nd	Sm	Eu	Gd	Tb	Yb	Lu
$-\Delta G$ hydr.cr	-	22	24	27	27	30	33.6	37.6	34 ± 4
$-\Delta H$ hydr.cr.	33	33.5	35.5	37.4	-	-	-	45.4	-

e. Actinides

Energy	$UO_2(NO_3)_2$	UO_2Cl_2	UO_2Br_2	$ThCl_4$
$-\Delta G$ hydr.cr.	16.1	-	-	-
$-\Delta H$ hydr.cr.	20 x)	25.7	27.3	56.7

x) For hexahydrate - 5.4 kcal/mole

It can be seen from table 1 that $-\Delta G_{hydr}$ increases with ion charges growth and with a decrease of ion radii. The values of

$-\Delta G_{hydr.l}$ for Li, Na, K chlorides and nitrates as well as for HNO_3 and HCl are well described if the $-\Delta G_{hydr.l}$ values of 8.0; 4.4; 3.2; 3.0 and - 1.2 kcal/mole are assumed for ions of Li^+, Na^+, K^+, Cl^- and NO_3^-, respectively (NO_3^- is negatively hydrated!).

Now consider the data from the extraction viewpoint. One can conclude that since the free energy of hydration of univalent ions is of order of - 10 kcal/mole and that of di- and trivalent ions is - 20-40 kcal/mole the extraction becomes weaker with an ion charge growth due to the hydration reinforcement; a similar effect is produced by a substitution of a nitrate-ion by a more powerfully hydrated chloride ion. To provide for an appreciable extraction the free solvation energy (the binding energy) must be of the same order as the energy and enthalpy of hydration, i.e., 10-40 kcal/mole which is characteristic of electron donor acceptor(EDA) complexes.

Using the data obtained one can determine the constants of complexing in an organic phase and to estimate the fraction of unsolvated salt molecules present in the organic phase. For uranyl nitrate, e.g., on TBP-extraction ($K=10^2$, $\Delta G_{ex}=-2.74$ kcal/mole find $\Delta G_{solv} = \Delta G_{ex} + \Delta G_{hydr} = -2.7-16.1 = 18.8$ kcal/mole, $\beta_{org} \sim 10^{14}$, i.e., the fraction of uncomplexed molecules is negligible ($\sim 10^{-14}$); for HNO_3 this fraction is $\sim 10^{-4}$, which does not rule out the feasibility of finding out uncomplexed molecules with physical methods.

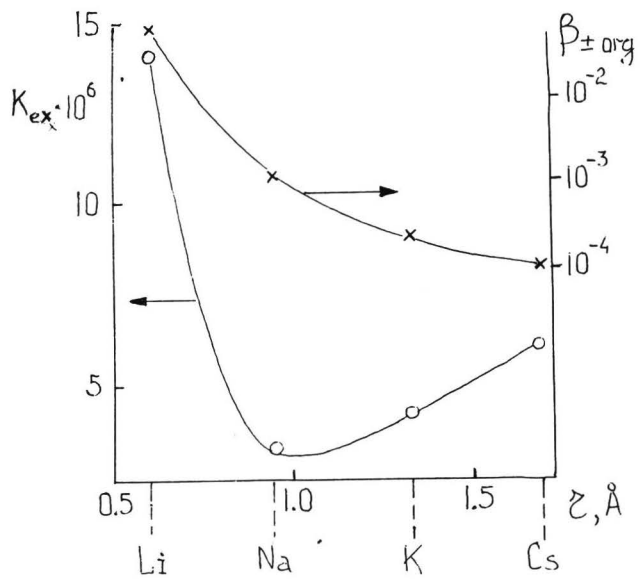


Fig. 1. Extraction constants K_{ex} for alkaline metal chlorides and complexation constants β_{org} vs metal ion radius

Using the data presented the contributions made by hydration and solvation can be separated. It can be shown that, e.g., the low TBP extractability of HCl (and metal chlorides) as compared to HNO_3 (and nitrates) is mainly due to a more powerful Cl^- hydration rather than to a weaker bond to TBP (see table 2).

Table 2

Comparison of HNO_3 and HCl extraction with TBP

	Extraction constant	ΔG_{extr} kcal/mole	ΔG_{hydr} kcal/mole	ΔG_{solv} kcal/mole	β_{org}
HNO_3	2×10^{-1}	0.95	-7.3	-6.3	5×10^4
HCl	2×10^{-4}	5.0	-10.7	-5.7	2×10^4

The extremal atomic number dependence of alkaline element extractability (minimum for sodium) (see fig.1) is due to hydration, solvation varies monotonously.

Thus, the dependence of complexing and extraction constants on the site of an element in Mendeleev Periodic Table can differ significantly.

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EXTRACTION OF RARE EARTHS BY NAPHTHENIC ACID AND STRUCTURE OF THE EXTRACTED COMPLEX

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ABSTRACT

The effect factors in the extraction of rare earths by naphthenic acid have been studied. The tetrad effect in D-Z curve of this system was observed. Results show that the separation factors are varying with the variation of the relative contents of the two elements separated, which is caused by the formation of heteronuclear complex in the organic phase. The crystal structure of the model molecule of the extraction complex has been reported as well.

INTRODUCTION

Naphthenic acid (noted as HA) is a mixture of carboxylic acids obtained from petroleum industry, having a general molecular formula of $R(CH_2)nCOOH$, where n>1, R represents one or more poly-membered rings. As an extractant, it is stable, cheap, nontoxic, and the metal ions extracted are easily stripped back to the aqueous phase. The extraction of some metal ions with HA were reviewed by F.Miller[1] and the extraction of La. Gd. Y with HA were studied by R. A. Alekperov and his coworkers[2-4]. The aggregation of naphthenic acid in nonpolar and polar solvents were studied by Tian-Zhu Jin and his coworkers[5].

1.THE TETRAD EFFECT IN D-Z CURVE

A sample from Kelamayi, China was vacuum distilled into several fractions and their average molecular weights were determined by titration as shown in Table 1.

Data show that in this naphthenic acid, the alkane content is about 10% and the acidic content increases with the boiling point until b.p. >200°C.

TABLE 1. COMPOSITION OF NAPHTHENIC ACID FROM KELAMAYI

	Distillation range	Colour	Acidic value g/mol COO-		Weight (%)
1	120-140°C / 0.5 mm Hg	yellowish	1489*		8
2	140-160°C / 0.7 mm Hg	light yellow	520*	525**	25
3	160-180°C / 0.8 mm Hg	light yellow	312*	317**	27
4	180-200°C / 1.0 mm Hg	brown	296*	301**	30
5	>200°C	dark, sticky	443*		10
6	original	deep brown	351*		

* right after distillation ** Three month after distillation

Results indicate that the extraction behavior of naphthenic acid with rare earth is not effected by their molecular weight obviously. When the extraction distribution ratio D was plotted against its atomic number Z, the tetrad effect was observed on the D-Z curve (see Fig.1). As it is well known, the tetrad effect is the reflection of the configuration of the 4f electrons. So it appears in all the properties of rare earth elements along with their atomic number Z. However, usually this factor appears with lots of other factors simultaneously. For instance, in the case of extraction, it appears at least with the following factors: the equilibrium pH value of aqueous phase; the coordination of the extractant with metal ions; the coordination of anions with metal ions in aqueous phase; the hydrolysis of the metal ions and the salting out effect. Since these factors effect D-Z curve not in the same order, it results in a large difference in the form of tetrad effect in D-Z curve.

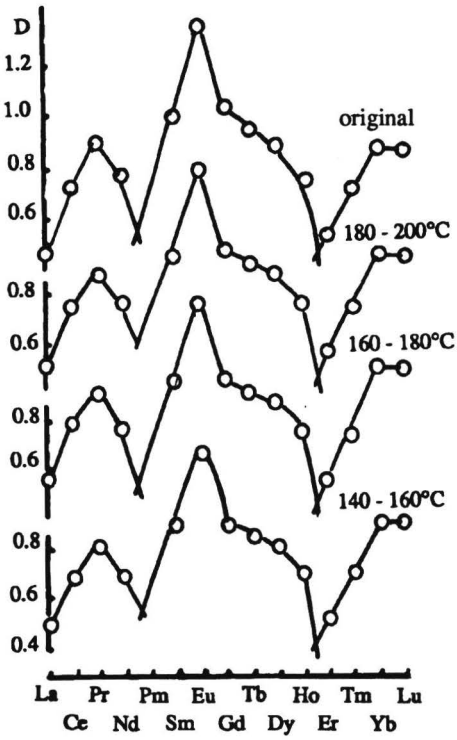


Fig.1. The distribution ratio D of the extraction of $RECl_3$ by naphthenic acid (HA) distillation collected in different range, diluent: 15% octanol and sulfurized paraffin hydrocarbon, O/A=1, t=25°C.

2. THE FACTORS AFFECTING THE EXTRACTION OF RARE EARTHS BY HA

When rare earth ion RE^{3+} is extracted by HA, the reaction could be simply represented by the following equation:

$$RE^{3+} + 3HA = REA_3 + 3H^+ \quad (1)$$

$$Kex = [REA_3][H^+]^3/[RE^{3+}][HA]^3 = D_0\ [H^+]^3/[HA]^3 \quad (2)$$

where D_0 is the distribution ratio when the coordination and salting out effects are not taken into consideration. When the coordination reaction between RE^{3+} and anion L^- (Cl^- or NO_3^-) is considered, let Y_0 represents the coordination degree, defined by:

$$Y_0 = C_{RE}/[RE^{3+}] = ([RE^{3+}]+[REL^{2+}]+[REL_2^+]+...)/[RE^{3+}] \quad (3)$$

$$Kex = [REA_3][H^+]^3/[RE^{3+}][HA]^3 = [REA_3][H^+]^3Y_0/C_{RE}[HA]^3 = DY_0[H^+]^3/[HA]^3 \quad (4)$$

$$D = D_0/Y_0 \quad (5)$$

When the salting out reagent is added into the system, then we have:

$$D = XD_0/Y_0 \quad (6)$$

where X represents the salting out effect, which is always larger than one.

Based on these considerations mentioned above, the following facts are worthy to be noticed.

2.1 Comparing the curves a and b in Fig 2, we can find that the distribution ratio for $RECl_3$ is larger than that for $RE(NO_3)_3$ in similar conditions because the coordination degrees Y for NO_3^- is larger than Cl^-[7].

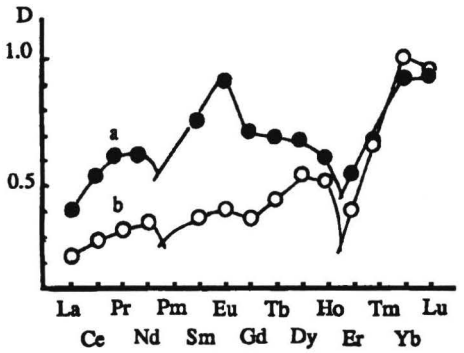


Fig2. The Extraction of Rare Earth by HA
(a) $RECl_3$=1.0M [HA]=0.608M pH=5.40
(b) $RENO_3$=1.0M [HA]=0.608M pH=5.42

2.2 In the nitrate system, when 3.0 M NH_4NO_3 is added into the system, the distribution ratio D of RE^{3+} will decrease due to the coordination effect of NO_3^- with RE^{3+}. On the other hand, as a salting out reagent, NH_4NO_3 will increase D. In the range of light and middle rare earths, the coordination effect is larger than salting out effect, it results in decrease of D. In the range of Tm-Lu, the situation is in contrast with that mentioned above, the value of D increases with Z gradually. When the concentration of NH_4NO_3 increases to 6.0 M, the dominative range of salting out effect is enlarged. This effect will be further strengthened by replacement of NH_4NO_3 with $LiNO_3$, as shown in Fig 3. That is, the addition of salting out agent $LiNO_3$ will result in an enlargement of the separation factor $\beta(Z/Z+1)$.

2.3 In the chloride system, as it is well known, the changes between the stability constants of individual rare earths are very small. So the shape of the D-Z curve does not change very much, when NH_4Cl is added into the aqueous phase.

It is very interesting to find that $RECl_3$ could be extracted by naphthenic acid through neutral coordination mechanism at lower pH range and high concentration of $RECl_3$ as shown below:

$$nHA + RECl_3 = RECl_3 \cdot nHA \quad (7)$$

For instance: when 2.70 M of $RECl_3$ is extracted by 0.661 M naphthenic acid with O/A=1:1.

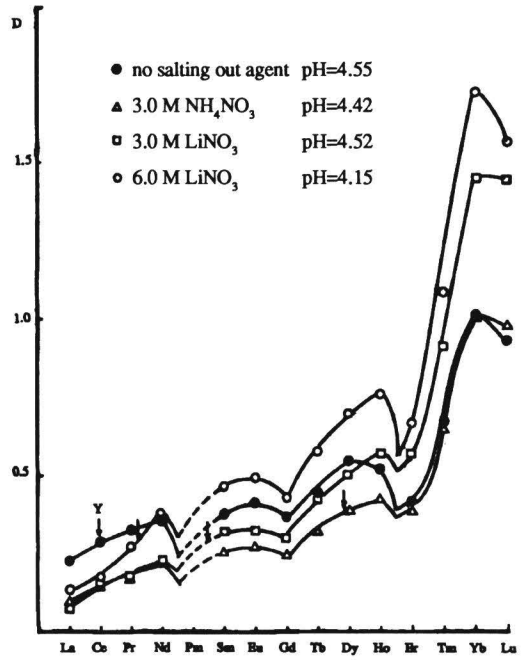


Fig3. The Influence of salting out agent on the extraction of RE by Naphthenic acid
$RE(NO_3)_3$=1.0 M, [HA]=0.698 M

0.104 M RE^{3+} ions is transfered from the aqueous phase into the organic phase, while the transfer of H^+ ion from organic phase to aqueous phase is very small, which cause only a small pH changes from 4 to 3.

The $RECl_3$ could also be extracted by HA according to the following reaction when HA is neutralized partly, for instance 50%:

$$RE^{3+} + (3\text{-}n)Cl^- + nA^- + mHA = RECl_{3-n}\cdot A_n\cdot mHA \qquad (8)$$

This fact is supported by the structural data of the extracted complexes reported in the next paragraph.

3.THE STRUCTURE OF THE EXTRACTED COMPLEX

It is well known, a separation factor $\beta_{A/B}$ of an extraction system is equal to the quotient of two extraction equilibrium constants of elements A and B, that is:

$$\beta_{A/B} = K_A/K_B \qquad (9)$$

Normally, $\beta_{A/B}$ does not change neither with the changing of the total concentrations of A and B, nor with the changing of the ratio of A/B in the extraction system.

It is very interesting to find that in the carboxylic acid system, the situation is quite unusual. This fact indicates that a heteronuclear complex may be formed in the system. After an evidence has been got by thermodynamic study that the heteronuclear complex La-Y-HA is more stable than Y-HA and La-HA, we have succeeded to synthesize $\{[LaY(C_6H_{11}COO)_4(C_6H_{11}COOH)_4]\cdot 2Cl\cdot 3CH_3COCH_3\}_n$, which is the first heteronuclear extraction complex ever reported. X-ray single crystal diffraction studies show that the complex is monoclinic with space group $P2_{1/2}$. The cell parameters are a=28.379(7), b=26.210(1), c=10.113(4)Å, β=92.43(2)°, V=7515(5)Å^3, Z=4. La and Y both are coordinated by nine oxygen atoms, from four $C_6H_{11}COO$-groups. The coordination polyhedrons of La and Y take tricapped triangular prism arrangement and are linked together by sharing one edge.

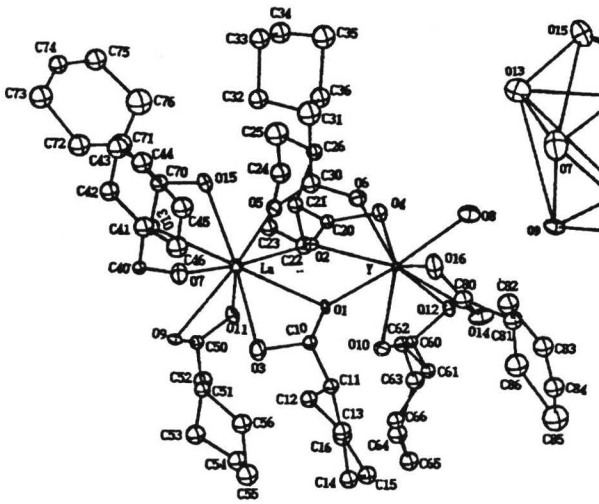


Fig4. The structure of $[LaY(C_6H_{11}COO)_4(C_6H_{11}COOH)_4]^{2+}$

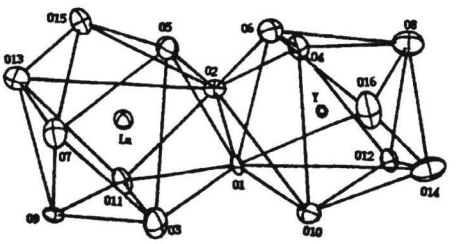


Fig5. The polyhedron of $[LaY(C_6H_{11}COO)_4(C_6H_{11}COOH)_4]^{2+}$

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SOLVENT EXTRACTION EQUILIBRIUM OF CADMIUM(II) BROMIDE COMPLEXES WITH 4-METHYL-2-PENTANONE IN THE PRESENCE OF TETRABUTYLAMMONIUM IONS.

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Abstract

The solvent extraction of cadmium(II) in 1 $mol \cdot dm^{-3}$ $Na(Br,NO_3)$ ionic media into 4-methyl-2-pentanone containing none or a certain amount of tetraethyl-, tetrapropyl-, or tetrabutylammonium ions was measured and the results were statistically analyzed. It was found that in the absence of such bulky large cations, both $CdBr_2$ and $Na^+ \cdot CdBr_3^-$ species were extracted and the addition of tetraethylammonium ions changed the extractions only slightly. However, the addition of tetrapropyl- or tetrabutylammonium ions (B^+) enhanced the extraction very much. This was explained in terms of an extraction of the $B^+ \cdot CdBr_3^-$ ion-pairs and when the B^+ was the latter, the extraction was about 100 times better than when it was the former. It was also found that an extraction of $B^+ \cdot NO_3^-$ ion-pairs from the back ground salt occurred and this interfered with the extraction of the anionic metal bromide complex.

Introduction

The solvent extraction of cadmium(II) as halide complexes with trioctylphosphine oxide (TOPO) in hexane was found to be very complicated because of the extractions of not only the uncharged complex but also several charged ones as ion-pairs.(Iwahori, et al., 1985) In the present study, the distribution ratio of cadmium(II) between 4-methyl-2-pentanone (MIBK) and aqueous 1 $mol \cdot dm^{-3}$ $Na(Br,NO_3)$ ionic media has been determined in the absence and presence of bulky tetraalkylammonium ions. The results were statistically analyzed and the equilibrium constants for the metal spices in the both phases were calculated.

2 Experimental

Experiments were made at 298 K. The reagents were of a reagent grade. Stoppered glass tubes (capacity 20 cm^3) were used for the solvent extraction. The aqueous phase was a 1 $mol \cdot dm^{-3}$ $Na(Br,NO_3)$ solution containing 2×10^{-5} $mol \cdot dm^{-3}$ of Cd^{2+} and none or a certain amount of tetraalkylammonium ions and being buffered at pH about 7

by a small amount of hydrogen carbonate. A 6 cm3 portion of this aqueous solution was placed in the tube and the same volume of water-saturated MIBK was added. The two phases were agitated by a mechanical shaker for 30 min and centrifuged. The amount of cadmium(II) in the both phases was determined by atomic absorption.

3 Results and Discussion

The distribution ratio of cadmium(II) in the present study may be written as;

$$D=([CdBr_2]_{org}+[Na^+\cdot CdBr_3^-]_{org}+[B^+\cdot CdBr_3^-]_{org}+[Na^+_2\cdot CdBr_4^{2-}]_{org} +[B^+\cdot Na^+\cdot CdBr_4^{2-}]_{org}+[B^+_2\cdot CdBr_4^{2-}]_{org})/([Cd^{2+}]+[CdBr^+]+[CdBr_2] +[CdBr_3^-]+[CdBr_4^{2-}]) \quad (1)$$

where the subscript "org" denotes those chemical species in the organic phase and B^+ denotes a tetraalkylammonium ion. The extraction constants for the metal species into the organic phase may be defined as;

$$Kex_{a,b,c}= [B^+_c\cdot Na^+_b\cdot CdBr_a^{2-a}]_{org}/[Cd^{2+}][Br^-]^a[Na^+]^b[B^+]^c \quad (2)$$

where a, b, and c denotes the number of Br^-, Na^+, and B^+, respectively, in the extracted species.

By introducing the extraction and stability constants, eqn.(1) can be rewritten as;

$$D=(Kex_{2,0,0}[Br^-]^2+Kex_{3,1,0}[Br^-]^3+Kex_{3,0,1}[Br^-]^3[B^+] +Kex_{4,2,0}[Br^-]^4+Kex_{4,1,1}[Br^-]^4[B^+]+Kex_{4,0,2}[Br^-]^4[B^+]^2)/ (1+\beta_1[Br^-]+\beta_2[Br^-]^2+\beta_3[Br^-]^3+\beta_4[Br^-]^4) \quad (3)$$

where $\beta_n=[CdBr_n^{2-n}]/[Cd^{2+}][Br^-]^n$.

The sodium(I) concentration was always unity. The distribution ratio was determined as a function of the bromide concentration at a certain B^+ concentration. The distribution data experimentally obtained were analyzed on the basis of eqn.(3) by using a least squares computer program.

Figure 1 shows the distribution ratio as a function of the bromide concentration at the given tetrabutylammonium concentration. Figure 2 compares the effect of addition of tetrabutyl-(tba^+), tetrapropyl-(tpa^+) and tetraethylammonium(tea^+) on the

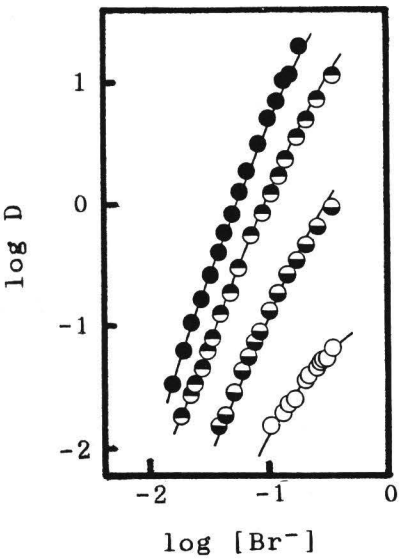


Fig.1

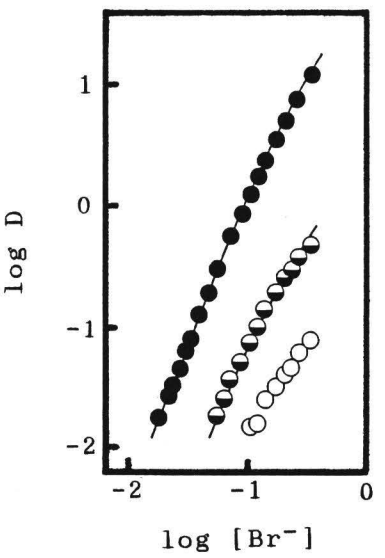


Fig.2

Fig.1 Extraction of Cd(II) bromide complexes as a function of aqueous bromide concentration containing none or a certain amount of tba^+.

Solid curves were calculated on the basis of eqn.(3) by introducing the values of constants in Table 1.

(○) : $[tba^+]_{init.} = 0$ mol·dm^{-3}
(◒) : $[tba^+]_{init.} = 5\times10^{-4}$ mol·dm^{-3}
(◓) : $[tba^+]_{init.} = 5\times10^{-3}$ mol·dm^{-3}
(●) : $[tba^+]_{init.} = 1.5\times10^{-2}$ mol·dm^{-3}

Fig.2 Extraction of Cd(II) bromide complexes as a function of aqueous bromide concentration initially containing 5×10^{-3} mol·dm^{-3} tea^+, tpa^+, or tba^+.

Solid curves were calculated on the basis of eqn.(3) by introducing the values of constants in Table 1.

The data in the presence of 5×10^{-3} mol·dm^{-3} of tea^+ are quite similar to those obtained in the absence of it. Thus no curve is drawn.

(○) : tea^+, (◒) : tpa^+, (●) : tba^+

extraction. The ion-pairs with tetraalkylammonium ion, nitrate ion, or bromide ion were also to some extent extractable into MIBK. These extractions of the large cations were determined by a similar method described in a previous paper.(Kusakabe, et al., 1989) Under the conditions of the experiments in Figs. 1 and 2, the initial concentration of tpa^+ and tba^+ was 5×10^{-3} mol·dm^{-3} in

the 1 mol·dm-3 Na(Br,NO_3) media and the concentration in the aqueous phase at equilibrium was about 4.9×10^{-3} mol·dm^{-3} with tpa^+ and 1.4 to 1.7 mol·dm^{-3} with tba^+. This was affected by the bromide concentration in the aqueous phase. The data analysis was made by using these concentrations at equilibrium. The equilibrium constants obtained from these date are listed in Table 1. From these equilibrium constants, the percentage distribution of each species in the aqueous phase and in the organic phase was calculated as a function of the bromide concentration as shown in Fig.3.

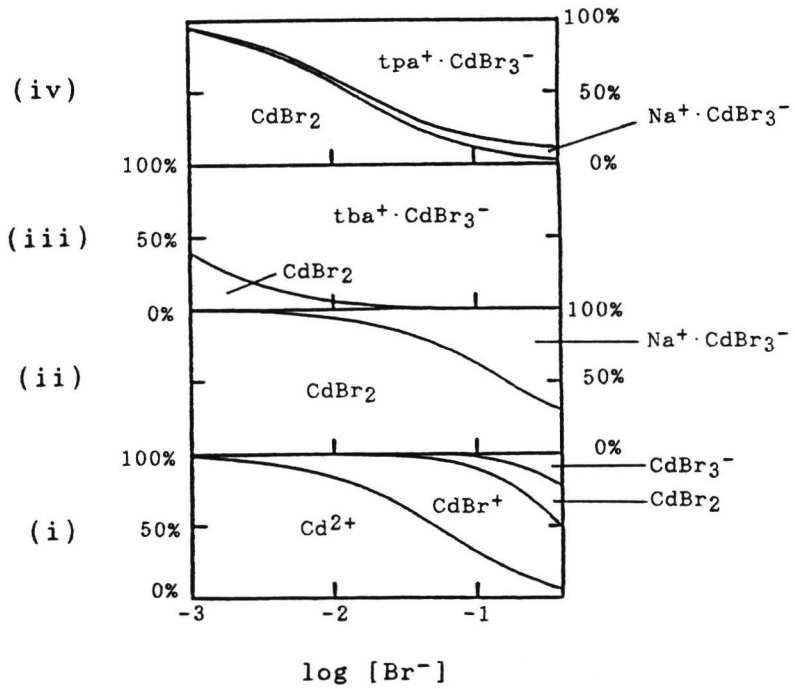


Fig.3 Percentage distribution of Cd(II) species as a function of bromide concentration calculated from the constants in Table 1.
(i) 1 mol·dm^{-3} Na(Br,NO_3).
(ii) MIBK which is in an equilibrium with (i).
(iii) MIBK which is in an equilibrium with (i) containing 5×10^{-3} mol·dm^{-3} (at initial) tba^+.
* a slight amount of $Na^+ \cdot CdBr_3^-$ is also extracted in this system but since it is always less than 0.5%, this is not clear in this figure.
(iv) MIBK which is in an equilibrium with (i) containing 5×10^{-3} mol·dm^{-3} (at initial) tpa^+.

TABLE 1

Stability and extraction constants of Cd(II) bromide complexes in 1 $mol \cdot dm^{-3}$ $Na(Br,NO_3)$-MIBK systems at 298 K.

B^+	$log\beta_1$	$log\beta_2$	$log\beta_3$	$logKex_{2,0,0}$	$logKex_{3,1,0}$	$logKex_{3,0,1}$
tpa^+	1.3	1.4	1.8	0.39	1.2	4.5
tba^+	1.3	1.4	1.8	0.39	1.2	6.4

The data are well explained if the following extractions are assumed.

(i) In the absence of tetraalkylammonium ions, both the neutral complex $CdBr_2$ and the anionic complex $CdBr_3^-$, as an ion-pair with a sodium ion, are extracted. The extraction is, however, rather poor under the present experimental conditions.

(ii) Addition of tetraalkylammonium ions enhanced the extraction except tetraethylammonium ions. As seen from Fig.2, the extraction is enhanced more with tetrabutylammonium ions. When $[Br^-]$ is 0.1 $mol \cdot dm^{-3}$ and the initial concentration of the ammonium ions was 5×10^{-3} $mol \cdot dm^{-3}$, the distribution ratio is enhanced 5 times by the addition of tetrapropylammonium and about 100 times by the addition of tetrabutylammonium. However, as it will be considered later, a tetrabutylammonium ion is well extracted as an ion-pair with a nitrate ion into MIBK. Thus the concentration of tba^+ in the aqueous phase at equilibrium is much lowered and the true effect of tba^+ is much greater than these.

(iii) Since the extraction of the anionic complex, $CdBr_3^-$, is more favorable with the bulkier cations, the extracted species in the presence of tba^+ is mainly the ion-pair with the anionic complex, $tba^+ \cdot CdBr_3^-$. However, the organic phase in the system where tpa^+ is added, contains not only the $tpa^+ \cdot CdBr_3^-$ species but also those found when no tetraalkylammonium ions were added, that is, $CdBr_2$ and $Na^+ \cdot CdBr_3^-$.

(iv) As is seen from (ii), the effect of the tetraalkylammonium ions cannot be estimated directly from the experimental results because of the extraction of these cationic extractant with nitrate ions. Such estimation can be made by the extraction constants in Table 1. The difference in the values of $logKex_{3,0,1}$ of tba^+ and tpa^+ is about 1.9. Thus the extraction of the ion-pairs with the former is about 100 times more effective than with the latter.

The extraction of cadmium(II) bromide with TOPO in hexane in the previous paper was very different from the present results which have been obtained by using MIBK as the solvent.

The results in Fig.2 indicate that the extraction of the anionic complex is better when the size of counter cation is larger as it is expected from the general tendency of solvent extraction. However, it should be noted that an extraction of ion-pairs with the anions of back-ground salt in the aqueous phase could occur together with the anionic metal complex. This impairs the efficiency of the extraction of the anionic metal complex. This should be more marked when the size of cationic extractant is larger. The decrease in the cationic extractant concentration by this extraction with the back ground anion in the aqueous phase was only 2% with tpa^+ but 72% to 66% with tba^+. Stability constants of bromide complexes of cadmium(II) (Martell and Smith, 1976) was reported previously and the formation of ever the tetrakis complex in 1 $mol \cdot dm^{-3}$ aqueous ionic media was pointed out. However,the higher complexes than $CdBr_3^-$ was not found by the analysis of the data of present experiments.

Use of bulkier cations as the counter-ion of the anionic metal complexes seems to be more favorable, at least apparently. However, as seen from the present results, the efficiency of the bulkier cations as the extractant is very much affected and this should be taken into account when this type of extractants are used. When the anion of the back ground salt is small and/or the concentration is low, the impairment of the efficiency as the extractant should not be affected very much and the use of bulkier cations should be more favorable although bulkier cations are tend to form precipitates with the anions and also micelles in the organic phase.

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EQUILIBRIA IN THE $NI(NO_3)_2$ – LIX63/N–HEXANE EXTRACTION SYSTEM

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ABSTRACT

The effects of changing pH and LIX63 concentration on Ni(II) distribution coefficient (D_L) have been studied. Log D_L was found to depend as 0.5[LIX63]. D_L was not strongly dependent on pH below 1.5 but increased as pH was was increased above 1.5.

A model was developed which interprets these results. The overall distribution coefficient is represented by the sum of a contribution due to Ni(II) exchange plus another contribution due to ion–pairing. It is proposed that LIX63 monomers adsorbed at the aqueous–organic interface associate with nitrate ions, forming negatively charged intermediate species that subsequently combine with Ni(II) as ion–pairs extracted into the organic phase. Thus according to this interpretation previously suggested in literature for mineral acids other than nitric the extract loads nitrate together with metal. Former knowledge about speciation, interfacial adsorption and ionization of the extractant is implemented in the model. An estimate for the dimerization equilibrium constant of LIX63 was obtained from data fitting in reasonable agreement with a previously reported value.

1. INTRODUCTION

The chemistry of Ni(II) extraction by the diethylhydroxydodecane oxime LIX63 (H_2L, Henkel Corp.) in hydrocarbon solvents is complicated by the existence of several complexes that coexist in the extract. The proportion between the concentrations of those complexes is dictated by the pH of the raffinate and the ratio of the metal ion to extractant concentrations. Renninger and Osseo–Asare (1983) reviewed work done on extraction equilibria of nickel and cobalt with LIX63, and tabulated reported pH dependences of the distribution coefficient D_L. For Ni(II), log D_L was found to vary as 1.3 pH to 2.0 pH in the range 4.45 pH $\leq$ 7.2. The relative importance of the various complexes proposed would depend on pH, with doubly charged complexes predominating at pH $\leq$ 4. This hypothesis is consistent with the fact that LIX63 is a weak acid which does not appreciably ionize under these conditions, as suggested by the electrophoretic mobility (EM) measurements of Lin and Osseo–Asare (1984), but it would still be able to extract Ni(II) by ion–pairing. Cation exchange, instead, would be the predominant mechanism at higher pH. In the pH range 6.5 to 8.5, Preston (1975) found that LIX63 exchanged Ni(II) by two H^+, and the 1:2 stoichiometry for the extracted species. Hummelstedt (1977) reviewed work on the extraction of copper by LIX63 and showed that no cation exchange took place at low pH and that $SO_4^{=}$ and HSO_4^- were coextracted. The uptake of mineral acids was confirmed by Al–Diwan *et al* (1977), who proposed the formation of the species $(H_3R)HSO_4$.

Zapatero *et al* (1987) studied the extraction of copper from nitrate solutions by LIX63. Log D_L was found to depend as 1*pH at high acidity, and as 2*pH in the range $2.5 \leq pH \leq 3.0$. Those authors suggested five different types of extractable species with nitrate–copper cation pairs present in two of them, thereby offering an explanation for the varying dependence of D_L on pH and for the coextraction of nitrate.

In this work, the effect of pH and LIX63 concentration ($\bar{C}_{LT}$) on the equilibrium distribution of Ni(II) between 0.5 M KNO_3 and n–hexane solutions was investigated.

2. EXPERIMENTAL

LIX63 was purified as proposed by Tammi (1976), with the modifications introduced by Lin (1985). Elemental analysis of the product showed deviations from theoretical values equal to 2.5% for N, 2.0% for C and 8.6% for H. Concentrations of stock solutions were evaluated from ultimate loading tests, assuming a 1:2 stoichiometric ratio and a formula weight of 271 (Lin, 1984; Keeney and Osseo–Asare, 1984; Tammi, 1976). In ultimate loading experiments, equal volumes of both phases with Ni(II) concentrations around 1000 times higher than LIX63 concentrations and at pH = 1.6 were shaken at room temperature during 3 hours. Extracts were stripped with equal volumes of 4N HNO_3 and Ni(II) concentrations in the strippates were measured by atomic absorption spectrophotometry. N–hexane 95%+ (Aldrich Chemicals Co.) was used as diluent. All other chemicals were of AR grade, and were used as received. Extract loadings were estimated *a priori* from the work of Renninger and Osseo–Asare (1983), and extract/strippate volume ratios were chosen in such a way that metal concentrations in the strippates fell within the spectrophotometer linearity limit without further dilution.

To verify nitrate extraction, LIX63 solutions in n–hexane were equilibrated with 0.1 N HNO_3, then injected into a Perkin Elmer Series 4 high pressure liquid chromatograph, fitted with a VYDAC 302 IC column and a Perkin Elmer conductivity detector. The eluant was 2mM acid potassium phthalate, pH adjusted to 4.9 with saturated sodium tetraborate. Two peaks were resolved, respectively around 1 and 3 minutes after injection, of heights proportional to $\bar{C}_{LT}$.

3. RESULTS AND DISCUSSION

Ni(II) distribution coefficients (D_L) were calculated from raffinate and strippate concentrations in the usual way. The dependency of D_L on $\bar{C}_{LT}$ is shown in Figure 1. The values of D_L are in the range 1.10^{-3} to 1.10^{-2}, similar to those reported for copper (Zapatero *et al* 1987) and for nickel (Renninger and Osseo–Asare, 1983). Linear regression of the data shows that D_L correlates at $\bar{C}_{LT}^{0.49}$, close within error to a square root dependency.

The effect of changing acidity on D_L is shown in Figure 2. D_L was found to rise slightly as pH was increased from 0.5 to 2.5.

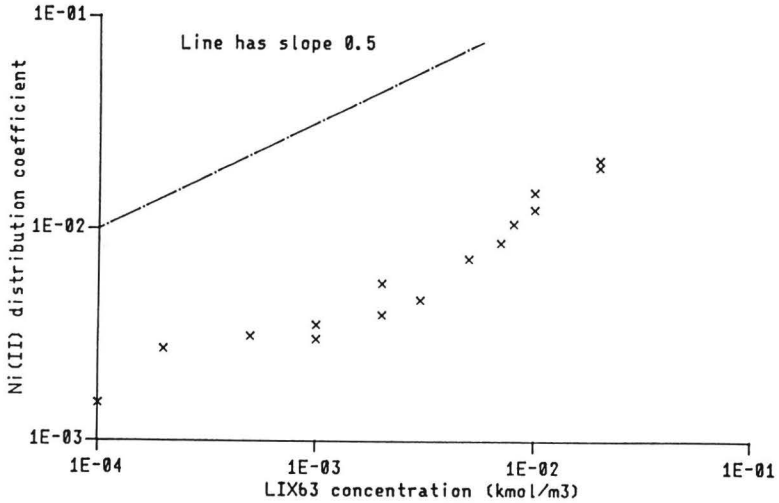


Figure 1: Effect of $\bar{C}_{LT}$ on D_L. Ni conc. 0.005 M, ionic strength = 0.5 M, pH = 2.5.

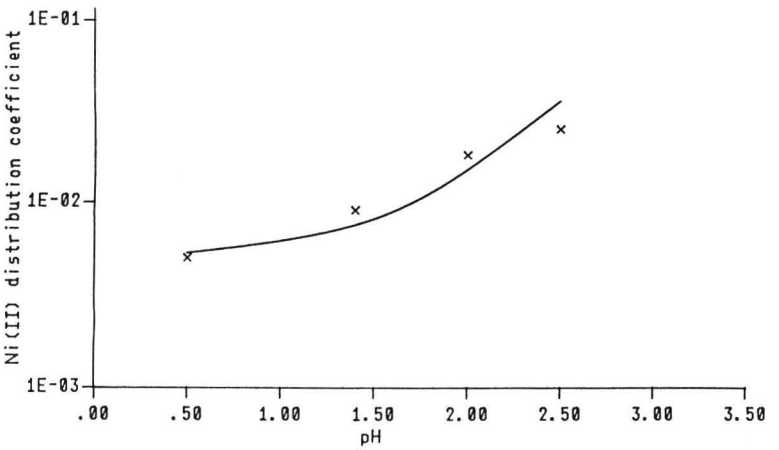


Figure 2: Effect of pH on D_L. $\bar{C}_{LT}$ = 0.01 M, Ni conc. = 0.005 M, ionic strength = 0.5 M.

No trace of potassium was found in the strippates that could suggest its simultaneous extraction. It was confirmed that nitrate was extracted by LIX63 solutions. The following data (chart divisions versus concentrations) indicate a linear relationship between NO_3^- concentration in the organic phase and $\bar{C}_{LT}$. Duplicates are sometimes presented.

$\bar{C}_{LT}$x10³ k mol m⁻³	20	10	7	5	1
1st peak	20/29	21	18/14	16	3
2nd peak	9/9	5	4/3	2.5	0.5

The results shown in Figure 1 suggest that LIX63 is extensively dimerized, in agreement with the vapour pressure osmometry measurements of Zheng and Osseo–Asare (1987). Equation 1 describes the dimerization equilibrium.

$$2\,\overline{H_2L} \Leftrightarrow (\overline{H_2L})_2 \;;\; K_d = \frac{\bar{C}_2}{\bar{C}_1^2} \qquad (1)$$

where $\bar{C}_1$, $\bar{C}_2$ stand respectively for monomer and dimer concentrations. Thus the oxime balance about the organic phase is

$$\bar{C}_{LT} = 2\,\bar{C}_2 + \bar{C}_1 = 2\,\bar{C}_2 + (\bar{C}_2/K_d)^{1/2} \cong 2\,\bar{C}_2 \qquad (2)$$

The approximation, valid at relatively high values of $\bar{C}_{LT}$ and large values of dimerization constant K_d, is supported by the half order dependency of D_L on $\bar{C}_{LT}$ observed (Figure 1) and it will be used in the analysis below.

Interfacial tension measurements indicate that LIX63 adsorbs at the O/W interface (Savastano, 1988). Calculations using also the data of Al–Diwan *et al* (1977) lead to the conclusion that the interfacial adsorption density was approximately constant in the concentration range used. The interfacial concentration of extractant (C_1^{ad}) was accordingly taken as a constant. The EM work of Lin and Osseo–Asare (1984) suggests that the dissociation of the adsorbed oxime can be safely neglected under the present conditions of pH and ionic strength. The pH dependence of D_L indicates that Ni^{2+} was not extracted by cation exchange only, but also by solvation. Both types of mechanisms were proposed for the extraction of Cu^{2+} by LIX63 (Zapatero *et al* 1987). Based on the above arguments two reaction schemes are proposed, one consisting of partial neutralization by aqueous anions and cation exchange (A), and the other consisting of neutralization and ion pairing (B).

(A) *Cation exchange*

$$NO_3^- + H_2L^{ad} \Leftrightarrow NO_2^-.H_2L^{ad} \qquad (3a)$$

$$M^{2+} + NO_3^-.H_2L^{ad} \Leftrightarrow M(NO_3).HL^{ad} + H^+ \quad (3b)$$

$$M(NO_3).HL^{ad} + \overline{(H_2L)_2} \Leftrightarrow \overline{M(NO_3).HL\ (H_2L)_2} \quad (3c)$$

A disproportionation would follow to yield the 1:2 complex:

$$\overline{(MNO_3).HL\ (H_2L)_2} \Leftrightarrow \overline{M(NO_3).HL\ (H_2L)} + \overline{H_2L} \quad (3d)$$

The superscript "ad" identifies species absorbed at the o/w interface, M^{2+} is the Ni(II) cation (water of hydration is not shown for clarity), and the bar indicates species in the organic phase. The overall LMA constant for steps 3a, 3b, 3c and 3d, K_o, is given by

$$K_e = \frac{\bar{C}_{Me}}{C_H} \frac{C_H}{C_a} \frac{\bar{C}_1}{C^{ad}\ \bar{C}_2} = K_a K_b K_c K_d \quad (4)$$

where C_a is the concentration of the main aqueous anion (i.e. nitrate). Substitution of equations 1 and 2 into equation 4 leads to the contribution of cation exchange to the distribution coefficient:

$$D_e = \frac{\bar{C}_{Me}}{C_M} = \frac{K_d^{1/2}\ K_e\ C_1^{ad}}{\sqrt{2}} \frac{C_a\ \bar{C}_{LT}^{1/2}}{C_H} \quad (5)$$

(B) *Ion pairing*

$$2\ NO_3^- + H_2L^{ad} \Leftrightarrow (NO_3^-)_2.H_2L^{ad} \quad (6a)$$

$$M^{2+} + (NO_3^-)_2.H_2L^{ad} \Leftrightarrow M(NO_3)_2.H_2L^{ad} \quad (6b)$$

$$M(NO_3)_2.H_2L^{ad} + \overline{(H_2L)_2} \Leftrightarrow \overline{M(NO_3)_2(H_2L)_3} \quad (6c)$$

$$M(NO_3)_2(H_2L)_3 \Leftrightarrow \overline{M(NO_3)_2(H_2L)_2} + H_2L \quad (6d)$$

The global equilibrium constant for steps 6a to 6d is K_{ip}:

$$K_{ip} = \frac{\bar{C}_{Mip}}{C_M\ C_a^2} \frac{\bar{C}_1}{C_1^{ad}\ \bar{C}_2} = K_a'\ K_b'\ K_c'\ K_d' \quad (7)$$

The contribution due to ion pairing is defined similarly as above

$$D_{ip} = \frac{\bar{C}_{Mip}}{C_M} = \frac{K_d^{1/2}\ K_{ip} C_1^{ad}}{\sqrt{2}}\ C_a^2\ \bar{C}_{LT}^{1/2} \qquad (8)$$

At pH $\leq$ 3 and I = $[NO^3]$ = 0.5 as used in this work, NO_3^- in preference to HO^- coordinates with Ni(II), as calculations with stability constants of Ni(II) hydrolysis products confirm. The total (observed) distribution coefficient is the sum of D_c and D_{ip}, i.e.:

$$D_L = \frac{(2\ K_d)^{1/2}}{2}\ C_a\ C_1^{ad} \left[\frac{K_e}{C_H} + C_a K_{ip} \right] \bar{C}_{LT}{}^{1/2} \qquad (9)$$

Figure 2 and equation 9 suggest that as pH is increased ion pairing becomes less important and exchange more dominant in the extraction mechanism. The $\bar{C}_{LT}^{1/2}$ dependence of D_L predicted by equation 9 is supported by the experimental evidence of LIX63 dimerization and agrees well with the dependence shown in Figure 1, found from linear regression of the data to be $D_L = 0.103\ \bar{C}_{LT}^{0.48}$. The pH dependence of D_L can be approximated by a line of equation $D_L = a + \frac{b}{x}$, where $x = C_H$, and the parameters a and b are explicit in equation 9. For C_a = 0.5 M the values a = 0.005 and b = 0.001 fitted the data best and give the solid line shown in Figure 1. From these values the calculated ratio K_{ip}/K is equal to 100. A mean value of K_d equal to 158 was estimated from the data which is similar to $K_d \simeq 126$ reported by Akiba and Freiser for LIX65N (1982).

4. CONCLUSIONS

The distribution of Ni(II) between nitrate media and n–hexane solutions of LIX63 was studied experimentally. An equilibrium model is proposed that satisfactorily simulates the observed effects of pH and extractant concentration on the distribution coefficient.

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THERMODYNAMIC STUDY ON THE SOLVENT EXTRACTION OF PERCHLORATES OF UNI-CHARGED CATION WITH TRIOCTYLPHOSPHINE OXIDE IN HEXANE

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Abstract

Uni-charged ions in an aqueous 1 mol·dm^{-3} $NaClO_4$ solution were extracted with trioctylphosphine oxide in hexane as ion pairs with perchlorate ions at different temperatures from 7 to 45°C. The enthalpy (ΔH_{ex}) and entropy (ΔS_{ex}) of the extraction were calculated from the temperature dependence of the extraction constant. The values of ΔH_{ex} were in the range from -84 (Li^+) to -117 (Cs^+)kJ·mol^{-1} and ΔS_{ex} from -237 (Li^+) to -363 (Cs^+) J·mol^{-1}·deg^{-1}. These results were compared with the standard enthalpy and entropy of hydration of the cations. It is suggested that the smaller ions retain some amount of the hydration water in the organic phase.

1 INTRODUCTION

The authors studied the extraction of a number of metal perchlorates with trioctylphosphine oxide (TOPO) in hexane at 298 K and considered the behavior of the metal ions in the absence of any ligand in the aqueous phase (Kusakabe, et.al., 1980, 1981, 1983). The solvation number of TOPO in the extracted species has been found to be four for bi- and tervalent cations (five for chromium ion, exceptionally). For uni-charged metal ions it was also four for Rb^+ and Cs^+, however, it was three for Li^+, Na^+, K^+, Ag^+, Tl^+, and NH_4^+. A thermodynamic study on these univalent cations was made in order to find the reason for the solvation number three.

2 EXPERIMENTAL

2.1 *Reagents*

Sodium perchlorate and TOPO were purified by the similar method in the previous studies. Potassium, rubidium, and cesium chloride, silver and thallium nitrate, and lithium hydroxide were used as the source of the cations.

2.2 *Distribution measurements*

A portion of 1 mol dm^{-3} sodium perchlorate solution containing

a certain amount of a cation in question and a portion of hexane solution containing various amount of TOPO were placed in a stoppered glass tube (capacity 20 cm^3). The two phases were agitated in a thermostated water bath where the temperature was controlled at a certain value from 7 to 45°C. After the agitation for 30 min, the two phases were settled for a while. Then the organic phase was transferred to another tube and centrifuged. The metal ions in this sample was washed with a dilute nitric acid containing a certain amount of sodium nitrate and then analyzed by atomic absorption (Rb^+, Ag^+, and Tl^+) or flame spectrometry (Li^+, Na^+, K^+, and Cs^+). The metal ions in the equilibrated aqueous phase were also analyzed. The distribution ratio of ammonium ion was measured by an ammonia electrode (Sekine, 1982).

2.3 *Data treatment*

The distribution equilibrium in the present system may be given by Eq. 1. The extraction constant is defined by Eq. 2.

$$M^+ + ClO_4^- + nTOPO(org) = MClO_4(TOPO)_n(org) \quad (1)$$

$$K_{ex} = [MClO_4(TOPO)_n]_{org}/[M^+][ClO_4^-][TOPO]^n_{org}. \quad (2)$$

When only one kind of the solvated species with TOPO is extracted, the distribution ratio of the metal ion, D, is related with the TOPO concentration as:

$$D = [M^+]_{org}/[M^+] = K_{ex}[ClO_4^-][TOPO]^n_{org}. \quad (3)$$

The TOPO concentration is calculated on the basis of its material balance;

$$[TOPO]_{org,total} = [TOPO]_{org} + 3[NaClO_4(TOPO)_3]_{org} + n[MClO_4(TOPO)_n]_{org}$$

$$= [TOPO]_{org} + 3K_{ex(Na)}[Na^+][ClO_4^-][TOPO]^3_{org}$$

$$+ nK_{ex}[M^+][ClO_4^-][TOPO]^n_{org}. \quad (4)$$

Since the concentration of sodium ion is usually much larger than that of the metal ion in question, it is indispensable to correct the TOPO concentration decreased by the extraction of sodium perchlorate. The distribution data were processed with a least squares program in conjunction with a successive approximation of

the TOPO concentration. The extraction constants obtained were plotted against the reciprocal value of the temperature. The enthalpy and entropy change of the extraction, denoted by ΔH_{ex} and ΔS_{ex} respectively, were calculated from the slope and intercept of the plot drawn on the basis of Eq. 5.

$$\log K_{ex} = -\Delta H_{ex}/2.303RT + \Delta S_{ex}/2.303R \qquad (5)$$

3 RESULTS AND DISCUSSION

Distribution ratio of rubidium(I) and silver(I) at various temperature was shown in Fig. 1. In a previous paper (Kusakabe, 1980), the extracts of rubidium(I) and cesium(I) were reported as the mixture of three and four solvates of TOPO. In the present study, however, the solvation number of these metal ions was both concluded to be four at all the temperature studied.

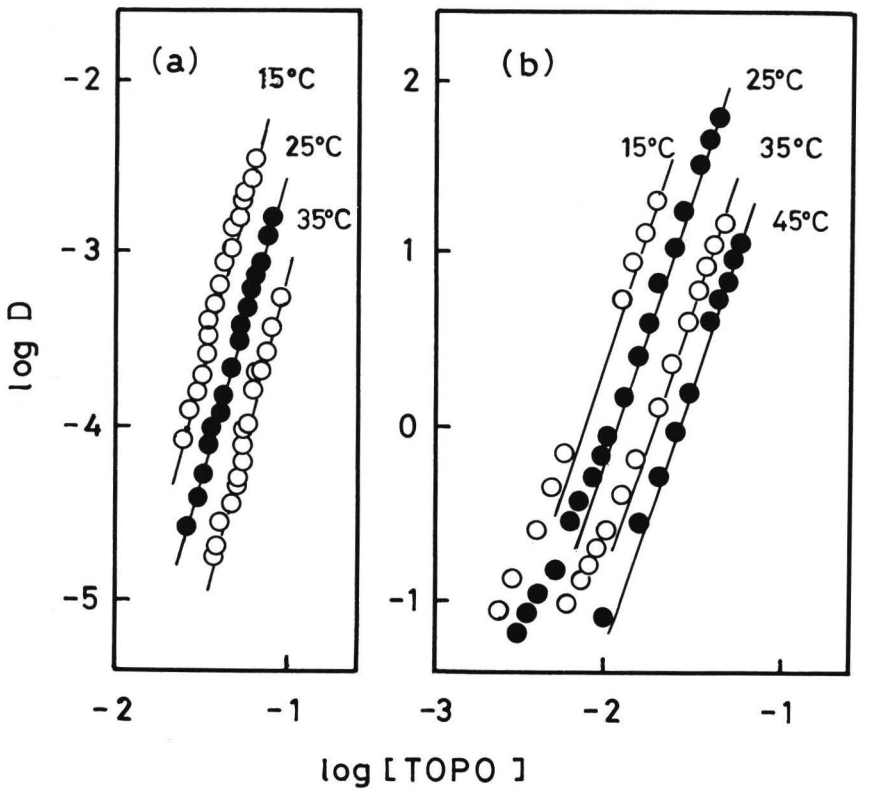


Fig. 1 Extraction of (a) rubidium(I) and (b) silver(I) perchlorate at various temperatures. The slope of the solid lines is four for rubidium(I) and three for silver(I).

When the TOPO concentration was low, silver(I) was extracted better than expected on the basis of Eq. 3 as is seen in Fig. 1b. This additional extraction was concluded to be of chloro-complexes caused by contaminating chloride ions. Therefore, the data at higher TOPO concentrations were used for the calculation of silver(I) extraction. The temperature dependence of the extraction constant is presented in Fig. 2. The calculated values of enthalpy and entropy of the extraction are given in Table 1.

The values of ΔH_{ex} and ΔS_{ex} obtained indicate that this type of extraction is exothermic and a negative enthalpy change compensates for a large decrease in entropy term. Since the hydrated water molecules on a metal ion should be released on transferring from aqueous phase to the organic solvent, hydration energy should be linked up with the extraction process. The standard enthalpy and entropy of hydration of ions (ΔH_h and ΔS_h) are listed in Table 1 together with the ionic radius of the cations.

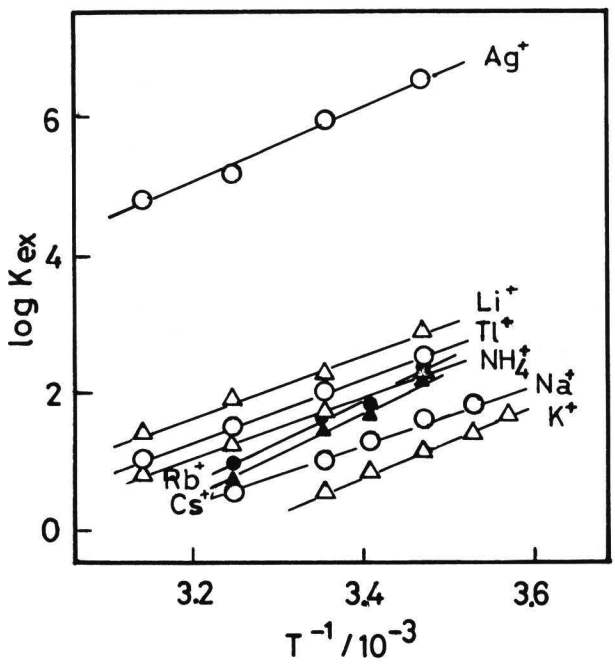


Fig. 2 Extraction constants at various temperatures.

TABLE 1

Thermodynamic parameters and ionic radii[1)]

Ion	$-\Delta H_{ex}$	$-\Delta H_h$	$-\Delta H_{ex}-\Delta H_h$	$-\Delta S_{ex}$	$-\Delta S_h$	$-\Delta S_{ex}-\Delta S_h$	r_c
	kJ·mol^{-1}			J·mol^{-1}·deg^{-1}			pm
Li^+	83.9	551.8	636	237	140	377	68
Na^+	86.1	442.7	529	269	108	377	97
K^+	97.0	358	455	314	72.7	387	133
Rb^+	112.1	333	445	345	60.6	406	147
Cs^+	116.5	301	418	363	57.5	421	167
Ag^+	104.2	512.5	617	236	114	350	126
Tl^+	86.1	363	449	250	68.6	319	147
NH_4^+	87.4			260			
ClO_4^-		200			58.2		236

1)The values of $-\Delta H_h$ and $-\Delta S_h$ are taken from Rosseinsky,F.D., *Chem.Rev.*, 1965, 467, **65** and ionic radii are Ahrens's values from "Landolt-Börnstein Zahlenwerte und Funktionen," I Band, 4 Teil, p523-525, Springer-Verlag (1955).

In general, the values of ΔH_h and $-\Delta S_h$ are both negatively larger in smaller ions. However, the magnitude of the extraction enthalpy and entropy seems to be in the reverse tendency, namely, they are negatively larger in the larger ions. Suppose that the hydration water molecules are completely released when one molar metal ions transfer to the organic phase, the dehydration energy should be as much as the oppositely signed amount of the standard hydration energy and this energy should be compensated with other energies of extraction motive processes such as ion-pair formation and solvation with TOPO. The extraction motive processes should be as a whole with a negative enthalpy and negative entropy enough to reach the ΔH_{ex} and ΔS_{ex} values in Table 1 after compensating for the dehydration terms. Therefore, the sum of the standard hydration and the extraction enthalpy (or entropy) terms, which is given in Table 1, will represent a roughly estimated amount of the enthalpy (or entropy) of the extraction motive processes in the case of the complete dehydration. If the dehydration process is not completed and the extracted cations retain a part of the hydration water in the organic phase, the energies of the extraction motive processes may not be necessary to compensate for the whole amount of the standard hydration energy.

The reason why the most of the uni-charged metal ions are

solvated with three TOPO molecules but rubidium and cesium are with four is not clear from the data in Table 1, although a meaning difference in the thermodynamic data should be expected between potassium and rubidium. Since the size of the smaller alkali metal ions is not always smaller than Be^{2+}, Sc^{3+}, or Ga^{3+} all of which are solvated with four TOPO molecules, steric hindrance around the metal ions should not be the reason for the smaller solvation number. If TOPO molecules combine to a metal ion via hydration water molecules, namely, they bind with the protons of the hydration water, it will be easy to explain the large solvation number for the small ions such as Be^{2+}. Solvation of TOPO to the hydration water seems to be certain for Cr^{3+} because chromium perchlorate was extracted to hexane with five TOPO molecules and the extraction equilibrium was completed within a few minutes. Since chromium(III) ion is inert for ligand exchange reactions, such a rapid replacement of the hydrating water with TOPO molecules is implausible. In contrast, ferric perchlorate is extracted with four TOPO. Although the solvation number is smaller, the extraction is much better than Cr^{3+}. Comparing the extraction of these two tervalent ions, it may be concluded that Fe^{3+} ions will release the hydration water at least partly on the extraction and retain lesser amount of water in the organic phase than Cr^{3+} ions do.

On the basis of these discussions, the idea that lithium ion might hold some amount of water but rubidium and cesium will have less amount in the organic phase may not be unreasonable. This will explain the apparent tendency of the extraction enthalpy and entropy of the alkali perchlorates; they are negatively larger in larger ions. Further thermodynamic study will be necessary for finding the more reliable conclusion.

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FLUID DYNAMICS OF PULSED SIEVE-PLATE EXTRACTION COLUMNS

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INTRODUCTION

An extensive research has been done on the fluid dynamics of two pulsed sieve-plate extraction columns on a pilot scale. The object was to improve the basis for design as well as to investigate the scale-up of this type of extraction column. Special emphasis was placed on the hydrodynamic behaviour of the pulsed sieve-plate extraction column as a function of the liquid-liquid system and the plate geometry. The investigations encompass measurements of the drop size distribution, hold-up, flooding throughput and mixing in both phases.

1 EXPERIMENTAL AND TECHNIQUES OF MEASUREMENT

The measurements were carried out for different column-diameters (D=80 and 225 mm), sieve-plate geometry (hole diameter of d_h=2, 4 and 6 mm, fractional free area of φ=23, 39 and 49%), plate distance (from 50 to 100 mm), load (v_d+v_c: 60 and 80 per cent of the maximum throughput), pulsation frequency (from f=0.0 to 2.5 Hz), pulsation amplitude (from a=6 to 12 mm) and phase ratio (v_d/v_c: between 0.5 and 5.0). Water was used as the continuous phase and toluene ($\sigma=35.4\cdot10^{-3}$ N/m, ρ=867 kg/m^3, $\eta=0.586\cdot10^{-3}$ Pa·s), butylacetate ($\sigma=14.1\cdot10^{-3}$ N/m, ρ=882 kg/m^3, $\eta=0.730\cdot10^{-3}$ Pa·s) or butanol ($\sigma=1.75\cdot10^{-3}$ N/m, ρ=810 kg/m^3, $\eta=2.948\cdot10^{-3}$ Pa·s) as the dispersed phase.

The experimental set-up of the column with an active length of 4.3 m and the positions of the measuring devices are shown schematically in Fig. 1. With the exception of the butanol/water system, the drop size distribution was measured with photoelectric suction probes at five positions along the length of the column (DSD in Fig. 1). For the butanol/water system this measurement was done photographically at a height of 3.5 m above the distributor (DSDP in Fig. 1). The integral hold-up was determined over the active length of the column by means of the displacement method. In addition, an average hold-up was measured over a column section for all experiments with the differential pressure method (DP in Fig. 1). The flooding point was determined for a constant throughput by a stepwise increase or decrease of the pulsation frequency. Flooding, which is characterized by a nonsteady-state behaviour of the column, was recognized by visual observation of the individual column

sections. For the determination of the residence time behaviour of both phases, a nonsteady-state tracer injection method was applied. An aqueous salt solution was employed as tracer for the continuous phase. The concentration of this tracer was measured with conductivity probes. For the dispersed phase a fluorescent tracer was used which allows the measurement of the concentration with photomultipliers.

2 RESULTS AND DISCUSSION

The results presented in this paper were obtained at a phase ratio of one, a plate spacing of 100 mm, and a pulsation amplitude of 8 mm. The effect of these operating parameters on the fluid dynamics of pulsed sieve-plate extraction columns is already known from earlier investigations (Aufderheide, 1985 and Reissinger, 1985).

2.1 Drop size distribution

As is the case for all extractors, the drop size distribution which is established in pulsed sieve-plate columns results from the interaction between drop breakage and drop coalescence. For the systems under consideration, coalescence is only of minor importance in the technically significant operating range of the column. Since the dispersed phase was only coarsely predispersed at the distributor during the investigations, the Sauter diameter and the standard deviation of the drop size distribution decreased in the direction of flow of the dispersed phase as a result of repeated breakage at the sieve-plates. As shown by motion pictures and single-drop experiments performed in parallel, breakage occurs exclusively during the passage of the drops through the holes of the sieve-plates (Haverland, 1988).

As the measured drop size profiles show, the decrease in the average drop diameter occurs essentially during the passage through the first sieve-plates immediately above the distributor. Thereafter, a stable drop size distribution is established which depends on the sieve-plate geometry and the interfacial tension of the system, in addition to the pulsation intensity. For a constant pulsation intensity, the stable drop size is attained sooner with smaller hole diameter or fractional free area of the sieve-plates, and a lower interfacial tension of the system. The drop size profile is a function only of the number of sieve-plates. Thus the average drop diameter of the stable drop size distribution in the upper section of the column is independent of the sieve-plate distance.

The dependence of the stable drop size on the pulsation intensity, the sieve-plate geometry and the liquid-liquid system is illustrated in the upper part of Fig. 2 (DSD3 position of measuring). Because of the increasing energy

input and the associated increase in the forces which destabilize the drops, the Sauter diameter decreases with increasing pulsation intensity. Due to the different dispersive action of the sieve-plates, the drop size distribution is shifted toward smaller drop sizes with decreasing hole diameter. A decrease in the interfacial tension results in a decrease in drop stability and thus in smaller Sauter diameters under otherwise constant operating conditions. The standard deviation, which characterizes the width of the distribution, exhibits the same dependence on the operating parameters as does the average drop size.

The measurements have demonstrated that the drop size which is established in the column is independent of the column diameter, the phase ratio and the throughput in the usual operating range of a pulsed sieve-plate extraction column. Moreover, the drop size essentially depends on the pulsation intensity, that is, on the product of amplitude and frequency. No significant separate effect of pulsation amplitude or frequency was observed (Aufderheide, 1985).

2.2 Hold-up

The hold-up is directly influenced by the throughput of both phases and by the relative velocity of the drop swarm which depends on the drop size, system properties and the retarding effects on the drop motion associated with the pulsation and the sieve-plates. Under all operating conditions, the local hold-up continuously augments in the flow direction of the dispersed phase because of the decreasing drop size and the associated decrease in the relative velocity of the drops. The throughput of the dispersed phase thereby exerts a far more pronounced influence on the hold-up than the throughput of the continuous phase. At a constant total throughput, the hold-up, therefore, augments with increasing phase ratio.

The dependence of the total hold-up on the pulsation intensity, the liquid-liquid system, and the sieve-plate geometry is illustrated in the lower part of Fig. 2 for values of the throughput of about 80% of the flooding load. The integral hold-up value plotted as a function of the pulsation intensity for a constant throughput exhibits a more or less pronounced parabolic curve with a minimum at the transition between the mixer-settler and dispersion range. This typical shape of the hold-up curves is caused by the interaction between the free movement of drops and the delay caused at the sieve-plates. The minimum of the hold-up curve is shifted towards lower pulsation intensity with decreasing interfacial tension of the system.

As already mentioned, the motion of the drops in the mixer-settler range is influenced by the blocking action of the sieve-plates. As indicated by investigations by Hussain et al. (1988), the blocking action of the sieve-plates

decreases with decreasing ratio of the drop to the hole diameter, increasing fractional free area of the sieve-plates, and augmenting pulsation intensity. With the dependence of the drop size on the operating parameters taken into account, the hindrance of the drop motion by the sieve-plates thus increases with augmenting interfacial tension and diminishing intensity of pulsation. For this reason, the increase in hold-up with decreasing pulsation intensity is most pronounced with the toluene/water system.

The evaluation of the measurements has shown that the hold-up does not depend on the column diameter for equal superficial velocities. Earlier investigations did not indicate any unequivocal separate dependence of the hold-up on the amplitude and frequency in the range of variation for the pulsation conditions (Aufderheide, 1985). The data available from literature (i. e. Kumar, 1988) indicate that a decrease in plate spacing results in a decrease of the average velocity of drop ascent and consequently in an increase in hold-up, especially at a low pulsation intensity.

2.3 Flooding

The flooding point curves measured for three different liquid-liquid systems as a function of the sieve-plate geometry and the pulsation intensity at a constant phase ratio of one in the column with D=80 mm are presented in Fig. 3. The measured flooding curves exhibit the well known shape as a function of the pulsation intensity. The displacement of the maximum flooding throughput towards lower pulsation intensities with decreasing interfacial tension is clearly recognizable. This flooding characteristic results from the dependence of the drop size and average relative velocity on the pulsation intensity, the sieve-plate geometry and the system properties explained in the preceding sections.

A conspicuous feature, however, is the observation that the respective flooding throughput for the sieve-plate geometry with a hole diameter of 2 and 4 mm for the toluene/water and butylacetate/water systems, respectively, are of the same order of magnitude. The visual observation of the drop pictures during the flooding point determination of the butylacetate/water system indicates the relatively high hold-up values in the proximity of the flooding point and more pronounced drop-drop coalescence. Because of this deviation, an additional increase in throughput can be achieved until the countercurrent flow is completely disturbed and finally disrupted.

The investigations have shown that the flooding throughput slightly increases with augmenting column diameter. No significant separate dependence of the flooding throughput on the amplitude or frequency is observed in analogy with the drop size and the hold-up (Aufderheide, 1985).

Further conclusions on the dependence of the flooding throughput on the system and sieve-plate geometry result from the investigations of Berger et al. (1985) and Hirschmann (1984). The measured data of these authors and the presented ones confirm the well known relationship from the literature that a higher flooding load can be achieved with increasing plate spacing.

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position of measuring:

DSD	drop size distribution (photoelectric suction)
DSDP	drop size distribution (photographic)
DP	differential pressure (wet/wet transmitter)
T	temperature (thermocouples)

tracer injection:

CPTI	continuous phase (salt tracer)
DPTI	dispersed phase (luminescent tracer)

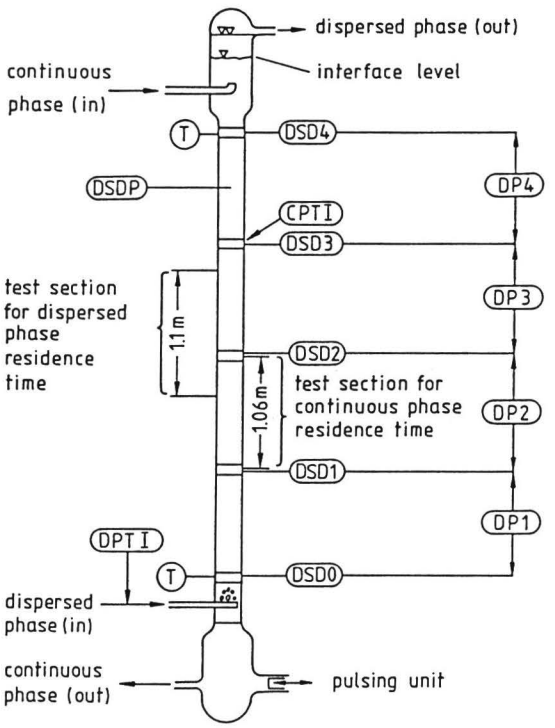


Fig. 1. Experimental set-up

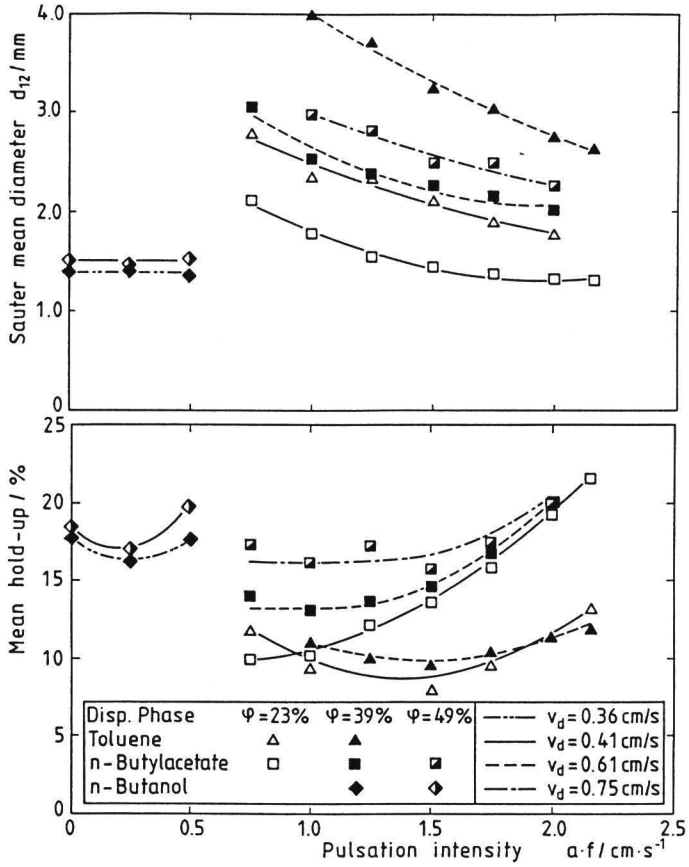


Fig. 2. Sauter diameter and mean hold-up as a function of pulsation intensity (Location DSD3, D=80 mm, ■ D=215 mm)

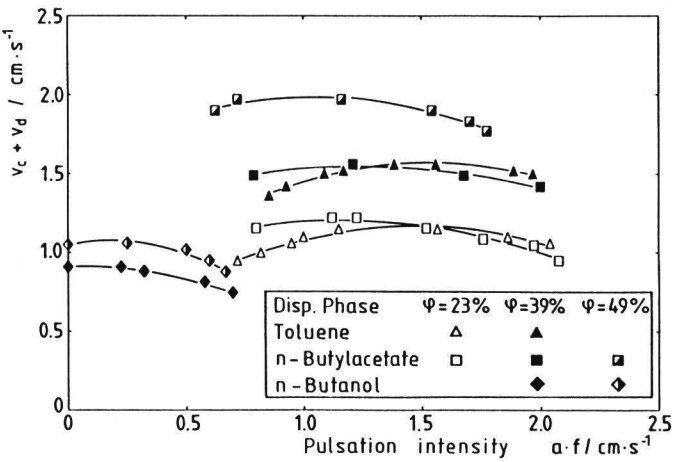


Fig. 3. Maximum of throughput as a function of pulsation intensity (D=80 mm)

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ON THE MECHANISM OF COBALT EXTRACTION FROM CHLORIDE SOLUTIONS USING TRI-ISO-OCTYLAMMONIUM CHLORIDE.

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The distribution of cobalt between a chloride solutions and a tri-iso-octylammonium chloride (R_3NHCl=A) has been investigated under different conditions. The effects of the ionic composition of the aqueous phase ($0 \leqslant LiCl \leqslant 15m$; $0 \leqslant NiCl_2 \leqslant 4.5m$; $0 \leqslant HCl \leqslant 14m$ (m = mol/kg)), the extractant concentration and the type of diluent have been considered. The measurements of water and HCl contents of the organic phase were carried out in addition to the partition of cobalt ; the aggregation of the extractant was also investigated by two-phase emf titrations. The experimental data have been treated by means of a generalized minimizing program, AFFINEX based on real phenomena i.e. physical and chemical interactions. All these experiments can be explained by the formation in the organic phase of species $A(H_2O)$; $A(H_2O)_2$; $[A(H_2O)]_2$; A_2CoCl_2 ; $A_3CoCl_2(H_2O)$ and $A(HCl)(H_2O)_2$; $A(HCl)_2$; $[A(H_2O)]_2(HCl)$; $A_4(HCl)(CoCl_2)_2(H_2O)$ in the presence of HCl solutions. In spite of the existence of $A_3CoCl_2(H_2O)$, a fairly good agreement is obtained by applying our model to literature experiments which concluded to the formation of a single 2:1 complex and an explanation will be proposed. At high HCl molalities, the extraction results from the competition between cobalt and hydrochloric acid species with the appearence of a mixed entity $A_4(HCl)(CoCl_2)_2(H_2O)$.

The study of cobalt extraction from chloride solutions using tri-iso-octylammonium chloride : R_3NHCl leads to (i) a general model based on chemical and physical interactions describing the extraction of the metal in chloride media. (ii) This model will be then compared to literature data.

1) The setting up

The cobalt extraction model has been established thanks to the measurements of water and HCl contents of the organic phases as well as the extraction isotherms in $NiCl_2$, LiCl and HCl media. The measurements have been treated by means of a generalized minimizing program AFFINEX (1). The experimental methods have been described in proceedings ISEC 86 (2).

Cobalt concentrations have been measured by two ways :

- Absorption spectrophotometry (VARIAN DMS 90, λ = 622 nm)
- Inductively coupled plasma atomic emission spectrometry (ARL 3510)

The research of the best model is carried out :

a) with the already obtained stability constants of the cobalt chlorocomplexes (2).

b) by fixing the equilibrium constants relative to the aggregation and hydration of the extractant and to the extraction of an excess of HCl in HCl media.

c) by introducing the following hypothesis :

$ACoCl_2$, A_2CoCl_2 , A_3CoCl_2 which are underscored (2)

d) by varying the number of moles of water fixed to the different previous species.

e) by fixing the interactions parameters at Bromley's values (3) for $Ni^{2+}(Li^+, H^+)$, Cl^- and Co^{2+}, Cl^- and by refining the interactions between chlorocomplexes and $Ni^{2+}(Li^+, H^+)$.

It has been considered that interactions between chlorocomplexes and other ions are the same whatever the degree of formation e.g. $B_{Co,Cl} = B_{CoCl,Cl} = B_{CoCl_2,Cl} = B_{Co,CoCl_2} = B_{Co,CoCl_3} = B_{Co,CoCl_4}$

idem $B_{Ni(Li, H), CoCl_2} = B_{Ni(Li,H), CoCl_3}$ .....

The species found to give the best fits, their stability constants as the introduced interaction parameters are listed in Table I.

TABLE 1 : General model for cobalt extraction bu R_3NHCl from chloride solutions.

Components					Species		
R_3NHCl,H_2O	$Co(H_2O)_6^{2+}$	Cl^-	H^+	H_2O		$\log_T$	Phase
0	1	1	0	-1	$CoCl(H_2O)_5^+$	-0.340	aq.
0	1	2	0	-1	$CoCl_2(H_2O)_2$	-3.240	"
0	1	3	0	-5	$CoCl_3(H_2O)^-$	-6.070	"
0	1	4	0	-6	$CoCl_4^{2-}$	-8.640	"
1	0	0	0	+1	$R_3NHCl(H_2O)_2$	0.145	org.
2	0	0	0	0	$(R_3NHCl,H_2O)_2$	1.570	"
1	0	1	1	+1	$R_3NHCl,HCl(H_2O)_2$	-1.903	"
1	0	2	2	-1	$R_3NHCl(HCl)_2$	-7.893	"
2	0	1	1	0	$(R_3NHCl,H_2O)_2HCl$	-0.764	"
2	1	2	0	-8	$(R_3NHCl)_2CoCl_2$	0.28	"
3	1	2	0	-8	$(R_3NHCl)_3CoCl_2(H_2O)$	2.414	"
4	2	5	1	-15	$(R_3NHCl)_4HCo_2Cl_5(H_2O)$	-0.988	"

Interactions parameters : $B_{Co,Cl}=0.1016$; $B_{H,Cl}=0.1433$; $B_{H,CoClx}=0.10$
$B_{Ni,Cl}=0.1039$; $B_{Ni,CoClx}=0.0463$; $B_{Li,Cl}=0.1283$; $B_{Li,CoClx}=0.01$

To get from a media to another, for example from HCl to LiCl, it is sufficent to substitute $B_{H,Cl}$ by $B_{Li,Cl}$.

1.1. Highly concentrated solutions have been considered until 4,5m for $NiCl_2$(fig. I), 15 m for LiCl, 14m for HCl.
However the great coherence of the model makes it valid for any media.

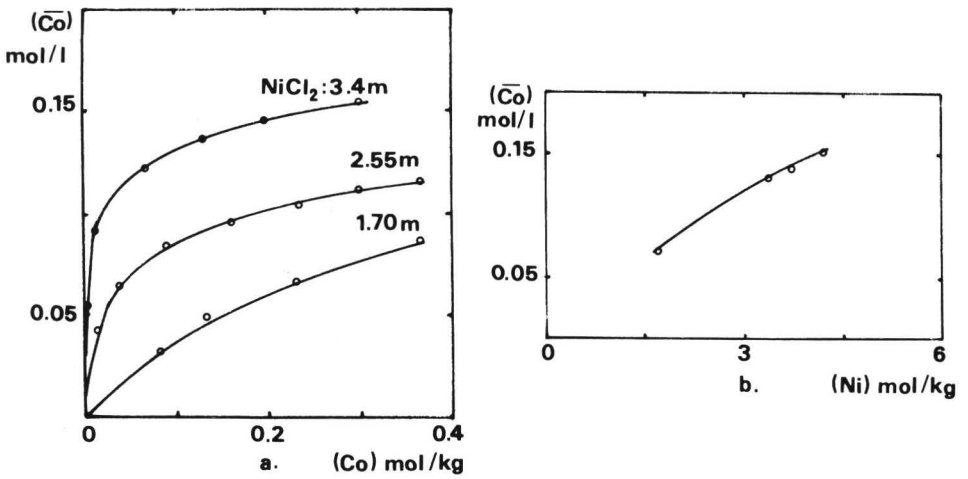


Fig.1. Cobalt extraction from $NiCl_2$ solutions by R_3NHCl=A (industrial diluent)
a) Extraction isotherms (A ≅ 0,399 M)
b) Evolution of cobalt extraction as a function of $NiCl_2$ molality
(A = 0,388 M ; Co initial = 0,4 m)
∘ experimental data — Calculated curves

1.2. The influence of diluent has been considered : industrial diluent, (supplied by MINEMET RECHERCHE), aromatic solvent (Solvesso 150, supplied by ESSO),Xylene.
The change from the industrial diluent to xylene needs only the refinement of the organic chlorocomplexes of cobalt stability constants. The stability constants remain approximatly the same, thus R_3NHCl has the same behaviour in the two diluents (Fig. II.a)
However when Solvesso 150 is used as diluent, only one complexe seems to be formed : $\overline{A_3CoCl_2(H_2O)}$ (Fig.II.b).
This phenomenon is probably due to the aggregation of the extractant in a medium whose dielectric constant is weak. (A third phase appears when $(NiCl_2) \geqslant 1,3$ m).

The final model is made up of :

1) The aqueous chlorocomplexes of Co

$Co(H_2O)_xCl_n^{2-n}$ $\quad (1 \leqslant n \leqslant 4 \ ; \ 0 \leqslant x \leqslant 5)$.

2) Organic species due to the aggregation, the hydration and chlorohydration of the extractant A, that is to say :

a) $\overline{A(H_2O)_n}$ n = 1, 2

b) * $\overline{(A,\ H_2O)_2(HCl)_m}$ (m = 0,1) ; * $\overline{(A,\ HCl,\ H_2O)_2}$; * $\overline{A\ (HCl)_2}$

These species have been brought to the fore :

a) by refinement of two-phase emf titrations.
(Biphas Program, to be published)

b) by following the extraction of water and HCl without cobalt.

3) The extracted species :

$\overline{A_2CoCl_2}$, $\overline{A_3CoCl_2(H_2O)}$, * $\overline{A_4HCo_2Cl_5(H_2O)}$

4) The interaction parameters between ions of opposite charges or between ions and neutral molecules :

- $B_{Co,Cl}$ and $B_{N,Cl}$ (N = Ni, Li, H) at Bromley's values
- $B_{N,CoCl_x}$ introduced in the refinement.

(* only in HCl medium).

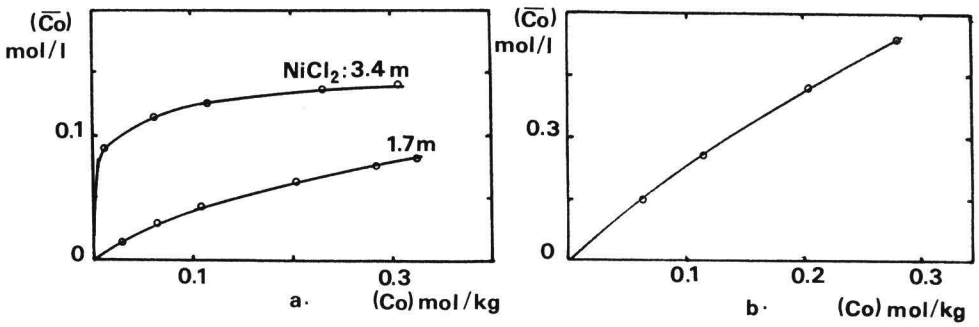


Fig.II. Experimental and calculated extraction isotherms of Co, from $NiCl_2$ solutions.

a - by R_3NHCl : 0,392 M, diluent : Xylene

b - by R_3NHCl : 0,403 M, diluent : Solvesso 150

2) Validity of the model

The fact that the model used fits so well the data found in the literature proves the validity and unicity of the model.

However this method goes against the classical method used to know the stoichiometry of the extracted species by plotting log (partition coefficient) versus f (extractant concentration). Although $\overline{A_3CoCl_2(H_2O)}$ can be predominant in some fields, the slope of the straight line remains constant and equal to 2. Our model applied to Brooks and all results predicted it (Fig.III).

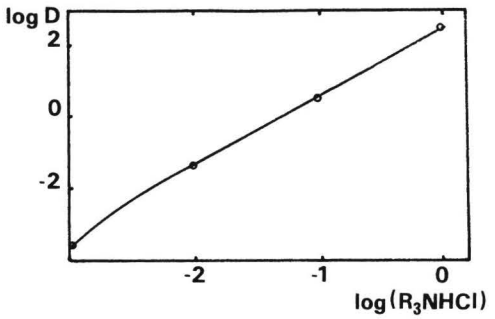


Fig.III : Distribution of cobalt between R_3NHCl and $NiCl_2$ as function of R_3NHCl concentration

This all calls into question the currently used that is to say the "anion exchange reaction" :

$$2\,\overline{A} + CoCl_4^{=} \rightleftharpoons \overline{A_2CoCl_2} + 2\,Cl^-$$

First of all, $CoCl_4^{=}$ doesn't need be present for this extraction. On the other hand, $\overline{A_3CoCl_2(H_2O)}$ seems to predominant especially for weak Co concentrations in aqueous media.

Figure IV proves that it's more complicated than usually postulated.

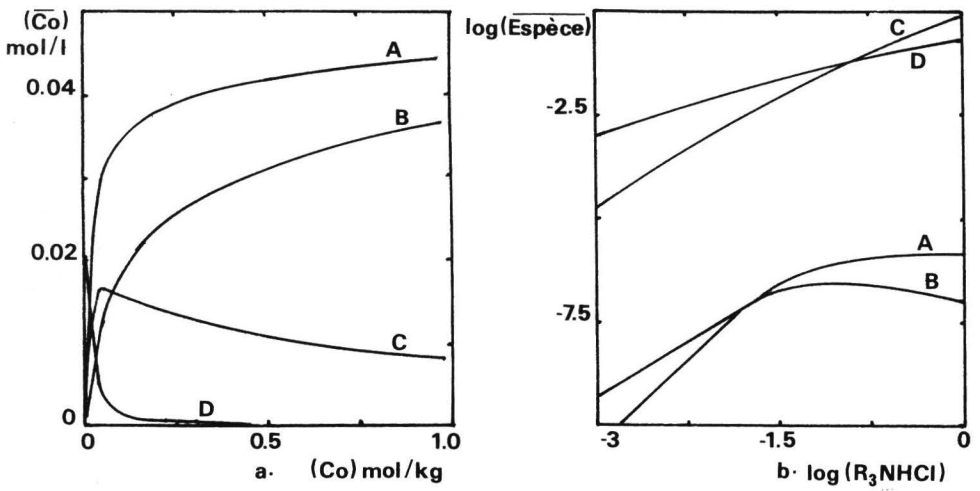


Fig.IV. Distribution of the indicated organic cobalt species.

a. as function of cobalt concentration
(A) general extraction isotherm for Co = B + C
(B) $(R_3NHCl)_2\,CoCl_2$; (C) $(R_3NHCl)_3CoCl_2(H_2O)$; (D)$(R_3NHCl, H_2O)_2$

b. as function of R_3NHCl
(A)$(R_3NHCl)_3CoCl_2(H_2O)$; (B) $(R_3NHCl)_2CoCl_2$; (C) $(R_3NHCl,H_2O)_2$
(D) $R_3NHCl,H_2O + R_3NHCl(H_2O)_2$

So when the extractant is very diluted, the aggregation is not any more significant and the usual mechanism is true. In the same time, the aggregation of the extractant and $\overline{A_3CoCl_2(H_2O)}$ increase. When the concentration overcomes about 0,02 M, $\overline{A_3CoCl_2(H_2O)}$ becomes more important than $\overline{A_2CoCl_2}$. Indeed, the slope of two coincides first of all with the real mechanism of extraction and then to the mechanism of aggregation of the extractant.

Our model also agrees with the results of Sato (4) (fig.V) despite the different extractant $\overline{TOA}$.

In fact, the limiting value of 0,5 for $(Co)_{org}/\overline{(TOA)}$ fit only the major specie when there is an excess of Co i.e. $\overline{A_2CoCl_2}$.

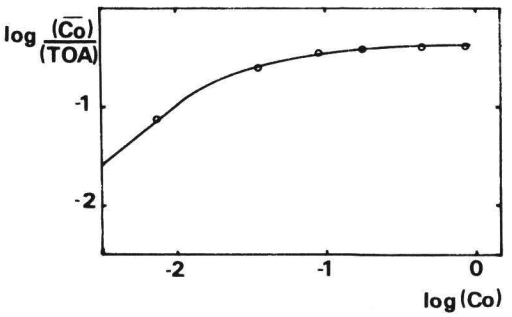


Fig.V. Varying extracted cobalt by tri-n-octylamine as function of aqueous cobalt.

3) Conclusions

The general model is very consistent, it allows a good representation of a lot of very different experimental data : extraction of metal, of water and of HCl. It is valid for aqueous phases of very different ionic composition (nature and concentration) and for an extractant of variable concentration. The hydration part is very important since its misunderstanding leads to adjustements whose quality is not that good, even when you just pay attention to the extraction of metal.

Up to now the different models had proposed some constants depending on the initial conditions, like the media so their use could not be extended to any system.

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SOLUBILITY OF FATTY ACID METHYL ESTERS IN WATER

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ABSTRACT

Solubility data of fatty acid esters in water are important for the purification of biologically active fatty acids. In this study, solubility in water of four fatty acid methyl esters and liquid-liquid equilibria for two ternary systems were measured by a gas chromatographic method. Solubilities decreased exponentially with increasing carbon number. The NRTL model was found to be successful in predicting equilibria for the ternary systems, in which NRTL binary parameters were determined from mutual solubilities.

1. INTRODUCTION

Some fish oils and vegetable oils include biologically active long-chain fatty acids. A potential candidate of purification scheme for these fatty acids consists of separation in the form of their esters using liquid-liquid contact operations such as extraction and liquid membrane permeation which require solubility data of esters in aqueous phase and predicting methods of them. Although solubilities of fatty acids and their ethyl esters in water have been studied by several investigators (Ralston and Hoerr,1942; Eggenberger et al., 1949; Sobotka and Kahn, 1931), solubility data of fatty acid methyl esters could not been found in literature.

This paper describes solubility of fatty acid methyl esters in water and liquid-liquid equilibria for ternary systems consisting of two methyl esters and water. The NRTL model was used to predict the equilibria.

2. EXPERIMENTAL

2.1 Materials

Four fatty acid methyl esters, methyl pentanoate(C5), methyl hexanoate(C6), methyl heptanoate(C7) and methyl octanoate(C8), were reagent grade chemicals supplied by Kanto Chemical Co. Water used was ion-exchanged and distilled one.

2.2 Procedures

Glass tubes (length : 80 mm) were used to make equilibrium between ester and aqueous phases. The glass tubes had two screwed ends on both sides. Both ends were sealed with Teflon sheets and screw caps having 5 *mm* bored holes. Initially 8 *ml* of water and 1 *ml* of pure ester or a two-component ester mixture were poured into the tube. The tube was shaken

in a constant temperature water bath for a day and then ester droplets dispersed in aqueous phase were settled using a centrifuge. After settling, the tube was again kept at the initial temperature without disturbing for more than two days.

Equilibrium concentrations in aqueous phase were determined by a gas chromatograph (Shimadzu Manuf. Co., GC-14A) with a FID detector and Unisol-3000 as a packing material. One μl of aqueous phase was sampled by a micro cylinge through the bottom-side Teflon sheet. Relations between ester concentrations and peak areas had been calibrated in advance. Water concentration in the ester phase was determined by a Karl Fischer Analyzer. Water-free compositions of esters in ester phase were assumed to be equal to the compositions of feed ester mixtures because the amount of ester transferred to the aqueous phase was negligibly small in comparison with the amount remaining in the ester phase.

Solubilities of four pure esters in water were measured at 283.2K and 303.2K. Liquid-liquid equilibria for two ternary systems, C5-C6-water and C7-C8-water, were examined at 283.2K.

3. RESULTS AND DISCUSSION

3.1 Solubility of pure component

Solubility data of fatty acid methyl ester in water and those of water in ester phase are summarized in Table 1, while the relations between solubility and the carbon number of fatty acid group in ester are shown in Fig. 1. Logarithm of the solubility of esters decreased linearly with increasing carbon number (Fig. 1), while that of water in ester phase attained plateau where carbon number of ester was greater than 7 (Fig. 2). The solubilities of methyl esters distributed in the middle between those of fatty acids and ethyl esters having the same carbon number (Fig. 1).

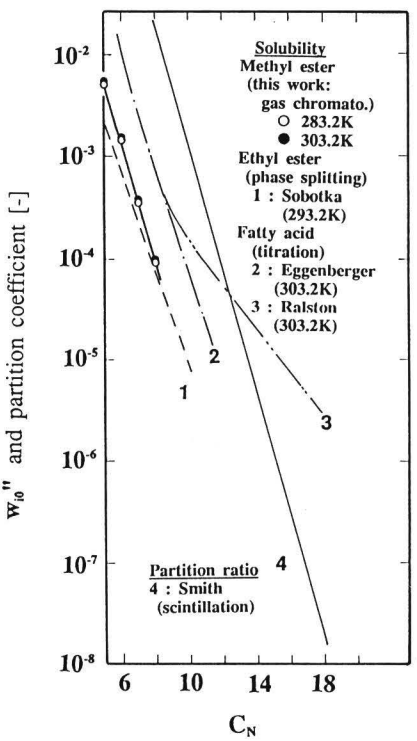


Fig. 1 Solubility of fatty acid and their esters and partition coefficient of fatty acid

3.2 Liquid-liquid equilibria for ternary systems

Fig. 3 shows liquid-liquid equilibria for methyl pentanoate(1) - methyl hexanoate(2)

TABLE 1

Solubility of fatty acid methyl esters and water

			283.2K		303.2K
Methyl ester(i)	w_{i0}''	x_{i0}''	w_{30}'	x_{30}'	w_{i0}''
pentanoate(C5)	5.10×10^{-3}	7.95×10^{-4}	0.00660	0.0411	5.59×10^{-3}
hexanoate(C6)	1.36×10^{-3}	1.89×10^{-4}	0.00455	0.0320	1.57×10^{-3}
heptanoate(C7)	3.50×10^{-4}	0.46×10^{-4}	0.00315	0.0246	3.94×10^{-4}
octanoate(C8)	0.95×10^{-4}	1.08×10^{-5}	0.00275	0.0236	9.73×10^{-5}

TABLE 2

NRTL binary parameters (α_{12}=0.3)

Methyl ester	τ_{12}	τ_{21}
C5(1) - water(2)	2.6483	5.9655
C6(1) - water(2)	3.0990	7.3533
C7(1) - water(2)	3.5359	8.7489
C8(1) - water(2)	3.7782	10.2042
C5(1) - C6(2)	0.1179	-0.1116
C7(1) - C8(2)	0.0723	-0.0697

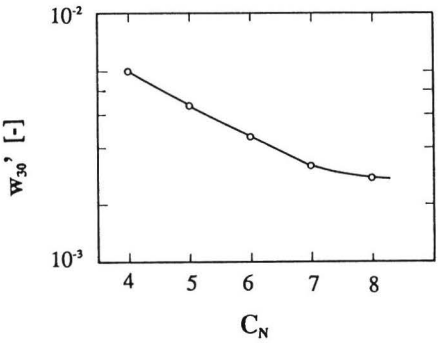


Fig. 2 Solubility of water in ester (283.2K)

- water(3) system. The vertical bars crossing data points indicate data ranges determined from multiple measurements, while circles show their averages. Because the solubilities of esters and water are very low, phase splitting area was close to the coordinate triangle.

Renon and Prausnitz (1969) demonstrated that the NRTL model (eqn. 1) is useful to predict activity coefficients in ternary liquid-liquid eqilibria for those systems having two immiscible binary pairs.

$$\ln \gamma_i = \frac{\sum_{j=1}^{N} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{N} G_{ki} x_k} + \sum_{j=1}^{N} \frac{x_j G_{ij}}{\sum_{k=1}^{N} G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_{i=1}^{N} x_i \tau_{ij} G_{ij}}{\sum_{k=1}^{N} G_{kj} x_k} \right) \qquad (1)$$

where $ln\ G_{ij} = -\alpha_{ij}\tau_{ij}$.

Therefore, in this work eqn.(1) was applied to predict the equilibria for the C5-C6-water system. NRTL binary parameters of ester-water systems were determined from mutual solubility data in Table 1 with 0.3 for α_{ij} recommended by Renon and Prausnitz (1968) for nonpolar-polar mixtures. Fig. 4 shows linear relations between carbon number and NRTL binary parameters.

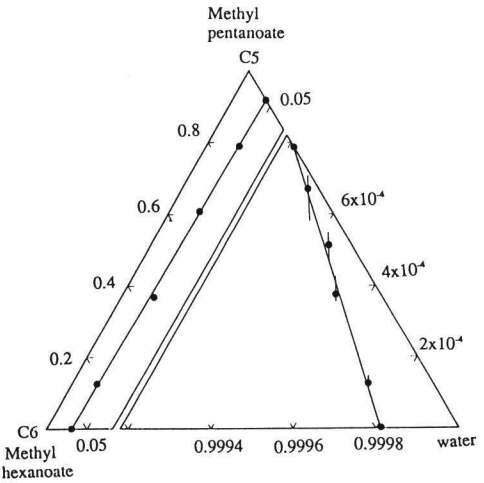


Fig. 3 Liquid-Liquid equilibria for C5-C6-water system (283.2K)

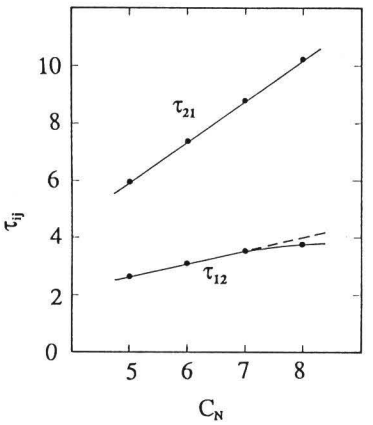


Fig. 4 Ralations between carbon number and NRTL parameters

NRTL parameters for the C5-C6 mixture were determined by use of activity coefficients at infinite dilution estimated by MOSCED method (Thomas, 1984): γ_5^{∞} =1.00223, γ_6^{∞} =1.00253. Table 2 shows these parameters. The condition of equilibrium in a ternary system is

$$\gamma_i' x_i' = \gamma_i'' x_i'' \quad (i = 1,2,3). \tag{2}$$

Solid lines in Fig. 3 show the ternary equilibria estimated using eqn.(2) in which the NRTL model was used for the prediction of activity coefficients; we can successfully predict the liquid-liquid equilibria by the NRTL model for a mixture of fatty acid methyl esters and water.

Fig. 5 shows a distribution composition curve (water-free base) for the C5-C6-water system. Because concentration ratios of esters can be accurately measured within 2 % of fluctuations, the maximum difference of about 10 % between measured and estimated water-free fractions may be due to the failure in the NRTL model. Predicted results were insensitive to the value of nonrandomness parameter α_{ij}: replacing 0.3 with 0.2 for α_{ij} caused only 2 % difference in predicting compositions. Furthermore, even if C5-C6 solution was assumed to be ideal solution ($\tau_{12}=\tau_{21}=0$), predicted values differed merely 1 %.

Fig. 6 shows direct relations between solubilities of esters in aqueous phase and ester phase composition. The solubilities show straight line against ester phase composition, which results from very low solubility of ester and water and also the ideality of C5-C6 solution. In a binary system, if $x_{30}' \approx 0$, then $\gamma_i' x_{i0}' \approx 1$. Therefore,

$$x_{i0}'' = 1 / \gamma_i'' \tag{3}$$

For a ternary system, if $x_3' \approx 0$, then $x_i' \approx x_i'/(x_1'+x_2')$ and $\gamma_i' \approx 1$ since activity coefficients even at infinite dilution were very close to unity. Therefore,

$$x_i'' = (1 / \gamma_i'') [x_i' / (x_1' + x_2')] \tag{4}$$

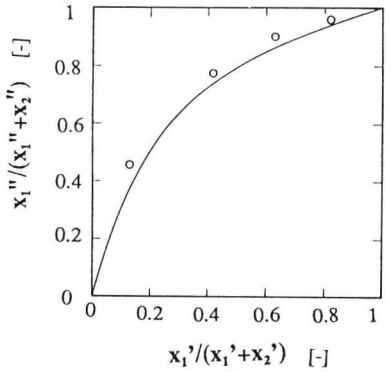


Fig. 5 Distribution composition curve for C5-C6-water system (283.2K)

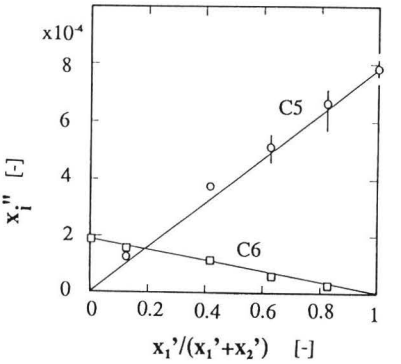


Fig.6 Relation between solubility and water-free mole fraction (283.2K)

If $x_i''\approx 0$ in both binary and ternary cases, the NRTL equation can be simplified as follows

$$\ln \gamma_i'' = \tau_{31} + \tau_{13}\, exp(-\alpha_{13}\tau_{13}) \qquad (5)$$

From eqns. (3),(4) and (5), eqn. (6) can be derived,

$$x_i'' = x_{i0}''\,[\, x_i' / (x_1' + x_2')\,] \qquad (6)$$

which is identical with the lines drawn on Fig. 6.

Figures 7,8 show solubility curves and distribution composition curve (water-free base) respectively for methyl heptanoate(1) - methyl octanoate(2) - water(3) system. Results appearing in these figures were very similar to those for C5-C6-water system.

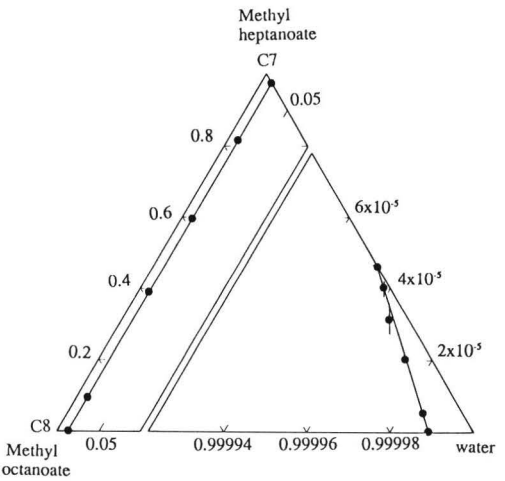


Fig. 7 Liquid-Liquid equilibria for C7-C8-water system (283.2K)

4. CONCLUSIONS

Mutual solubilities of each fatty acid methyl ester in water decreased exponentially with increasing carbon number and they distributed in the middle between those of fatty acids and fatty acid ethyl esters.

Solubility curves for ternary systems were linear for both methyl pentanoate-methyl hexanoate-water system and methyl heptanoate-methyl octanoate-water system. NRTL model was

found to be successful in predicting these solubility curves.

5. SYMBOLS

C_N = carbon number of fatty acid group in ester
w_i = weight fraction of component i
x_i = mole fraction of component i

Superscripts
' = ester phase
" = aqueous phase

Subscripts
i,j = component or ester i,j
0 = binary
1,2 = ester 1,2
3 = water

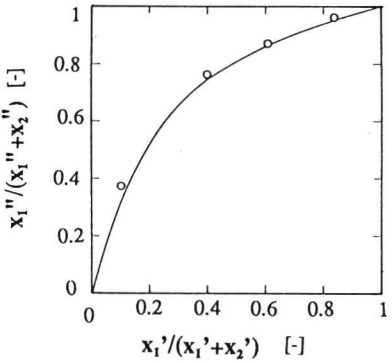


Fig. 8 Distribution curve for C7-C8-water system (283.2K)

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EXTRACTION OF DIVALENT METALS WITH MONO(2,4,4-TRIMETHYLPENTYL)PHOSPHINIC ACID.

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ABSTRACT

Mono(2,4,4-trimethylpentyl)phosphinic acid (HMTMPP) was synthesized and characterized by measurements of several physical properties (refractive index, acid-dissociation constant, IR, ^{31}P NMR).

The extraction of Cu(II), Zn(II), Cd(II), Pb(II), Co(II) and Fe(III) from 1 mol.dm^{-3} aqueous nitrate solutions by HMTMPP dissolved in toluene has been studied with relation to the equilibrium pH in the aqueous phase.

Results are compared with those obtained with bis(2,4,4-trimethylpentyl)phosphinic acid (HBTMPP).

The influence of the addition of some extractants as TLA and TOPO to the HMTMPP system has been tested.

INTRODUCTION

In recent years several new organophosphorus compounds have been studied. Among these, much work has been devoted to the study of phosphinic acids, especially bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) and its ability to separate cobalt(II) from nickel(II). In particular, Danesi et al. (1985), Preston et al. (1988) and Yuan et al.(1988) have carried out comparatives studies of the extraction with dialkylphosphoric, alkyl alkylphosphonic and dialkylphosphinic acids. However, only Peppard et al. (1966) studied some monoalkylphosphinic acids, such as mono(n-octyl)phosphinic acid and mono(2-ethylhexyl)phosphinic acid.

In this work the extraction of copper(II), zinc(II), cadmium(II), lead(II), cobalt(II), as well as iron(III), from aqueous nitrate solutions, by mono(2,4,4-trimethylpentyl)phosphinic acid dissolved in toluene, has been studied at 25 ^{o}C. Results are compared with those obtained with bis(2,4,4-trimethyl pentyl)phosphinic acid (Cyanex 272). The influence of the addition of some extractants as TLA and TOPO to the HMTMPP system has been tested.

2 EXPERIMENTAL

2.1 Reagents and solutions

Mono(2,4,4-trimethylpentyl)phosphinic acid (HA) was synthesized by reaction of diisobutylene with sodium hypophosphite in the presence of tert-butyl perbenzoate in a water-ethanol medium, and was purified as described (Herranz et al., 1989)

Toluene, provided by Merck a.r., was used as solvent and sodium nitrate, provided by U.C.B. a.r., was used as the ionic medium.

2.2 Characterization of the reagent

The refractive index was determined at 23º C and was found to be 1.4590. I.R. and RMN P^{31} were also made.

The pK_a value was determined by potentiometric titration of samples dissolved in a mixture of 75% ethanol-water against a sodium hydroxide in a vessel termostatted at 20ºC.

A rough estimation of the aggregation constant, pK_a and distribution constant of HMTMPP between toluene and 0.05 $mol.dm^{-3}$ sodium nitrate was obtained from distribution data of HMTMPP as a function of pH and reagent concentration at 25º C. The aqueous HMTMPP concentration was determined using an ICP tecnique (Ke-an et al., 1985)

2.3 Metal distribution procedure

The entire experiment was carried out at 25º C. The experiments for metal distribution were performed as described previously (Sastre et al., 1990).

3 RESULTS AND DISCUSSION

3.1 Extractant properties

Potentiometric titration in 75% aqueous-ethanol showed the product to be a monoprotic acid. The pk_a value was calculated using normalized curves and is given in Table 1. This value is in the range of those obtained by Peppard et al.(1966) for different monoalkylphosphinic acids.

TABLE 1.

pK_a values in 75% aqueous-ethanol.

	pK_a
mono(n-octyl)phosphinic acid	3.77
mono(2-ethylhexyl)phosphinic acid	4.08
mono(2,4,4-trimetilpentyl)phosphinic acid	3.69<*>

<*> this work.

Some results obtained for the distribution of HMTMPP between toluene and sodium nitrate are shown in Figure 1. The distribution constant, pk_a and association constant were calculated numerically.

The results are given in Table 2. These show that HMTMPP is dimeric at the experimental conditions used. The pk_a value obtained in aqueous media is one unit

lower than in water-alcohol media.

TABLE 2.

Values of the distribution constant (K_d) of HMTMPP between toluene and 0.05 mol.dm^{-3} sodium nitrate, pK_a and dimerization constant (K_2).

$HA = HA_{org}$	$\log K_d = 0.3$
$2\ HA_{org} = HA_2$	$\log K_2 = 2.3$
$HA = A^- + H^+$	$pK_a = 2.5$

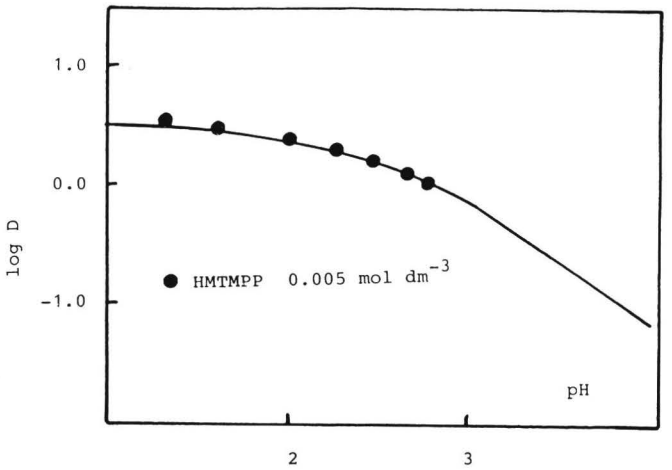


Fig. 1. Plot of log D versus pH for the distribution data for HMTMPP.

3.2 Metal distribution studies

The extraction of metals with mono(2,4,4-trimethylpentyl) phosphinic acid (HA) may be described with the following reaction:

$$M^{p+} + (p+q)/2\ (HA)_{2\ org} = MA_p(HA)_{q\ org} + p\ H^+ \qquad (1)$$

where

$$K_{pq} = \frac{[MA_p(HA)_q]_{org}\ [H^+]^p}{[M^{p+}]\ [(HA)_2]_{org}^{p+q/2}} \qquad (2)$$

is the stoichiometric equilibrium constant. This leads to the expression

$$\log D = \log K_{pq} + (p+q)/2 \log [(HA)_2]_{org} + p\ pH \qquad (3)$$

where D is the distribution coefficient of the metal. Making a plot of log D versus pH at constant reagent concentration gives a slope of p=2 for divalent metals. From equation 3, a plot of log D - 2 pH versus log $[(HA)_2]_{org}$ should give a straight line of slope (p+q)/2. Polynuclear metal complexes in the organic phase have been excluded because of these are independent of metal concentrations. The results obtained are given in Table 3.

TABLE 3.

Values of q and log K_{pq}, obtained graphically, for the extraction of several metals by HTMPP.

	q	$\log k_{2q}$
Zn(II)	2	-0.8
Pb(II)	3	-1.0
Cu(II)	2	-2.4
Cd(II)	3	-2.2

The results of this study of the $pH_{0.5}$ show that the extraction of metal ions follow the order Fe(III) > Zn(II) > Pb(II) > Cu(II) > Cd(II) > Co(II), which is the same as that found with HBTMPP (Table 4). The values of $pH_{0.5}$ were compared with those obtained by Sastre et al. (1990) for the extraction of some metals with bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) and it was observed that $pH_{0.5}$ values are lower for monoalkylphosphinic acid than for dialkilphosphinic acid, in accordance with the increasing pK_a of the extractants. On the other hand, the difference in extraction behaviour between HMTMPP and HBTMPP, expressed as $\triangle pH_{0.5}$, follows the order Cd(II) > Cu(II) > Zn(II). The separation of Zn/Cu, Zn/Cd and Cu/Cd, shown as differences of $pH_{0.5}$, increases as the extractant is changed from HMTMPP to HBTMPP, and is similar for Zn/Cd separation.

TABLE 4.

Values of $pH_{0.5}$ for the extraction of various metals with HMTMPP and HBTMPP at 0.05 $mol.dm^{-3}$ of HA, and separations between metals as differences of $pH_{0.5}$

	$pH_{0.5}$ HMTMPP	$pH_{0.5}$ HBTMPP	$\triangle pH_{0.5}$
Zn(II)	2.1	2.3	0.2
Cu(II)	2.9	3.9	1.0
Cd(II)	3.1	4.4	1.3
Pb(II)	2.6		

	$\triangle pH_{0.5}$ HMTMPP	$\triangle pH_{0.5}$ HBTMPP
Zn(II)/Cu(II)	0.8	1.6
Zn(II)/Cd(II)	1.0	1.1
Cu(II)/Cd(II)	0.2	0.5
Zn(II)/Pb(II)	0.5	
Pb(II)/Cd(II)	0.5	
Pb(II)/Cu(II)	0.3	

In order to improve metal separations, several experiments were carried out using mixtures of extractants. In this context, the extraction of Zn(II), Cu(II),

Cd(II), Pb(II) and Co(II) by mixtures of HMTMPP and TOPO and HMTMPP and TLA was studied, and the results obtained are shown in Figures 2 and 3, respectively. The addition of TOPO to HMTMMP causes a pronounced shift to higher pH values for Pb(II), Cu(II) and Cd(II), while for Zn(II) and Co(II) there is practically no shift, and there is no variation in the order of extraction of the different metal ions. However, the addition of a more basic extractant such as TLA produces a greater shift of the curves to higher pH values for all the metals. This shift is especially large for lead and cobalt.

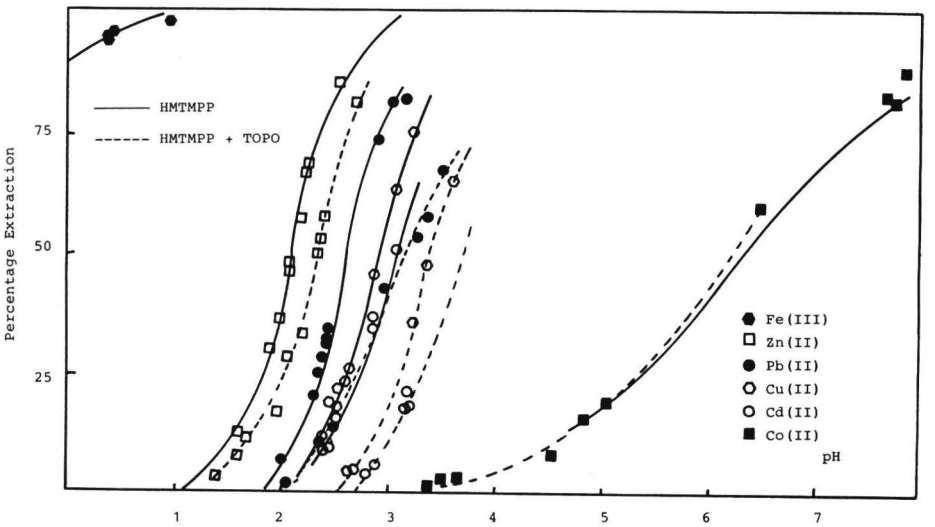


Fig 2. Percentage of extraction versus pH for the systems HMTMPP and HMTMMP+TOPO.

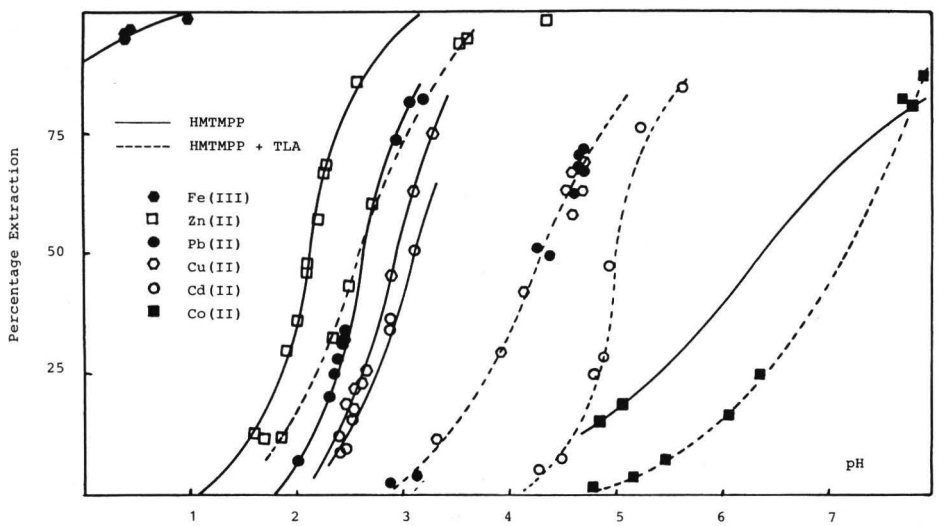


Fig 3. Percentage extraction versus pH for the systems HMTMPP and HMTMMP+TLA.

TABLE 5

Values of separations between metals, as differences of $pH_{0.5}$, for the extractioon of several metals by mixtures of HMTMPP+TOPO and HMTMPP+TLA.

	$\triangle pH_{0.5}$ HTMPP+TOPO	$\triangle pH_{0.5}$ HTMPP+TLA
Zn(II)/Cu(II)	1.1	1.6
Zn(II)/Cd(II)	1.3	2.3
Cu(II)/Cd(II)	0.2	0.7
Pb(II)/Cd(II)	0.5	0.7
Zn(II)/Pb(II)	0.9	1.6
Pb(II)/Cu(II)	0.3	0.0

As seen in table 5 the addition of TLA to HMTMPP shows a higher separation factor than the addition of TOPO especially for Zn/Cu, Zn/Cd and Zn/Pb.

4 CONCLUSIONS

At the experimental conditions used, mono(2,4,4-trimethylpentyl)phosphinic acid extracts to higher pH values than bis(2,4,4-trimethylpentil)phosphinic acid, and shows a similar behaviour to the latter in the extraction of metal ions studied but with a lower separation factor. The addition of basic extractant improves the separation between metals.

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SUBSTITUENT EFFECTS ON DIMERIZATION OF COPPER(II) CARBOXYLATES IN EXTRACTION OF COPPER(II) WITH MONO-SUBSTITUTED BENZOIC ACIDS

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ABSTRACT

The solvent extraction of copper(II) with ortho-, meta-, and para-isomers of mono-substituted benzoic acids was carried out at 25 °C and aqueous ionic strength of 0.1 mol dm^{-3}($NaClO_4$), and the substituent effects on the dimerization of copper(II) carboxylates, which is one of important factors in the extraction of copper(II) carboxylates, were investigated. It has been found that the extraction of copper(II) with aromatic carboxylic acids(mono-substituted benzoic acids) proceeds through a stoichiometry different from that with aliphatic carboxylic acids. Irrespective of a substituent group which was introduced into the benzene ring of benzoic acid, each of the three positions of substitution in benzene ring results in an individuality in the extraction behavior for copper(II). The introduction of the substituent group at the *p*-position in benzoic acid leads to the lowering of the solubility of the acid and its copper(II) compound in both the aqueous and organic phases in comparison with the other isomers. While the substitution of hydrogen atom at the *m*-position by a substituent can enhance the extractability of copper(II). The introduction into *o*-position is the most complicated, and can be subject to the steric effect exerted by the substituent upon the carboxyl group.

INTRODUCTION

In the previous paper,[a] it has been noted that copper(II) benzoate cannot be extracted in benzene but can be extracted in 1-octanol as a monomeric copper(II) species CuA_2. In the subsequent investigations[b,c] on the extraction of copper(II) with mono-substituted benzoic acids, it has been found that the introduction of methyl group at the *o*- and *m*-positions and chloro group at *m*-position in benzoic acid results in the formation of the dimeric copper(II) carboxylate, and leads to the enhancement of the extractability. On the other hand, methyl and chloro substituents at the *p*-position in benzoic acid lowers the extracting capability for copper(II). Then the extraction of copper(II) with the mono-substituted benzoic acid has proved to be appreciably influenced by the positions and properties of the substituent groups.

The present paper reports on the extraction of copper(II) with *o*-, *m*-, and *p*-methoxybenzoic acids in 1-octanol. It was found that even in the extraction of copper(II) by *o*- and *m*-methoxybenzoic acids the dimerization of copper(II) species does not occur to any appreciable extent, and copper(II) is scarecely extracted by *p*-methoxybenzoic acid in 1-octanol.

From the present and previous results the extractability of mono-substituted benzoic acid for copper(II) was found to be estimated by the value of $K_{D,HA}/K_a$ on the acid.

2 EXPERIMENTAL

Reagents and Procedure.

o-, *m-*, and *p*-methoxybenzoic acids: The reagent grade methoxybenzoic acids were dissolved in purified 1-octanol. Coppper(II) and sodium perchlorates, and 1-octanol were same as employed previously.[a)]

Partition was performed in a bath thermostated at 25.0 °C. Shaking for about 30 minutes was sufficient for complete equilibration.

3 RESULTS AND DISCUSSION

3.1 *Partition of Methoxybenzoic Acids.*

It is essential to examine the partition behavior of a carboxylic acid in order to investigate the extraction of a metal ion with a carboxylic acid. The partition behavior of a carboxylic acid HA are governed by the following equilibria: (1) The dissociation of HA in the aqueous phase, (2) the partition of HA between the aqueous and organic phases, and (3) the dimerization of HA in the organic phase. The dissociation constants of three kinds of methoxybenzoic acids were potentiometrically estimated at the ionic strength of 0.1 mol dm^{-3}($NaClO_4$). The values obtained are shown in Table 1. The distribution ratio of the respective methoxybenzoic acids between 1-octanol and 0.1 mol dm^{-3} perchloric acid, in which the dissociation of the acids can be neglected, was observed to be the intrinsic values, respectively, irrespective of the concentration of the acids. This suggests that the dimerization of the acids in 1-octanol does not occur to any appreciable extent. Then the distribution ratio of each acid is equal to its partition constant $K_{D,HA}$. The values obtained are summarized in Table 1. The value of *o*-methoxybenzoic acid is significantly small compared with the other acids. This seems to be caused by hydration of the acid.

3.2 *Extraction of Copper(II) with Metoxybenzoic Acids.*

Taking into account the extraction of the j-merized copper(II) species, the following extraction equilibrium is set up:

$$jCu^{2+} + (2j+a)(HA)_o \overset{K_{ex(ja)}}{\rightleftharpoons} (Cu_jA_{2j}(HA)_a)_o + 2jH^+.$$

On the assumption that only $Cu_jA_{2j}(HA)_a$ is responsible for the extration, the following expression can be obtained:

$$\log C_{Cu,o} = j(\log[Cu^{2+}] - 2\log[H^+]) + (2j+a)\log[HA]_o + \log j + \log K_{ex(ja)}, \quad (1)$$

where $C_{Cu,o}$ is the total concentration of copper(II) in the organic phase. The

concentration of copper(II) in the aqueous phase can be represented as follows: $[Cu^{2+}] = C_{Cu,w}/\alpha_{Cu}$, (2)

where α_{Cu} denotes the side-reaction coefficient of copper(II) ion in the aqueous phase. According to Eqs. 1 and 2, the degree of polymerization of the extracted species can be determined from the slope of the plot: $\log C_{Cu,o}$ vs. ($\log C_{Cu,w} - 2\log[H^+]$) at constant $[HA]_o$. The results for *o*- and *m*-methoxybenzoic acids are shown in Fig. 1. While, copper(II) was scarecely extracted with *p*-methoxybenzoic acid in 1-octanol. In Fig. 1, the slope of the plots for

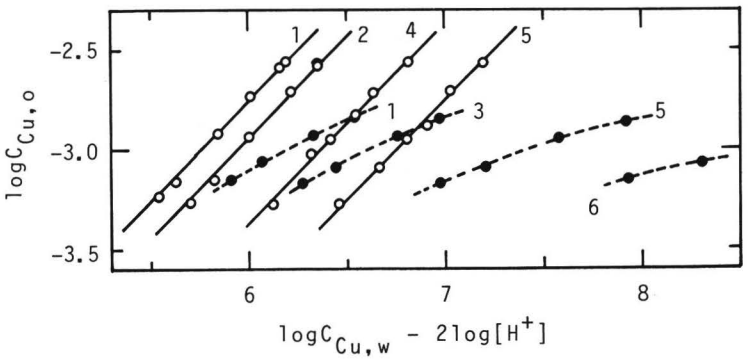


Fig. 1. Determination of the degree of polymerization of the extracted species. Closed and open symbols are *o*- and *m*-methoxybenzoic acids, respectively. C_{HA}; 1: 0.3, 2: 0.25, 3: 0.2, 4: 0.15, 5: 0.1, 6: 0.05 mol dm^{-3}. Solid lines are the straight lines with slope of 1.0.

o-isomer is less than 1.0, and tends to be lowered with increasing copper(II) concentration in the organic phase. Then it suggests that the monomeric copper(II) species can be responsible for the extraction and side-reaction of copper(II) ion in the aqueous phase cannot be neglected in the *o*-methoxybenzoic acid systems. On the other hand, the open symbols fall on a straight line with slope of 1.0. It was found that only the monomeric copper(II) species is responsible for the extraction in the *m*-methoxybenzoic acid systems, and the side-reaction of copper ion in the aqueous phase does not occur to any appreciable extent, that is, $j = 1$ and $\alpha_{Cu} = 1$. Then the following equation can be obtained from Eq. 1:

$$\log C_{Cu,o} - \log[Cu^{2+}] + 2\log[H^+] = (2+a)\log[HA]_o + \log K_{ex(1a)}. \quad (3)$$

According to Eq. 3, the number of the acid molecules involved in the monomeric copper(II) species can be determined from the slope of the plot of ($\log C_{Cu,o} - \log[Cu^{2+}] + 2\log[H^+]$) against $\log[HA]_o$. The plots falled on a straight line with slope of 2.0. Therefore, the monomeric species was found to be CuA_2. And the extraction constant $K_{ex(10)}$ of CuA_2 can be estimated from the intercept of the straight line.

Taking into account K_a, $K_{D,HA}$ of *o*-methoxybenzoic acid, the hydrogen ion

concentration in the aqueous phase, and the side-reaction of copper(II) ion with *o*-methoxybenzoate anion, the concentration of the monomeric *o*-methoxybenzoic acid in the organic phase, $[HA]_o$ cannot be kept constant under the present extraction conditions. Then it is convenient to adopt the following equation instead of Eq. 1:

$$\log C_{Cu,o} - a\log[HA]_o = j(\log C_{Cu,w} - 2\log[H^+] + 2\log[HA]_o) - j\log\alpha_{Cu(A^-)} + \log j + \log K_{ex(ja)}, \quad (4)$$

where $\alpha_{Cu,(A^-)}$ denotes the side-reaction coefficient of Cu^{2+} ion with *o*-methoxybenzoate anion in the aqueous phase, and represents as follows:

$$\alpha_{Cu(A^-)} = 1 + \beta_1[A^-] + \beta_2[A^-]^2, \quad (5)$$

where β_1 and β_2 are the over-all formation constants: $\beta_1 = [CuA^+]/[Cu^{2+}][A^-]$ and $\beta_2 = [CuA_2]/[Cu^{2+}][A^-]^2$, respectively. $[HA]_o$ can be calculated from Eq. 6:

$$[HA]_o = K_{D,HA}C_{HA}/(K_{D,HA} + 1 + \frac{K_a}{[H^+]}) \quad (6)$$

From the coordination number of coppper(II) ion, the possible values of 'a' can be predicted to be 0, 1, or 2. From the plots of ($\log C_{Cu,o} - a\log[HA]_o$ for a = 0, 1, and 2) against ($\log C_{Cu,w} - 2\log[H^+] + 2\log[HA]_o$) on the basis of Eq. 4, the extracted species can be estimated. Only in the case of a = 0, the plots were found to fall on the identical curve with slope of less than unity. Then the monomeric species CuA_2 can be estimated as an extracted species and the side-reaction of copper(II) ion with *o*-methoxybenzoate anion in the aqueous phase influences the extraction equilibrium on this extraction system. Therefore, the following expression can be obtained from Eqs. 4 and 5:

$$C_{Cu,o}{}^{-1}C_{Cu,w}[H^+]^{-2}[HA]_o{}^2 = K_{ex(10)}{}^{-1} + \beta_1 K_{ex(10)}{}^{-1}[A^-] + \beta_2 K_{ex(10)}{}^{-1}[A^-]^2, \quad (7)$$

where A^- denotes the *o*-methoxybenzoate anion in the aqueous phase. The plot of the values of left-hand side of Eq.7 against $[A^-]$ was found to be linear. Then the third term of the right-hand side of Eq. 7 can be negligible for the first and second terms, that is, the existence of CuA_2 species in the aqueous phase can be negligible for Cu^{2+} and CuA^+ species. The extraction constant $K_{ex(10)}$ and the formation constant β_1 were calculated from the intercept and slope of the straight line by the least-squares method as follows: $\log K_{ex(10)} = -7.32$ and $\log\beta_1 = 2.01$.

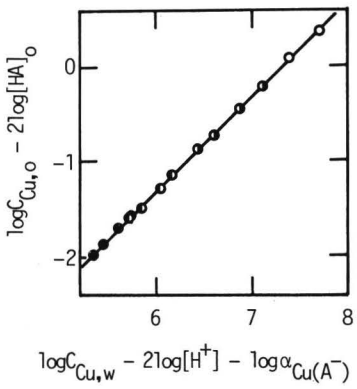
The partition constant of the monomeric copper(II) *o*-methoxybenzoate can be predicted to be small from the much lower partition constant of *o*-methoxybenzoic acid than the other isomers. Nevertheless, the species CuA_2 didn't exist in the aqueous phase to any appreciable extent. This suggests that the second *o*-methoxybenzoate anion is hard to attach to CuA^+. This seems to result from the steric hindrance by a methoxy group, and to cause a lowering of the extractability.

According to the resulting informations for *o*-methoxybenzoic acid, the following expression can be derived from Eq. 4:

$$\log C_{Cu,o} - 2\log[HA]_o = \log C_{Cu,w} - 2\log[H^+] - \log\alpha_{Cu(A^-)} + \log K_{ex(10)}. \quad (8)$$

Then, the plots of $(\log C_{Cu,o} - 2\log[HA]_o)$ against $(\log C_{Cu,w} - 2\log[H^+] - \log\alpha_{Cu(A^-)})$ should fall on the straight line with slope of unity and intercept of $\log K_{ex(10)}$. As shown in Fig. 2, the calculated line has proved to be in good agreement with the observed values.

Consequently, the extraction equilibria for the present extraction systems are represented as follows.



o-, and m-Methoxybenzoic acids:

$$Cu^{2+} + 2(HA)_o \underset{}{\overset{K_{ex(10)}}{\rightleftharpoons}} (CuA_2)_o + 2H^+.$$

In the former, the concentration of CuA^+ species cannot be neglected compared with that of Cu^{2+} ion. Then, the partition ratio of copper(II) should be represented as :

$$D = [CuA_2]_o/([Cu^{2+}] + [CuA^+])$$
$$= K_{ex(10)}[HA]_o^2[H^+]^{-2}\alpha_{Cu(A^-)}^{-1}, \quad (9)$$

where $\alpha_{Cu(A^-)} = 1 + \beta_1[A^-]$.

Fig. 2. The correction by considering the side-reaction of copper(II) ion with *o*-methoxybenzoate anion. Solid line is the calculated one with slope of 1.0 and intercept of $-7.32(\log K_{ex(10)})$. Symbols are as follows: C_{HA}; ○ :0.05, ◑ : 0.1, ◐ :0.2, ● :0.3 mol dm^{-3}.

p-Methoxybenzoic acid: Copper(II) was scarecely extracted. The emulsion appeared in the region where the percent extraction of copper exceeds only a few percent under the present extraction conditions.

TABLE 1

Dissociation and partition constants of aromatic carboxylic acids, and extraction constants of copper(II)-aromatic carboxylates.

Acids	pK_a	$\log K_{D,HA}$	$\log K_{ex(10)}$	$\log K_{ex(20)}$	$\log K_{ex(22)}$	$K_{D,HA}/K_a$
o-MOBA	3.90	1.21	- 7.32			1.3×10^5
m-MOBA	3.90	2.05	- 7.75			8.9×10^5
p-MOBA	4.34	1.97				2.0×10^6
o-MBA	3.73	2.21	- 7.84	- 12.84		8.7×10^5
m-MBA	4.09	2.41	- 7.84	- 13.15		3.2×10^6
p-MBA	4.21	2.33	- 7.84			3.5×10^6
o-CBA	2.74	2.07	- 6.75			6.5×10^4
m-CBA	3.66	2.65	- 7.03	- 12.20	- 12.04	2.0×10^6
p-CBA	3.95	2.67	- 7.15			4.2×10^6
BA	4.04	1.88	- 7.70			9.1×10^5

Solvent: 1-Octanol. MOBA, MBA[b], CBA[c], and BA[a]: Methoxybenzoic, methylbenzoic, chlorobenzoic, and benzoic acids, respectively.

An increase in $[A^-]$ should be essentially favorable for extracting a metal ion, since it facilitates the formation of the extracted species. On the other hand, it results in an increase in $\alpha_{Cu(A^-)}$ and leads to a lowering of the partition ratio of copper(II). Therefore, the extracting agent anion is required to a concentration low enough to avoid this reduction of the partition ratio of copper(II). In the present extraction systems, in which the dimerization of a carboxylic acid does not occur to any appreciable extent, the concentration of carboxylate anion can be calculated by Eq. 10, provided the concentration of the acid is much higher than the copper(II) concentration.

$$[A^-] = C_{HA}/\{1 + ([H^+]/K_a)(K_{D,HA} + 1)\} \quad (10)$$

According to Eq. 10, the value of $K_{D,HA}/K_a$ must be sufficiently large in order that the concentration of A^- can be maintained at a low enough. The values of $K_{D,HA}/K_a$ for mono-substituted benzoic acids are given in Table 1 with the other constants. The value for *o*-methoxybenzoic acid as well as *o*-chlorobenzoic acid[c)] is significantly small compared with the other acids. In these extraction systems, a lowering of the partition ratio of copper(II) was observed, as expected by Eq. 9. Then, the value of $K_{D,HA}/K_a$ on the extracting agent is anticipated to be one of factors for its extractability. Irrespective of the large $K_{D,HA}/K_a$, the application of *p*-substituted benzoic acids to extraction of copper(II) should be restricted to the lower range of copper concentration, owing to the poor solubility of *p*-isomers and their copper(II) compounds in both the aqueous and 1-octanol phases, that is, a high enough partition ratio of copper(II) can be attained provided the extraction of copper(II) is carried out under such a condition that no precipitates of *p*-isomers and their copper(II) compounds appear.

Although both the methoxy and methyl groups are electron-releasing group, a considerable difference in the extraction equilibrium on copper(II) has been recognized. The difference can be ascribed in part to a lone pair of electrons on an oxygen atom in the methoxy group, which may take part in the conjugated system in benzoic acid, and through which water molecules may be linked by a hydrogen bonding.

It has been noted that no dimerization of copper(II) carboxylate occurs to any appreciable extent in the extraction of copper(II) with methoxybenzoic acids different from methyl- and chlorobenzoic acids.

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PREPARATION AND CHARACTERIZATION OF MACROPOROUS RESINS IMPREGNATED WITH ORGANOPHOSPHOROUS COMPOUNDS.

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ABSTRACT
DEHPA has been impregnated in Amberlite XAD2 polymeric resin by both wet and dry methods. In both cases a known amount of resin was shaken with a mixed solvent solutions and total DEHPA loadings were estimated. Water capacity was determined and C_{HL}^{max} was extrapolated from water capacity versus C_{HL} plot. Distribution coefficients of DEHPA between the aqueous and resin phase was obtained as a function of pH. Total P was measured by using ICP. Results show a S shape curve which may indicate the attainment of chemical equilibrium. Impregnated XAD2-DEHPA was used in the extraction of Cu^{2+} and Zn^{2+} in nitrate media. In both cases mass action law holds and is kept constant after 240 min. Results of metal extraction indicate 80% and 100% of extraction for Cu^{2+} and Zn^{2+}, respectively, and preliminary treatments may explain the existence of complexes of known stoichiometries.

1 INTRODUCTION

Solvent Impregnated Resins (SIR) have been postulated as a new technological alternative for problems associated with metal separation and recovery. In this context several SIR have been prepared and different studies have been published (Warshaswky,1981). These works reveal the necessity of additional experimental information.

In our case detailed investigations on the fundamental parameters (loading, water capacity, distribution coefficient, metal recovery...) have been undertaken. The system was chosen because of industrial importance of organophosphorous compounds as well as due to our previous knowledge of these solvent extraction behaviors (Sastre, 1984; Muhammed, 1984) which will facilitate our experimental approach.

2 EXPERIMENTAL.

2.1 Reagents and solutions.

Di-(2-ethylhexyl) phosphoric acid (DEHPA = HL) was supplied by BDH,(UK). Ethyl and Methyl Alcohol, Merck, p.a., were used without further purification.

Amberlite XAD-2 Adsorber Resin (20-69 mesh), Merck, size particule 0.3-0.9 mm was used.

Sodium, Copper and Zinc Nitrates, Phosphoric, Hydrochloric and Nitric acids, Merck p.a., were used for the preparation of the different solutions.

Solid Support preparation. XAD-2 was kept in contact during 12 h with a 50% methanol-water solution containing 4 mol.dm^{-3} HCl in order to eliminate inorganic impurities as well as monomeric material and other inorganic traces. The solid was washed with water until no Cl^- ion was detected in the filtrate.

2.2 Impregnation process.

The impregnation of XAD-2 beads was done according to the following two procedures (Warshaswky, 1976):

a) Dry method. An appropriate amount of dry polymer was placed for 24 h in a (67:33) ethanol-water mixture containing DEHPA of different concentrations. After this time, which seems to be sufficient for completing the swelling process, the diluent was removed by slow evaporation.

b) Wet method. After XAD-2 was kept in contact for 24 h under identical experimental conditions, polymeric beads were separated through a porous filter in a water pump and then stored in water.

3 RESULTS

3.1 Evaluation of the impregnation process.

The amount of DEHPA impregnated was evaluated for several samples after washing the resin with ethanol and determination of DEHPA with NaOH titration. From this data using the following variables:

C'_{HL} =weight of DEHPA in g/weight XAD-2 in g

and C_{HL} = mol of DEHPA/weight XAD-2 in Kg

the information in Table 1 was obtained.

TABLE 1.

Data on the Impregnation of DEHPA in XAD-2 under different experimental conditions.

Resin	W_{XAD2} (g)	W_{HL} (g)	V_{EtOH} ml	V_{H2O} ml	$C_{Im,s}$ (gHL/ml)	Method	C'_{HL} (gHL/gXAD)	C_{HL} (molHL/kgXAD)
M1	4.0011	1.096	15	0	0.073	Wet	0.126	0.391
M2	4.0009	1.403	10	5	0.094	Wet	0.230	0.713
M3	4.0013	1.808	10	5	0.120	Wet	0.270	0.838
M4	4.0008	2.214	10	5	0.148	Wet	0.350	1.085
M5	4.0000	2.809	10	5	0.187	Wet	0.406	1.259
M6	4.0012	1.365	10	5	0.092	Wet	0.248	0.769
M7	4.0006	0.943	10	5	0.066	Dry	0.237	0.735
M8	4.0000	1.822	10	5	0.122	Dry	0.438	1.360
M9	4.0013	1.840	10	5	0.123	Dry	0.433	1.370

where $C_{Im,s}$ is the concentration of DEHPA in the impregnation solution.

From these data it seems that the impregnation with dry method is more effective, the amount of impregnated resin is always higher than for the wet method. Concerning the mixed solvent phase the impregnation seems to be independent of the solvent composition for the dry method while in the case of

the wet method the increase of water percentage facilitate the transfer of organic reagent to the resin phase. On the other hand, a linear relationship between the amount of DEHPA impregnated in the resin C_{HL} and $C_{Im.s}$ has been found.

3.2 Water capacity.

Experiments have been made in order to determine the amount of water absorbed by the polymeric resin both in the presence and in absence of DEHPA. For this purpose, the resin was equilibrated with a mixed solvent phase of different composition. After appropriate filtration, water content in the resin was estimated by weight difference.

The results of these experiments plotted in Fig. 1, show a linear relationship between the weight of water absorbed and DEHPA concentration. From the straight line in Fig 1, the extrapolated value of the maximum loading concentration C_{HL}^{max} was estimated as 1.7mol.kg^{-1}. After this value exudation process takes place.

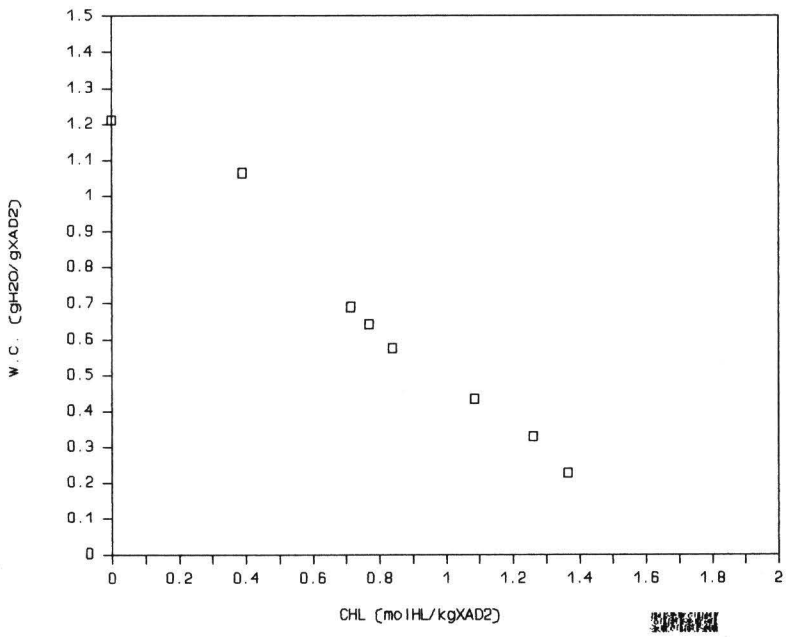


Figure 1. Water capacity (W.C.) of the impregnated amberlite XAD2 support as a function of its DEHPA content.

Another set of experiments was done in order to investigate the evaluation of the impregnation process as a function of the pH. Batch experiments were carried out in which different amounts of XAD-2-DEHPA resin were mechanically shaken for 24 h with an aqueous phase containing 0.05 mol.dm^{-3} $NaNO_3$. After phase

separation, both pH and total DEHPA concentration were determined. Total P determination was done using the 213.618 nm first order atomic emission line of phosphorus with the aid of a inductively coupled plasma atomic emission spectrometer (ICP). Calibration curves were constructed using H_3PO_4 solutions in the range of $3.2x10^{-6}$ to $1.6x10^{-4}$ $mol.dm^{-3}$ corresponding to 0.1 to 50 ppm of P atoms. From these data, the "distribution" coefficient of DEHPA was determined by means of the following expression:

$$D = \frac{C_{HL}}{[HL]} = \frac{C_{HLi} - [HL]\ (V_a / m_{res})}{[HL]} \qquad (1)$$

where Va denote the volume of aqueous phase , m_{res} the mass of impregnated resin, C_{HL} the concentration of DEHPA in the resin and [HL] the concentration of DEHPA in the aqueous phase. Subscript i refers to initial concentration of DEHPA, and the others are equilibrium concentrations. The results of these experiments are shown in Fig. 2.

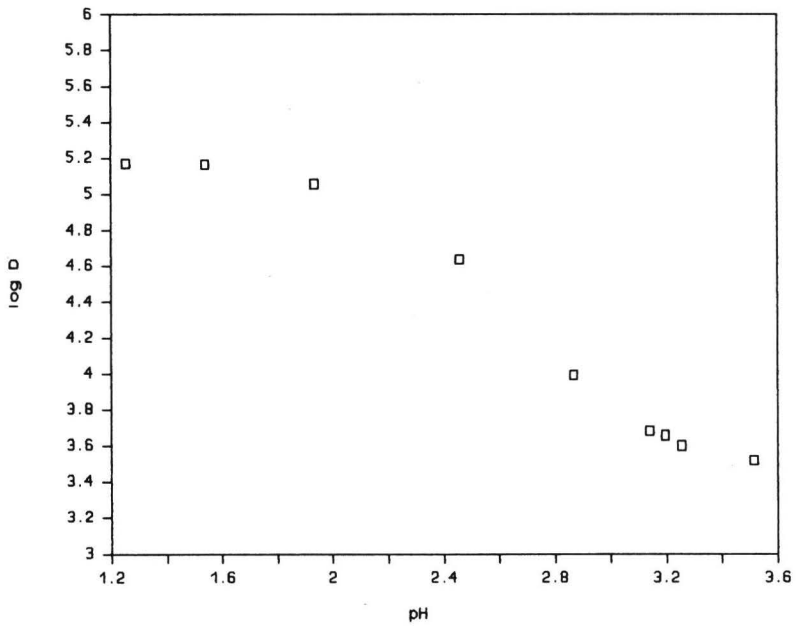


Figure 2 .LogD versus pH for XAD2-DEHPA resin in the pH range 1.4 to 4.5 with initial concentration of DEHPA in XAD2 resin being 1.36 $molxkg^{-1}$.

The typical S shape curve shows a region (pH<2) where the distribution

function is independent of pH while a continuous decrease of the value of this function is observed as pH increases. In this sense, it is interesting to point out the similarity of the function in Fig. 2 with the typical liquid-liquid distribution curves (Ken et all,1985) although SIR curve seems to be moderately shifted upwards.

3.3 Metal extraction.

In order to estimate the extraction of Zn^{2+} and Cu^{2+} an aqueous solution of the following general composition was prepared:

$[M^{2+}]$= 1mg.dm^{-3}, $[NO_3^-]=[Na^+]$= 0.1 mol.dm^{-3} and $5x10^{-2} > [H^+] > 1x10^{-4}$mol.dm^{-3} (where M^{2+} = Zn^{2+} and Cu^{2+})

Experiments were carried out at 298 K by shaking 20 ml of aqueous phase with 0.21 g of XAD-2-DEHPA resins using stoppered glass tubes in a continuous rotary during 3 h. After equilibrium was attained metal and proton concentrations were determined. In a separate experiment it was checked that the system follows the mass balance while it was estimated that 2h was enough to attain equilibrium.

Results in metal extraction are shown in Fig 3. This seems to indicate a high extraction percentage for Cu^{2+} while Zn^{2+} is completely extracted after pH=2.6.

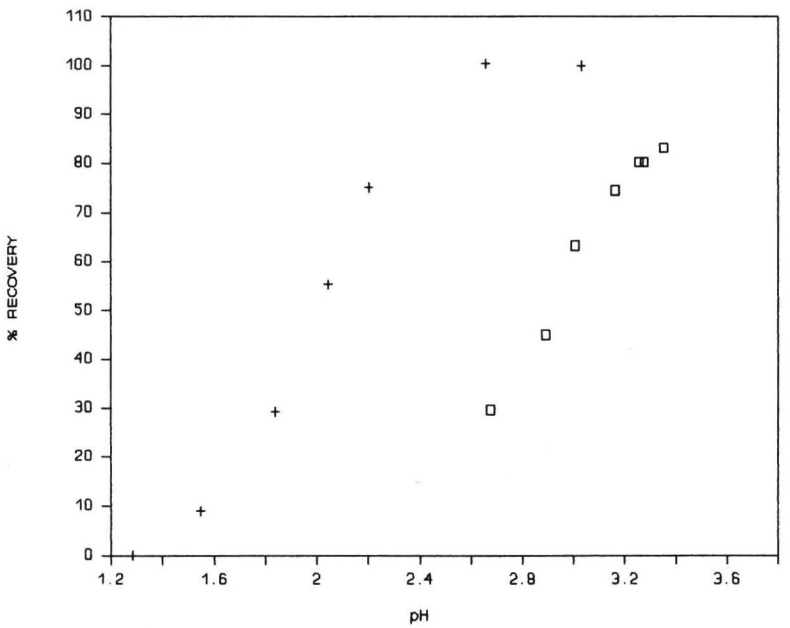


Figure 3. pH dependence of the recovery of Zn^{2+} and Cu^{2+} with the impregnated XAD2-DEHPA resin. The concentration of metals in the sample solutions is 2mg.dm^{-3}.
(+): Zn^{2+} (■): Cu^{2+}

4 CONCLUSIONS.

The results of this work seem to indicate a good performance for the SIR-Metal systems. Nevertheless the diversity of data and results make us to the following considerations.

Talking from a preliminary experimental information it seems that XAD-2-DEHPA impregnation is a favorable procedure where a great amount of the reagent can be loaded (C_{max} =1.7 mol.kg^{-1}) and both operations seem to behave reversibly. On the other hand, additional information seems to indicate the establishment of chemical equilibrium between loaded reagent and the aqueous phase. This possible equilibrium, which seems similar to those encountered in liquid-liquid systems, strongly shifted towards the resin phase, indicating that the link of DEHPA to the resin phase acts as a driving force for the displacement of DEHPA molecules towards the polymer.

Concerning metal extraction, it seems to take place at moderate speed and mass balance for the different metals holds within 100%. On the other hand metal extraction percentages are high for both Cu^{2+} and Zn^{2+} and in both they are higher than the corresponding SX systems. Finally, preliminary graphical and computer treatments seem to indicate the existence of metal complex species in the resin phase.

5 ACKNOWLEDGEMENTS

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COMPARISON OF AGGREGATES FORMED BY ACIDIC ORGANOPHOSPHORUS EXTRACTANTS AND METALS (Ni AND Co) IN SOLVENT EXTRACTION

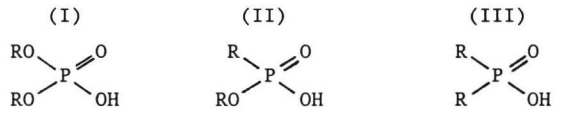
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ABSTRACT

The structure of three classes of acidic organophosphorus extractants, HDEHP, di(2-ethylhexyl)phosphoric acid (I), PC 88A, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (II), and CYANEX 272, di(2,4,4-trimethylpentyl) phosphinic acid (III), has been characterized by NMR and FT-IR spectroscopy. In solvent extraction systems, after equilibration of the aqueous phase at the same pH and nickel ion concentration with the organic phase containing (I), (II), or (III) in n-heptane, bulk water was identified by FT-IR spectra with the solubilization ability: (I) > (II) > (III). On the other hand, when the extractants were partially saponified by a concentrated sodium hydroxide solution and then equilibrated with an aqueous nickel chloride solution, the solubilization ability for water in the organic phase was inverted: (I) < (II) < (III). Aggregates formed by organophosphorus extractants and cobaltous ions retain bulk water only under appropriate conditions. On the basis of the FT-IR results, the three acidic organophosphorus extractants form reversed micelles in hydrometallurgical solvent extraction systems.

INTRODUCTION

Three classes of organophosphorus extractants, i.e., (I) HDEHP, di(2-ethylhexyl)phosphoric acid, (II) PC 88A, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester, and (III) CYANEX 272, di(2,4,4-methylpentyl)phosphinic acid, have proved to be the most versatile extractants to date for their efficiency of the extraction of zinc, uranium, vanadium, cobalt, nickel and rare earths (Lo et al., 1983; Eccles and Naylor, 1986; Szilassy et al., 1986; Tavlarides et al., 1987). Structures for the three classes of extractants are



phosphoric (HDEHP) | phosphonic (PC 88A) | phosphinic (CYANEX 272)

Although the three extractants can be used successfully in solvent extraction processes, it has been reported that under the same conditions

their selectivity in Co/Ni separation is so different that the separation factor of CYANEX 272 is about 500 times that of HDEHP (Rickelton et al., 1983). Thus, a structural comparison of the three organophosphorus extractants and a knowledge of the physicochemical nature of the metal-extractant aggregates are essential in understanding the mechanism of the solvent extraction process.

2 EXPERIMENTAL MATERIALS AND METHODS

The organophosphorus extractants were purified following the procedures of Partridge and Jensen (1969). The n-heptane (Fisher, HPLC grade) was doubly distilled. All inorganic reagents including nickel chloride, cobalt chloride, sodium hydroxide and hydrochloric acid were ultra-high purity grades.

Three series of samples were prepared: (i) solvent extraction systems of nickel at the same pH by equilibrating equal volumes of an aqueous phase containing $NiCl_2$ (0.35 M) with an organic phase of the extractant (1.0 F) in n-heptane at 20°C, (ii) solvent extraction systems of nickel by adding the appropriate amount of concentrated NaOH solution (10 M) to the extractant (1.0 F) in n-heptane to obtain an organic phase with the composition of 2NaR·HR and equilibrating with 0.35 M $NiCl_2$ solution, and (iii) solvent extraction systems of cobalt prepared in the same manner as (ii).

The aggregates formed by the metal-extractant complexes in the organic phase of the various solvent extraction systems were examined by NMR and FT-IR spectroscopy. The NMR and FT-IR spectra were recorded using Bruker AM400 NMR and Nicolet Model 5SXC FT-IR spectrometers, respectively.

3 RESULTS AND DISCUSSION

3.1 Organophosphorus Extractants

The results of structural characterization of the three extractants by ^{1}H-NMR and ^{31}P-NMR spectroscopy are given in Table 1. Interesting features can be seen, for example, the differences in chemical shifts for POH-protons of the three samples show the influence of the adjacent $POCH_2$-group. The small ^{31}P-chemical shift of HDEHP relative to phosphoric acid indicates the structural similarity of P in HDEHP and phosphoric acid. On the other hand, phosphinic acid reveals a chemical shift as large as 53 ppm due to the marked structural difference of P in the given extractant and phosphoric acid as the result of direct binding of two hydrocarbon chains to the phosphorus atom. Spectra for the phosphonic acid, which contains a $POCH_2$-group, show a reasonable intermediate ^{31}P-chemical shift of 33.7 ppm.

The characteristic absorption bands obtained from FT-IR spectra for various groups of the three extractants are summarized in Table 2. The

results show that the vibrational frequency of the P=O group is also affected by the adjacent groups binding to P such that the frequency decreases as P-O-R is replaced by P-R. The strong band at 1034 cm^{-1} for the P-O-C group in HDEHP is again an indication of the presence of two P-O-C groups per molecule, and the weaker band at 1036 cm^{-1} in the case of PC 88A is due to only one P-O-C group. For CYANEX 272 the given band disappears completely (see Table 2).

TABLE 1

Chemical shifts for (I) HDEHP, (II) PC 88A, and (III) CYANEX 272.

	Chemical Shift (ppm)		
Sample	POH-^{1}H	$POCH_2$-^{1}H	^{31}P
HDEHP	12.1	3.0	1.0
PC 88A	11.9	3.0	33.7
CYANEX 272	10.8	--	53.4

TABLE 2

FT-IR absorption bands for (I) HDEHP, (II) PC 88A, and (III) CYANEX 272.

	Absorption Bands (cm^{-1})				
Sample	P-O-H	P-O-C	P=O	H-C-H (bending)	C-H (stretching)
HDEHP	886(?)	1034	1229	1463	2801-2960
PC 88A	984	1036	1197	1462	2860-2959
CYANEX 272	959	--	1171	1468	2869-2953

3.2 Extraction of nickel by organophosphorus extractants at same pH: HR/n-heptane/$NiCl_2$ solution (0.35 M, pH 5.7)

FT-IR spectra of liquid water reported previously (Weng et al., 1985) are shown in Fig. 1, where the broad stretching vibrational band of liquid water near 3400 cm^{-1} can be resolved into 8 peaks of rational fine structure. FT-IR spectra for the three nickel-organophosphorus extraction systems at constant

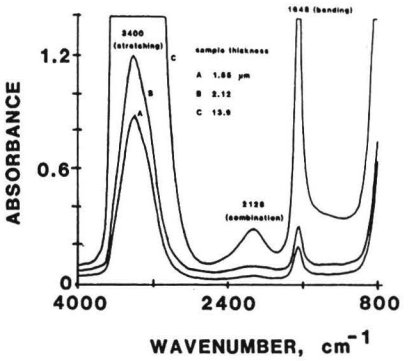


Fig. 1. FT-IR spectra of liquid water (from Weng et al., 1985).

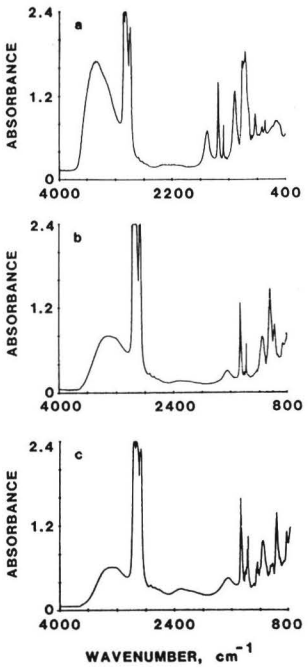


Fig. 2. FT-IR spectra of the extraction system HR/n-heptane/$NiCl_2$ (0.35 M and pH 5.7). (a) HDEHP, (b) PC 88A, and (c) CYANEX 272.

pH are shown in Fig. 2. The absorption band at ca. 3400 cm^{-1} indicates an appreciable amount of bulk water solubilized in the organic phase. The sequence of solubilization ability of the three extractants evaluated from the absorption band is as follows: (I) > (II) > (III). This sequence can be interpreted by the difference in pK values of the three extractants.

3.3 Extraction of nickel by saponified extractants: 2NaR·HR/n-heptane/metal chloride solution (Ni^{2+} or Co^{2+}, 0.35 M)

An alternative comparison of the solubilization characteristics of the three extractants seems desirable since their pK values are not identical. Consequently, studies of extraction systems containing equally saponified organophosphorus extractants were carried out. The results for 67% saponified extractants are shown in Fig. 3, where the sequence of solubilization ability is inverted: (I) < (II) < (III).

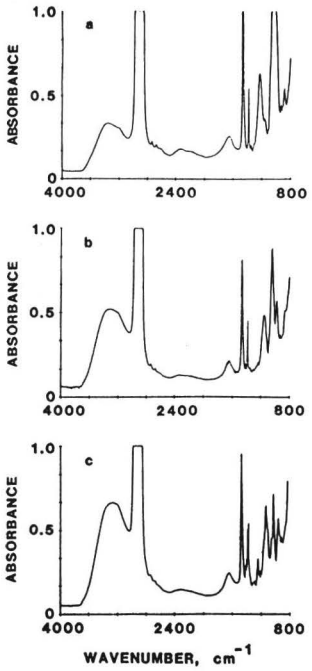


Fig. 3. FT-IR spectra of the extraction system 2NaR·HR/n-heptane/ $NiCl_2$ (0.35 M). (a) HDEHP, (b) PC 88A, (c) CYANEX 272.

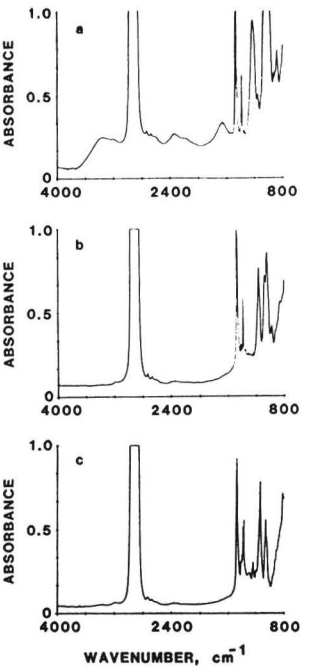


Fig. 4. FT-IR spectra of the extraction system 2NaR·HR/n-heptane/ $CoCl_2$ (0.35 M). (a) HDEHP, (b) PC 88A, (c) CYANEX 272.

However, organophosphorus extraction systems containing cobalt are more complicated. Figure 4 shows the FT-IR spectra under the same conditions as in Fig. 3. Upon comparison to the nickel extraction systems, the aggregates formed by cobaltous ions and extractant ligands cannot solubilize as much water. The coordination structure of metal ions seems determinative in the aggregation process with extractant molecules. Nickel ions can form octahedral coordination structures, while cobaltous ions coordinate with organophosphorus extractants in n-heptane to form tetrahedral structures as identified by the maximum absorption at 626 nm in VIS absorption spectra. It seems likely, therefore, that the higher separation factor of CYANEX 272 in Co/Ni separation is due to the stronger coordination affinity of the extractant for cobaltous ions.

Interesting findings also include the following: (i) when sodium ions are present in the cobalt extraction system at lower cobaltous ion loading, an appreciable amount of water can be solubilized in the organic phase, and (ii) the addition of a co-extractant, e.g., 2-octanol, can help solubilize water by forming a large "water pool" in the core of metal-extractant aggregates. In this latter case, cobaltous ions display an octahedral coordination structure, as indicated by the pink color and the maximum absorption at 518 nm. Although the addition of a co-extractant can increase water solubilization and enhance the extraction of metal ions, a decrease in the separation factor of Co/Ni is predictable.

In conclusion, although there are differences in the solubilization of bulk water by the various metal-extractant complexes, reversed micellar formation appears to be a general phenomenon in hydrometallurgical solvent extraction systems which employ the acidic organophosphorus extractants HDEHP, PC 88A, or CYANEX 272.

4 ACKNOWLEDGMENTS

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COMPARISON BETWEEN LIQUID-LIQUID EXTRACTION AND IMPREGNATED RESIN SYSTEMS. THE EXTRACTION OF Au(III) FROM CHLORIDE MEDIA BY TRI-n-DODECYLAMMONIUM CHLORIDE.

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ABSTRACT

Amberlite XAD-2 polymeric resin was impregnated with tri-n-dodecylammonium chloride (TLAHCl). The higher impregnation obtained was 1.77 mg TLAHCl/ g XAD-2. The extraction of Au(III) from hydrochloric acid media by this system was almost quantitative even at low resin loading. The liquid-liquid extraction of Au(III) showed that $AuCl_4TLAH$ and $AuCl_3$ were the species in the organic phase. Both species can also explain the behaviour observed by the SIR extraction.

1 INTRODUCTION

During the last few years, Solvent Impregnated Resins (SIR) have been proposed as a technological alternative for metal extraction, separation and recovery under the idea that these new materials gather the versatility and potentiality of the Solvent Extraction (SX) Reagents with the advantage of using solid phase as extractant system. In this context, several types of resins have been tested and studies on impregnation and metal extraction have been published (Warshaswky, 1981; Tavlarides et al, 1987). These works reveal the great capacity and versatility of the new systems for metal extraction. However, more information is needed in order to ascertain the physico-chemical parameters which govern the different steps of the whole process.

Although some thermodynamic data on impregnation have been published, little is known about chemical reactions which may either facilitate or hinder the transfer of the reagent to the resin, mainly because the experimental difficulties of the different steps. A methodological approach to this problem may be to consider that SIR and SX systems behave similarly, so all the information on SX reaction could be used as a reference to orientate the experimental procedure.

Therefore, studies of the extraction of Au(III) in chloride media by tri-n-dodecylammonium chloride (TLAHCl) both with SIR and SX have been undertaken. The TLAHCl was selected because previous works with divalent metals (de Pablo et al, 1984; Masana and Valiente, 1987) have allowed us to describe composition of the organic phase, influence of the ionic strength, determination of extraction constants, etc. The behaviour of this extractant in SX could be similar to that

observed in the SIR extraction.

2 EXPERIMENTAL

2.1 Reagents and solutions

Tri-n-dodecylammonium chloride (TLAHCl) was synthesized and purified.

Organic solvents: toluene, ethanol, acetone, Merck, p.a. were used without further purification.

Tetrachloroauric (III) acid, Merck, p.a. was purified by recrystallization.

Hydrochloric acid, Merck, p.a.

Amberlite XAD-2 (20-69 mesh) Adsorber Resin (Merck) with a particle size between 0.3-0.9 mm has been used in this work.

3 RESULTS

3.1 Impregnated resin preparation

Amberlite XAD-2 was used in this work as the polymer support for the preparation of the impregnated resin. XAD-2 was purified with a solution of 50% methanol and 4 mol dm^{-3} hydrochloric acid overnight. The solid support was washed with water to remove the chloride from the resin.

The impregnation of XAD-2 beads was carried out by using the "wet method" (Warshawsky and Patchornik, 1976). In this method, appropiate amounts of dry XAD-2 were placed into organic solutions containing TLAHCl at different concentrations (0.012 to 0.225 mol dm^{-3}) during 2 hours. The selected organic solvents were toluene, acetone, methanol and ethanol. The impregnated resin was separated from the solution by filtration through a porous filter using a water pump, washed several times with water and stored in water. The TLAHCl remaining in the organic solution was determined gravimetrically.

The results of the XAD-2 resin impregnation by TLAHCl using ethanol as organic solvent are shown in figure 1. In order to improve this impregnation, some experiments were carried out with toluene, methanol and acetone. No important differences were observed with toluene and methanol. In acetone, due to the low solubility of the TLAHCl in it, only concentrations of 0.01 and 0.02 mol dm^{-3} were tested. In this case, a higher impregnation was obtained. This fact may be explained by taking into account a higher affinity of the TLAHCl to the XAD-2 than to the acetone.

3.2 Au(III) extraction by SIR

In order to study the extraction of Au(III), a weighed amount (0.1 g) of TLAHCl/XAD-2 was placed in contact during 2 hours with an aqueous phase with the following composition: $[Au(III)] = 5.1 \times 10^{-4}$ mol dm^{-3}, $[H^+]=[Cl^-] = 1$ mol dm^{-3}. After equilibrium was attained Au(III) was determined in aqueous phase by atomic absorption spectrometry. In separated experiments, the adsorption of the metal by

the XAD-2 resin was studied. The results of these experiments are collected in table 1. These results indicate a high capacity of the TLAHCl/XAD-2 resin which reaches 90% extraction even with a loading as small as 0.1 mg TLAHCL/ g XAD-2, as well as the high affinity of the polymeric material for the metal.

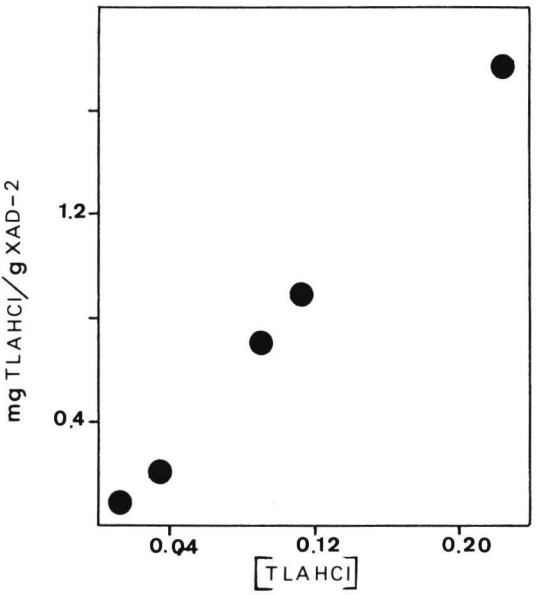


Fig. 1. Plot of mg TLAHCl/g XAD-2 vs concentration of TLAHCl in the ethanol impregnation solution.

TABLE 1

Extraction percentage of Au(III) at different concentration of TLAHCl in the XAD-2 resin. Initial Au(III) concentration 5.1×10^{-4} mol dm^{-3}.

mg TLAHCl/g XAD-2	% extraction
0	20
0.08	76
0.12	90
0.19	97
0.53	99
0.89	100
1.77	100

3.3 Au(III) Liquid-liquid extraction

The organic phase was prepared dissolving TLAHCl (s) in toluene. The total concentration of TLAHCl was varied from $5x10^{-5}$ to $5x10^{-4}$ mol dm^{-3}. The composition of the aqueous phase was $[H^+]=[Cl^-]= 1$ mol dm^{-3} and the concentration of Au(III) was kept constant at three values:0.106, 0.164 and 0.214 mmol dm^{-3}.

Experiments were carried out at 298 K by shaking equal volumes (15 cm^{-3}) of both phases using stoppered glass tubes in a continuous rotary during one hour when the equilibrium was attained. The Au(III) concentration in the aqueous phase was determined by atomic absorption spectrometry. The Au(III) stripping from the organic phase was carried out using 0.5 mol dm^{-3} thiourea.

The extraction of Au (III)from chloride media can be described by the following reaction:

$$q\ Au^{3+} + 3q\ Cl^- + p\ TLAHCl\ (org) = (AuCl_3)_q(TLAHCl)_p\ (org) \qquad (1)$$

The equilibrium constant can be written:

$$K_p = \frac{[(AuCl_3)_q(TLAHCl)_p]}{[Au^{3+}]^q\,[Cl^-]^{3q}\,[TLAHCl]^p} \qquad (2)$$

Experiments at different gold concentrations indicated the absence of polynuclear complexes in toluene, thus q=1.

In order to determine p, the following treatment was carried out:

$$[Au(III)]_{tot} = [Au(III)]_{org} + [Au(III)]_{aq}$$

where

$$[Au(III)]_{org} = K_p\,[Au^{3+}]\,[Cl^-]^3\,[TLAHCl]^p$$
$$[Au(III)]_{aq} = [Au^{3+}]\,(1 + \Sigma\,\beta_i\,[Cl^-]^i)$$

being β_i the formation constant of the gold chloro complexes (Högfeldt, 1982), the distribution coefficient defined as:

$$D = [Au(III)]_{org} / [Au(III)]_{aq}$$

can be written:

$$D = K_p'\,[TLAHCl]^p \qquad (3)$$

where

$$K_p' = K_p [Cl^-]^3 / (1 + \Sigma \beta_i [Cl^-]^i)$$

The equilibrium concentration of TLAHCl was calculated taking into account trimerization of the amine salt in toluene (Coello, 1986).

Equation (3) can be written as:

$$\log D = \log K_p' + p \log [TLAHCl]$$

In figure 2, log D is plotted versus log [TLAHCl]. From this plot, the slope equal to 1 is the value of p and log K_p' = 5. These results agree with those obtained in the extraction of also strong complexes as metal cyanide complexes (Figuerola 1988) where p depended on the negative charge of the complex, in this case $AuCl_4^-$ and log K presented similar values.

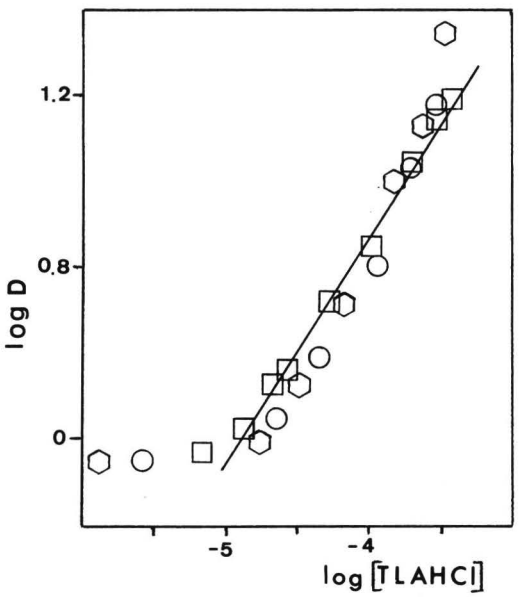


Fig.2. log D as a function of log [TLAHCl] at $[H^+]=[Cl^-]=$ 1 mol dm^{-3}. Full line has a slope equal to 1.

Deviations from this model at low TLAHCl concentration where log D is independent on log [TLAHCl] have been explained by the following reaction:

$AuCl_3$ (aq) = $AuCl_3$ (org)

This extraction process has been proved by using toluene without TLAHCl. The extraction of the metal by the solvent was confirmed in a separated experiment. Similar results were obtained in the Pb(II) extraction (Masana and Valiente, 1987).

4 CONCLUSIONS

The results of this work allow us to make the following remarks:

The SIR TLAHCl/XAD-2 presents a low loading capacity compared to other systems although the metal extraction efficiency is very high. This may be related to the fact that the solid support extracts Au(III) by itself, contributing to facilitate the extraction process.

The SX study showed that the predominant species in organic phase is $AuCl_4$TLAH and $AuCl_3$ is also extracted by the toluene. Both species can be also responsible to the Au(III) extraction by SIR. The $AuCl_3$ would be extracted by the XAD-2 while TLAHCl/XAD-2 would extract $AuCl_4^-$.

5 ACKNOWLEDGEMENTS

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SOLVENT EXTRACTION OF PHOSPHOROUS ACID FROM PLATING BATH SOLUTION

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ABSTRACT

Mishima, K., Nagatani, M. and Arai, Y.,1990. Solvent extraction of phosphorous acid from plating bath solution.

Solvent extraction of phosphorous acid and hypophosphorous acid from the alkaline aqueous solution with trioctylmethylammonium chloride (TOMAC) dissolved in benzene was investigated at 25 ^{o}C. The equilibrium relation of this system was measured. And the selectivity of TOMAC for phosphorous acid and hypophosphorous acid was found to be sufficient for practical separation of these acids.

INTRODUCTION

Electroless deposition (chemical plating) technique using hypophosphite is widely used in electronics industry for plating, because uniform thickness metal can be deposited on polymers and intricately shaped surfaces. However, when metal deposition progresses in this process, the phosphorous acid increases in the plating bath solution as impurity. A large quantity of phosphorous acid causes degradation of the plating bath solution. However, it seems to be difficult to remove phosphorous acid from the mixture composed of hypophosphite, phosphorous acid and metal ions (Mishima et al.,1989).

It is important to develop the extraction technique removing the phosphorous acid from the plating bath solution. It is necessary to find an effective extractant which has the selectivity to extract hypophosphorous acid or phosphorous acid. The extractions of such acids to the organic phase are only possible with the use of carriers. We used trioctylmethylammonium chloride (TOMAC) which was used as the extractant for d,l-phenylalanine (Haensel et al.,1986). The knowledge on the chemical equilibrium is required to design the extraction system. In this work, benzene is chosen as an organic solvent because inorganic substances have poor solubility in benzene. The extraction of hypophosphorous acid and phosphorous acid was carried out by the flask shaking method at 25 ^{o}C.

2 EXPERIMENTAL

2.1 Reagents

Hypophosphorous acid, phosphorous acid, sodium hydroxide and benzene (Ishizu Pharmaceutical Co., Ltd.) were used without further purification because no impurities was detected by ion chromatography or gas chromatography. All reagents were of analytical reagent grade. Trioctylmethylammonium chloride (Wako Pure Chemical Ind. Ltd.) was used without further purification. Water used in this work was distilled and deionised one.

2.2 Method of solvent extraction

The organic solution was prepared by dissolving trioctylmethylammonium chloride in benzene. The aqueous solution was prepared by dissolving the acids and sodium hydroxide in distilled and deionized water. Equal volumes (25 ml each) of the aqueous and organic phases, placed in 100 ml stoppered conical flasks, were shaken for 10 h with a mechanical shaker at 25 ^{o}C to attain the equilibrium. The mixtures were separated, and the concentrations of hypophosphorous acid, phosphorous acid or chloride ion were determined with the ion chromatography or the titration method in the aqueous phases. The instrument used in this research was a Tosoh Model 8010 ion chromatography system equipped with a conductivity detector (CM-8010). The conductivities detected for each solution were converted to concentrations of anions with the aid of conductivity-anion concentration calibration obtained from preliminary experiments. The anion separator column was a TSK-gel IC-anion-SW column (4.6mmX5cm). The all operating conditions of this system are given in Table 1. The eluent used for the separation of the anions was 0.002 M tartrate buffer (pH = 2.8). The working eluent was prepared from analytical reagent grade salts. The stock solution of eluent was prepared weekly. If the eluent was prepared and stored for long period, there was a chance of bacterial growth. The detection limit was $1x10^{-5}$ M for all anions. The concentration of those anions in the organic phase were determined by a SEIKO Model SPS-1200VR ICP (Inductively coupled plasma) system. The extraction constant Kex were obtained from the acid concentration measured by ion chromatography, ICP and titration. The amount of water in organic phase were measured with the titration using the Karl Fischer's reagent (Mitsubishi Chem. Ind. Ltd.).

2.3 Equilibrium

The following processes play a role during the extraction of hypophosphorous acid and/or phosphorous acid with trioctylmethylammonium chloride in the organic phase denoted by subscript o: hypophosphorous acid HA' or phosphorous acid H_2A'' in the aqueous phase denoted by the subscript a into acid anion A'^- or A''^{2-} :

$$HA'_a + H_2O \rightleftharpoons H_3O^+A'^-_a \qquad (1)$$

$$HA''_a + 2H_2O \rightleftharpoons (H_3O^+)_2A''^{2-}_a \quad (2)$$

The reactions of hypophosphorous acid anion or phosphorous acid anion with trioctylmethylammonium chloride as the anion exchager Q^+Cl^- at interface were expressed as follows,

$$A'^-_a + Q^+Cl^-_o \rightleftharpoons Q^+A'^-_o + Cl^-_a \quad (3)$$

$$A''^{2-}_a + 2Q^+Cl^-_o \rightleftharpoons Q^+_2A''^{2-}_o + 2Cl^-_a \quad (4)$$

The extraction constants Kex' and Kex'' for each system were described as follows,

$$Kex' = \frac{[Q^+A'^-]_o\,[Cl^-]_a}{[A'^-]_a\,[Q^+Cl^-]_o} \quad (5)$$

$$Kex'' = \frac{[Q^+_2A''^{2-}]_o\,[Cl^-]^2_a}{[A''^{2-}]_a\,[Q^+Cl^-]^2_o} \quad (6)$$

The distribution ratios of hypophosphorous acid and phosphorous acid between the organic phase and aqueous phase, D' and D'' were respectively expressed as follows,

$$D' = [Q^+A'^-]_o/[A'^-]_a \quad (7)$$

$$D'' = [Q^+_2A''^{2-}]_o/[A''^{2-}]_a \quad (8)$$

3 RESULTS AND DISCUSSION

A chromatogram obtained using the ion chromatography is given in Fig. 1. There are four peeks of hypophosphorous acid, phosphorous acid, phosphoric acid and chloride ion. This illustrates the possibility of concentration detection for the mixtures composed with water, hypophosphorous acid, phosphorous acid, phosphoric acid and chloride ion. The concentration of all species in organic phase and aqueous phase are obtained by ion chromatography, ICP and titration. By plotting $[Q^+A'^-]_o[Cl^-]_a$ versus $[Q^+Cl^-]_o[A'^-]_a$ according to Eq.(5) as shown in Fig.2, the constant of extraction equilibrium Kex' is calculated to be Kex'=24.8. Fig. 3 shows the constant of extraction equilibrium Kex'' as Kex''= 48.6 for phosphorous acid.

The effect of concentration of hypophosphorous acid in the aqueous phase on the distribution ratio of hypophosphorous acid, D' is shown in Fig.4. The distribution ratio D' decreases with increase in hypophosphorous acid concentration. The same effect is obtained for phosphorous acid as shown in Fig. 5. And the distribution ratio of phosphorous acid is larger than that of hypophosphorous acid under the same condition .

The results of extraction are obtained for the aqueous solution which contains hypophosphorous acid and phosphorous acid as shown in Fig.6. It illustrates that the TOMAC has the enough selectivity in extraction for phosphorous acid and hypophosphorous acid. From this result, TOMAC seems to be useful for separation of these acids in the recycle system of the plating bath solution .

TABLE 1

Operating conditions of the ion chromatography

Eluent	0.002 M tartrate buffer (pH = 2.8)
Flow-rate	0.5-2.0 ml min^{-1}
Separator column	TSK-gel IC-anion-SW (Tosoh , CA) as an anion separator
Column temperature	35 ^{o}C

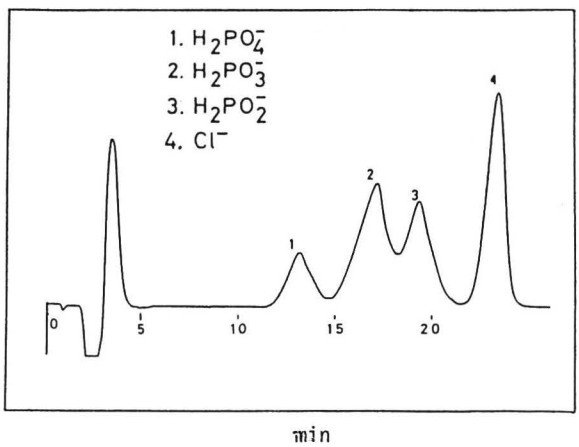


Fig. 1. The chromatogram for the aqueous solution composed of phosphoric acid, phosphorous acid, hypophosphorous acid.

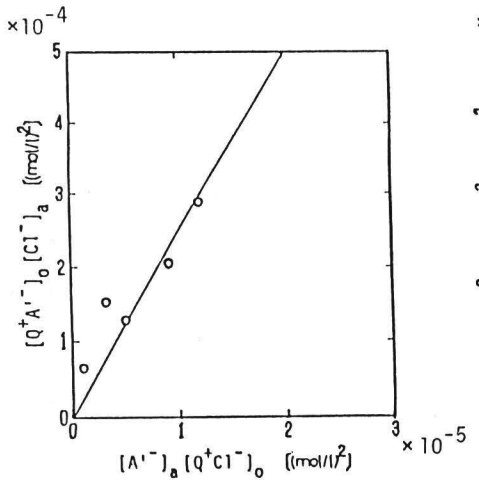


Fig. 2. Evaluation of equilibrium constant of anion exchange reaction in hypophosphorous acid/benzene/ TOMAC system.

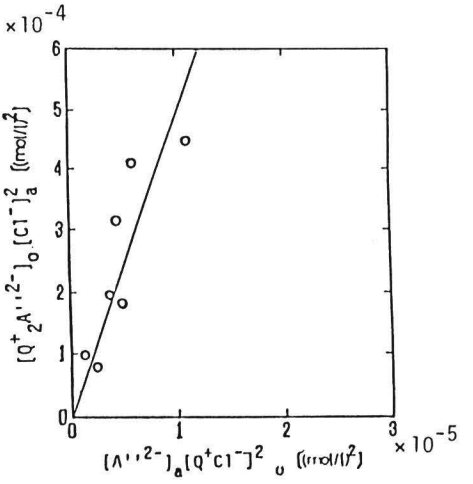


Fig. 3. Evaluation of equilibrium constant of anion exchange reaction in phosphorous acid / benzene /TOMAC system.

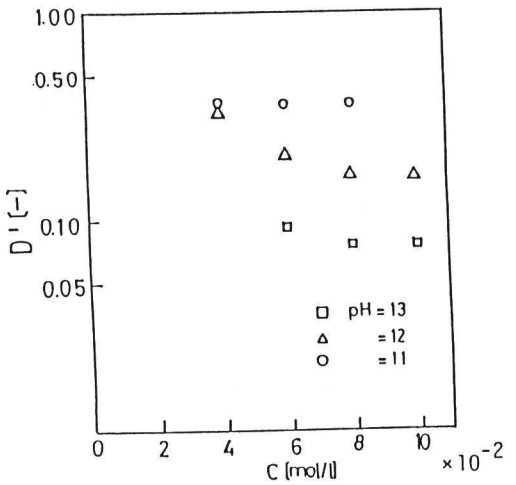


Fig.4. Distribution ratio of hypophosphorous acid.

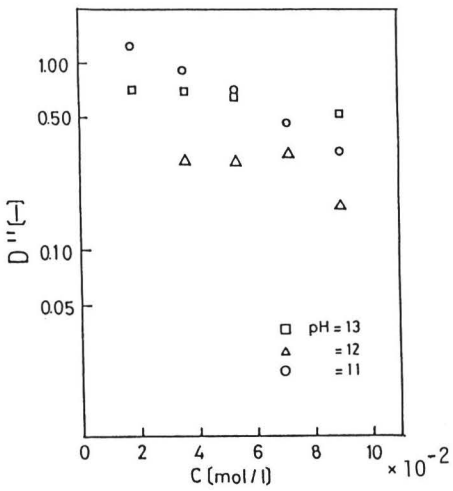


Fig. 5. Distribution ratio of phosphorous acid .

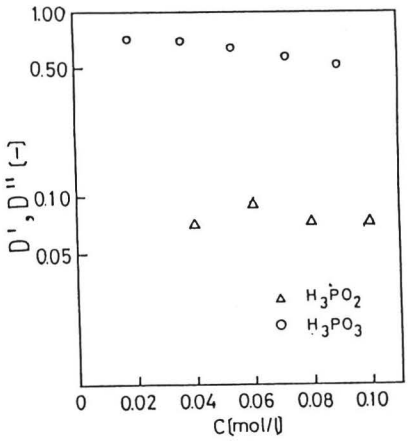


Fig. 6. Distribution ratio of hypophosphorous acid and phosphorous acid at pH = 13 and 25 °C.

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NEPTUNIUM (VII) EXTRACTION FROM ALKALINE MEDIA

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ABSTRACT

Rozen A.M., Nikiforov A.S., Kartasheva N.A., Nikolotova Z.J., Tananaev J.G., 1990. Neptunium (VII) extraction from alkaline media. The possibility of Np(VII) extraction from alkaline media with extractants of different classes has been investigated. Neutral organophosphorus mono- and bidentate compounds and crown ethers do not practically extract Np(VII), $D \leq 0.01$. Alkylphenols and especially their oligomers extract Np(VII) adequately. The highest distribution coefficients ($D \sim 10^2$) are reached on extraction with alkyl tin salt, enanthic acid, β-diketones.

INTRODUCTION

Actinides in their highest oxidation state (VII) discovered by Krot and co-workers are unstable. Therefore until recently their extraction was a failure. The aim of these notes is to study the possibility of actinide (VII) extraction with different extractant classes using most stable Np(VII) as an example.

Like other actinides Np(VII) is known to be stable only in alkaline media. Hence, Np(VII) extraction was studied using alkaline solutions. The aqueous phase contained LiOH or KOH (from 0.1 to 2.0 mole/l); under the indicated conditions Np(VII) is available as $NpO_4(OH)_2^{3-}$ anion.

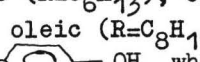
EXTRACTANTS

The following extractants were tested:

neutral: organophosphorus - TBP, TOPO, bidentate compound tetra-tolylmethylene diphosphine dioxide (4 tol)
crown-ethers-dicyclohexyl-18-crown-6 (DCH)
Alkyl tin salts with mineral (HNO_3) and organic (D2FHPA) acids.

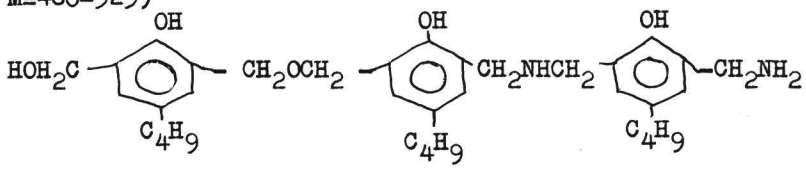
Chelate - -diketone $C_6H_5C(O)CH_2C(O)CF_3$ (DK)

Acids - di-2-ethylhexylphosphoric acid (D2EHPA), carboxylic acids RCOOH-enanthic ($R=C_6H_{13}$), caprylic ($R=C_7H_{15}$), pelargonic ($R=C_8H_{17}$) and oleic ($R=C_8H_{17}CH=CH(CH_2)_7$) acids.

Alkylphenols (APh)  OH, where $R=C_7-C_9$ (technical product, M=209) or

R = CH_3- C(CH$_3$)$_3$ - paratertbutylphenol (M=150)

Oligomer: p-tertbutylaminophenolphormaldehyde (BAPPO or Yarresin, M=460-525)



RESULTS

It was established that a very strong hydration of $NpO_4(OH)_2^{3-}$ anion is responsible for a very weak Np(VII) extraction with neutral organic compounds from alkaline media. Extraction with TBP or TOPO was not revealed at all.

For extraction with the most efficient crown-ether-dicyclohexyl-18-crown-6 (1 mole/l in 100% TBP) the distribution coefficients were

from KOH (2 mole/l) D=0.005

from LiOH (1.7 mole/l) D=0.0006

When the most powerful neutral compound - tetratolylmethylenediphosphine dioxide - (1 mole/l in TBP, extraction from 1-7 mole/l LiOH solution) is used D=0.012; the same results was found for extraction with 0.5 mole/l ditolyldiphenylmethylenediphosphine dioxide in methylisobutylketone, i.e., these most powerful extractants are incapable of overcoming hydration forces.

Spivakov, Shkinev and Zolotov recommend (1984) alkyl tin nitrate $R_2Sn(NO_3)_2$ for extraction of trivalent anions (e.g., PO_4^{3-}). They have kindly given us R_2SnO_2(R-octyl); the nitrate was prepared by neutralization with nitric acid. The distribution coefficients were D=0.3-0.4 on extraction with 0.2 mole/l solution of alkyl tin in TBP from 0.16 mole/l HNO_3 (1 ml) with the added 0.1 ml solution of 2 mole/l KOH containing Np(VII) or with the added 0.1 ml of 1.7 mole/l LiOH containing Np(VII). However, due to the salt hydrolysis pH of the equilibrium phase did not exceed 2.0 and the retention of the valency in the organic phase could not be expected.

To suppress the salt hydrolysis, i.e., the acid back extraction to the aqueous phase alkyl tin salt with D2EHPA in dichlorobenzene was tested. The resultant distribution coefficients are listed in table 1.

The data of table 1 conform to the ratio Np: $(D2EHPA)_2$ = 1:1 in the complex.

Table 1 *

Distribution coefficients for Np(VII) extraction with $(C_{18}H_{17})_2SnO$ solutions in 1:1 D2EHPA-DCB mixture

$(C_{18}H_{17})_2SnO$ concentration, mole/l	0.025	0.05	0.1	0.125	0.25
Np(VII) distribution coefficients, D	3.0	6.3	10.0	16.6	33-40

* Aqueous phase: 1 ml of 0.15 mole/l HNO_3 + 0.1 ml of Np(VII) solution in 1.7 mole/l LiOH.

The experiments revealed that D2EHPA effectively extracts Np(VII) in the absence of alkyl tin. For 100% D2EHPA extraction from 0.05 mole/l solution of KOH (1 ml of 0.15 mole/l HNO_3 with an additive of 0.1 ml of 2 mole/l KOH containing Np(VII))D=9.4. In this case the organic phase was stained green, which is inherent in the aqueous neptunium solution.

It was checked if the extraction was improved when D2EHPA was replaced by its zirconium salt $ZrA_4(HA)_2$. The result was negative, the distribution coefficient dropped to 0.19.

The unexpectedly effective extraction with D2EHPA was a stimulus to test also carboxylic acids - enanthic and caprylic ones. The extraction was conducted from a 0.4 mole/l LiOH solution (the separation deteriorated with the alkalinity). Longer chain acids (pelargonic and oleic ones) when in contact with an alkali (0.4 mole/l LiOH) produced thick white precipitates of RCOOMe salts which prevented their usage. When the system containing caprylic acid was held, the second organic phase was formed (as an intermediate layer between the aqueous and major organic phases) and this makes its practical usage inconvenient. The distribution coefficient for caprylic acid varied from 3 (third phase formation) to 30 (retention of the two phase system). In case of enanthic acid the stable value $D \sim 10^2$ resulted. On extraction a dark-brown precipitate was formed at the phase interface; it quickly dissolved and went to organic phase making it bright green. The study of the spectra (with a spectrophotometer SP-20) showed that Np is available in the oxidation states V (the maximum of 985 nm growing with time) and VI; in the 600-640 nm range (Np(VII)) no maximum was revealed.

The precipitate was likely to be a $LiNp^{VII}O_4xH_2O$ salt that forms by the reactions:

$$NpO_4(OH)_2^{3-} + 2\,H_2O = NpO_4^- \cdot 2H_2O + 2\,OH^-$$

$$LiOH + NpO_4^- \rightarrow \underset{\text{brown precipitate}}{LiNpO_4 \downarrow} + nH_2O$$

subsequently Np transforms to a cation and since pH≈6 Np(VII) is reduced to form Np(V) and (VI).

On extraction with alkyl phenol (AP) (0.5 mole/l in decane) from 0.4 mole/l LiOH the distribution coefficient was D=0.05. At the AP concentration of 2 mole/l (in octane containing 0.05 mole/l NaOH) D=1.0 was found for extraction from 1 mole/l NaOH.

The following distribution coefficients were found D=0.08 and D=0.25 for extraction with 1 mole/l paratertbutylphenol in toluene from the solutions containing 0.4 mole/l LiOH and 0.4 mole/l KOH + 0.25 mole/l K_2CO_3, respectively. During extraction the colour of the solution was observed to change from green to brown and then colourless, which corresponds to Np(VII) and (VI).

It should be pointed out that tertbutylphenol extraction proceeds by a micellar mechanism (with micelles in organic phase).

The following results were obtained for extraction with BAPPO (table 2).

Table 2

Np(VII) extraction with BAPPO

Extractant	Aqueous phase composition	Np distribution coefficient
0.1 mole/l BAPPO in 20% octyl alcohol in dodecane	0.4 mole/l LiOH	0.74
	0.4 mole/l KOH + 1 mole/l K_2CO_3	0.8
0.25 mole/l BAPPO in 20% octyl alcohol in decane	0.4 mole/l KOH+ + 0.25 mole/l K_2CO_3 pH=13.0	1.64
0.1 mole/l BAPPO in toluene	1.0 mole/l NaOH	1.0
	1.0 mole/l NaOH+ 1.0 mole/l K_2CO_3	0.55
	1.0 mole/l K_2CO_3	0.3

It follows from table 2 that K_2CO_3 added to the aqueous phase increases extraction if the diluent is dodecane/octylalcohol and decreases it if the diluent is toluene.

Good results (D~ 40) were obtained for a diketone DK extraction (100% DK) from 1 mole/l KOH (at 25% and 50% in dichlorobenzene D=10 and 25, respectively). If ammonium persulphate is added

(0.1 M) the distribution coefficient grows four times.

So, the best extractants for Np(VII) are alkyl tin salts, enanthic acid, β -diketones.

APPENDIX

Np(VII) solution (10^{-2} mole/l) was prepared by ozonization of Np(V) hydroxide suspension in LiOH solution (2 mole/l) up to full suspension dissolution.

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SOLUTION STRUCTURE OF SYNERGISTIC LANTHANOID DIBUTYLPHOSPHATE COMPLEXES

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ABSTRACT
Takahashi, T., Suzuki, Y, and Yamasaki, A, 1990. Solution structure of synergistic lanthanoid dibutylphosphate complexes.

Proton magnetic resonance study of lanthanoid dibutylphosphate complexes in deuteriochloroform solution made it possible to elucidate the solution structure of synergistic complexes. The remarkable chemical shift change of oxymethylene protons suggested the much crowded chelate rings arrangement in the tris-chelates than those in the hexakis-chelates.

Dibutyl phosphoric acid has been widely used as the good chelating synergistic extractant for various metal ions, especially actinoids and lanthanoids(Sekine and Hasegawa, 1977). The stoicheiometry of lanthanoid complexes were determined to be 1:3 and 1:6 from the equilibrium study, and the existence of dimeric free acid is well recognized in the low-polar organic solvent like many carboxylic acids. The isolation of lanthanoid dibutylphosphate has been carried out already by the thermal decomposition of tributyl phosphate adducts of their nitrate(Shin-ike, Shiokawa and Ishino, 1967), but their waxy(and probably polymeric) character prevented us to extend further research even today.

We have tried to investigate the structural characteristics of dibutylphosphato ligands in the lanthanoid(III) complexes by proton magnetic resonance and found several interesting characteristics, the results are shown below.

EXPERIMENTAL

Preparation of complexes: An acetonitrile solution of dibutyl phosphoric acid is added to the water/acetonitrile(1:1) solution of lanthanoid nitrates in the stoicheiometric ratio. The resulted solution was neutralized with 1M aqueous sodium acetate. The neutralized solution was stayed overnight and the precipitated solid was filtered off and washed with acetonitrile/water mixture and dried in vacuo. The ratio of metal ion(chelometry)

and the phosphate(gravimetry) were reasonably consistent with the estimated 1:3 and 1:6 respectively. (The neutralization with dilute aqueous ammonia could not yield the satisfactory analyses in almost all cases.) The infrared spectra of these products were nearly consistent with those previously reported by Shinike et al.(1967)

Lanthanide shift reagent (tris(dipivaloylmethanato)praseodymium(III)) were purchased from Dojin Chemical Lab. and used without further purification.

Spectral Measurement: Proton nuclear magnetic resonance(pmr) spectra were recorded at 90 MHz with Varian nmr spectrometer. The complexes were dissolved into deuteriochloroform containing 1% tetramethylsilane(TMS) as internal standard. The lower solubility and high viscosity of the prepared complexes made it difficult to record clear spectra in many cases.

The concentration dependence of chemical shift was carried out by the addition of tris(dipivaloylmethanato)lanthanoid(III) chelates in dibutyl phosphoric acid-deuteriochloroform solution. (see Discussion)

RESULT and DISCUSSION

The typical spectra of proton nmr are shown in Figure 1(a-c) for free dibutyl phosphoric acid and paramagnetic praseodymium (III) complexes. The overlapped methyl-methylene spectra and small chemical shift change could not give the clear information for the geometry of these complexes. Fortunately, the paramagnetic lanthanoid(III) complexes have been widely used for "shift reagents" for their large pseudocontact shift. The solution geometry can be elucidated for many organic compounds from their stereochemical (dipolar) term $(3\cos^2\theta-1)/r^3$ in the adducts.

We have tried to apply here the tris(dipivaloylmethanato) complexes of lanthanoids (mainly praseodymium), because of their large pseudocontact shift range. These complexes are dissolvable in dibutyl phosphoric acid solution, and their β-diketonato ligands are easily replaced by the dibutylphosphate groups, which was proved from the chemical shift of dipivaloylmethane without any paramagnetic shift and line broadening.

The praseodymium complexes were most extensively studied because of their large pseudocontact shift and small line broadening. The typical pmr spectra and the concentration depend-

ence of the chemical shift are shown in Figure 2. The extremely large paramagnetic shift of OCH_2 protons and the much smaller shift of methyl and other methylene protons can suggest the structure of the 1:3 complex of praseodymium in deuteriochloroform solution. The oxymethylene(-OCH_2-) protons situate in the upfield shift region, and the other protons are at around the surface of cones which separate the upfield and downfield shift regions. On the other hand, all the protons in the 1:6 complexes do not show the upfield shift. This means the site of all protons are outside of upfield shift cones. From these spectral characteristics, the estimated structure are shown in Figure 3, which was been roughly estimated from the calculation of simple personal computer.

Of course there exist the rapid ligand exchange and stereochemical movement of chelate rings in the solution in ambient temperature, the exact geometry seems to be hardly determined precisely. However, the resemblance of the trend of chemical shift change for the other lanthanoid complexes would suggest the similar solution structure for the two kinds of lanthanoid dibutylphosphates.

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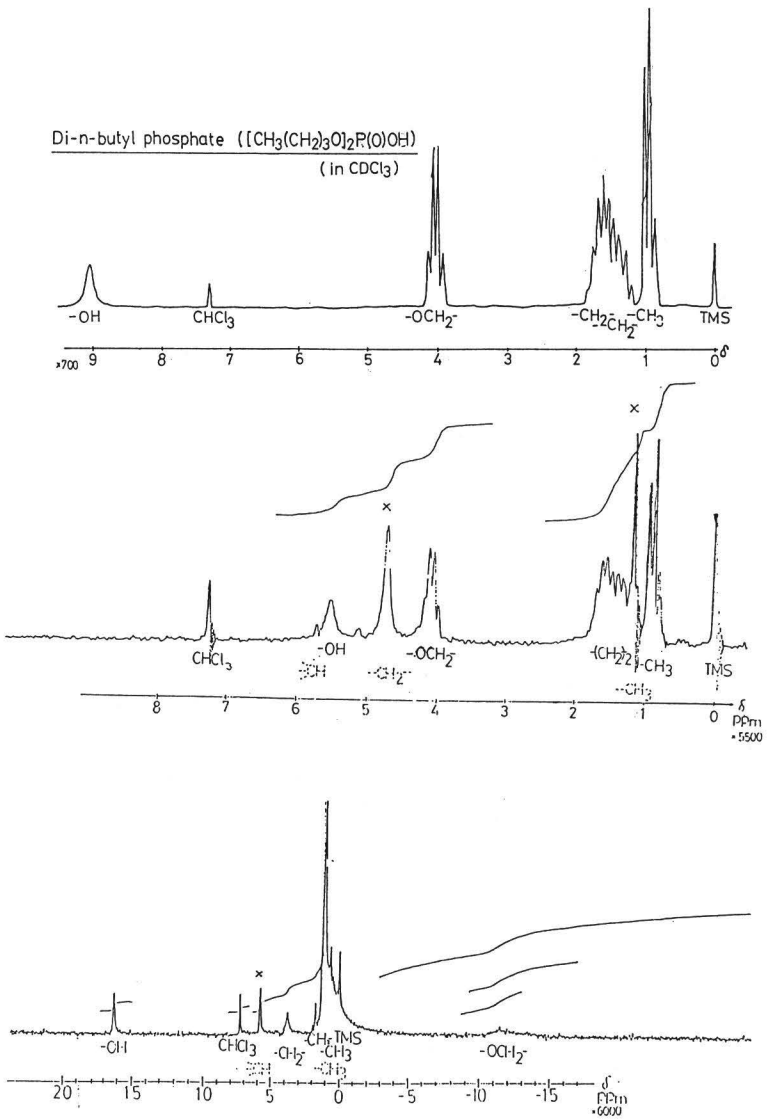


Figure 1. Pmr spectra of
a) dibutyl phosphoric acid in deuteriochloroform.(0.5mol/l)
b) tris(dipivaloylmethanato)praseodymium(III) added dibutyl phosphoric acid/deuteriochloroform. Pr(dpm)3/HDBP = 0.042:1
c) tris(dipivaloylmethanato)praseodymium(III) added dibutyl phosphoric acid/deuteriochloroform. Pr(dpm)3/HDBP = 0.277:1

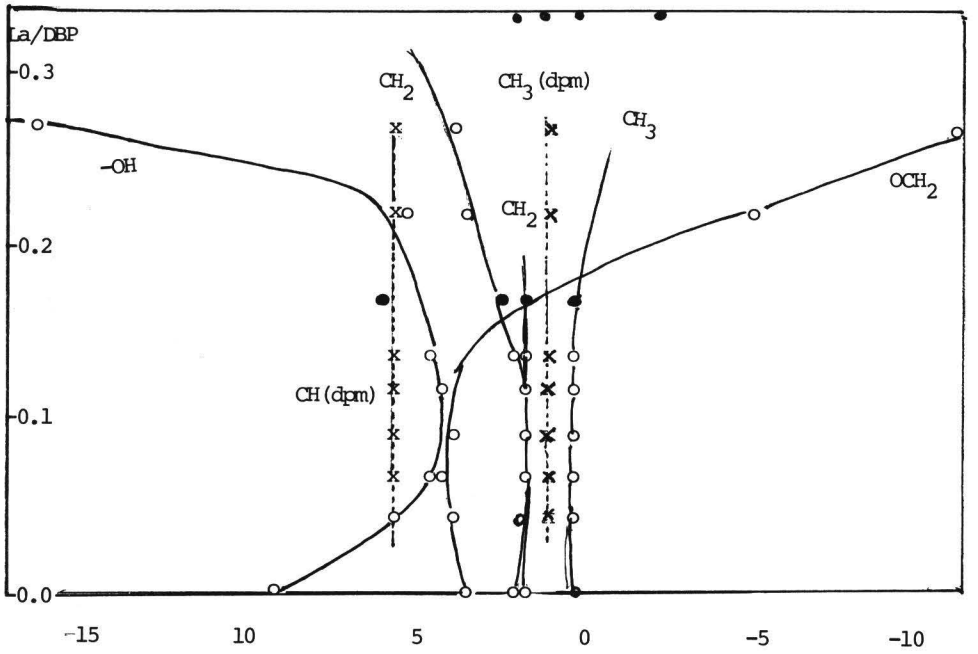


Figure 2. Proton chemical shift dependence on the ratio of praseodymium to dibutyl phosphoric acid in deuteriochloroform.
open circle : dibutyl phosphoric acid--tris-(dipivaloylmethanato)praseodymium(III) solution.
filled circle : dissolved dibutyl phosphate complexes
cross : proton signals of free dipivaloylmethane

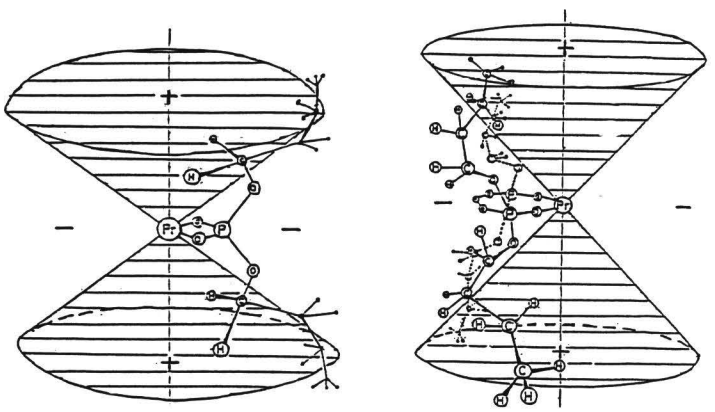


Figure 3. Proposed Structure of Lanthanoid(III) dibutylphosphate complexes in solution.
a) Ln(DBP)3
b) Ln(H(DBP)2)3

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W/O MICROEMULSIONS FORMED BY ACIDIC EXTRACTANTS AND EFFECT OF LANTHANIDES

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ABSTRACT

W/O microemulsions are involved in the practical process of rare earth separation by solvent extraction. In this study, naphthenic acid (I), HDEHP, di(2-ethylhexyl)phosphoric acid (II), PC 88A, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (III), and CYANEX 272, di(2,4,4-trimethylpentyl) phosphinic acid (IV) were employed. FT-IR spectra show the coordination between lanthanides and extractant molecules, and FT-IR and PCS (photon correlation spectroscopy) provide direct evidence of the existence of W/O microemulsion or microemulsion-like droplets. The extraction of rare earths by saponified naphthenic acid in mixed solvent has been confirmed to be a process of destruction of the W/O microemulsion. A possible mechanism is discussed.

INTRODUCTION

W/O microemulsions are involved in the practical process of rare earth separation by solvent extraction. It was suggested in previous studies (Wu et al., 1980a,b) that the saponification of acidic extractants such as naphthenic acid, HDEHP, etc., is a process of W/O microemulsion formation, while the extraction of rare earths by the saponified extractant is a process of destruction of the microemulsion.

However, it has been observed also in our laboratories that under restrictive conditions, such as low lanthanide ion loadings, the organic diluent can also hold an appreciable amount of water with a microemulsion-like appearance. Then, questions arise: (i) is it a stable W/O microemulsion system? (ii) what is the aggregate size? (iii) what is the effect of different lanthanides on the stability of the W/O microemulsion? It is believed that these questions are important in understanding the physicochemical nature of aggregates formed by lanthanides and acidic extractants in solvent extraction systems.

Accordingly, in this work FT-IR spectroscopy was employed to verify the interaction between lanthanides and extractant molecules and to identify the existence of bulk water. In order to identify the formation and stability of microemulsion droplets containing lanthanides, PCS (photon correlation spectroscopy) measurements were also performed carefully (Neuman et al., 1990).

2 EXPERIMENTAL MATERIALS AND METHODS

In this study the following acidic extractants were employed: (I) naphthenic acid, (II) HDEHP, di(2-ethylhexyl)phosphoric acid, (III) PC 88A, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester, and (IV) CYANEX 272, di(2,4,4-trimethylpentyl)phosphinic acid. The organophosphorus extractants were purified following the procedures of Partridge and Jensen (1969) as reported previously (Gaonkar and Neuman, 1984). Naphthenic acid (Fluka) was used as received. The diluent used for the three organophosphorus extractants (II), (III) and (IV) was double-distilled n-heptane (HPLC grade, Fisher). For naphthenic acid the diluent was a mixture of 80% n-heptane and 20% 2-octanol (v/v). All extractants were properly saponified by concentrated sodium hydroxide solution (10 M), and then the organic phase was equilibrated with aqueous solutions of $LaCl_3$, $PrCl_3$, or $EuCl_3$. After separation of the two bulk phases, the organic phase was subjected to FT-IR spectroscopic measurements. The samples employed in PCS measurements were prepared by adding a known amount of water or lanthanum chloride solution to the organic solution containing the saponified extractant without forming a separate phase.

3 RESULTS AND DISCUSSION

3.1 Coordination between lanthanum and naphthenate

FT-IR spectra for the lanthanum-naphthenic acid extraction system are shown in Fig. 1. The symmetrical stretching vibrational absorption band of the carboxylic group for naphthenic acid and the saponified extractant are 1408 and 1404 cm^{-1}, respectively. In the lanthanum-sodium naphthenate extraction system at 67% loading, the corresponding frequency is 1416 cm^{-1}. These findings can be explained by the stronger interaction between rare earths and extractant molecules so that the symmetrical stretching vibration shifts to a higher frequency and, therefore, indicate the coordination between lanthanum ions and naphthenate ligands. Similar results were reported in previous studies (Wu et al., 1980a, 1985) by the method of spectra subtraction. In this work the sampling technique was improved so that the symmetrical stretching frequency could be measured directly.

3.2 W/O microemulsion formed by sodium naphthenate in mixed solvent and effect of lanthanum on the microemulsion stability

The phase diagram for the 0.2 M sodium naphthenate-water system is shown in Fig. 2 where W_o is the water-extractant molar ratio. The homogeneous region denotes the composition range of the W/O microemulsion. The measured relative scattering light intensity, which is a measure of the hydrodynamic radius of the aggregates, versus temperature plots are shown in Fig. 3. The results show that the particle size of the W/O microemulsion droplets depends on temperature and water content, i.e., the higher the temperature, the

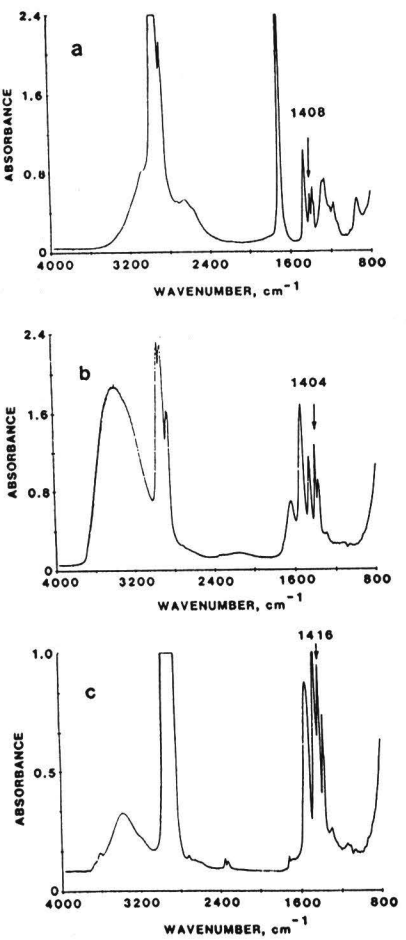


Fig. 1. FT-IR spectra of lanthanum-naphthenic acid extraction system. (a) naphthenic acid, (b) sodium naphthenate-water, and (c) sodium naphthenate/mixed solvent/$LaCl_3$ solution (67% loading).

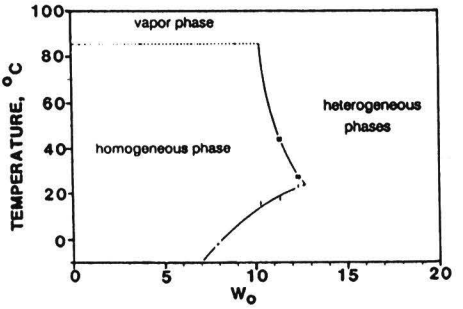


Fig. 2. Phase diagram of sodium naphthenate-water system in mixed solvent of n-heptane (80%) and 2-octanol (20%).

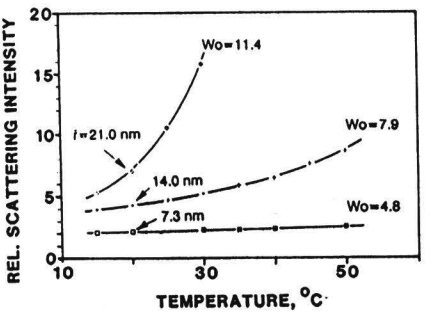


Fig. 3. Relative scattering intensity of sodium naphthenate-water system as a function of temperature and water content.

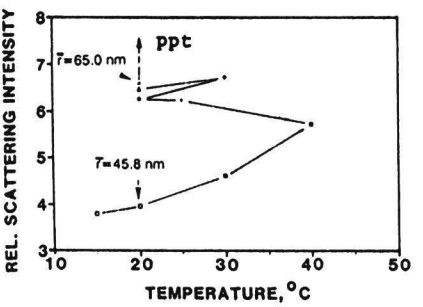


Fig. 4. Relative scattering intensity of sodium naphthenate-water system containing lanthanum (7.8% loading and W_o = 3.2).

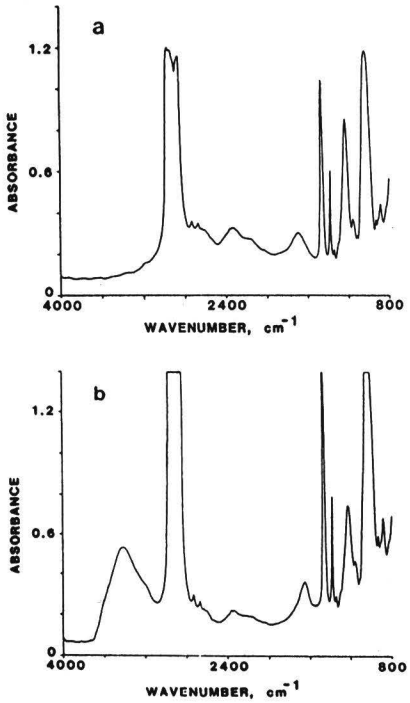


Fig. 5. FT-IR spectra for HDEHP.
(a) HDEHP in n-heptane, and
(b) 25% saponified HDEHP.

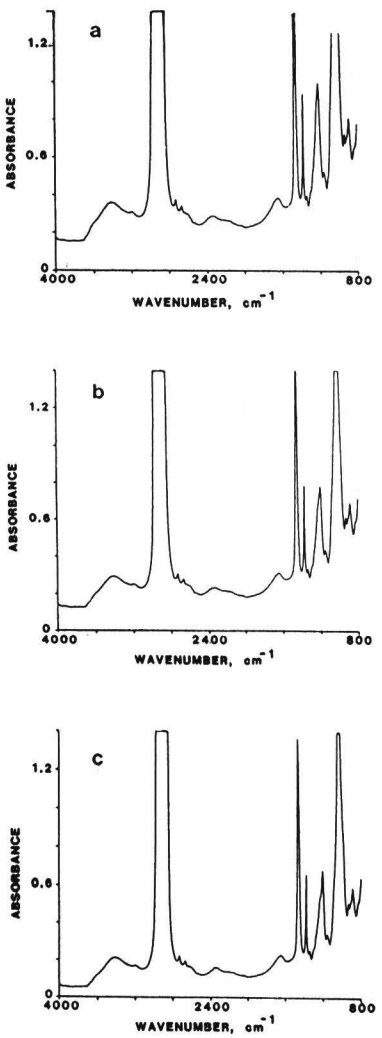


Fig. 6. FT-IR spectra of lanthanide-NaDEHP·3HDEHP extraction systems at 50% loading: (a) lanthanum chloride, (b) praseodymium chloride, and (c) europium chloride.

larger the aggregates, and the higher the water content, the larger the aggregates. For reference, the mean effective hydrodynamic radius (r) obtained from PCS measurements at 20°C is given in Fig. 3. What should be emphasized is that the W/O microemulsions shown in Fig. 3 are independent of repeat heating/cooling cycles or aging. Accordingly, the unstable microemulsion-droplets can be distinguished from a thermodynamically stable microemulsion by examining the stability of the system upon repeated heating and cooling and aging.

When rare earths were added to a sodium naphthenate-water microemulsion system, or the organic phase of the extraction system was equilibrated with an aqueous solution of rare earths, the W/O microemulsion was destroyed. However, under restrictive conditions, for example at metal ion loadings < 10%, a homogeneous organic phase can exist for a period of days. Figure 4 shows the result for a representative system containing sodium naphthenate-water and lanthanum ions at 7.8% loading. PCS measurements showed that the particle size increased (compare the results with those shown in Fig. 3). In addition, at higher loadings, it was visually observed that the addition of $LaCl_3$ solution reduced the water solubilization (also see Fig. 1). Also, the temperature effect on the particle size was irreversible, and the particles grew slowly with time. After aging the given sample at 20°C for 10 days, precipitates appeared in the organic phase.

The mechanism of coagulation between the W/O microemulsion droplets is not clear. Nevertheless, based on its chelate coordination structure (Wu et al., 1980a,b), lanthanum naphthenate may attach with one hydrocarbon tail to the surface film of a microdroplet producing a "penetration" effect. This increases the curvature of the surfactant film around the microdroplet and thus decreases the water content. On the other hand, a similar "penetration" of the second tail may occur with another microdroplet and thereby build bridges between microdroplets resulting in a size growth. At lower loadings, this coagulation is a slow process, but it can be accelerated by heating.

3.3 Reduction of water solubilization by lanthanides

The stretching vibrational absorption band of liquid water near 3400 cm^{-1} in the FT-IR spectra (Weng et al., 1985) can be used to compare the ability of lanthanides to reduce solubilized water. The FT-IR spectra for HDEHP and saponified HDEHP, i.e., NaDEHP·3HDEHP, in n-heptane are shown in Fig. 5. The FT-IR spectra in Fig. 6 show the ability of lanthanides to reduce the solubilized water. The effect also depends on the lanthanide ion loading, i.e., the higher the loading, the greater the reduction of solubilized water. In fact, the FT-IR spectra in Figs. 5 and 6 show less amount of solubilized water than that in the lanthanum-naphthenic acid system shown in Fig. 1, therefore the aggregates formed from organophosphorus extractants (HDEHP) are

more likely reversed micelles. FT-IR spectra for PC 88A and CYANEX 272 systems (not shown in this report) also show the reduction of solubilized water upon the extraction of lanthanides. A detailed discussion will be communicated elsewhere.

4 CONCLUSIONS

(1) The saponified naphthenic acid can form W/O microemulsions in the mixed solvent 80% n-heptane and 20% 2-octanol (v/v).

(2) In the extraction of La^{3+}, a coordination reaction takes place between La^{3+} and naphthenate ligands, thereby forming a chelate complex of lanthanum naphthenate.

(3) W/O microemulsions are destroyed by the extraction of La^{3+} and accompanied by a size growth and water content decrease, which is proposed to result from the possible effect of hydrocarbon tail penetration of lanthanum-naphthenate complexes and bridging between microdroplets.

(4) In the extraction of lanthanides by partially saponified HDEHP in n-heptane, a reduction of solubilized water occurs and the effect depends on the lanthanide loading, i.e., the higher the loading, the lower the water content.

5 ACKNOWLEDGMENTS

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EXTRACTION OF NICKEL FROM NITRATE MEDIA WITH DI(2-ETHYLHEXYL)PHOSPHORIC ACID UNDER HIGH LOADING CONDITIONS

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ABSTRACT

The extraction of nickel(II) from nitrate media of ionic strength 0.25 M by di(2-ethylhexyl)phosphoric acid (HDEHP) in n-heptane has been studied under constant high nickel loading conditions (0.4) and pH 5.7 to further understand hydrometallurgical solvent extraction. The experimental techniques of dynamic light scattering and FT-IR spectroscopy, as well as classical physicochemical and extraction measurements, were employed to characterize the nickel-HDEHP complexes formed in the organic phase. It was found that there were two regimes for the [HDEHP] dependence of the equilibrium nickel distribution coefficient. The enhancement in nickel extractability at higher [HDEHP] is presumably due to differences in the nature of the nickel-HDEHP complexes. Indeed, the characterization study provided strong evidence that cylindrical reversed micelles form in the organic phase.

INTRODUCTION

Di(2-ethylhexyl)phosphoric acid (HDEHP) is a typical extractant for recovery of nickel from acidic leach solutions. Under low nickel loading conditions (<0.04), the nickel-extractant complexes exist as a single "monomeric" species (Komasawa et al., 1981). On the other hand, as the loading ratio increases above 0.04, the composition of the nickel-extractant complexes changes and aggregates (or polymeric species) begin to form. However, conventional slope analysis based on equilibrium metal distribution can not be applied to highly loaded systems because the extraction equation varies with the loading ratio in a complex manner.

Recently, Neuman and co-workers (Gaonkar et al., 1987, 1989; Neuman et al., 1990a,b) investigated various solvent extraction systems containing HDEHP and metal ions. These investigators employed colloid and surface science concepts in their study of the aggregation behavior of metal-HDEHP complexes. They concluded that the aggregation in solvent extraction is analogous to that for classical surfactants in nonpolar solvents and proposed that the aggregates were reversed micelles. In addition, a general model (see Fig. 1) for aggregation of metal-extractant complexes in acidic organophosphorus solvent extraction systems was proposed.

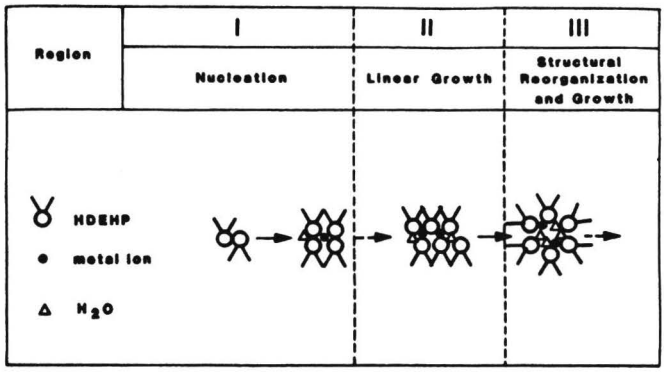


Fig. 1. Simplified model for aggregation of metal-extractant complexes in acidic organophosphorus solvent extraction systems (from Neuman et al., 1990b).

In these studies, however, the metal loading ratio was not well controlled. Accordingly, in the present work, a systematic investigation of nickel extraction was performed under more controlled high loading conditions in order to further the fundamental understanding of nickel(II) extraction by HDEHP and, in general, the solvent extraction of metal ions by acidic organophosphorus extractants.

2 EXPERIMENTAL MATERIALS AND METHODS

HDEHP (Morton Thiokol, 98%) was purified by the copper salt method described elsewhere (Partridge and Jensen, 1969). The diluent, n-heptane, (Aldrich, 99+%) was purified by simple distillation, and water was purified by a reverse-osmosis/NANOpure II (Barnstead) system. Nickel nitrate (AESAR, 99.9999%) was used as received. All other chemicals were analytical reagent grades.

In measurements of the equilibrium nickel distribution coefficient, D, the initial concentrations of nickel nitrate and those of HDEHP were varied from 0.0025 to 0.1000 M and from 0.0003 to 0.229 F, respectively. Equal volumes of the aqueous and n-heptane solutions were adjusted to pH 5.7 and equilibrated at 20.0 + 0.1°C. The nickel content of the aqueous phase was determined by back-titration against EDTA with standard thorium solution.

The following methodology was adopted for determination of D at constant loading. For a given initial nickel concentration, a series of experiments was conducted to obtain the equilibrium nickel distribution coefficient and loading, L, corresponding to various initial concentrations of HDEHP. Then, the concentration of HDEHP, which yielded a loading ratio of 0.4, was obtained from the plot of loading versus log [HDEHP]. At this HDEHP

concentration, D was determined from the plot of log D versus log [HDEHP]. Next, the nickel concentration was varied, and the same procedures were repeated to obtain another [HDEHP] value at which the organic phase was 80% loaded, i.e., L = 0.4. In this study, [HDEHP] was the corrected value obtained by subtracting the aqueous phase HDEHP concentration from the total HDEHP concentration. The HDEHP concentration in the aqueous phase was determined by the method of Bhattacharyya and Murthy (1974). Ionic strength also was kept constant at 0.25 M. In order to maintain constant ionic strength, however, a different amount of $NaNO_3$ was added to each aqueous solution since different initial nickel nitrate concentrations were used for the constant loading experiments. The nickel-extractant complexes in the organic phase were characterized by dynamic light scattering and FT-IR spectroscopic measurements using the apparatus and procedures described elsewhere (Neuman et al., 1990a,b). Furthermore, the water content of the organic phase was determined using a Fisher L/I aquametry apparatus.

3 RESULTS AND DISCUSSION

Figure 2 shows the effect of total HDEHP (free and complexed) concentration in the organic phase on the equilibrium nickel distribution coefficient at constant loading ratio. As shown in Fig. 2, two different regimes for the HDEHP dependence of D are observed. In fact, at higher HDEHP concentrations, nickel extraction is enhanced. If the nickel-extractant complexes in the organic phase are identical throughout the

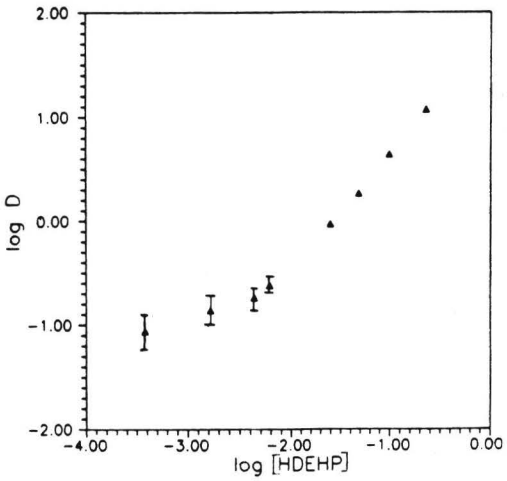


Fig. 2. Equilibrium nickel distribution coefficient as a function of HDEHP concentration in the organic phase at loading ratio 0.4 and pH 5.7.

entire extractant concentration range, the log D-log [HDEHP] plot should be a straight line under constant loading conditions. Accordingly, we can infer that different nickel-extractant complexes (chemically or physically) are formed in the organic phase depending on the extractant concentration. Table 1 shows the size of the aggregates formed by the nickel-HDEHP complexes in the organic phase as determined by dynamic light scattering. The mean effective hydrodynamic radius, $\bar{r}$, increases as the total [HDEHP] increases at constant loading. On the other hand, the polydispersity index, Q, which is a measure of the width of the size distribution, decreases with increasing HDEHP concentration. These results also indicate that the aggregate size and polydispersity index are consistent with those of reversed micelles.

TABLE 1

Dynamic light scattering measurements of organic phase of solvent extraction system HDEHP/n-heptane/nickel(II) nitrate solution*.

Sample No.	$[Ni^{2+}]_{initial}$, M	$\log[HDEHP]_{org}$	$\bar{r}$, Å	Q
A	0.1000	-0.64	52.0	0.13
B	0.0500	-1.00	31.5	0.14
C	0.0301	-1.31	22.5	0.25
D	0.0202	-1.61	~15	0.27

*Loading ratio 0.4, pH 5.7, 20°C.

The FT-IR spectra of the organic phase for the system HDEHP/n-heptane/nickel(II) nitrate solution are given in Fig. 3. The spectra show the O-H stretching and bending absorption bands of liquid water at about 3400 and 1630 cm^{-1}, respectively. Accordingly, it appears that the aggregates are reversed micelles since the FT-IR results indicate the existence of "bulk" water in the core of the aggregates formed by nickel-HDEHP complexes. However, the O-H stretching vibrational absorption band observed at 3200 cm^{-1} implies that the aggregates also contain bound water molecules to complete the coordination number (6) of nickel. Therefore, the most probable unit structure of the nickel-HDEHP complexes in the aggregates is $Ni(DEHP)_2n(H_2O)$ where n, the number of coordinated water molecules, is equal to two under high loading conditions.

In addition to the FT-IR spectra, the water content in the organic phase was determined. Table 2 shows that the absolute water content increases

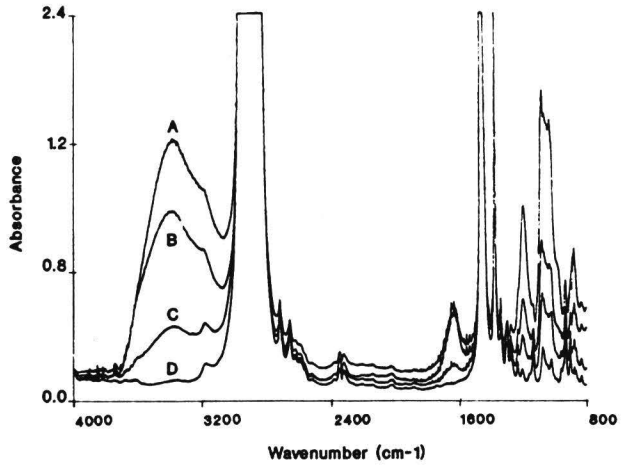


Fig. 3. FT-IR spectra of the organic phase of the solvent extraction system HDEHP/n-heptane/nickel(II) nitrate solution. log[HDEHP]: A=-0.64, B=-1.00 C=-1.31 and D=-2.21.

with increasing HDEHP concentration (or size of aggregates). However, W_o, the molar ratio of water to HDEHP in the organic phase, does not vary significantly with HDEHP concentration. Thus, the shape of the reversed micelles appears to be cylindrical (or rodlike). The approximate size of the cylindrical reversed micelles was estimated by taking into consideration the hydrodynamic radius of the aggregates and the molecular dimensions of HDEHP, water and nickel ions. The ratio of length to radius of the cylindrical reversed micelles was about 5-7, for example, 130 Å length and 23 Å radius in the case of sample A.

TABLE 2

Water content of the organic phase of the solvent extraction system HDEHP/n-heptane/nickel(II) nitrate solution*.

Sample No.	Water content, g/L	W_o
A	23.6	5.8
B	9.70	5.4
C	4.73	5.4
D	2.18	4.8

*Loading ratio 0.4, pH 5.7, 20°C.

Therefore, the present study shows that the general model proposed by Neuman et al. (1990b) can be applied to the nickel extraction system under

high loading conditions. In addition, the metal-extractant aggregates can grow either into spherical (e.g., Na-HDEHP) or cylindrical (e.g., Ni-HDEHP) reversed micelles.

4 CONCLUSIONS

The equilibrium nickel distribution results show that there are two regimes for the D dependence on [HDEHP] at constant loading. Furthermore, nickel extraction was enhanced when the nickel-HDEHP complexes formed cylindrical reversed micelles.

5 ACKNOWLEDGMENTS

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EXTRACTION OF MONO AND POLYNUCLEAR COMPLEXES OF ZINC(II) WITH DI(2-ETHYLHEXYL)PHOSPHORIC ACID

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ABSTRACT

The distribution of zinc(II) between solutions of di(2-ethylhexyl)phosphoric acid in dodecane, decalin or heptane and aqueous solutions has been studied in sulphate and perchlorate media. The dependence of the distribution ratio of zinc(II) on the concentration of H^+ ions, the extractant concentration and the initial concentration of zinc(II) was measured at room temperature. Small amounts of zinc are extracted as mononuclear complexes of the type $ZnA_2 \cdot 2HA$. Polynuclear zinc complexes with Zn/HDEHP ratios up to 1/2 are extracted at >0.01 *M* Zn(II) in the organic phase. The possible composition of the polynuclear complexes was estimated by a computer evaluation of the distribution data. Substitution of dodecane by decalin suppresses slightly the extraction of zinc(II). Changes in temperature and ionic strength have no significant influence on the distribution ratio.

INTRODUCTION

Di(2-ethylhexyl)phosphoric acid (hereafter HDEHP, in formulas HA) has been shown to be an effective extractant for the separation of a large number of divalent metals in hydrometallurgical processes (Baes, 1962; Komasawa, 1981; Lo, 1983). The aim of this work was to obtain and interpret extensive distribution data for a model extraction system. Among divalent transition metals, zinc is extracted by HDEHP more effective than copper, cadmium, cobalt or nickel (Kolarik, 1974).

EXPERIMENTAL

HDEHP (Bayer) was purified by precipitating a copper salt (Partridge, 1969). The other chemicals (Merck, Ventron-Alfa) were used as received.

The organic phase was a solution of HDEHP in dodecane, decalin or heptane. The aqueous phase was a solution of sodium sulfate or perchlorate, sulfuric or perchloric acids and zinc sulfate or perchlorate in deionized water. The ionic strength was 0.75 and temperature was 23°C±1°C, with the exception of those cases in which the effect of the ionic strength and temperature was investigated. The initial concentration of zinc(II) in the aqueous phase was varied from traces (about 10^{-6} *M*) to 0.058 *M* in the sulfate medium and to 0.055 *M* in the perchlorate medium.

The experiments were carried out in one way bottles, which were shaken for

about 30 min. at a middle frequency. The zinc sulfate and perchlorate solutions used in the extraction were labeled with a $^{65}ZnCl_2$ solution. A relation between the molarity of zinc and the gamma counting rate was determined for each series of measurements. The pH value expresses the concentration and not the thermodynamic activity of hydrogen ions. The glass electrode used for the measurements was calibrated with solutions containing known amounts of respective acids at a desired ionic strength.

The program LETAGROP DISTR (Liem, 1971) was used for the evaluation of the distribution data.

RESULTS AND DISCUSSION

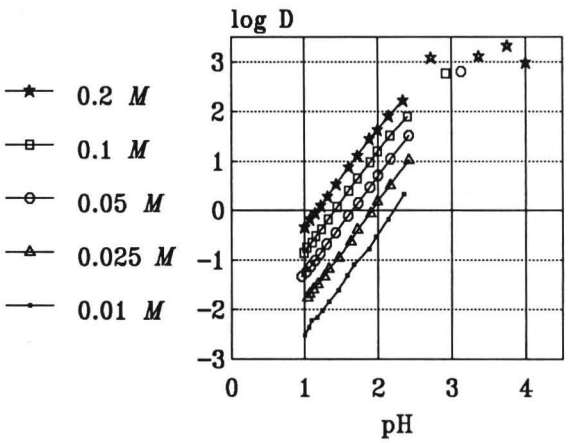


Fig. 1: Zinc extraction at different HDEHP concentrations in dodecane. Zn(II): ~10^{-6} *M*, 0.75 *M* $(Na,H)ClO_4$, 23°C.

The distribution of zinc(II) traces in a system with dodecane diluent is shown in Fig. 1. Results analogous to those in Fig. 1 were obtained at pH 1.7 to 4.0 in the sulfate medium (dodecane diluent). Analogous results were also obtained at pH 1.0 to 2.0 in the perchlorate medium with decalin and heptane diluents. The distribution ratio of zinc is suppressed by a factor of 1.4, if temperature is increased from 23°C to 45°C (dodecane diluent, perchlorate medium). The distribution ratio of zinc is increased by a factor 1.15, if the ionic strength is decreased from 0.75 to 0.1.

The distribution ratio is a ~1.7 power function of the HDEHP concentration. Two explanations are possible:

1- HDEHP is predominantly dimeric in the organic phase, and the complexes $ZnA_2 \cdot HA$ and $ZnA_2 \cdot 2HA$ are extracted.
2- HDEHP exists in the organic phase as a mixture of a dimer and a trimer, and only the complex $ZnA_2 \cdot 2HA$ is extracted.

Partial trimerisation of HDEHP in aliphatic or alicyclic diluents is indicated by data reported in the literature (Ferraro, 1961). Moreover, a mathematical treatment of the data gave a better fit with the latter model. Thus, the distribution equilibrium of zinc(II) can be expressed as

$$Zn^{2+} + 2\ (HA)_{2,org} = (ZnA_2 \cdot 2HA)_{org} + 2\ H^+ \qquad (1)$$

and, in systems with a sulfate containing aqueous phase

$$Zn^{2+} + n\ SO_4^{2-} = Zn(SO_4)_n^{(2n-2)-} \qquad \text{with } n=1,2,3 \qquad (2)$$

The logarithm of the equilibrium constant of the reaction (1) is 0.52±0.02 with dodecane diluent. It is slightly lower (0.4) with heptane diluent, and a value of 0.3±0.1 was found with decalin diluent. The dissociation constant of the bisulfate ion was not determined in our work. A value of 0.0667 was derived from data given in (Smith, 1976, p.79). The logarithms of the formation constants of the Zn(II) monosulfate, disulfate and trisulfate complexes (reaction 2) are 0.94±0.07, ~1.7 and 2.47±0.06, respectively. The formation of a sodium salt of HDEHP in the organic phase plays a marginal role at pH≤2.4. Nevertheless, it was taken into account in the calculations of equilibrium constants. A value of 0.0008 was estimated from the published literature (Lanin, 1972; Dubuquoy, 1967) for the equilibrium constant of the formation of the species $NaA \cdot 3HA$.

The results at pH≥3 are badly reproducible and possibly are impaired by a micelle or colloid formation. The appearance of a maximum on the pH dependence of the distribution ratio of zinc(II) (Fig. 1) can be ascribed to increasing conversion of HDEHP to a sodium salt in the organic phase.

The distribution of variable amounts of zinc(II) is shown in Fig. 2 and 3 for sulfate and perchlorate systems, respectively.

Polynuclear zinc complexes are extracted at $[Zn^{2+}]_{org} > 0.01$ *M*. As the amount of Zn(II) in the system increases, the overall HDEHP/Zn(II) ratio in the organic phase decreases below 4 and can become as low as 2.1. The coordination number of the zinc ion in the polymeric complexes was supposed not to be higher than 4. This supposition is justified by the fact that the zinc(II) ion exhibited no tendency to a coordination number of >4 even in the extraction of zinc(II) traces. The simplest consideration assumes chain complexes with eight-membered Zn/HDEHP rings as links. Two zinc ions are bridged by two HDEHP anions in the link rings. Eight-

membered rings involving each an undissociated HDEHP molecule and a HDEHP anion are attached to the end zinc ions of the chain (Kolarik, 1976). The composition of such complexes would be $Zn_nA_{2n}\cdot 2HA$.

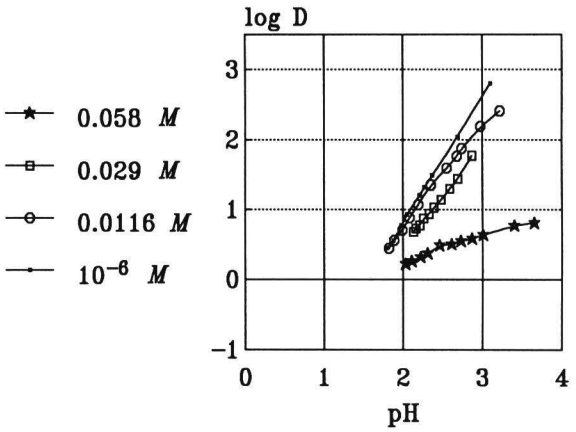


Fig. 2: Zinc extraction with 0.2 *M* HDEHP in dodecane at different concentrations. Zn(II): ~10^{-6} *M* up to 0.058 *M*, 0.25 *M* $(Na,H)_2SO_4$, 23°C.

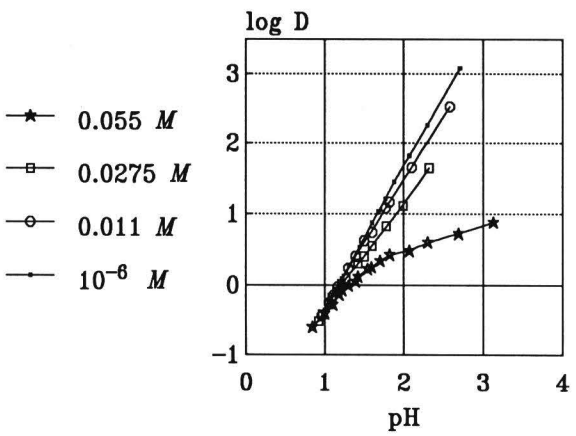


Fig. 3: Zinc extraction with 0.2 *M* HDEHP in dodecane at different concentrations. Zn(II): ~10^{-6} *M* up to 0.055 *M*, 0.75 *M* $(Na,H)ClO_4$, 23°C.

A plausible model of the extraction equilibrium includes the complexes $ZnA_2 \cdot 2HA$, $Zn_2A_4 \cdot 2HA$, $Zn_4A_8 \cdot 2HA$, $Zn_{15}A_{30} \cdot 2HA$ and $Zn_{45}A_{90} \cdot 2HA$. Also mixed complexes like $Na_3Zn_{10}A_{23} \cdot 2HA$ can be formed in the organic phase.

However, only a moderately good fit of experimental and calculated results could be reached with this model. The fit could markedly be improved by two additional assumptions, namely

1- the extraction of complexes of the type $Zn_nA_{2n-k}(ClO_4)_k \cdot 2HA$

2- the formation of HDEHP complexes in the aqueous phase.

Since perchlorate ions could not reliably be detected in the loaded organic phase, the first assumption was rejected. Whatever the plausibility of the second assumption is, we reached a good fit by adding the complexes ZnA^+ and $Zn_6A_{11} \cdot HA^+$ in the aqueous phase to the above model involving four oligomeric complexes in the organic phase.

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DIFFERENCE IN MECHANISM OF SOLVENT EXTRACTION OF IRON(III) AND CHROMIUM(III) WITH SEVERAL β-DIKETONES INTO 4-METHYL-2-PENTANONE

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ABSTRACT

The rate of solvent extraction of iron(III) and chromium(III) in aqueous perchlorate solutions into 4-methyl-2-pentanone with several β-diketones has been measured and the mechanism of extraction was considered. The extraction of iron(III) was found to proceed through two routes; one was the extraction of the metal chelate formed in the aqueous phase and the other was the extraction of ion-pairs followed by chelate formation in the organic phase. The extraction of chromium(III) was found to proceed also through these two routes but besides these, an extraction of a precursor species formed in the aqueous phase occured and the rate of extraction through this route was about 10^2 times higher than that of the others.

1 INRODUCTION

It was observed that the rate of extraction of certain metal ions in aqueous perchlorate solutions with β-diketones into 4-methyl-2-pentanone (MIBK) was much higher than that into carbon tetrachloride. (Sekine et al., 1971, 1975, 1980) This was explained in terms of an extraction of the metal perchlorate and that of ion-pairs of cationic metal complex with perchlorate ions. In the present study, the rate of complex formation of iron(III) and chromium(III) with β-diketones in aqueous perchlorate solutions and in MIBK solutions was determined and the contribution of these reactions in each phase to the whole extraction process was considered.

2 EXPERIMENTAL

All the experiments were carried out at 298 K. The reagents and diluents were similar to those in the previous papers. (Inaba et al., 1985, 1989) The β-diketones used were; acetylacetone (Haa), trifluoroacetylacetone (Htfa), and benzoyltrifluoroacetone (Hbfa). The experimental procedures were also similar to those in previous papers. (Inaba et al., 1985, 1989, Sekine et al., 1984, 1985, 1988)

(i) Rate of solvent extraction. An aqueous 4 mol dm^{-3} sodium perchlorate solution of iron(III) or chromium(III) and the same volume of an MIBK solution of a β-diketone were placed in a stoppered glass tube and they were agitated

vigorously for a given time. The amount of metal extracted was determined by spectrophotometry or atomic absorption spectrometry.

(ii) Rate of complex formation in aqueous solutions. An aqueous 4 mol dm^{-3} perchlorate solution containing iron(III) or chromium(III) was mixed up with an aqueous solution of a β-diketone. The solution was left standing in the dark for a given time. The complex in the solution was determined by spectrophotometry or from the amount extracted into an organic solvent.

(iii) Rate of complex formation in MIBK. An MIBK solution which extracted the metal perchlorate was mixed up with an MIBK solution of a β-diketone. The resulted solution was left standing in the dark for a given time. The amount of complex formed was determined by spectrophotometry.

3 STATISTICAL

The subscript "org" in the present paper denotes chemical species in the organic phase. Then the ditribution equilibrium of a β-diketone, HA, can be written as:

$$HA \rightleftharpoons HA_{org}; \qquad K_d = [HA]_{org}/[HA] \tag{1}$$

The rate of solvent extraction and that of complex formation in an aqueous soluton and in MIBK may be expressed as:

$$V_{SE} = k_{obsdSE}[M(III)] \tag{2}$$

$$V_{CF(aq)} = k_{obsd(aq)}[M^{3+}] \tag{3}$$

$$V_{CF(org)} = k_{obsd(org)}[M^{3+}]_{org} \tag{4}$$

Here, $[M^{3+}]_{org}$ denotes the total concentration of the metal ions which are not complexed with the β-diketone in an MIBK solution.

4 RESULTS AND DISCUSSION

The values of distribution constant for the β-diketones used are listed in Table 1. (Inaba et al., 1985, Sekine et al., 1988)

TABLE 1. Distribution constants of β-diketones.

	Haa	Htfa	Hbfa
log K_d	0.39	1.16	3.30

4. 1 *Iron(III)-Htfa, Hbfa system*

(i) Rate of complex formation in aqueous solutions. It was observed that the rate of complex formation was first order with respect to the metal ions and the reagent. The rate was zero to inverse first order with respect

to the hydrogen ions. From these, the following rate equation can be written.

$$V_{CF(aq)} = (k_{0aq} + k_{1aq}[H^+]^{-1})[HA][Fe(III)] \quad (5)$$

The rate constants obtained are listed in Table 2.

(ii) Rate of complex formation in MIBK solutions. It was found that the rate was first order with respect to the metal ions and HA. It was apparently inverse first order with respect to the hydrogen ions in the aqueous solution from which the metal ions were extracted into MIBK solution as perchlorate at equilibrium. From these results, the rate can be expressed by the following equation.

$$V_{CF(org)} = k_{1org}[HA]_{org}[H^+]^{-1}[Fe(III)]_{org} \quad (6)$$

The rate constants obtained are summarized in Table 2.

TABLE 2. Summary of rate constants for iron(III).

(a) Rate constants of complex formation.

	$\log k_{0aq}$ ($M^{-1}s^{-1}$)	$\log k_{1aq}$ (s^{-1})	$\log k_{1org}$ ($M^{-1}s^{-1}$)
Htfa	-1.2	-1.6	-0.9
Hbfa	-1.4	-1.4	-1.4

(b) Rate constants of solvent extraction.

	$\log k_{0SE}$ ($M^{-1}s^{-1}$)	$\log k_{1SE}$ (s^{-1})	$\log k_{0SE}^*$ ($M^{-1}s^{-1}$)	$\log k_{1SE}^*$ (s^{-1})
Htfa	-2.2	-2.5	-2.1	-2.5
Hbfa	-2.6	-3.4	-2.8	-3.4

(iii) Rate of solvent exrtaction into MIBK. Figures 1(a) and 1(b) give the experimental results of the rate of solvent extraction. In order to analyze these results, Eq. 2 can be rewritten as:

$$V_{SE} = (k_{0SE} + k_{1SE}[H^+]^{-1})[HA]_{total}[Fe(III)] \quad (7)$$

where $[HA]_{total}$ is similar to the initial concentration of HA in the organic phase. When the concentration of iron(III) in the aqueous phase, [Fe(III)], is nearly equal to $[Fe^{3+}]$, the rate of solvent extraction can be introduced by the sum of the rate of complex formation in the both phases. The solid line in each figure was calculated on the basis of the following equation:

$$\begin{aligned} V_{SEcal} &= V_{CF(aq)} + V_{CF(org)} \\ &= (k_{0aq} + k_{1aq}[H^+]^{-1}) \times (K_d+1)^{-1} \times [HA]_{total}[Fe(III)] \\ &\quad + k_{1org} \times K_d \times (K_d+1)^{-1} \times [HA]_{total} \times D_{Fe} \times [Fe(III)] \\ &= (k_{0SE}^* + k_{1SE}^*[H^+]^{-1})[HA]_{total}[Fe(III)] \end{aligned} \quad (8)$$

where D_{Fe} denotes the distribution ratio of the metal ions as ion-pairs with perchlorate anions. As seen from these figures, the calculated rate assuming that complex formation takes place in the both phases nearly agree with the experimental results. However, the calculated rate which was made by assuming that the complex formation took place only in the aqueous phase (given by the broken line) is much lower than that experimentally obtained.

The values of rate constant obtained experimentally and those from the calculation are summarized in Table 2.

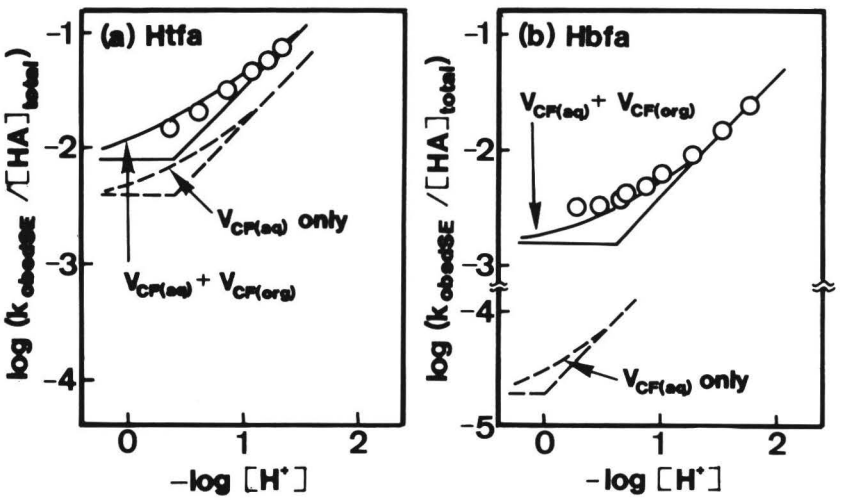


Fig. 1. Dependence of rate of solvent extraction of iron(III) with (a) Htfa and (b) Hbfa into MIBK as a function of hydrogen ions.

4. 2 *Chromium(III)-Haa, Htfa system*

(i) Rate of complex formation in aqueous solutions. It was observed that the rate was first order with respect to the metal ions and HA, and inverse first order with respect to the hydrogen ions when the extractant was Haa and inverse first to second order with respect to the hydrogen ions when it was Htfa. From the results, the following rate equation can be written as;

$$V_{CF(aq)} = (k_{1aq}[H^+]^{-1} + k_{2aq}[H^+]^{-2})[HA][Cr(III)] \quad (9)$$

The rate constants obtained are listed in Table 3.

(ii) Rate of complex formation in MIBK solutions. It was found that the rate was first order with respect to the metal ions and HA. It was inverse first order with respect to hydrogen ions when the ligand was Htfa while it was somewhat lower in the Haa system; about -0.8 order with respect to the hydrogen ions. This can not be explained clearly. However, in the present

study, we treated the dependence of the rate on the hydrogen ions as -1. From these, the rate equation may be written as:

$$V_{CF(org)} = k_{1org}[HA]_{org}[H^+]^{-1}[Cr^{3+}]_{org} \quad (10)$$

The rate constants obtained are summarized in Table 3.

TABLE 3. Summary of rate constants for chromium(III).

(a) Rate constants of complex formation.

	log k_{1aq} (s^{-1})	log k_{2aq} ($M\ s^{-1}$)	log k_{1org} (s^{-1})
Haa	-8.9	-	-6.7
Htfa	-8.8	-11.6	-7.1

(b) Rate constants of solvent extraction.

	log k_{1SE} (s^{-1})	log k_{2SE} ($M\ s^{-1}$)	log k_{1SE}^* (s^{-1})	log k_{2SE}^* ($M\ s^{-1}$)
Haa	-7.2	-	-8.7	-
Htfa	-7.1	-10.4	-9.0	-12.8

(iii) Rate of solvent extraction into MIBK. Figures 2(a) and 2(b) give the experimental results of the rate of solvent extraction. It was found that the rate was inverse first and second order with respect to the hydrogen ions with the extraction of chromium(III). Thus Eq. 2 can be rewritten as:

$$V_{SE} = (k_{1SE}[H^+]^{-1} + k_{2SE}[H^+]^{-2})[HA]_{total}[Cr(III)] \quad (11)$$

where $[HA]_{total}$ and [Cr(III)] were defined the same as in Eq. 7.

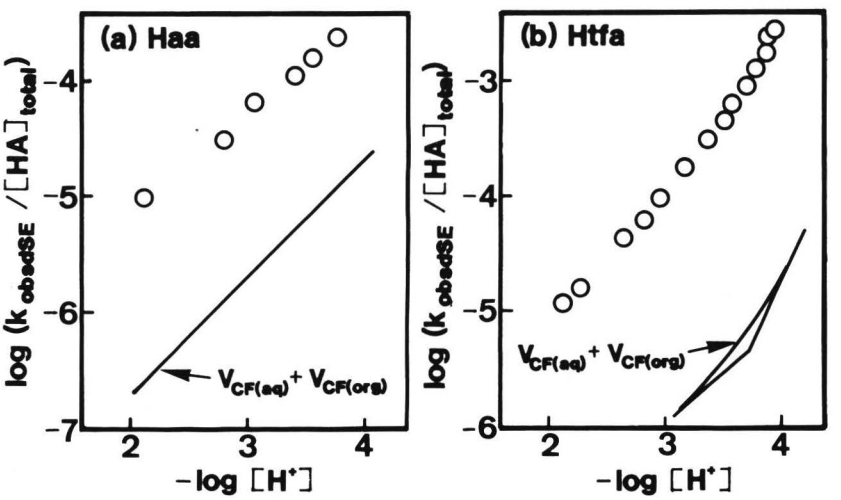


Fig. 2 Dependence of rate of solvent extraction of chromium(III) with (a) Haa and (b) Htfa into MIBK as a function of hydrogen ions.

The solid line in each figure was calculated by the following equation:

$$V_{SEcal} = V_{CF(aq)} + V_{CF(org)}$$

$$= (k_{1aq}[H^+]^{-1} + k_{2aq}[H^+]^{-2}) \times (K_d+1)^{-1} \times [HA]_{total}[Cr(III)]$$

$$+ k_{1org} \times K_d \times (K_d+1)^{-1} \times [HA]_{total} \times D_{Cr} \times [Cr(III)]$$

$$= (k_{1SE}^*[H^+]^{-1} + k_{2SE}^*[H^+]^{-2})[HA]_{total}[Cr(III)] \quad (12)$$

where D_{Cr} denotes the distribution ratio of the metal ions as ion-pairs with perchlorate anions. The values of rate constant obtained are summarized in Table 3. As seen from these figures, the extraction rate experimentally obtained with both Haa and Htfa is much higher than that calculated by Eq. 12. This indicates that an extraction of a chromium(III) species whose rate of formation is about 10^2 times higher than that of the species in the both phases already described should be occured.

It has been pointed out that the rate of solvent exrtaction of these metal ions with the β-diketones into MIBK is much higher than that into carbon tetrachloride. As seen from the present results, the higher rate of exrtaction of iron(III) into MIBK can well be explained by consideration of the complex formation in the organic phase. However, the rate of extraction of chromium(III) is still much higher than that estimated by assuming that the complex formation takes place in the both phases. This was explained in a previous paper (Inaba et al., 1989) to be due to an extraction of a "precursor" species.

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DILUENT INFLUENCE ON THE EXTRACTION OF DIVALENT COBALT BY THENOYLTRIFLUOROACETONE, DIBENZO-18 -CROWN-6 AND THEIR MIXTURES FROM PERCHLORATE AQUEOUS MEDIUM.

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ABSTRACT

The extraction of Co(II) by thenoyltrifluoroacetone (HTTA), dibenzo 18-crown-6 (Db18C6) and their mixtures in different diluents from perchlorate aqueous medium was investigated. The stoichiometric formulae of the extracted species were found to be Co $(TTA)_2$, Co OH(Db18C6)(ClO_4) and Co $(TTA)_2$.Db18C6, in each of the diluents used. The stability of extracted chelate was found to increase by increasing the dielectric constant (ϵ) of the diluent, while the stability of the adduct decreased with increasing ϵ .The same trend was observed with other physicochemical parameters of the diluents. The non specific interaction between the diluent and the solute was also elaborated for the systems studied, via the solubility parameter of the extracted species.

INTRODUCTION

Diluents have a great effect on the extraction of metals. In some cases, this influence may exceed the synergic effect itself as mentioned by Akiba (1973). The metal extractability was related with the diluents dielectric constant, Aly et al(1979), the dipole moment, Cobble and Maddock (1958), Hammett's substituent constants, Stronski and Nahlik (1972), and the solubility parameter, Irving and Al-Jarrah (1973). Nazarenke et al (1983) found that the extraction of alkali metal from picrate medium by 15-crown-5 in chloroform is twice in benzene. Bunecl et al (1984) found the sequence : adiponitrile > isobutyronitrile > acetophenone > cyclohexanone > methylenechloride > phenylaceto-nitrile during the extraction of potassium P - nitrophenoxide by different crown ethers of these solvents. The effect of nitro-benzene (Nb), toluene (Tol) and their mixtures on the extraction

of cobalt (II) by HTTA and Db18C6 was previously investigated by Khalifa (1987). In the present work, the effect of various solvents on the extraction of Co-60 by HTTA, Db18C6 and their mixtures was studied and discussed.

EXPERIMENTAL

Dibenzo - 18-crown - 6 (Db18C6), Fluka product, was used without further purification. HTTA and all other reagents were of analytical reagent (A.R.) grade. The Co-60 radioactive tracer and the extraction procedure were identical to those previously reported by Aly et al (1985).

RESULTS AND DISCUSSION

The effect of thirteen diluents on the extraction of radioactive cobalt from aqueous perchlorate medium, 0.1 (H^+, $NaClO_4$), by HTTA was investigated. Slope analysis of the experimental results indicated the following extraction equilibrium for all diluents used ,

$$Co^{2+} + 2\ \overline{HTTA} \rightleftharpoons \overline{Co(TTA)_2} + 2\ H^+ \qquad (1)$$

where bared symbols point to the organic phase.

Cobalt was slightly extracted by Db18C6 according to the following eqilibrium,

$$Co(OH^+) + \overline{Db18C6} + ClO_4^- \rightleftharpoons \overline{Co\ OH.\ Db18C6\ (ClO_4)} \qquad (2)$$

Synergic extraction of Co(II) by HTTA mixed with Db18C6 was found for the different diluents used, as exemplified by O-nitrotoluene and carbon tetrachloride, Fig.(1).

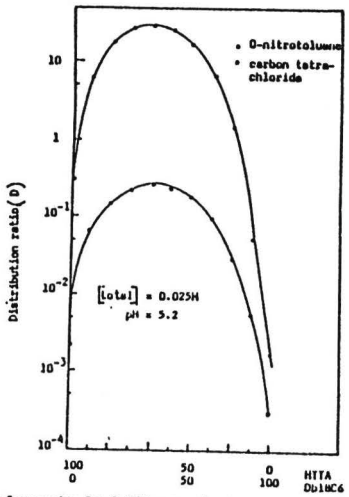


Fig.1 Test of synergism for Co(II) extraction by HTTA and Db18C6 in thirteen different diluents, represented by O-nitrotoluene and carbon tetrachloride.

The effect of $[H^+]$, [HTTA] and [Db18C6] when fixing two of the three parameters and slope analysis of the results showed that the extraction equilibria are repesented by

$$Co^{2+} + 2\ \overline{HTTA} + \overline{Db18C6} \rightleftharpoons \overline{Co(TTA)_2 . Db18C} + 2\ H^+ \qquad (3)$$

The adduct formation reaction in the organic phase can be represented by

$$\overline{Co(TTA)_2} + \overline{Db18C6} \rightleftharpoons \overline{Co(TTA)_2 . Db18C6} \qquad (4)$$

For all diluents used, the stoichiometric formulae elucidated is $Co(TTA)_2 . Db18C6$.

The extraction constants K_{20}, K_{11} and K_{21} of reaction 1,2 and 3 were calculated for different diluents and included in Table 1 with the synergic factor (S.F) and the formation constant (β_{21}) of the synergic reaction, as calculated from reaction (4).

TABLE 1

Extraction constants K_{20}, K_{11} and K_{21}, formation constant (β_{21}) and synergic factor (S.F) of Co(II) extracted by HTTA and Db18C6 in different diluents from perchlorate aqueous medium.

diluents *'	$K_{20} \times 10^{0}$	$K_{11} \times 10^{6}$	$K_{21} \times 10^{5}$	$\beta_{21} \times 10^{-4}$	$S.F_{(max)}$
1	37.6±0.5	18.5±0.3	67.7±1.6	1.8±0.1	178
2	24.8±0.5	39.1±0.5	52.4±1.0	2.1±0.1	203
3	19.8±0.4	29.7±0.4	45.7±0.7	2.3±0.1	221
4	8.8±0.1	5.1±0.1	27.9±0.6	3.2±0.1	314
5	6.1±0.1	4.1±0.1	22.4±0.4	3.7±0.1	362
6	2.5±0.4	3.9±0.1	20.2±0.4	8.2±0.2	782
7	2.0±0.1	2.2±0.1	16.9±0.4	8.4±0.3	813
8	1.7±0.1	6.6±0.1	0.14±0.1	0.1±0.1	7
9	1.1±0.1	2.8±0.1	8.0±0.1	7.2±0.3	674
10	0.9±0.1	4.7±0.1	4.9±0.1	5.5±0.2	477
11	0.8±0.1	1.9±0.1	7.5±0.2	9.2±0.1	865
12	0.7±0.1	2.5±0.1	5.8±0.1	8.3±0.3	763
13	0.6±0.1	2.5±0.1	4.5±0.1	8.0±0.2	714

cont.

Table cont

* 1- nitrobenzene	2- O- nitrotoluene	3- m-nitrotoluene
4- methylisobutylketone	5- O-dichlorobenzene	6- ethylenechloride
7- benzene	8- chloroform	9-trichloroethylene
10- chlorobenzene	11- carbon tetrachloride	
12- xylene (mixtures)	13- toluene	

The stoichiometeric formulae of the different extracted species $Co(TTA)_2$, Co OH(Db18C6)(ClO_4) and $Co(TTA)_2$.Db18C6 were found to be the same in all diluents used indicating that the diluents used has no specific effect on the stoichiometric ratios. These results run parallel to various reported data by Marcus and Kertes (1969) and Aly et al (1979). The different constants determined for different diluents indicated that a large variations is observed by changing the diluent, Table 1. To discuss these results, K_{20}, K_{11} and β_{21} were correlated to dielectric constant (€), polarizability and solubility parameter of the used diluents.The increase of both K_{20} and K_{11} by increasing € can be ascribed to the hydrophobic character of the extracted cobalt hydrated complex species prefer media with high dielectric constants, Denesi et al (1975). The decrease in the stability constant (β_{21}) by increasing € can be attributed to change in the hydrophobic character of the formed adduct which is less hydrophobic and prefer organic media with low € . Deviations of some points (fig. 2) is, however, notable for such relations as mentioned by Kandil and Ramadan (1979).

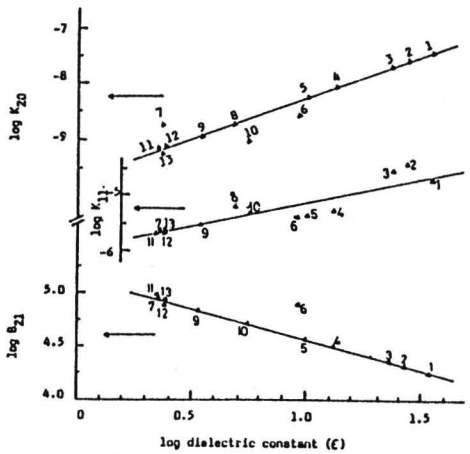


Fig.2 Variation of log dielectric constant with log K_{20}, log K_{11} and log β_{21} of the Co(II) extraction by HTTA,Db18C6 and HTTA-Db18C6 mixture in the thirteen diluents.

When K_{20}, K_{11} and β_{21} (as calculated on molal basis) was related with $\epsilon \cdot \delta^{-1}$ as proposed by Mottola and Freiser (1966), a high scattered linear relation was obtained, which exclude the applicability of this relation.

The polarizability (P_o, P and ΔP) of the investigated diluents were calculated where P_o, P and ΔP are the optical polarizability, the molar polarizability and electric moment alternatively. The relationships between the constants K_{20}, K_{11} and β_{21} with the respective values of P_o, P and ΔP gave the same trend which indicates the increase in K_{20} and K_{11} with increasing each of the polarizability values, P_o, P or ΔP, while for log β_{21} an opposite trend was obtained. The best fit of this trend was observed with the molar polarizability (fig.3)

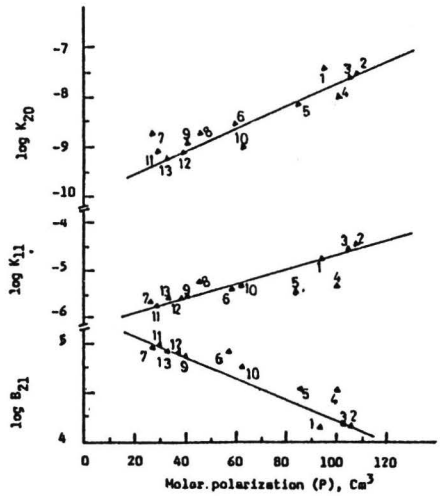


Fig.3 Variation of the molar polarization of the thirteen diluents with log K_{20}, log K_{11} and log β_{11} for the Co(II) extraction by HTTA, Db18C6 and HTTA-Db18C6 mixture.

These results can be explained as being due to the presence of a simple columbic force variations within the different diluents.

The last approach considered to explain the diluent effect is the solubility parameter $\overline{\delta}$ as a determining factor for the non specific diluent - solute interaction as studied by Irving (1972). In this concern, a plot between log $\overline{K}$ or log $\overline{\beta}$ and the respective $\overline{\delta}$ (calculated on molal basis) should give a parabolic form. This form was realized in fig.(4) for the variations of $\overline{\delta}$ with the respective values of $\overline{K_{20}}$, $\overline{K_{11}}$, $\overline{K_{21}}$ and $\overline{\beta_{21}}$ which indicate the importance of the non specific interactions occured between used diluents and the extracted species in each case.

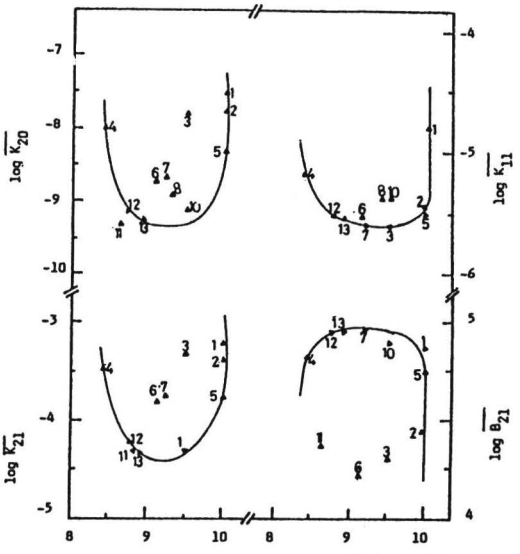


Fig.4 Variation of the solubility parameter of the thirteen diluents with log K_{20}, log K_{11} and log β_{21} for the Co(II) extraction by HTTA, Db18C6 and HTTA-Db18C6 mixture.

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STUDY OF SOLVENT EXTRACTION PROCESS BY ION-TRANSFER POLAROGRAPHY AT THE LIQUID/LIQUID INTERFACE

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ABSTRACT

Ion-transfer across the aqueous/organic solutions interface which is involved in the solvent extraction reaction was investigated by potential-scan polarography using aqueous electrolyte dropping electrode. The neutral carrier type 1,10-phenanthroline (phen) and 1,2-dichloroethane (DCE) were employed as extractants and the solvent. The polarograms for the transfer of phen-complex ions of proton and such metal ions as Ni(II), Co(II), Fe(II), Fe(III), Mn(II), Cu(II), Zn(II), and Cd(II) were examined. Results with Ni(II), Co(II), Fe(II), Fe(III), and Mn(II) suggest that the magnitude of the limiting currents for the transfer of complex ion from the aqueous to the DCE phases can be correlated to the rate of H_2O-substitution of the respective hydrated ion.

INTRODUCTION

The mass transfer process of various species across the interface of such an immiscible solvent pair as aqueous/organic (w/o) solutions which is involved in the solvent extraction system has fundamental significance in elucidating both equilibrium and kinetic aspects of the solvent extraction phenomena.

The voltammetry or the polarography for the ion transfer at the w/o interface is a powerful method to investigate the dynamic feature of the ion transfer, because of the unmatched advantage that the transfer free energy and the amount of ions transferred can be measured simultaneously. This technique, therefore, has been applied to studies of the solvent extraction reactions (Yoshida, et al., 1984a, b).

In the present work, the ion transfer process involved in the ion-pair extraction system with 1,10-phenanthroline as extractant and water/1,2-dichloroethane as solvents pair is studied.

EXPERIMENTAL

The polarogram for the ion transfer with the aqueous electrolyte dropping electrode, AEDE, was recorded using the cell shown

in Fig. 1. The aqueous electrolyte solution, w, was forced upward dropwise through a glass capillary into the organic solution, o, containing 0.02 M crystalviolet tetraphenylborate, CV^+TPhB^-, as a supporting electrolyte. The flow rate of w and the drop time of the AEDE were controlled by adjusting the height of the w-reservoir. The reference electrode in o was a tetraphenylborate ion-selective electrode, TPhBE, which can be related to a tetraphenylarsonium(TPhAs)-tetraphenylborate(TPhB) ion electrode potential, i.e., TPhE, where the transfer energy is equal to be zero on the basis of the extrathermodynamic assumption that the transfer energy of $TPhAs^+$ and that of $TPhB^-$ across a liquid/liquid interface are equal. Potentiostat, wave-function generator, and recorder which were identical to those reported previously(Kihara et. al. 1986) and iR-drop compensation instrument, Hokuto Denko Co., Ltd., Type HI-203, were employed to record the polarogram.

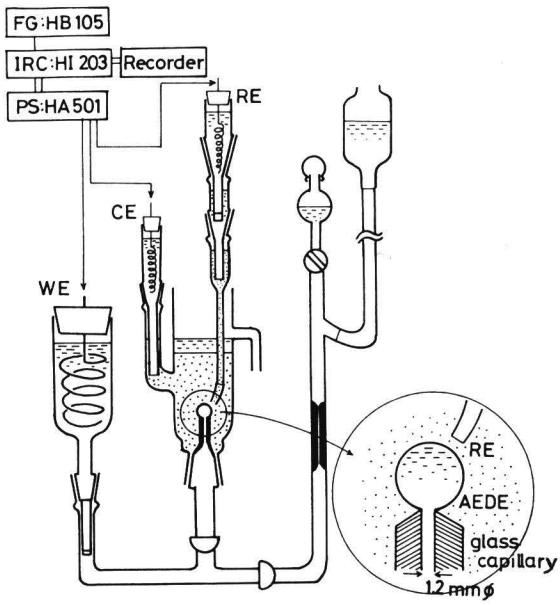


Fig. 1 Polarographic Cell

RESULTS AND DISCUSSION

In the following, we define the transfer of cation from w to o as the anodic reaction. With this definition, the polarogram of the cation which transfers with a small Gibbs energy should appear at the less positive potential.

Polarograms in Fig. 2 were obtained with AEDE; 1 M $MgSO_4$ 0.05 M CH_3COOLi buffer (pH 4.7) with and without Co^{2+} (10^{-3} M), and DCE; 0.05 M CV^+TPhB^- with and without phen (10^{-3} M). Curve (3) is the residual polarogram obtained in the absence both of Co^{2+} and phen.

The anodic wave in polarogram (1) shows a reversible charac-

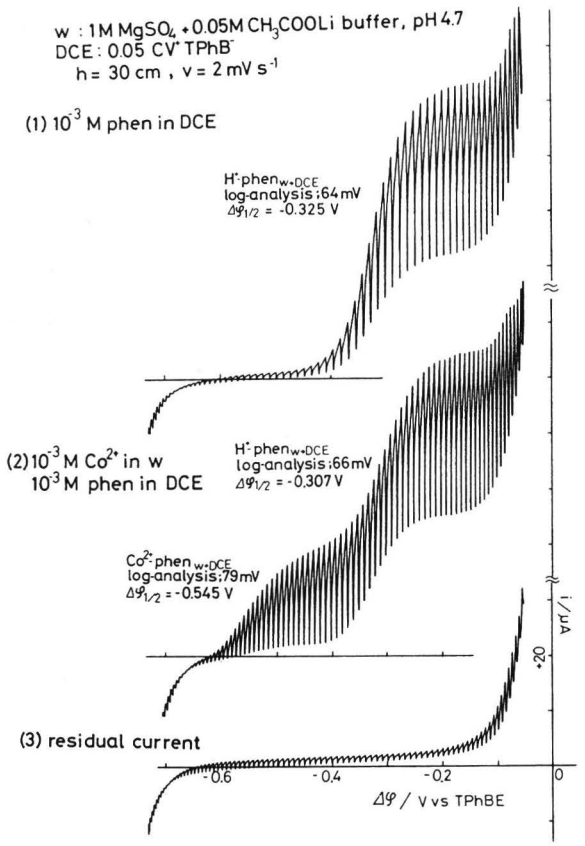


Fig. 2 Ion Transfer Polarograms

teristics and can be concluded to be attributable to the transfer of protonated phen (HP^+) from w to DCE, and the transfer reaction is rapid and controlled by the diffusion of phen in DCE. As shown in curve (2) obtained in the presence both of Co^{2+} and phen, two anodic waves are observed, which suggests that two ionic species may transfer across the interface. The first and the second waves are attributed to the transfer of metal-phen complex, $Mphen_x^{n+}$, and HP^+, respectively. The first wave shows a kinetically controlled characteristics, whereas the second wave shows reversible ones even in the presence of metal ion in w.

Identical polarograms as polarogram (2) in Fig. 2 were investigated with w containing various kinds of metal ions instead of Co^{2+} and results are realized in Fig. 3a. Based on the feature of the anodic waves for the transfer of $Mphen_x^{n+}$ and $Hphen^+$ in the polarogram, seven metal ions studied can be classified into three groups as follows; (1) such ions as Ni^{2+} giving no wave for the transfer of $Mphen_x^{n+}$, (2) ions, Mn^{2+}, Fe^{2+}, and Co^{2+}, giving kinetic controlled wave for the transfer of $Mphen_x^{n+}$ and diffusion controlled wave for the transfer of $Hphen^+$, and (3) ions, Zn^{2+}, Cu^{2+}, and Cd^{2+}, giving a diffusion controlled wave for the transfer of $Mphen_x^{n+}$.

The i-E curve recorded at single drop of AEDE containing Ni^{2+} is shown in Fig. 3b. In this experiment, the drop time of the AEDE was 90 sec and the potential was at -0.55 V vs TPhBE. With such long drop time the anodic wave due to the transfer of $Mphen_x^{n+}$

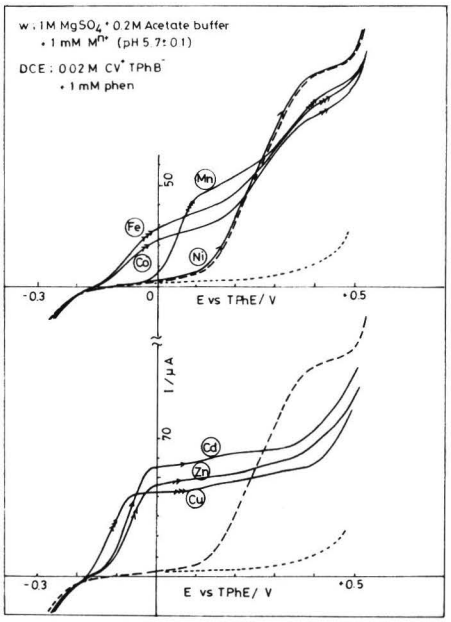


Fig. 3a Polarograms for the transfer of metal-phen complex ions from w to DCE.

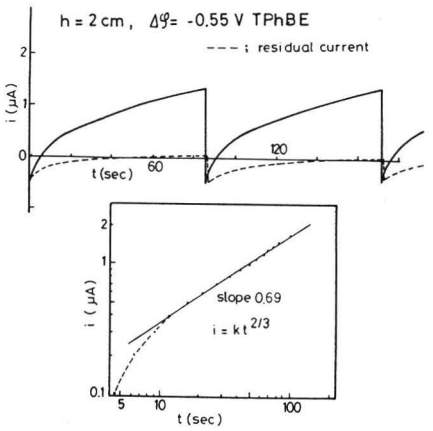


Fig. 3b i-t curves at single drop of AEDE for the trasfer of Ni^{2+}-phen complex.

can be observed even for Ni^{2+}, though the current is still small. The log-plot in Fig. 3b indicates the linear relation with slope 0.69, which supports that the transfer of $Niphen_x^{2+}$ is completely controlled by the kinetics.

To elucidate the characteristics of the kinetic controlled reaction, the limiting currents for the transfer of $Mphen_x^{n+}$ are plotted against the reported values of the rate of substitution of water molecule, k^{-H2O}, for the respective hydrated metal ions as given in Fig. 4. There observed distinct correlation between the limiting current and k^{-H2O}, which indicates that main kinetic factor determining the rate of the ion transfer process of $Mphen_x^{n+}$ is considered to be the dehydration of M^{n+}. As typical example, no wave for the transfer of $Mphen_x^{n+}$ was observed for Ni^{2+} with such small k^{-H2O} as 10^4 sec, although the stability constant of Ni^{2+}-phen complex is enough large. Metal ions, Co^{2+}, Fe^{2+}, or Mn^{2+}, with k^{-H2O} between 10^5 and 10^7 sec forms $Mphen_x^{n+}$ complex and the amount of $Mphen_x^{n+}$ formed during a life time of the AEDE increases with the increase of k^{-H2O}. In this case, phen molecule

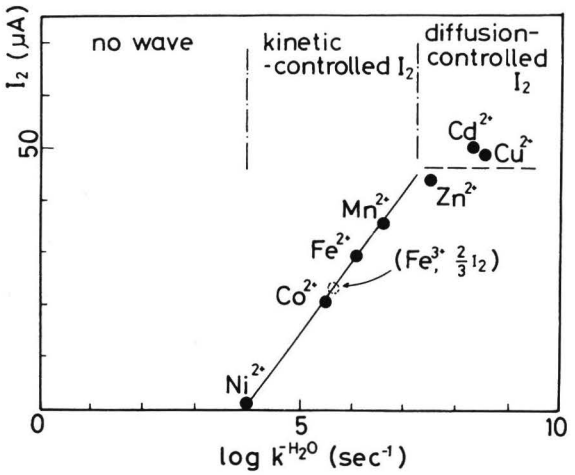


Fig. 4 Relation between the limiting current for the transfer of metal-phen complex and the rate of substitution of water molecule from the hydrated ion.

distributed into the w phase near the interface forms both the complex, $Mphen_x^{n+}$ and $Hphen^+$. The ratio of the amount of $Mphen_x^{n+}$ to those of $Hphen^+$ increases with the increase of k^{-H2O}.

It is noteworthy that the half-wave potentials of the anodic waves for the transfer of $Mphen_x^{n+}$ in polarograms in Fig. 3a may reflect the stability constants, K_1, of M^{n+}-phen complex, which implies that the transferring ionic species across the w/DCE interface may be 1:1 complex, $Mphen^{n+}$.

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ION TRANSFER OF SOME METAL IONS ACROSS THE LIQUID-LIQUID INTERFACE FACILITATED BY ION CARRIER COMPOUNDS

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ABSTRACT

The transfer of some metal ions(Na^+,K^+,Li^+,Sr^{2+},Ba^{2+},and Pd^{2+}) across the liquid-liquid interface facilitated by 15-crown-5(15C5), or polyethylene glycol-400(PEG),or 1,4,8,11-tetrathiacyclotetradecane(TTCT) has been studied by ion-transfer voltammetry. The interfacial half-wave potential equation is deduced in terms both of the mechanism proposed and of the equilibria of distribution. The standard Gibbs transfer energies, $\Delta G_{tr}^{W\to 0}$,of alkali metal complex with 15C5 and alkali earth metal complex with PEG were caluculated. For the Ba^{2+} ion transfer by PEG,DP voltammogram showed the existence of three transfer waves. For the palladium(II) ion transfer by TTCT, cyclic voltammogram was obtained successfully. Ion-transfer voltammetry was found to be a powerful technique for understanding mechanism of the single-ion solvent extraction.

INTRODUCTION

A new voltammetric study using the polarizable interface between two immiscible electrolyte solutions(ITIES),so-called ion-transfer voltammetry[1-3], offeres a promising possibility to understand the mechanism of the solvent extraction processes. This technique provides quantitative information on the interfacial transfer of a single ion. ITIES studies have been intensively undertaken by Koryta and his group[4-6], Yoshida and Kihara[7],Fujinaga[8],Freiser[9], and Senda[10-12] using various techniques. There is a few report about the transfer of alkali metal ion by neutral carrier ligand. But,there is no report about the transfer of the class-b metal ions by thiacrown ethers.

In this study,the transfer of alkali metal ion (Na^+,K^+,Li^+), alkali earth ion (Sr^{2+},Ba^{2+}) and transition metal ion (Pd^{2+}) across nitrobenzene(NB)/water(W) or 1,2-dichloroethane(DCE)/water (W) interface facilitated by neutral carrier ligand(15C5,TTCT or hydrophobic ligand,PEG has been examined by ion-transfer voltammetry.

2 EXPERIMENTAL

2.1 Materials

The reagent,TTCT , was synthesized according to the method by

Rosen and Bush[13] and recrystallized twice from ethanol. 15C5 and PEG were obtained from Nakalai tesque Co. Most of the other reagents and solvents was also obtained from Nakalai tesque Co.

2.2 Electrochemical measurements

Cyclic voltammetry (CV),normal pulse voltammetry(NPV) and differential pulse voltammetry(DPV) were carried out with a microcomputer-controlled system[14]. The detail of voltammetric measurements have been described elsewhere[15].

The electrical cell system used was water-jacketted at 25 ± 0.1 °C. The cells to be studied can be expressed as follows:

Ag-AgCl (RE1)	c mM 15C5 (water)	0.1 M NaCl or LiCl	*	0.1 M TBATPB (NB)	0.1 M TBACl (water)	Ag-AgCl (RE2)
Ag-AgCl (RE1)	c mM 15C5 (water)	0.1 M KCl	*	0.1 M TPATPB (NB or DCE)	0.02 M TPACl 0.1M $MgSO_4$ (water)	Ag-AgCl (RE2)
Ag-AgCl (RE1)	c mM PEG 400	0.1 M $SrCl_2$ or $BaCl_2$ (water)	*	0.1 M TBATPB (NB or DCE)	0.1 M TBACl (water)	Ag-AgCl (RE2)

Ag-AgCl (RE1)	0.5 M $MgCl_2$ (water)	0.5 M $MgCl_2$ (salt bridge)	x mM $PdSO_4$	0.5 M $MgCl_2$ (water)	pH=1	*	y mM TTCT	0.1 M TBATPB (NB or DCE)	0.1 M TBACl (water)	Ag-AgCl (RE2)

The potential difference at the interface shown by"*" was controlled by a laboratory-made potentiostat. The solution resistance was compensated for by a circuit of positive feedback.

The electric cells used are shown in Fig. 1.1 and 1.2.

The cell potential,E, is the potential of the right-hand terminal of the cell,E_{right}, referred to that of the left-hand,E_{left}; $E = E_{right} - E_{left}$. Let the potential difference across the interface between the solvent and the aqueous solution be $\Delta_o^w \Phi$ (here, w and o stand for the aqueous and solvent phases, respectively, and $\Delta_o^w \Phi$ indicates the potential of w phase referred to that of o phase). For each cell, we have

$$E = \Delta_o^w \Phi + \Delta E_{ref}(R) \qquad (1)$$

where $\Delta E_{ref}(R)$ is the constant which is determined by the couple

of the right- and left- hand reference electrodes in each cell.

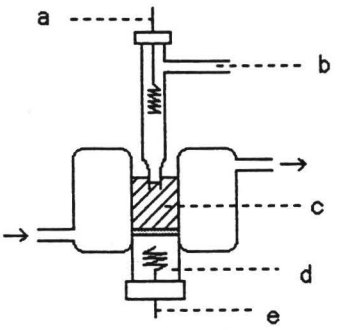


Fig. 1.1

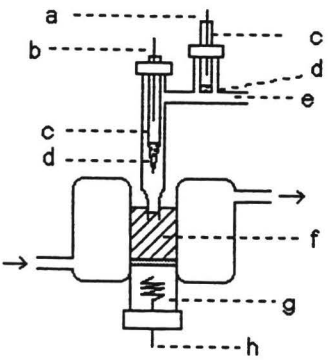


Fig. 1.2

Fig. 1.1 Electric cell for amphiphilic ligand system
a: Ag-AgCl electrode (as RE1) b: test solution(water)
c: test solution(oil) d: liquid junction e: Ag-AgCl electrode (as RE2)
Fig. 1.2 Electric cell for hydrophobic ligand system
a: Ag-AgCl electrode (as CE) b: Ag-AgCl electrode(as RE1)
c: liquid junction d: salt bridge e: test solution(water)
f: test solution(oil) g: liquid junction h: Ag-AgCl electrode (as RE2)

3 RESULTS and Discussion

3.1 Ion transfer of Na^+, Li^+ and K^+ facilitated by 15C5

A possible mechanism of the ion transfer of alkali metal(M^+) at liquid-liquid interface facilitated by 15C5(L) can be represented by

$$\begin{array}{ccccc} & & \overset{K^w}{\rightleftharpoons} & & \\ M^{n+}(w) + jL(w) & & ML_j^{n+}(w) & & \text{water phase} \\ \uparrow\downarrow D_M & \uparrow\downarrow D_L & \uparrow\downarrow D_{ML} & & \\ M^{n+}(o) + jL(o) & & \underset{K^o}{\rightleftharpoons} ML_j^{n+}(o) & & \text{oil phase} \end{array} \qquad \text{scheme (I)}$$

The equilibrium parameters in scheme (1) are combined to obtain next equation.

$$\Delta(\Delta\Phi) = \Delta\Phi_{1/2,M} - \Delta\Phi_{1/2,ML} = \frac{RT}{nF}\left(\log K^o + \log D_L - \log K^w\right) \qquad (2)$$

where $\Delta(\Delta\Phi)$ is an ability to facilitate ion transfer and $\Delta\Phi_{1/2,M}$ and $\Delta\Phi_{1/2,ML}$ are interfacial half-wave potential of metal ion and metal complex,respectively. The above equation shows that $K^o$is

calculated by K^W, D_L and Δ ($\Delta\Phi$) and that $\Delta\ \Phi_{1/2,ML}$ is independent on the concentrations of metal ion and L. log $D_L$was 0.12 (Table 1). The transfer of Na^+ facilitated by 15C5 at NB/W interface has examined by CV (Fig.2) and NPV. For the cyclic voltammogram, the positive - current peak corresponds to the transfer of Na^+ from W to NB, while the negative-current peak to its transfer back to W. The peak separation was about 60 mV, showing that the ionic charge of the transfer species is unity and reversible reaction occurs. Since the midpoint potential of CV(reversible half-wave potential, ($_rE_{1/2}$) was independent of the concentration of 15C5 in the range of 50 - 500 μM,this potential should be regarded as the ion-transfer potential of Na-15C5 complex . From the value of $_rE_{1/2}$, the $\Delta\ \Phi_{1/2}$ and $\Delta\ G_{tr}^{W\to O}$ were calculated to be 13 mV and 1.26 kJ.mol^{-1}, respectively. For the normal-pulse voltammogram,the currents were linearly dependent on the concentration of 15C5 in the above range. $\Delta\ \Phi_{1/2}$ and $\Delta\ G_{tr}^{W\to O}$ of Li- and K- 15C5 complex were calculated to be 83 and - 38 mV and 80.4 and - 36.8 kJ.mol^{-1}.

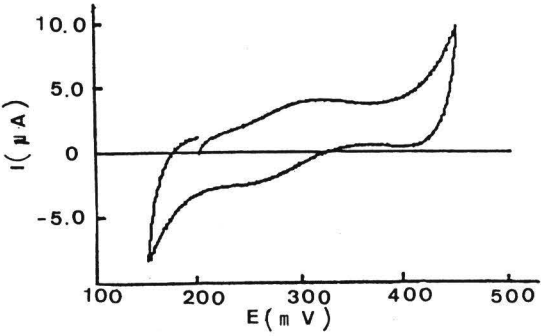


Fig. 2 Cyclic voltammogram of the 0.1 M TBATPB(NB)/0.1 M NaCl(W) interface in the presence 0.2 mM 15C5 in W. Scan rate 100mV/s.

TABLE 1

$\Delta\phi_{1/2,ML}$, $\Delta G_{tr}^{W\to O}$, $\Delta\phi_{1/2,M}$, $\Delta(\Delta\phi)$, log K^W, and log K^O of the transfer of alkali metal ions (Li^+, Na^+, K^+) facilitated by 15C5.

metal ion	$\Delta\phi_{1/2,ML}$ (mV)	$\Delta G_{tr}^{W\to O}$ (kJ·mol^{-1})	$\Delta\phi_{1/2,M}$ (mV)	$\Delta(\Delta\phi)$ (mV)	log K^W (l/mol)	log K^O (l/mol)
Li^+	83	8.04	395	312	~0	5.1
Na^+	13	1.26	354	341	0.70	6.3
K^+	-38	-3.68	242	278	0.74	4.7

The stability constants sequence is $Na^+ > Li^+ > K^+$. It seems to follow mainly the change in the cation solvation; i.e. the cavity size effect no longer dominates.

3.2 The transfer of alkali earth metal ions (Sr^{2+} and Ba^{2+}) facilitated by PEG.

The transfer of Sr^{2+} and Ba^{2+} at NB/W and DCE/E interface facilitated by PEG was examined by CV,NPV and DPV. For Sr^{2+}, a well-defined voltammogram was observed as shown in Fig.3. In the same fashion as the above Na^+ ion transfer, the $\Delta G_{tr}^{w\to o}$ for Sr-PEG complex was calculated to be 20.2 and 21 $kJ.mol^{-1}$ for transfer from W to NB and to DCE, respectively. In contrast to Sr^{2+} ion transfer, Ba^{2+} transfer at DCE/W by PEG showed an ill-defined voltammogram with successive three current peaks(Fig.4). This result suggests that Ba^{2+} forms some different kinds of complexes which can be transferred in the polarizable potential range.

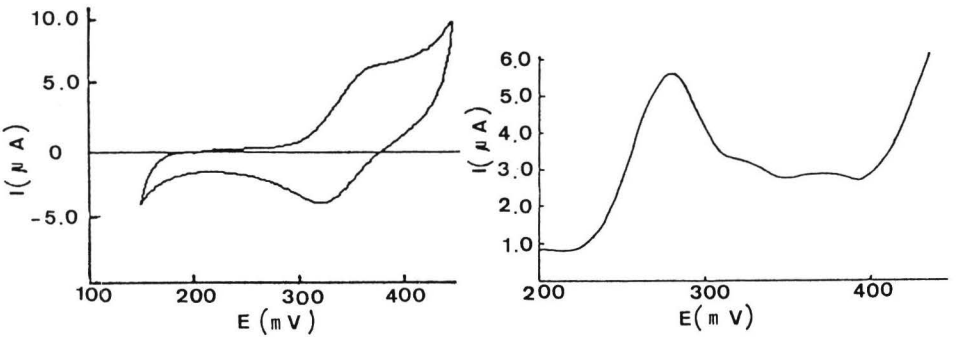
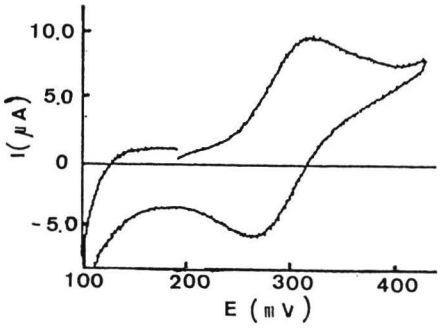


Fig.3 Cyclic voltammogram of the 0.1M TBATPB(DCE)/0.1 M $SrCl_2$(W) interface in the presence of 0.2 mM in W. Scan rate 100 mV/s^2.
Fig.4 Differential-pulse voltammogram of the 0.1 M TBATPB(DCE)/ 0.1 M $BaCl_2$(W) interface in the presence of 0.2 mM PEG in W. Scan rate 100 mV/s .

3.3 The transfer of Pd^{2+} facilitated by TTCT.

The transfer of Pd^{2+} facilitated by TTCT at NB/W and DCE/W interface has been studied by CV and NPV. In this experiment, the ligand(TTCT) was added to the organic phase. A well-defined voltammogram was obtained as shown in Fig.5. In this case, $_rE_{1/2}$ was affected by the concentrations of TTCT and metal ion to some extent. The peak separation was about 30 mV , showing reversible reaction. Although further study is in progress , a proposed mechanism of this facilitated transfer is given by scheme (II) . The transfer species is a complex ion formed by TTCT with Pd^{2+} and the

complex stoichiometry is 1:1.



$$\begin{array}{ccccc} M^{n+} & & & & \text{water phase} \\ \uparrow\downarrow & & & & \\ M^{n+} & + & jL \rightleftarrows & ML_j^{n+} & \\ & & \uparrow\downarrow & \uparrow\downarrow & \text{oil phase} \\ & & jL & ML_j^{n+} & \end{array}$$

scheme (II)

Fig. 5. Cyclic voltammogram of the 0.1 M TBATPB(DCE)/0.1 M $MgCl_2$ (pH 1.0)(W) interface in the presence of 0.2 mM $PdSO_4$ in W and 10 mM TTCT in DCE. Voltage scan rate 100 $mV \cdot s^{-1}$

Ion transfer is governed by the standard Gibbs energies of partition of the individual ion between water and the organic solvent employed but can be varied by the potential difference applied across the water/oil interface.

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POLYENERGETIC CONJUGATION OF KINETIC FACTORS IN SYNERGISTIC SOLVENT EXTRACTION PROCESSES

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ABSTRACT

Nature of the limiting stage of the mass transfer in synergistic extraction process can be ascertained on the basis of the polyenergetic conjugation relationship of the thermodynamics of accumulation processes, obtained as a further development of the Extended Arrhenius Equation. The polyenergetic conjugation relationship associates the velocity constant with intensity and/or capacity factors of the investigated system in exponential equations. Exponent values of factors in the equations ensure the assessment of the nature of interfacial resistance. Experimental results show that the resistence nature cannot be of pure chemical or physical type in the most cases, and that the combined nature can vary with the system conditions.

INTRODUCTION

At present, the thermodynamics of accumulation processes /TAP/ and the thermodynamics of irreversible processes are the two branches of non-equilibrium thermodynamics /Mehandjiev and Mehandjieva, 1986, pp 331-338/. TAP became an object of study in Bulgaria in 1967; it deals with phenomena associated with the introduction, transformation, and accumulation of mass, or energy, or both, in the affected systems, i.e., in non-isolated, open, or closed systems. The phenomena's processes and effects, due to the work done upon the systems by positive exogenous impacts /influences/ during a measurable impact time are called accumulation processes and effects respectively. TAP always deals with processes which proceed with real velocities, and it is not opposed to the thermodynamics of irreversible processes. TAP should be considered as a link between classic equilibrium thermodynamics and the thermodynamics of irreversible processes, since the beginning of every irreversible process is always preceded by an introduction and accumulation of mass, or energy, or both /i.e., by accumulation phenomena/ in an equilibrium, before the impact, system. Proofs regarding the difference of principle between the accumu-

lation and irreversible processes can be found in each hysteresis phenomenon.

Processes and effects are expressed in TAP by the change velocities and by the final changes of intensity /P/ and capacity /X/ factors of state, defining various elementary energy kinds in the system. The conjugation existing between the intensity and the capacity factors of one and the same elementary energy kind is a monoenergetic one:

$$P_r X_r = \Psi_r^o = \text{constant}, \; /P_{k \neq r} = \text{constant}; \; k=2,3,.., \; n/. \qquad /1/$$

2. POLYENERGETIC CONJUGATION OF FACTORS OF STATE

A polyenergetic conjugation relationship existing between the intensity or capacity factors, or both, which define different elementary energy kinds, has been developed in TAP /Mehandjiev, 1978/. The polyenergetic conjugation between the variables is expressed by exponential equations, e.g.,:

$$\prod_{r=1}^{j} P_r^{\pm\theta_r^o} \prod_{i=j+1}^{n} X_i^{\pm\theta_i^o} = \text{constant}; \; /r \neq i; \; r+i = n \geqslant 2/; \qquad /2/$$

$$T \prod_{r=2}^{j} P_r^{\pm\theta_r} \prod_{i=j+1}^{n} X_i^{\pm\theta_i} = \text{constant}; \; /r \neq i; \; r+i+1 = n \geqslant 2/. \qquad /3/$$

Assuming the exponent of the Kelvin temperature T to be equal to unity, as in eqn./1/, the relative exponents of all other P and X are approximately constant: $|\theta_r| \approx 0.3$; $|\theta_i| \approx 0.4$, in expressions for processes /effects/ without qualitative transformation. In TAP, qualitative transformation is appearance or disappearance of an indispensable and observable elementary energy kind in the system. Ordinary examples are appearances /disappearances/ of phases, or of chemical substances. Exponents in eqn./3/ vary in qualitative transformation cases, and their mean relative values for various elementary energy factors, representing impacts upon affected systems, experimentally obtained, are shown in Table 1. In eqns./2,3/ n equals the number of the elementary energy kinds, which are indispensable and sufficient for the characterization of an affected system, or of an impact, in a degree

which corresponds to the purposes of the thermodynamic study. The significance of polyenergetic conjugation equations has been proved in many investigation cases /Mehandjiev, 1984; Mehandjiev et al., 1983/. It has been proved also that the relative exponent values can be used independently of the T-participation in the expressions.

TABLE 1

Mean relative values of some elementary energy factor exponents in qualitative transformation cases.

Kind of impact	Exponent value
Heat impact	1.00
Values experimentally obtained:	
Impact by increased surface area	0.04
Ultrasonic impact	0.04
Pressure impact /up to 5 MPa/	0.14
Chemical /concentration/ impact	0.15
Maximum theoretical value for a possible impact with the exception of heat impact	0.70

3. POLYENERGETIC CONJUGATION OF KINETIC FACTORS

An Extended Arrhenius Equation has been developed /Mehandjieva and Mehandjiev, 1975/, which associates the velocity constant k not only with the Kelvin temperature, but also with all other various intensity and capacity factors of the process system:

$$\ln k = \ln A' - E_o/RT + \Psi_T \ln T + \sum_{r=2}^{j} \Psi_r \ln P_r + \sum_{i=j+1}^{n} \Psi_i \ln X_i \qquad /4/$$

Assuming T= constant, and $\Psi_T = 1$, $\Psi_T \ln T$ can be included in $\ln A = \ln A' T$, and all constants: Ψ_r; Ψ_i can have relative values, less than unity. It has been proved experimentally that Ψ_r-; Ψ_i-values are equal to those given in Table 1, for the respective energy kind. Assuming also only two kinds of activation impact factors: organic drops interfacial surface area s, and extractant concentration C in a synergistic solvent extraction system, and using symbols indexed by "1" and "2" for two diffe-

rent extraction cases, we can write from eqn./4/:

$$\ln k_1 = \ln A - E_o/RT + \Psi_s \ln s_1 + \Psi_C \ln C_1 \qquad /5/$$

$$\ln k_2 = \ln A - E_o/RT + \Psi_s \ln s_2 + \Psi_C \ln C_2 \quad . \qquad /6/$$

Multiplying eqn./6/ by /-1/ and substracting it from eqn./5/, we obtain:

$$\ln k_1 - \Psi_s \ln s_1 - \Psi_C \ln C_1 = \ln k_2 - \Psi_s \ln s_2 - \Psi_C \ln C_2 \quad , \qquad /7/$$

or:

$$\ln \frac{k_1}{k_2} = \Psi_s \ln \frac{s_1}{s_2} + \Psi_C \ln \frac{C_1}{C_2} \quad . \qquad /8/$$

An antilogarithm of eqn./7/ is:

$$k_1 s_1^{-\Psi_s} C_1^{-\Psi_C} = k_2 s_2^{-\Psi_s} C_2^{-\Psi_C} \quad . \qquad /9/$$

Eqn./9/ is a polyenergetic conjugation relationship written for the cases 1 and 2, which includes kinetic as well as state factors. The general form of that relationship is:

$$k\, s^{-\Psi_s}\, C^{-\Psi_C} = \text{constant} \; . \qquad /10/$$

By introduction of Ψ_s-; Ψ_C-values for surface, and concentration impacts respectively from Table 1 in eqn./10/, we obtain:

$$k\, s^{-0.04}\, C^{-0.15} = \text{constant} \; . \qquad /11/$$

The corresponding equations for $n = 2$ are:

For a pure physical nature of interfacial resistance:

$$k\, s^{-0.04} = \text{constant} \; ; \quad k_1 s_1^{-0.04} = k_2 s_2^{-0.04} \; ; \qquad /12/$$

and for a pure chemical nature of that resistance:

$$k\, C^{-0.15} = \text{constant} \; ; \quad k_1 C_1^{-0.15} = k_2 C_2^{-0.15} \quad , \qquad /13/$$

where the exponent of k should be equal to unity in both cases.

4. ASSESSMENT OF INTERFACIAL RESISTENCE NATURE

Eqns./11/-/13/, obtained by transformation of Extended Arrhenius Equation in polyenergetic conjugation relationships which include kinetic factor, can be used for ascertainment of the nature of the interfacial resistance in synergistic solvent extraction processes. It is obvious from those equations that the exponent of k should be, theoretically, equal to unity. Symbolizing that exponent by θ_k, from eqns./12/ and /13/ we can write:

$$k^{\theta_k} s^{-0.04} = \text{constant} ; \qquad /14/$$

$$k^{\theta_k} C^{-0.15} = \text{constant} , \qquad /15/$$

therefore, in cases of pure physical or chemical interfacial resistence nature, the equality: $\theta_k = 1$ will correspond to ideal process conditions in both equations. However, the use of eqns. /14/ or /15/ with the experimental data obtained for cases of combined interfacial resistence nature should result in θ_k-values less than 1. Moreover, in the last cases we should expect that θ_k-value will vary with the values of factors, such as droplets' surface area s and extractant concentration C respectively. From the point of view of polyenergetic conjugation dependence, we should expect also that the influence of s - excluded from eqn./15/ - will be bigger at low extractant concentrations in cases of combined resistance nature, i.e., θ_k-value will be undoubtedly proportional to C in applications of eqn./15/. Thus, by a deviation: $\theta_k < 1$, we can evaluate the existence and the magnitude of a combined interfacial resistance nature.

All those conclusions have been fully proved applicating eqns./14,15/ with the data for the extraction of U/VI/ from phosphoric acid by HDEHP-TOPO/TBP systems, as the experimental results of Maher and Pareau /1986/. For example, we calculated $\theta_k = 0.038$ in cases of $C = 0.27$ mol/l TBP, and $\theta_k = 0.13$ at $C = 0.50$ mol/l. However, we cannot accept without reservation the conclusion of those authors that the synergistic effect is not related to an improvement of the transfer rate, since the influences of other factors in eqn./10/-type relationships of polyenergetic conjugation are not fully investigated.

5. CONCLUSION

Application of polyenergetic conjugation relationships associating kinetic factors and factors of system state, developed from the Extended Arrhenius Equation on the base of the regularities of thermodynamics of accumulation processes, can ensure important information about the nature of interfacial resistance in synergistic extraction processes.

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EXTRACTION OF 12-TUNGSTATOSILICIC ACID AND 12-TUNGSTATOPHOSPHORIC ACID BY PETROLEUM SULFOXIDE

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ABSTRACT

Using petroleum sulfoxide as extractant, the extraction behavior of heterotungstic acids was studied. It was proved by IR spectrometry that the extracted species were 12-tungstatosilicic and 12-tungstatophosphoric acids which keep tne α-Keggin structure in the complexes. An **oxonium** extraction mechanism was suggested.

1 INTRODUCTION

The solvent extraction of heteropolytungstic acid was studied by many researchers. The majority of their studies concerned the extraction of heteropolyacid from strong acidic solutions. Lakshmanan (1970) investigated extraction of heteropolyacids with many oxygen-containing and phosphorus-containing extractants. Yatirajam (1977) extracted tungstatophosphoric acid with MIBK. Gu (1985) prepared 12-tungstatophosphoric acid by extraction method with dibutyl ether. The present authors (1990) reported an extraction process for separating small amounts of phosphorus from tungsten by using petroleum sulfoxide (PSO). This paper is to report the extraction of 12-tungstatophosphoric acid and 12-tungstatosilicic acid from weak acid solution.

2 EXPERIMENTAL

2.1 Extractant

Petroleum sulfoxide (PSO) is a mixture of sulfoxides of different **molecular** weights having a general formula R_1R_2SO, where R_1, R_2 being alkyl groups with 4 to 5 carbon atoms. The physical and chemical properties are shown in Table 1.

TABLE 1

Appearance	Clear brown liquid
Average molecular weight	176.2
Density, d_4^{10}	1.0253
Refractive index, n_D^{20}	1.4853
Sulfoxide concentration, kmol/10^3 kg	1.369

The IR spectrum of PSO is shown as A in Figure 4. The S-O bond of the sulfoxide shows a stretch vibration absorption peak at 1033 cm^{-1}. There are other peaks, which are attributed to symmetric and dissymmetric stretch vibrations of sulfone, at 1117 cm^{-1} and 1299 cm^{-1} indicating the presence of sulfone due to over oxidation.

2.2 Diluents

Octanol and decanol of C.P. grade were used as diluents.

2.3 Aqueous feed solution

Aqueous feed solutions containing tungsten and silicon or phosphorus were prepared by dissolving sodium tungstate and sodium silicate or sodium phosphate in deionized water, and then adjusted to proper pH values by adding hydrochloric acid or sodium hydroxide. These aqueous solutions contained a large excess of tungsten in comparison with the amount of silicon or phosphorus.

2.4 Apparatus and procedure

Extraction experiments were carried out in an extraction equilibrator with magnetic stirrer and thermostatic jacket (Dai, 1984). The time required to attain phase equilibrium was found to be less than 15 minutes. Therefore, 30 minutes of equilibration were used to obtain all the experimental data.

2.5 Method of analysis

Tungsten and silicon were analyzed by the thiocyanate and silicomolybdate spectrophotometry respectively. To avoid the interference of tungsten in silicon analysis, samples was first diluted with NaOH solution and boiled for a few minutes to decompose the tungstatosilicic acid before determination. In the case of tungstatophosphoric acid, precipitation of phosphate with calcium salt was used for the separation of phosphorus from most of tungsten and then the phosphorus portion was analyzed. In several runs, arsenic was added to the tungsten solution instead of phosphorus or silicon. It was first separated by distillation and analyzed by hypophosphite turbidimetry. Sulfoxide was measured by titration according to Ashworth (1972).

3 RESULTS AND DISCUSSION

3.1 Effect of pH value

Figure 1 shows the effect of the equilibrium pH on the extraction of 12-heterotungstic acids, namely, $H_4SiW_{12}O_{40}$, $H_3PW_{12}O_{40}$ and $H_3AsW_{12}O_{40}$.

The percentage extraction of these heterotungstic acids is found to decrease with increasing pH value. $H_4SiW_{12}O_{40}$ can be effectively extracted at pH < 4.5 and its percentage extraction drops in the range of pH 4.5-5.5 and becomes almost zero at pH = 5.7. The percentage extraction of $H_3PW_{12}O_{40}$ drops sharply in the range pH = 3-4. Arsenic is extracted only at low pHs, i.e. pH = 1-2.5. These phenomena are very similar to the result illustrated by Kepert (1973, in Figure 32, p.662) on the degradation of heteropoly-anions as a function of pH. The coincidence can also lead to the conclusion that PSO only extracts 12-heterotungstic acids instead of others such as 11-heteropolyacids.

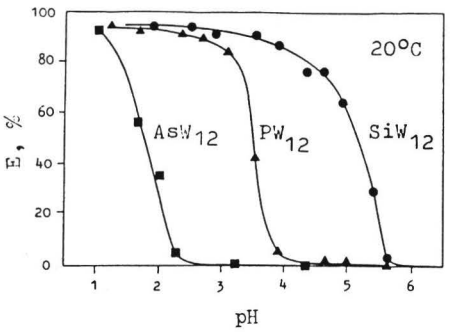


Fig. 1 Effect of equilibrium pH on the percentage Extraction E

organic phase:
PSO : DeOH = 7 : 3 (v/v)
initial aq. conc. (kmol/m^3)
● WO_3 = 0.543; Si = 5.44×10^{-3}
▲ WO_3 = 0.431; P = 5.48×10^{-3}
■ WO_3 = 0.431; As = 4.83×10^{-3}

If the concentration of HCl increases to 0.1 kmol/m^3, phase disengagement of the extraction system becomes difficult. More concentrated acid will cause the formation of an interphase emulsion layer. Therefore, this investigation deals mainly with the extraction of 12-tungstatosilicic acid and 12-tungstatophosphoric acid in the range of pH 1.5-6.

3.2 Effect of extractant concentration

The effect of concentration of extractant PSO in organic phase on the distribution coefficient is shown in Table 2. As expected, the higher is the concentration of PSO in solvent, the larger will be the distribution

TABLE 2 Effect of extractant concentration on the distribution coefficient

PSO, v%	-	10	30	50	70	100
$D_{SiW_{12}}$ *	0.00	0.05	0.76	5.55	9.19	13.3
$D_{PW_{12}}$ **	0.14	5.83	7.25	8.74	16.7	30.5

T = 293K, phase ratio = 1, initial pH = 2.0;
* diluent: DeOH; initial aqueous solution: $WO_3 = 53 \times 10^{-3}$kmol/m^3, Si = 5.44×10^{-3}kmol/m^3;
** diluent: OctOH; initial aqueous solution: $WO_3 = 208 \times 10^{-3}$kmol/m^3, P = 1.43×10^{-3}kmol/m^3.

coefficient. However, a certain amount of diluent should be added so as to keep the necessary density difference between two phases for phase disengagement, since the density of PSO is very near to that of water. Preliminary tests indicated that the extraction complexes are sparingly soluble in nonpolar solvents such as bezene and kerosene. Therefore, the polar solvents such as alcohols are used as diluents.

3.3 Ratio of tungsten to heteroatom in extraction complexes

The method of continuous variation was used to determine the atomic ratio of tungsten to heteroatoms in extraction complexes. The result is plotted in Figures 2 and 3. From the figures it indicates that when

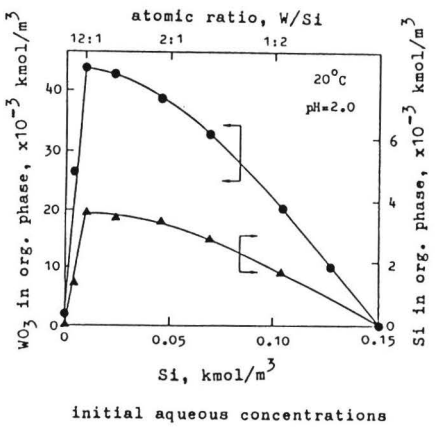


Fig. 2 Method of continuous variation

organic phase: PSO : DeOH = 7 : 3
aqueous feed: W + Si = 0.150 kmol/m^3
phase ratio = 1

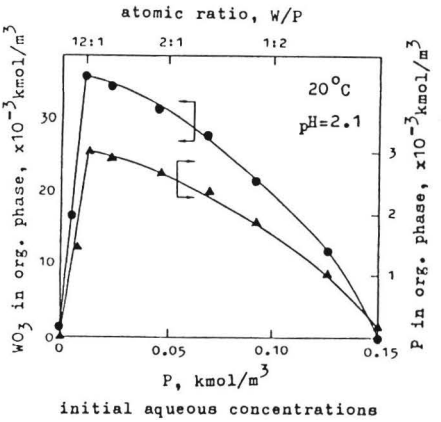


Fig. 3 Method of continuous variation

organic phase: PSO : DeOH = 7 : 3
aqueous feed: W + P = 0.150 kmol/m^3
phase ratio = 1

tungsten, silicon or phosphorus exists alone none will be extracted by PSO under the present experimental conditions and that when the heteroatom Si or P coexists with W, the extractable species conforms to the atomic ratio W/Si or P=12/1. This value is consistant with the result obtained by the direct analysis of the loaded organic phase.

3.4 IR study and extraction reactions

The IR spectra were obtained by liquid film method with the infrared spectrometer, Model FT-20sx produced by Nicolet Co. The sample was prepared by repeated contacts of 100% PSO with fresh portions of the feed solution for many times, so as to obtain sufficient concentration of heteropolytungstic acid in organic sample for the spectrogram. Figure 4 shows the IR spectra of the loaded organic phase and the fresh PSO (A of

Figure 4) for comparison. Absorption bands, which characterize the α-Keggin structure of 12-heteropolyacid anions, appear in the spectra of loaded PSO (B and C of Figure 4). The stretch bands attributed to the three kinds W-O bonds of the 12-tungstatosilicic acid are found respectively: ν_{W-Od} at 973 cm^{-1}, ν_{W-Ob-W} at 872 cm^{-1} and ν_{W-Oc-W} at 815 cm^{-1}, and Si-O stretch band ν_{Si-O} is at 919 cm^{-1} (B of Figure 4). For 12-tungstatophosphoric acid, stretch bands ν_{W-Od}, $\nu_{W-Ob=W}$, ν_{W-Oc-W} and ν_{P-O} are found at 979 cm^{-1}, 896 cm^{-1}, 825 cm^{-1} and 1078 cm^{-1}.

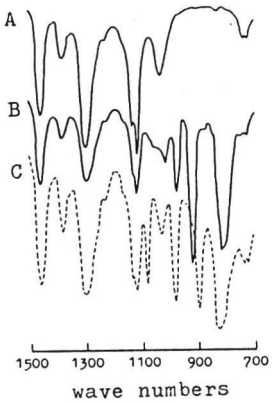


Fig. 4 IR spectra of organic phases

A: fresh extractant PSO
B: PSO loaded with SiW_{12}
C: PSO loaded with PW_{12}

In comparison with Rocchiccioli-Deltcheff's results (1976), when heteropolyacids associate with PSO all of their stretch bands shift slightly, which be probably due to the deformation of the frame of 12-heteropolyacid in extraction complexes. Likewise, the stretch band attributed to S-O bond of PSO shifts towards low frequency, e.g. in the case of 12-tungstatosilicic acid, ν_{S-O} shifts from 1033 to 1013 cm^{-1} and in the case of 12-tungstatophosphoric acid to 1031. According to Cotton et al. (1960), sulfoxide may coordinate through the oxygen atom to form the extraction complexes and the bands will shift to low frequency. The bands attributed to the sulfone in loaded organic phase are not changed. This means sulfone does not take part in extraction reaction.

On the other hand, if sulfoxide coordinates with metals as neutral ligand, namely, PSO directly coordinates with the tungsten atom in the frame of the 12-heteropolyacid, heteropolyacid anion will not keep their α-Keggin structure. Although the exact mechanism is still unclear, an oxonium extraction mechanism might be suggested as follows:

$$R_2S{=}O + H^+ = R_2S{=}OH^+ \qquad (1)$$

And then it associates with the 12-heteropolyacid anion to form extraction complexes. For example, the equations for extraction of 12-tungstatophosphoric acid may be

$$R_2S{=}OH^+ + H_2PW_{12}O_{40}^- = H_2PW_{12}O_{40}{\cdot}R_2S{=}OH \quad (2)$$

$$2\ R_2S{=}OH^+ + HPW_{12}O_{40}^{2-} = HPW_{12}O_{40}(R_2S{=}OH)_2 \quad (3)$$

$$3\ R_2S{=}OH^+ + PW_{12}O_{40}^{3-} = PW_{12}O_{40}(R_2S{=}OH)_3 \quad (4)$$

or by a single equation,

$$i\ R_2O{=}OH^+ + H_{3-i}PW_{12}O_{40}^{i-} = H_{3-i}PW_{12}O_{40}(R_2S{=}OH)_i \quad (5)$$

Likewise, the extraction equation of 12-tungstatosilicic acid may be

$$j\ R_2S{=}OH^+ + H_{4-j}SiW_{12}O_{40}^{j-} = H_{4-j}SiW_{12}O_{40}(R_2S{=}OH)_j \quad (6)$$

4 CONCLUSION

Petroleum sulfoxide can extract tungstatosilicic acid and tungstatophosphoric acid from low acid solutions. The percentage extractions of these heteropolyacids decrease with increasing pH value. The extraction complexes comprise 12-heteropolyacid anion $SiW_{12}O_{40}^{4-}$ and $PW_{12}O_{40}^{3-}$ which keep their α-Keggin structure in organic phase. The sulfoxide coordinates through the oxygen atom to form the extraction complexes.

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EXTRACTION OF EUROPIUM (III) BY 8-HYDROXYQUINOLINE AND SOME RELATED AMINES IN CHLOROFORM FROM NITRATE MEDIUM.

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ABSTRACT:

The extraction of radioactive Eu(III) by oxine (HOX) and trilaurylamine (TLA), trioctylamine (TOA), tributylamine (TbA), tripropylamine (TPA) and triallylamine (TAA) $\equiv$ Am in chloroform was investigated. The stoichiometric formulae of the extracted chelate and adduct species were established to be $Eu.(NO_3).(OX)_2$ and $Eu(NO_3).(OX)_2.Am$, respectively. The respective extraction constants of the extracted europium specices were elucidated. As related to the amines used,the extraction constants of the extracted species increased in the order: TAA < TPA < TbA < TOA < TLA. This sequence was discussed in the light of the inductive effect of the alkyl substituents in these tertiary amines.

INTRODUCTION:

In synergic extraction, the aqueous phase composition plays a main role in achieving the synergic phenomenon as reported by Healy (1961), Irving (1966) and Aggett (1970). The presence of certain chemical composition in the aqueous phase was found to be required for the formation of the synergic species to be extracted as reported by Deptula et al (1967). In the present work, the extraction of trivalent europium from nitrate buffer aqueous medium is investigated using pure and mixed extractants of 8-hydroxyquinoline and some related amines in chloroform.

EXPERIMENTAL:

8-hydroxyquinoline (HOX), sodium nitrate and chloroform were AR grade and obtained from Veb Lobor Chemie Apolda. The tertiary

amines; trilaurylamine (TLA), trioctylamine (TOA),tributylamine (TbA), tripropylamine (TPA) and triallylamine (TAA) were supplied from Fluka AG and used without further purification.Eu(152 + 154) was used as radiotracer. In all cases , the ionic strength of the aqueous medium was adjusted to be 0.1 (H^+,$NaNO_3$),unless otherwise stated. Extraction procedure was similar to that reported by Zakareia et al (1988).

RESULTS AND DISCUSSION

Slope analysis of the detailed extraction results of Eu(III) by HOX in chloroform from nitrate aqueous medium supported the following equilibrium:

$$Eu(III) + 2\,\overline{HOX} + NO_3^- \rightleftharpoons \overline{Eu.(NO_3).(OX)_2} + 2H^+ \qquad (1)$$

where bars refer to the organic phase.

The mean values of the extraction constant, K_{21},for this reaction was found to be $9.02 \pm 0.09 \times 10^{-6}$.

The enhancing effect of the tertiary amines TLA, TOA, TbA, TPA and TAA on the extraction of Eu (III) by HOX in chloroform together with these amines was expressed in terms of synergic factor (SF) values. The maximum SF values were found to exceed 4170, 3060, 1980, 77 and 35 for TLA, TOA, TbA, TPA and TAA, respectively, at equimolar mixture of 0.1 M total concentration.

The synergic extraction of Eu(III) by HOX and each of these amines(Am)in chloroform from the nitrate medium was systematically investigated in details covering the four parameters (f) affecting the Eu (III) extraction, $[H^+]$,[HOX],[Am] and $[NO_3^-]$ when fixing three of them. log D-log f relations were traced in Fig .(1)

Slope analysis of these data indicates that the molar ratio of Eu(III)to HOX to NO_3^- in the mixed species is 1:2:1 as that obtained in absence of the amines. The formation of the adduct in the organic phase can be represented by the equilibrium

$$\overline{Eu\,(NO_3)(OX)_2} + \overline{Am} \rightleftharpoons \overline{Eu.(NO_3).(OX)_2.Am} \qquad (2)$$

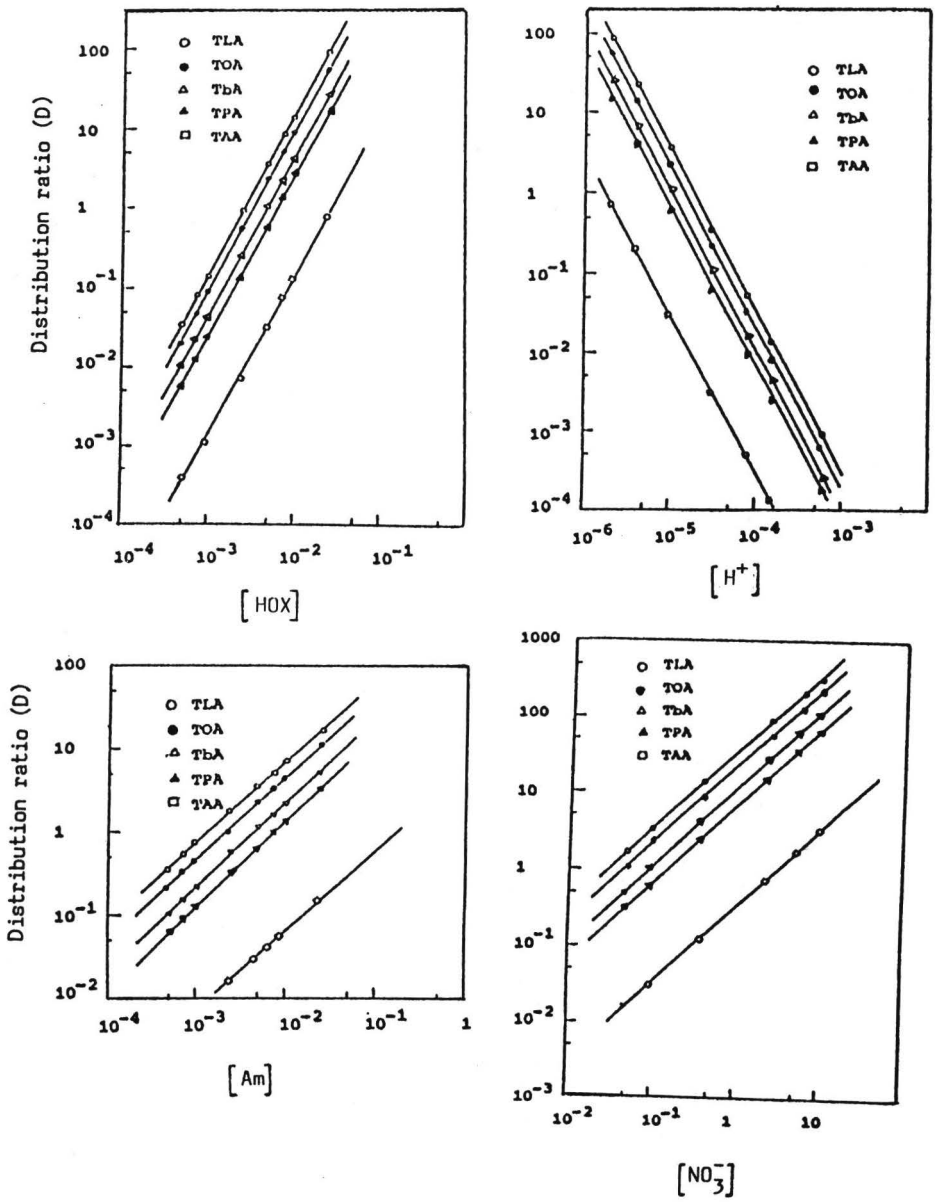


Fig.1 Effect of concentration of hydrogen ion , oxine , amines and nitrate on the extraction of Eu (III)

and the overall synergic reaction can be represented by the equilibrium:

$$Eu^{3+} + \overline{2\ HOX} + NO_3^- + \overline{Am} \rightleftharpoons \overline{Eu.(NO_3).(OX)_2.\ Am} + 2\ H^+ \qquad (3)$$

the mean values of the extraction constants, K_{211} of reaction(3) and the respective formation constants, β_{211} of the extracted adducts,reaction 2, are given in Table (1).

TABLE 1

Extraction of trivalant europium by 8-hydroxyquinoline (HOX) and HOX - amine mixtures.

Species	K_{21}	K_{211}	β_{211}
$Eu.NO_3^-\ (OX)_2$	9.02×10^{-6}		
$Eu.NO_3^-\ (OX)_2.TLA$		$2.84\pm0.05\times10^{-2}$	$3.10\pm0.005\times10^{3}$
$Eu.NO_3^-\ (OX)_2.TOA$		$1.8\pm0.04\times10^{-2}$	$2.00\pm0.006\times10^{3}$
$Eu.NO_3^-\ (OX)_2.TbA$		$8.38\pm0.1\times10^{-3}$	$0.93\pm0.010\times10^{3}$
$Eu.NO_3^-\ (OX)_2.TPA$		$5.11\pm0.06\times10^{-3}$	$0.57\pm0.01\times10^{3}$
$Eu.NO_3^-\ (OX)_2.TAA$		$2.33\pm0.06\times10^{-4}$	$0.26\pm0.008\times10^{2}$

The synergic effects as indicated by the synergic factors took the sequence TLA › TOA › TbA › TPA › TAA. The tabulated data indicate that both K_{211} and β_{211} values decrease, also, in the same sequence: TLA › TOA › TbA › TPA › TAA. this order is in agreement with a comparable system on Co(II) using thenoyltrifluoroacetone instead of HOX as reported by Khalifa (1977).

The extraction power of an amine is mainly related to its basicity as reported by Knoch (1985), Khegfeldt (1968) and Makarov et al (1967), which depends mainly on its composition and structure as reported by Shevedov et al (1972). The position of the unshared electron pair of the active nitrogen atom determines the amine basicity, which is governed by the inductive and steric effects of the attached groups. Considering these groups in the related amines used (TLA,TOA,TbA and TPA), their chains having

increasing number of carbon atoms (3,4,8 and 12, respectively). The successive increase obtained in β_{211} values with increasing the number of carbon atoms in the chains of the attached groups Fig(2)can be as ascribed to the inductive effect of these chains. This conclusion was supported by correlating log β_{211} to the respective inductive effect of these amines in their Taft constant, Fig (3).

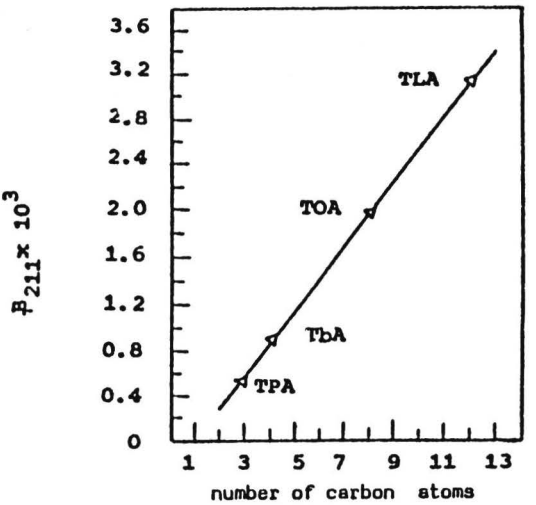


Fig. 2 Variation of β_{211} with the number of carbon atoms in the amine chain.

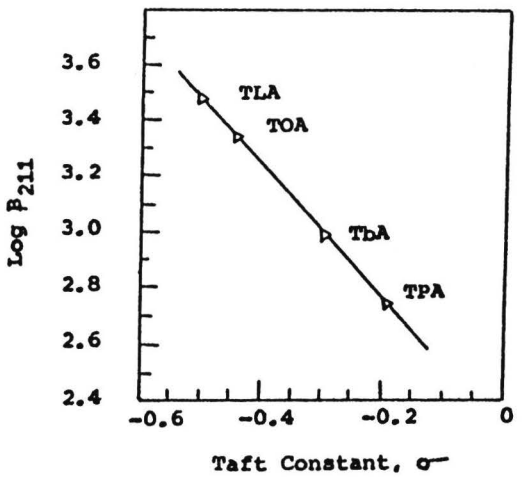


Fig. 3 Variation of β_{211} with the Taft constant of the amines.

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NEW METHOD OF ELECTROLYTE ACTIVITY COEFFICIENT DETERMINATION FROM EXTRACTION DATA

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ABSTRACT
Vlasov V.S. and Rozen A.M.,1990. New method of electrolyte activity determination from extraction data.

Activity coefficients are proposed to be determined from extraction data using expansion into a series for osmotic coefficients and computing the expansion coefficients. Electrolyte extraction constants are determined simultaneously. In case of extraction from multicomponent solutions the method envisages transfer to isopiestic conditions for the use of Mikulin-Zdanovsky rule. The reliability of the method was confirmed using as test the determination of uranyl nitrate activity coefficients from the data on its extraction with 100% and 30% TBP.

INTRODUCTION

If extraction proceeds by the solvate mechanism

$$Me^{z+}_{aq} + zA^{-}_{aq} + qL_{org} = MeA_zL_{q(org)} \qquad (1)$$

where Me is a metal, A is anion, L is organic ligand, the mass action law results in the following equilibrium equations :

$$y = \bar{K}[Me^{z+}][A^-]^z \gamma_{\pm}^{\nu} L^q;\ D = y/x = \tilde{K}[A^-]^z L^q \qquad (2)$$

where x and y are metal concentrations in aqueous and organic phases, D is distribution coefficient, $\bar{K}$ and $\tilde{K} = \bar{K}\gamma_{\pm}^{\nu}$ are effective and concentration constants of extraction, L is concentration of a free extractant (ligand) $L = L_o - qy$; $\nu = z + 1$.

Having the equilibrium data and knowing the solvate number q it is not difficult to find the concentration constant of exrtaction, its dependence on aqueous phase concentration of an element:

$$\tilde{K} = \bar{K}\gamma_{\pm}^{\nu} = y/x[A^-]^3L^q = f(x) \qquad (3)$$

By extrapolating $\tilde{K}$ to zero concentration (at which $\gamma_{\pm} = 1$) one can determine the effective extraction constant K and then also activity coefficients for any concentration (Rozen, Moiseenko,1959):

$$\gamma_{\pm} = (\tilde{K}/\bar{K})^{1/\nu} \qquad (4)$$

The most risky moment in this procedure is $\tilde{K}$ extrapolation to the zero concentration. Taking account of the fact that for ade-

quately dilute solutions according to Debye-Huckel theory, $\lg \gamma_{\pm} = -A\sqrt{I}$, where I is ionic strength, the extrapolation can be performed in $\ln K - \sqrt{I}$ coordinates. However, Debye-Huckel based extrapolation may be incorrect if extraction data on rather low concentrations of electrolyte are not available.

It is somewhat better to use Debye-Huckel second approximation or expansion is series (Rozen et al, 1976)

$$\ln\widetilde{K} = a_0 + a_1 I^{1/2} + a_2 I + a_3 I^{3/2} + \ldots \qquad (5)$$

where $a_0 = \ln\overline{K}$. The coefficients a_0, a_1, $\ldots\ldots a_n$ were found by the least square method. However, as it was shown in practice with $\widetilde{K}$ (I) adequately described in a wide concentration range the value of $a_0 = \ln \overline{K}$ does not wholly corresponds to the independently found constant $\overline{K}$ (for components with the known dependence of $\gamma_{\pm}$ on concentration, e.g., uranyl nitrate).

In this connection another way of determining activity coefficients and extraction constants from the extraction data is suggested below. It is based on determining activity coefficients in terms of the dependence of the osmotic coefficient Φ on the solution concentration (molality).

Systems with single dissolved component

In this case the shape of the osmotic coefficient vs molality dependence is known. It is advisable to consider it in two molality ranges : at low concentrations up to its certain value of m (e.g. $m_o = 0.1$)

$$\Phi_1 = 1 + A_1 m^{1/2} + A_2 m \qquad (6)$$

and at higher concentrations (usually above 0.1m) - for arbitrary power Series :

$$\Phi_2 = a_0 + a_1 m^p + a_2 m^q + a_3 m^r + \ldots \qquad (7)$$

where usually

$$p = 1;\ q = 2;\ r = 3 \text{ (a) or } p = \tfrac{1}{2};\ q = 1;\ r = 2 \text{ (b)} \qquad (8)$$

Then one should know only expansion coefficients (7) $a_0, a_1, a_2 \ldots\ldots a_n$; A_1 A_2 values will be found from the conditions of joining (smoothness) of curves (9) - (10) at $m = m_o$:

$$\Phi_1(m_o) = \Phi_2(m_o) \ ; \quad \Phi'_1(m_o) = \Phi'_2(m_o) \qquad (9)$$

where $m_o = 0.1$. From eqs.(6),(7) and (8) we find A_1 and A_2 from the data on a_i values

$$A_1 = -2\,(1 - a_o + a_2 m_o^2 + 2\,a_3 m_o^3)\ /\ \sqrt{m_o}$$
$$A_2 = (1 - a_o + a_1 m_o + 3\,a_2 m_o + 5\,a_3 m_o^3)\ /\ m_o \qquad (10)$$

If the Φ (m) dependence is known it is not difficult to determine $\gamma_{\pm}$:

$$\ln \gamma_{\pm} = (\Phi_2 - 1) + \int_0^{m_o} (\Phi_1 - 1)\, d\ln(m) + \int_{m_o}^{m} (\Phi_2 - 1)\, d\ln(m) \quad (11)$$

For the initial portion (up to $m = m_o = 0.1$)

$$\ln \gamma_{\pm} = 3 A_1 \sqrt{m} + 2 A_2 m \quad (12)$$

and for higher concentrations (above m_o) integration with respect to formula (11) results in expression :

$$\ln \gamma_{\pm} = 2A_1\sqrt{m_o} + A_2 m + a_o(\ln m - \ln m_o + 1) - 1 + (1+1/p)a_1 m^p + (1+1/q)a_2 m^q + (1+1/r)a_3 m^r - (a_1 m_o^p/p + a_2 m_o^q/q + a_3 m_o^r/r) \quad (13)$$

The transfer from the molality scale to the molar one is done with :

$$\gamma_{+c} c = \gamma_{+m} m \quad (14)$$

If tabulated data on osmotic coefficient values are available, then with the help of equations (7-10) they can be described and the mean ion activity coefficients $\gamma_{\pm}$ can be found without guaphical integration. Knowing $\gamma_{\pm c}$ from equation (3) one can also find the effective extraction constant $\bar{K}$.

When $\Phi_2(m)$ dependence is unknown and it should be determined from extraction data ($\tilde{K}$ values) a search is carried on for expansion coefficients (7-10) and extraction constant (constants) by minimization of misaligument at all experimental points (by the least square method).

To check the method consideration was given to uranium extraction with 100% TBP (Davis and Mrochek, 1967). In the search problem the effective extraction constant and four polynomial coefficients (7) in the form of (8b)(for area with $m > 0.1$ mole/kg) were determined. For the area of the concentrations $m < 0.1$ mole/kg equation (6) was used. The search resulted in $\bar{K} = 30$; $a_o = 0.91261$; $a_1 = -0.34712$; $a_2 = 0.69584$; $a_3 = 0.073138$.

Dependencies (7),(8b) with the found coefficients agree with the osmotic coefficients for uranyl nitrate (Robinson and Stokes) at the accuracy up to 3% and the $\bar{K}$ value corresponds to that found previously (Rozen, 1957). Close values of expansion coefficients a_i were found also using Rozen's and Kharkhorina data on uranium extraction with 30% TBP in neutral diluents; the calculated extraction constant $\bar{K} = 70$ also agrees with the found previously (Rozen, 1957).

Systems with Several Dissolved Substances

In case of several electrolytes osmotic coefficients and, hence, activity coefficients can be determined according to Zdanovsky-Mikulin rules by transfer to isopiestic conditions (i.e., conditions with the same activity of water).

Let dependences $\Phi_i(m)$ for individual components (in binary

salt-water system)be known in the system containing k components, then isopiestic conditions will be determined by a system of equations

$$\nu_1 m_1^* \bar{\Phi}(m_1^*) = \nu_2 m_2^* \bar{\Phi}(m_2^*) = \ldots = \nu_k m^* \bar{\Phi}(m_k^*) = R = 55.5 \ln(a_w)$$

$$m_1/m_1^* + m_2/m_2^* + \ldots + m_k/m_k^* = 1 \qquad (15)$$

$$\gamma_{\pm im} = \nu_i m_i^* \gamma_{\pm}(m_i^*) / \sum \nu_i m_i \qquad (16)$$

(the second equation is Zdanovsky rule, the third - is Mikulin rule), where m_i and m_i^* are molality of component in mixture and its isopiestic molality, a_w is activity of water in electrolyte mixture.

A number of algorithms for transfer to isopiestic conditions (see, e.g.,Denisov,1988) are available in literature, however all of them are ineffective and cannot be recommended for practical work with a personal computer. We offer the following iteration system for transfer to isopiestic conditions and, hence, determination of activity coefficients for each component of a mixture. Rewrite one of the equations of system (15) in the form convenient for numerical solution

$$m_1/m_1^* + m_2/m_2^* + \ldots + m_k/m_k^* - 1 = f(a_w) = 0 \qquad (17)$$

The value of a_w will be changed by the gradient method (Newton one) at each step matching $m_1^*, m_2^*, \ldots, m_k^*$ by the simple iteration method so that conditions

$$\nu_1 m_1^* \bar{\Phi}(m_1^*) = \nu_2 m_2^* \bar{\Phi}(m_2^*) = \ldots = \nu_k m_k^* \bar{\Phi}(m_k^*) = 55.5 \ln(a_w) \qquad (18)$$

be fulfilled.

As practical calculations show to reduce a system comprising 5 components to isopiestic conditions 4-5 iteration steps (18) and 6-10 steps to solve equation (17) are usually required.

The found values of m_i allow one to determine the activity coefficient of each component from eq.16 and then to go to the molar scale with eq.14.

Using the known dependences of $\bar{\Phi}_i(m)$ for each component in a binary salt-water solution this approach permits one to determine activity coefficients in electrolyte mixtures and, correspondingly, to calculate extraction of those components (on condition the stoichiometry and extraction constants are known).

On the contrary, if reliable extraction data are available and the extraction mechanism is known (i.e., the composition of complexes was determined at the high degree of probability and the extraction pseudoconstant $\tilde{K} = \tilde{K}(x)$ can be calculated but the dependence of $\bar{\Phi}_i(m)$ for one or several components is not available,

then by matching the expansion coefficients of (7-10) type and effective extraction constants in the problem of search for the best approximation one can determine $\Phi_i(m)$ and, hence, $\gamma_i(m)$. It is possible using data on microammount extraction from an electrolyte mixture to determine the molality dependence of the osmotic coefficient for its binary salt-water solution (when it is difficult to determine this dependence experimentally, e.g., for plutonium, americium nitrates).

The systems were considered :

1. 30% TBP - HNO_3 - H_2O - $Pu(NO_3)_4$
2. 30% TBP - HNO_3 - H_2O - $Am(NO_3)_3$
3. 100%TBP - H_2O - $NaNO_3$ - $Am(NO_3)_3$
4. 100%TBP - H_2O - $Al(NO_3)_3$ - $Am(NO_3)_3$

The results of the calculations are given in tables 1,2 and 3.

TABLE 1

Extraction constants and expansion coefficients of type (7).

System	K	a_0	a_1	a_2	a_3
1	1320	0.8568	-0.2544	0.1792	-
2	6.9	0.9567	-0.6892	0.3334	-0.01494
3	3.3	0.9590	-0.6900	0.3135	-0.01288
4	3.7	0.9511	-0.6547	0.3101	-0.01488

TABLE 2

Molality and osmotic data for Pu and Am nitrates in binary salt-water solutions.

Molality, mole/kg	$Pu(NO_3)_4$		$Am(NO_3)_3$	
	$\Phi(m)$	$\gamma_\pm(m)$	$\Phi(m)$	$\gamma_\pm(m)$
0.1	0.794	0.459	0.772	0.467
0.2	0.779	0.389	0.715	0.369
0.3	0.771	0.353	0.678	0.315
0.4	0.768	0.329	0.652	0.279
0.5	0.767	0.312	0.632	0.252
0.6	0.767	0.300	0.617	0.232
0.7	0.769	0.289	0.606	0.216
0.8	0.773	0.282	0.597	0.203
0.9	0.777	0.275	0.591	0.193
1.0	0.782	0.271	0.586	0.183
1.5	0.814	0.257	0.579	0.154
2.0	0.855	0.256	0.589	0.138

TABLE 3

Molar activity coefficients for Pu and Am nitrates in nitric acid solutions.

Molality,	$Pu(NO_3)_4$	$Am(NO_3)_3$
mole/l HNO_3	$\gamma_{\pm(m)}$	$\gamma_{\pm(m)}$
0.2	0.590	0.583
0.4	0.495	0.464
0.6	0.449	0.402
0.8	0.421	0.362
1.0	0.401	0.330
1.5	0.367	0.279
2.0	0.345	0.247

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INVESTIGATION OF URANYL AND THORIUM NITRATE COMPLEX FORMATION WITH TBP BY HIGH RESOLUTION NMR METHOD

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ABSTRACT
Rozen A.M., Nikiforov A.S., Kartasheva N.A., Neumoev N.V., Markov V.S., Yushmanov V.E., Shkarin P.Yu., 1990. Investigation of uranyl and thorium nitrate complex formation with TBP by high resolution NMR method.

Using NMR on ^{31}P and ^{1}H at a lower temperature (up to 180 K) uranyl and thorium nitrate-TBP complexes were visualized. The ^{31}P peaks of free TBP (the chemical shift δ = + 0.05 ppm) and uranyl nitrate disolvate (1.7 + 0,2 ppm) were separated. In the PMR spectrum the peaks of α-protons of TBP and the complex (the solvate shift $\Delta\delta$ = 0,4 ppm) are separated. A certain increase in the solvation shift on 31-P is noted with uranyl nitrate concentration growth, possibly because TBP outer-sphere molecules leave the complex. When TBP is saturated with uranium additional peaks A (δ = = 2,6 + 0,2 ppm) and B (1.0 + 0,2 ppm) appear in the 31-P spectrum; they belong to polymer complexes destructible with toluene dilution. The A peak intensity grows on a long-term phase contact; the A complex was obtained by dodecane scrubbing in which it is poorly soluble. In the 31-P spectrum of the thorium extract negative chemical shift are observed; the peaks of free TBP, two (and in one case three) complexes (δ = -4,5 and -5,15 ppm) can be seen.

According to the data of physicochemical investigations carried out by dilution and saturation methods the TBP extraction of uranyl nitrate results in a formation of a disolvate $UO_2(NO_3)_2(TBP)_2$ (Mc Kay 1954; Rozen 1957,1962); it is shown in the two latter papers; that this stoichiometry permits a full mathematical description of extraction equilibria. At the same time it was found (Rozen 1962) that the uranyl nitrate disolvate-TBP interaction is characterized by negative deviations from Raoult law at the non-ideality constant $A_{23} \approx -RT = -0,6$ kcal/mole (p. 44) which can be interpreted to be a weak chemical interaction, i.e., trisolvate formation (p. 51). Afanass'ev (1967) confirmed this by calorimetric measurements : in the disolvate-TBP system a heat release $h^E_{max} = -0,5$kcal /mole was observed which corresponds to A_{23} -2 kcal/mole. On thorium nitrate extraction disolvate and trisolvate were found; later based on the mathematical modelling of extraction isotherms it was

concluded that di- and trisolvates are present simultaneously (Torgov, 1978).

The objective of this paper is to visualize the complexes by the direct NMR method at a lower temperature, primarily, on ^{31}P, ^{1}H and partially on ^{15}N, ^{13}C (in the only known to us NMR investigation (Vashman, 1987)* of uranyl nitrate-TBP system the measurements were made at room temperature which did not allow the peaks of solvate and TBP to be separated).

Spectrometers Brooker AM-400 and AC-200 were used having ^{1}H resonance frequences 400 MHz and 200 MHz, respectively, and ^{31}P resonance frequences 162 and 81 MHz. The temperature was varied from room temperature to 180 K (the possibilities of lowering the temperature were limited by specimen vitrification effecting line broadening).

Uranyl nitrate-TBP system Through lowering the temperature one succeeded in separating the peaks of disolvate (D) and free TBP (fig. 1) in the ^{31}P spectra (standard 85% H_3PO_4).

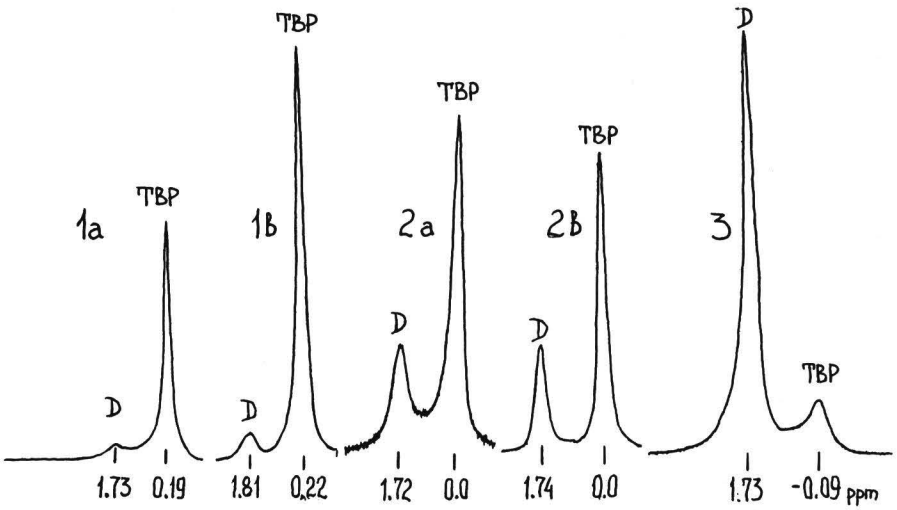


Fig. 1. ^{31}P spectra of uranyl nitrate extracts at different temperatures (100% TBP); 1 - uranium concentration of 65 g/l (a - - 215 K, b - 205 K); 2 - 180 g/l (a - 235 K, b - 220 K), 3 - - 315 g/l (230 K).

*The Vashman conclusion that at low U concentrations a "wet" complex $UO_2(NO_3)_2(TBP)_2(H_2O)_2$ is extracted was not confirmed by us.

With uranyl nitrate saturation of TBP the peak of free TBP (the chemical shift of 0.03 - 0.1 ppm) is reduced (disappears on full saturation), the peak of disolvate increases while the temperature T_d required to separate the peaks somewhat rises (at the uranium concentration y_U = 75 g/l; 200 g/l and 350 g/l it is 200, 220 and 230 K); the exchange rate is likely to decrease with a reduction in the free TBP concentration. The solvate chemical shift somewhat increases as the temperature lowers (at y_U = 75 g/l and T = 215, 203 and 196 K it is 1.50, 1.59 and 1.63 ppm, respectively; at 200 g/l and T = 235 and 220 K it is 1.63 and 1.77 ppm). The solvation chemical shift also grows with uranium concentration at y_U = 75 g/l, 200 g/l and 350 g/l and at the indicated growing T_d $\Delta\delta$ is 1.63, 1.76 and 1.82 ppm. On dilution with toluene δ increases by 0.15 ppm.

In the PMR spectra at the frequency of 400 MHz similar, but less pronounced (fig. 2) phenomena were observed : on solvation along with the α-protons peak of free TBP (standard TMS, δ =4.04

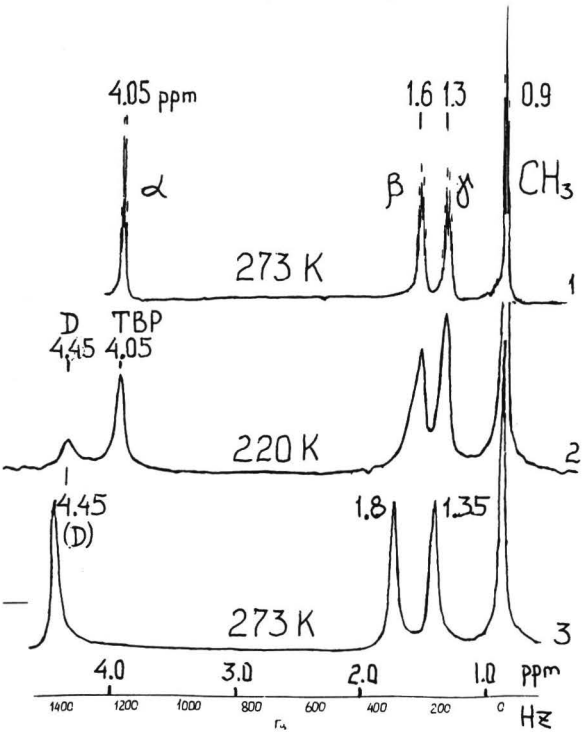


Fig. 2. Spectra of ^1H tributyl phosphate (1), extract (2, uranium concentration 180 g/l) and TBP fully saturated with $UO_2(NO_3)_2$ (3).

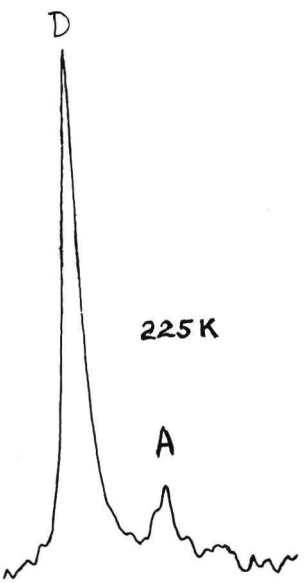


Fig. 3. ^{15}N spectrum corresponding to spectrum 1 in fig. 4.

ppm), there appeared a peak of α-protons of solvate (δ = 4.50 ppm), the solvation chemical shift $\Delta\delta$ was 170 Hz = 0.45 ppm, i.e., 4 times less than on ^{31}P. On solvation the peaks of CH_3 (δ = 0.90 ppm), α - and β-protons (δ = 1.3 and 1.6 ppm, respectively) last their fine structure and deformed, but ^{1}H shifts were small; for γ-protons $\Delta\delta$ = 18 Hz = 0.05 ppm; for β-protons $\Delta\delta$ = 70 Hz = 0.18 ppm.

We failed to separate the peak of tri- or tetrasolvate. It is possible that the availability of this complex is evidenced by the indicated growth of the solvation shift with the y_U growth. It in most likely that an additional TBP molecule or even two are in the outer sphere of the complex : the enthalpy of a disolvate formation is ~ 20 kcal/mole, the addition of the third molecule gives only ~ 1 kcal. Exchange between outer and inner sphere TBP molecules diminishes the chemical shift of the latter; on saturation all TBP molecules are only in the inner sphere and this effect disappears.

Changes in the spectra that point to a new complex formation are observed on a long-term contact of $UO_2(NO_3)_2 nH_2O$ crystals with TBP (fig. 4). At the contact time ~ 1 hour on both the sides of the disolvate peak (δ = 1.6 - 1.8 ppm) two small new peaks appear (fig. 4, spectrum 1) : peak A on the weak field side (δ = 2.6 $\pm$ $\pm$ 0.1 ppm) and peak B (is first to appear) on the strong field side (δ = 1.0 $\pm$ 0.1 ppm). The ^{15}N spectrum (fig. 3) of the extract reveals minimum two complexes. If one judges by the disappearance of peaks A and B on a four times dilution with toluene (1a spectrum) both the complexes are dimers or polymers.

On a long-term contact (more than a day) the intensity of peak A grows, its area constituses ~ 20% of the disolvate peak area (fig. 4 , spectrum 2). It turned out that the A complex is poorly soluble in saturated hydrocarbons that readily disolve common disolvate. This allows to obtain the A complex. Following 3 (spectrum 3) and 8 (spectrum 4) dodecane scrubs it prevails; with the temperature lowered to 15°C a solid phase precipitates; on heating to 30°C it is again dissolved.

In the IR-spectrum of the A complex a 10 cm^{-1} increase of the PO frequency shift was revealed (ω_{PO} = 1175 cm^{-1} instead of 1185 - 1189 cm^{-1} for common solvate), i.e., the TBP- UO_2 bond is strengthened; the frequencies of NO_3 (1269 and 1530) remain practically unchanged with the splitting of 260 cm^{-1} which evidences

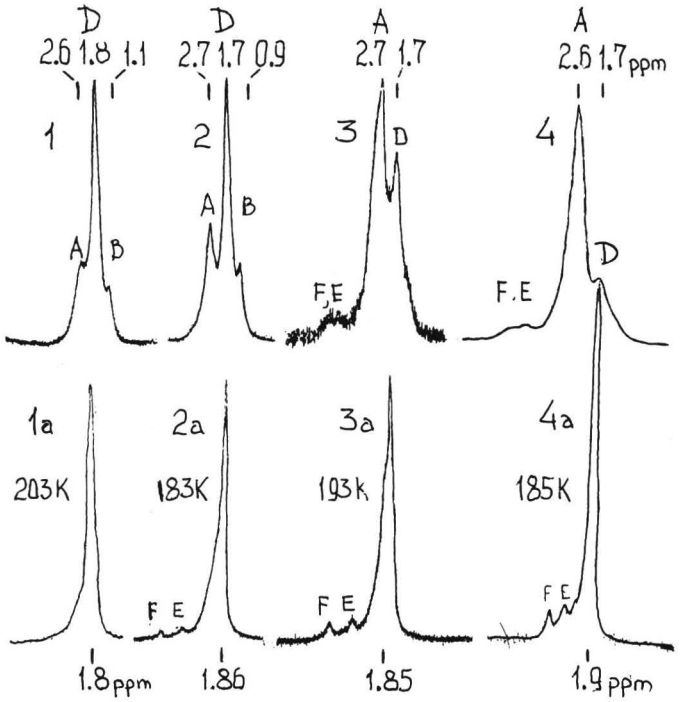


Fig. 4. ^{31}P spectra of extracts saturated with $UO_2(NO_3)_2.6H_2O$ 1 - contact time - 2 hours; 2 - days; 3 - specimen 2 after 3 wash-ups with dodecane; 4 - after 8 wash-ups (all spectra at 253K), 1a - 4a specimens 1-4 as 4 times diluted with toluene; peak F at 5.1 ± 0.1 ppm, E = at 4.5 ± 0.2 ppm (undiluted TBP) and at 3.8 ± 0.2 ppm - in toluene.

the bidentatic coordination; the UO_2 frequency grows by 4 cm^{-1}. From the IR spectra 0.3 mole/l of OH groups is found; and with the chemical analysis 0.2 mole/l HNO_3 is found which indicates a partial hydrolysis of uranyl nitrate.

According to the chemical analysis a fresh A complex can contain up to 600 g/l uranium, i.e., monosolvate, possibly $[UO_2OHNO_3 \cdot TBP]_n$ or more complicated mixed complexes, polymerized with OH bridges are formed (one OH group can coordinate up to three uranyl ones). The nature of the A complex needs further investigation, but we can see that it is tinted light brownish which is typical of hydroxoforms of uranyl; the polymerization is confirmed by the fact that the complex is essentially insoluble in dodecane.

On long-term holding a precipitate results and the uranium content of the organic solution diminishes up to 360-400 g/l which is close to that for disolvate.

The A complex formation is accompanied by E and F comple-

xes appearing (the peaks at 4 ± 0.3 and 5.2 ppm) both in 100% and diluted TBP (spectra 2 - 4 and 2a - 4a). Probably they are some other hydrolytic complexes, e.g., $UO_2(OH)_2TBP_n$. As distinct from E and F the A complex is significantly changed on 4-times dilution with toluene. It depolymerizes, a disolvate peak is primarily observed ($\delta^{31}P$ = 1.7 - 1.9 ppm) possibly due to the disproportionation with the E and F complexes.

The B complex is possibly an electrostatical polymer.

Thorium nitrate. On thorium nitrate solvation the negative ^{31}P chemical shifts are observed (fig.5), the peaks of free TBP, di- and trisolvate are seen. At fully saturation two or three (another thorium sample) peaks are seen (possibly $ThOH(NO_3)_3(TBP)_q$ is present).

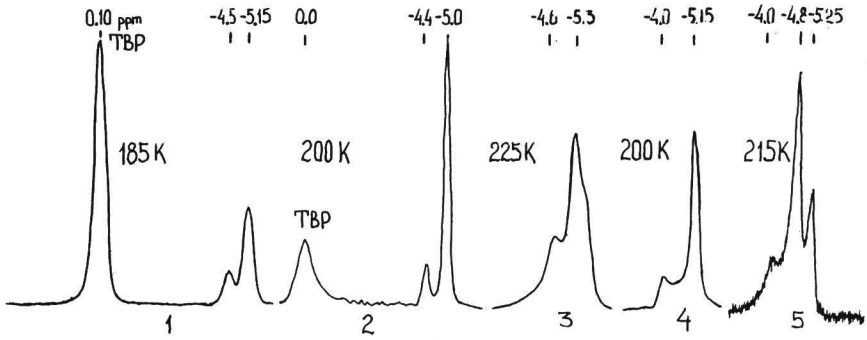


Fig.5. ^{31}P spectra of thorium nitrate extracts (100% TBP 4 times diluted with toluene, spectrum 3 - 2 times). Th concentrations (before dilution) 1 - 100 g/l, 2 - 200 g/l, 3-5 - TBP fully saturated with thorium nitrate.

Thus, di- and trisolvates of TBP with thorium nitrate and disolvate with uranylnitrate were visualized, new complexes in this trivial systems were revealed.

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MASS TRANSFER ON FREELY SUSPENDED SINGLE DROPLETS MEASURED BY SCINTILLATION QUENCHING AND SINGLE-PHOTON COUNTING TECHNIQUE

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ABSTRACT

Mass transfer of isomeric chlorobenzoic acids in aqueous phase/organic phase (xylene) systems is measured at different pH-values by partial optical quenching of γ-scintillation events, which were recorded by two photomultipliers in coincidence. The influence of the pH-value of the aqueous phase and the solute concentration on the mass transfer rate are ascertained. A two-dimensional distribution of the counting rates was determined by a single-photon-counting image-amplifier signal-processor system. The inner droplet coalescence in freely suspended liquid membrane drops is monitored by means of optical quenching of the scintillation measured by the latter technique.

INTRODUCTION

In order to avoid difficulties with the classical integral methods for the investigation of mass transfer between continuous and dispersed phases and to carry out different measurements for very short observation times as well, a modified liquid scintillation technique was developed to investigate the mass transfer on freely suspended droplets.

MEASURING METHODS

The droplet consisting of solvent or extractant + diluent and solute as well as scintillators were irradiated by low energy γ-ray (E_{max} =60 keV) by using a closed Am 241 source with a well focussed ray. As a consequence of the irradiation of the solvent, low energy electrons were formed by the photo- and Compton effect with an energy spectrum similar to that of tritium. They excited the solvent molecules, which transferred their energy to the primary and to the secondary scintillators (for better energy yield), which emitted this energy as fluorescent light at 300-400 nm. Hence, the external γ-source acted like a solvent label. The advantage of this labelling is that no open radioactive sources are needed. This energy transfer mechanism is disturbed in the pre-

sence of solutes with polar groups (chemical quench). Hence, when the solute was extracted from the droplet, the counting rate increased and, when it was transferred into the droplet, the counting rate diminished as time went on (Halwachs, Schügerl 1983).

A comparison of pulse height density distributions in absence and presence of chemical quench indicated that in the latter case, the distribution shifted to lower energies (pulse heights). This change of fluorescence emission was measured by two photomultipliers. The coincidence pulses of the two multipliers were counted into consecutive channels usually at equidistant time periods of 1 s. However, for measuring the mass transfer during the droplet formation equidistant time periods of 10 ms were used. Usually each run consisted of 1000 to 10 000 measured points. The measuring section consisted of the quartz nozzle with stainless steel grids located upstream from it and a stainless steel hypodermic needle for the formation of a droplet in the nozzle (Fig. 1). In the plane of the freely suspended droplet, a closed Am 241 source was mounted into the nozzle holder, and the two photomultipliers were optically coupled to the nozzle wall. With this setup it was possible to measure the solute concentration in the droplet, consisting of a nonquenching solvent, as a function of time for an extended period of time (several hours) with fixed and freely suspended single droplets, respectively, at different Reynolds numbers. This technique yielded high precision mass transfer data with high time resolution. Though it measured the solute amount by optical method, it did need the problematic sampling procedure of the other experimental techniques.

This method measured the scintillation counts integral over the entire volume of the droplet. An improved version of this method uses the single photon counting (Inuzuka et al. 1985), which allows the measurement of the local scintillation counts. By means of a VIM (Video Intensified Microscopy)-system consisting of a highly sensitive detector and image amplifier (three-stage microchannel plate) and real time processor (Tsuyoshi 1984), all of them leased from Hamamatsu Photonics, Germany, it was possible to evaluate the spacial concentration distributions of the solute in the droplet (for details, see Rhein 1988).

RESULTS

Freely suspended single droplet measurements

The concentration of the solute in the organic phase (droplet) $C_{HAo}(t)$ was measured with the modified liquid szintillation technique as a function of time t, and the mass transfer coefficients K_{tot} were calculated by the relationship for the mass transfer from the organic phase to the aqueous phase:

$$k_{tot} = \frac{d\,C_{HA,o}}{d\,t} \cdot \frac{V_o}{A} \cdot \frac{1}{C_{HA.o}(t)}$$

where A = the droplet surface area and V_o = droplet volume.

Figure 2 shows the variation of k_{tot} with the conversion X in the queous phase for 2-chlor-benzoic acida (2-CBA) at a high pH-value, and Figure 3 shows k_{tot} at a low pH-value. Both of them show the reduction of k_{tot} with an increasing conversion of the solute.
In Figure 4, k_{tot} is shown for the extraction of the solute from the aqueous phase into the organic droplet phase at a low pH as a function of the conversion. With this measuring technique, mass transfer coefficients on freely suspended droplets can be measured with high accuracy.

Liquid membrane emulsion droplet

Preliminary investigations were carried out with single liquid membrane droplets. The scintillators were dissolved in the membrane phase. However, in water/oil emulsions, the counting yield was very low because of the strong optical quench of the emulsion, and the strong chemical quench of the surfactants and carriers. Hence, a highly active Am-241-source (300 mCi) was used. The aqueous phase (0.1 n NaOH) was disperged in the organic phase (with LA-2 carrier, 3 w% Span 80, POP and POPOP scintillators in xylene) at a high stirrer speed (10 000 rpm). Rather rigid droplets were formed from this viscous emulsion. The chemical quench by Span 80, and the carrier and the optical quench by the emulsion were evaluated for each droplet volumina. The optical quench varied from 77,7% (100 μl droplet volume) to 24.8% (10 μl droplet volume). A linear relationship between the specific surface area of the aqueous droplets in the emulsion and the optical quench was detected. This allowed the determination of the interfacial area within the emulsion. With increasing time, the counting rate

increased (in 60 min by a factor of two), which indicates a coalescence of the small droplets and a decrease of the interfacial area (by 40%) within the emulsion drop. This allows the monitoring of the interfacial area in liquid membrane emulsions by an optical method. During extraction, the chemical quench changes due to the solute concentration variation and the optical quench by coalescence. In order to calculate the solute concentration as a function of time, the optical quench must be known. By assuming that the variation of the optical quench is caused by the droplet coalescence is not influenced by the solute concentration, and hence, the latter can be calculated. However, as long as this assumption is not proved, these results cannot be considered as quantitative ones.

Mass transfer on single droplets measured by single photon counting

Since the single-photon-counting technique measures local counts and evaluates a two-dimensional distribution of the counting rates by means of the image amplifier and processor, it is, in principle, possible to evaluate the three-dimensional concentration distribution of the solute within the droplet by means of a mathematical model.

CONCLUSION

The modified scintillation technique allows the measurement of the solute concentration in freely suspended liquid droplets by photomultipliers with high accuracy and high time resolution. By a single photon counting image intensifier processor system, one obtains the two-dimensional distribution of the counting rates in the droplet. In principle, it should be possible to evaluate the spacial distribution of the solute in the droplet by a mathematical model. These techniques can also be applied for the investigation of a liquid membrane droplet. It is possible to monitor the droplet coalescence in the liquid membrane drop by measuring the variation of the optical quench.

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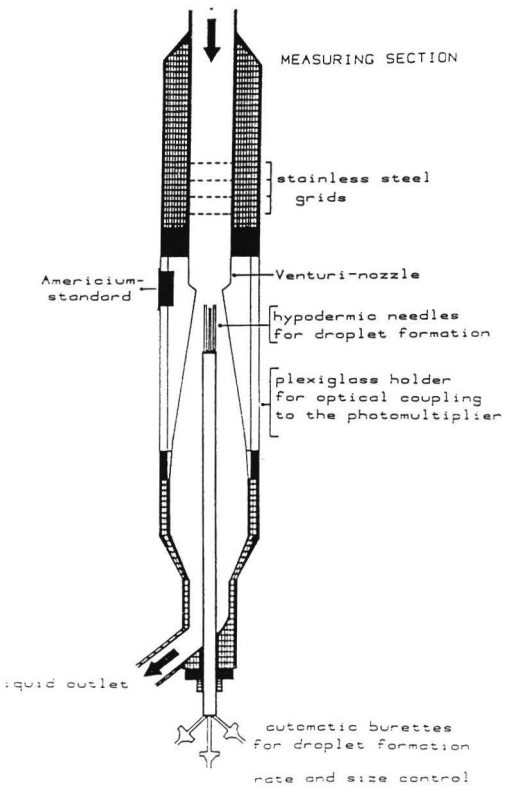


Fig. 1 Nozzle in the measuring section

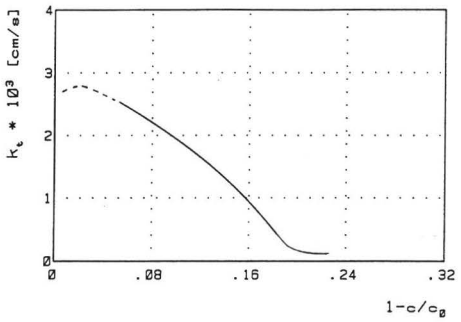


Fig. 2 Masstransfer coefficient k_{tot} for 2-CBA-extraction with 0.1 n NaOH solution from 80 droplet as a function of conversion . Initial concentration of solute in the organic phase 50 mmol/l

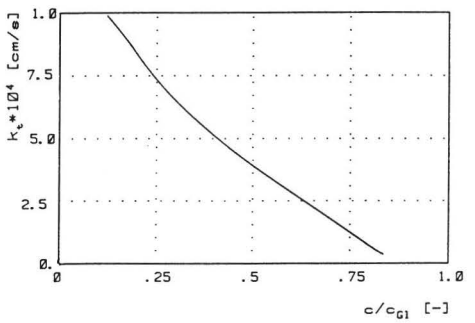


Fig. 3 Masstransfer coefficient k_{tot} for 2-CBA-extraction from the aqueous phase at pH1 into 80 1 droplet
Initial conc. of solute in the aqueous phase: 2 mmol/l

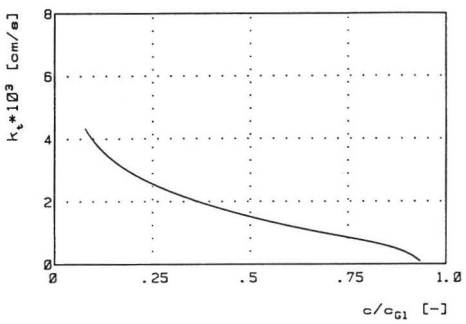


Fig. 4 Masstransfer coefficient k_{tot} for 2-CBA-extraction from the aqueous phase at pH1 into 80 1 droplet
Initial conc. of solute in the aqueous phase: 2 mmol/l, carrier conc.: 50 mmol/LA-2

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INVESTIGATION ON THE EXTRACTION BEHAVIOR OF CARBOXYL CROWN ETHERS FOR URANYL IONS

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ABSTRACT

8 benzocrown ether amidocarboxylic acids and 2 azacrown ether amidocarboxylic acids have been synthesized. New compounds were characterized by IR, NMR, MS. The extraction behavior of some crown ether carboxylic acids in nitromethane for uranyl ion from aqueous solution have been investigated and extraction equilibrium constants were evaluated. Acid dissociation constants and complex formation constants of azacrown ether carboxylic acids for UO_2^{2+}, La^{3+}, Cu^{2+} and other ions have been determined. Effects of substituted group and intramolecular synergistic action of complexing agents have been discussed.

INTRODUCTION

Since the exceptional selectivity of crown ethers for alkali and alkali earth metal cations was reported, quite a lot of papers on the extraction of various metal ions with different crown ethers have been published. However, for neutral crown ether molecule, extractability of metal ion from aqueous solution affects remarkably by the hydrophilic anion followed.

Designing new crown ether extractant to avoid the unfavorable affection of hydrophilic anion have been mentioned by several authors. Cram (1973) reported carboxylic acid derivative of binephthyl crown ether formed very stable coordination compound while it reacted with KOH. Strzelbicki (1981) synthesized 14 crown ether carboxylic acids and investigated their extraction for alkali and alkali-earth metal. They found the extractability of metal ion controlled by a balance between carboxyl and crown ether portions of the complexing agent.

It is reasonable to propose that while the allocation of crown ether and carboxyl portions is in appropriate position, certain crown ether carboxylic acids will exhibit excellent property both in extraction selectivity and extraction ability owing to intramolecular synergism.

Our laboratory found EDTA-diamino-dibenzo-18-crown-6 condensed polymer showed the synergism for the adsorption of uranyl ion (Liu, 1988). This paper reported the synthesis of a series of amido carboxylic acids of different crown and azacrown ethers and the extraction property of these new complexing agents for uranyl ion.

2 EXPERIMENTAL

2.1 Reagents

Dibenzo-18-crown-6, benzo-15-crown-5, benzo-18-crown-6, $(CH_3)_4NOH$, (no less than 10%) and $(CH_3)_4NBr$ were of A.R. grade. Reagents for organic synthesis were all of C.P. grade. Organic solvents and inorganic reagents were of A.R. grade. Glutaric anhydride and adipic anhydride monomer (Julian, 1930) were prepared freshly.

2.2 Apparatus

FTIR spectrometer, 170SX, Nicolet; NMR spectrometer, JEOLFX-90Q, Japan; GC-MS spectrometer, 4510, Finnigan; Organic Element Analyzer, 1106, Carlo Erba(Italy).

2.3 Synthesis

Derivatives of dibenzo-crown ethers

Nitration of dibenzo-18-crown-6 and their reduction were carried out following the description of Feigenbaum's paper(1971). Cis-NDB18C6 m.p. 208-212° C, cis-AmDB18C6 m.p. 179-182° C, trans-NDB18C6 m.p. 243-246° C, trans-AmDB18C6 m.p. 195-198° C.

Amidate reaction was carried out by heating bisamino-dibenzo-crown ether and relevant anhydride in DMF. Cis-product of bis(carboxyl-valeramido)-dibenzo-18-crown-6 was obtained with m.p. 213-217° C, tran-product m.p. 225-229° C.

Cis-bis(carboxyl-propionamido)-dibenzo-18-crown-6 m.p. 205-207° C, trans-product m.p. 247-249° C .

Derivatives of benzo-crown ethers

4-amino-benzo-15-crown-5, prepared following Ungaro's paper(1976), was acylated in toluene with relevant anhydride. 4-(carboxyl-valeramido)-benzo-15-crown-5, m.p. 183-186° C. 4-(Carboxyl-propionamido)-benzo-15-crown-5, m.p. 151-153° C and 4-(carboxyl-butanamido)-benzo-15-crown-5, m.p. 175-176° C.

Derivatives of Monoaza-15-crown-5 and 1,10-diaza-18-crown-6

a. Derivative of monoaza 15-crown-5

Monoaza-15-crown-5 was prepared following Maeda's paper(1983). Purified succinic anhydride was added in 200ml toluene solution of 8g monoaza-15-crown-5. Reactant was heated to 70° C with stirring and reaction processing monitored by TLC. The solvent was evaporated off. N-(Carboxyl-propionyl)-15-azacrown-5 was obtained as colorless sticky liquid after purification with petroleum ether.

b. Derivatives of 1, 10-diaza-18-crown-6

N, N'-Di(carboxyl-propionyl)-cryptand-[2,2]: 1,10-Diaza-18-crown-6 or cryptand-[2,2] was synthesized following Kulstad's paper(1979). White crystale of cryptand-[2,2] was obtained in a yield of 24%, m.p. 112-114° C.

Cryptand-[2,2] was acylated in toluene with purified succinic anhydride. After recrystalization from ethanol, a white solid product was obtained with yield of 51%, m.p. 140-142°C.

N,N'-Di(carboxyl-methyl)-cryptand-[2,2] (Tazaki, 1982): Alcohol solution of cryptand-[2,2], $ClCH_2COOEt$ and triethylene diamine was refluxed for 48 hrs to form the diethyl ester of objective compound. Then hydrolysis was carried out. Recrystalized with 80% EtOH, the objective compound was obtained with m.p. 165-167°C.

2.4 Solvent Extraction

Extraction experiments were carried out in a 10ml centrifugal tube with stopper. CH_3NO_2 was used as the solvent of crown ether carboxylic acids. For DB18C6 derivatives, di-n-butylamine was added to overcome the difficulty caused by slight solubility. Concentration of uranyl ion was determined by Arsenazo III spectrophotometry.

2.5 Determination of acid dissociation constants and complex formation constants

Acid dissociation constants were determined by PH potential titration at 25°C, I=0.1.

Cryptand-[2,2]-dicarboxylic acids dissociate in H_2O in two steps:

$H_2L \equiv\equiv\equiv H^+ + HL^-$ $\qquad k_1 = [H][HL]/[H_2L]$

$HL^- \equiv\equiv\equiv H^+ + L^{2-}$ $\qquad k_2 = [H][L]/[HL]$

While $k_1 >> k_2$, k_1 and k_2 were determined independently in different PH range by the following formula:

$$k_1 = \frac{[H](aC_L+[H])}{C_L-(aC_L+[H])}$$

$$k_2 = \frac{[H]((a-1)C_L-k_w/[H])}{C_L-((a-1)C_L-k_w/[H])}$$

Where a=mols of alkali added/mols of acid, C_L represents initial concentration of acid.

While $k_1=k_2$, these acid dissociation constants were determined by Schwarzenbach's method.

Coordination of crown ether carboxylic acid for metal ions depends on PH value of solution. While a>1.5, the acid will be mainly present in the form of carboxylate ion and the complex equilibrium might be proposed as:

$M^{2+} + A^{2-} \equiv\equiv\equiv\equiv MA$ $\qquad K_{MA}$

If $C_M=C_A$, K_{MA} can be calculated with equation:

$$K_{MA} = \frac{C_A-\alpha[A]}{[A]^2}$$

where $\alpha = \dfrac{[H]^2+k_1[H]+k_1k_2}{k_1k_2}$

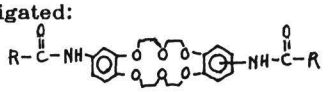
$$[A] = \frac{(2-a)C_A-[H]+[OH]}{2[H]^2+k_1[H]}\, k_1k_2$$

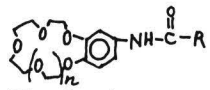
3 RESULT AND DISCUSSION

3.1 Characteristics of crown ether amidocarboxylic acids(be ommited)

3.2 Extraction of crown ether carboxylic acids for uranyl ion

The extraction behavior of following crown ether carboxylic acids have been investigated:





$H_2L(1)$ R=$(CH_2)_2COOH$, cis-
$H_2L(2)$ R=$(CH_2)_2COOH$, tran-
$H_2L(3)$ R=$(CH_2)_4COOH$, cis-
$H_2L(4)$ R=$(CH_2)_4COOH$, tran-

HL(5)R=$(CH_2)_2COOH$, n=1
HL(6)R=$(CH_2)_3COOH$, n=1
HL(7)R=$(CH_2)_4COOH$, n=1
HL(8)R=$(CH_2)_2COOH$, n=2

The influence of aqueous PH value upon the distribution ratio of uranyl ion was examined by holding the initial concentration of crown ether carboxylic acid in CH_3NO_2 constant. Plot of lgD vs. PH shows in Fig1. Fig2 records the variation of lgD as a function of the concentration of crown ether carboxylic acid by holding the equilibrated aqueous PH value constant.

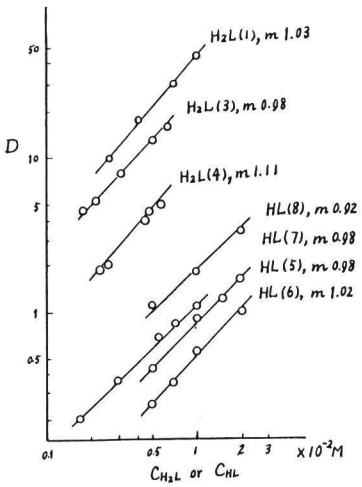


Fig 1 Plot of lgD vs. $LogC_{HL}$(orC_{H2L})

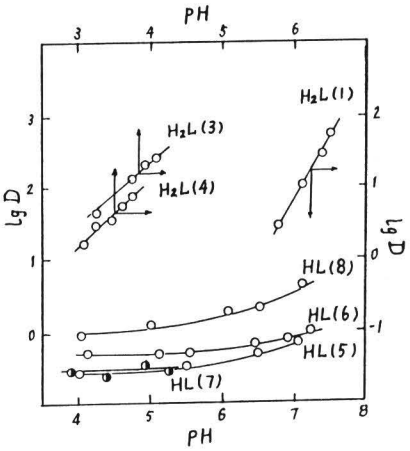


Fig 2 Plot of lgD vs. PH

Experimental results may be summarized as follows:

a. For 7 crown ether carboxylic acids, the plot of lgD vs. lgC are all straight line and the slopes are near by 1. It denotes the complexation ratio of crown ether carboxylic acid to uranyl ion is 1:1.

b. For $H_2L(1)$, the distribution ratio of uranyl ion increased as PH raised. The plot of lgD vs. PH is a straight line with slope near 2. Here the extraction of UO_2^{2+} belongs to acidic complexation extraction which can expressed as

$UO_2^{2+}+H_2L$ === UO_2L+2H^+

$H_2L(3)$ and $H_2L(4)$ extract uranyl ion effectively in lower PH range, the extraction reaction seems to be

$UO_2^{2+}+Cl^-+H_2L$ === $UO_2ClHL+H^+$

Extraction of HL(5), HL(6), HL(7), HL(8) for uranyl ion displayed different regularity. In the range of low PH value. The plot of lgD vs. PH is a straight line of slope 0. While PH raised to 5 to 7, the slope of curve increased. This denotes the extraction of above 4 compounds for uranyl ion is mainly neutral complexation extraction. Only in the neutral region nearby, there exists a small portion of acidic complexation extraction.

c. By comparison of K's, the factors of affecting extraction ability may deduced as: (i) while branch chain keeps the same, the extraction ability of B18C6 is a bit stronger than that of B15C5. Possibly it is because the cavity size of 18-member ring is nearer the diameter of uranyl ion than that of 15-member ring. (ii) length of branch chain with terminal carboxyl group on benzene ring affects extracting power in a negligible extent.

d. Extraction constants lgK_{ex} of benzocrown ethers for uranyl ion were evaluated as: HL(5) 4.45, HL(6) 4.73, HL(7) 4.43, HL(8) 5.0. For dibenzocrown ethers, only conditional extraction constants can be obtained: $H_2L(1)$ 1.68×10^{-11}, $H_2L(3)$ 0.41, $H_2L(4)$ 0.36.

3.3 Dissociation and complexing ability of azacrown ether carboxylic acids

a. N-(3-carboxyl-propionyl)-monoaza-15-crown-5 (HL(9))

Acid dissociation constant and complex formation constants of N-(3-carboxyl-propionyl)-aza-15-crown-5, were determined by PH potentiometry at 25°C and I=0.1. Complex formation constants were carried out in the presence of extra quantity of metal ion and calculated by the following equation:

$$K_{ML} = \frac{C_L-(HL)(1+k_a/[H])}{(HL)^2(1+k_a/[H])(k_a/[H])}$$

LgK's of 7 metal ions varied in the range of 1.16 and 3.23 with a sequence of

$$UO_2^{2+}>Pb^{2+}>Cu^{2+}>Ag^{+}>Tl^{+}>Sr^{2+}$$

Results denoted that the acidity of HL(9) is similar to that of n-butanic acid but weaker than acetic acid. The complexing ability of HL(9) for UO_2^{2+}, Pb^{2+}, Cu^{2+}, Co^{2+} and Sr^{2+} is of the same order comparing with that of acetic acid, and the values of lgK's of HL(9) are higher somewhat.

It implies that the donor atoms of N, O might attend the synergistic complexation with -COOH for metal ions.

b. N,N'-di(carboxyl-propionyl)-cryptand-[2,2] ($H_2L(10)$) and N, N'-di(carboxyl-methyl)-cryptand-[2,2] ($H_2L(11)$)

Dissociation and complex formation constants of these two cryptand-[2,2] carboxylic acids were determined by PH potentiometry.

Results are listed in Tab 1. Dissociation constants k_1 and k_2 differentiate in more than 5 orders for alkylcarboxylic acid $H_2L(11)$, but of the same order for amidocarboxylic acid $H_2L(10)$.

TABLE 1 Complex formation constants of azacrown ether carboxylic acids

H_2L M^{2+}	UO_2^{2+}	La^{3+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}	Ba^{2+}	Sr^{2+}
$H_2L(10)$	5.20	3.32	2.76	2.42	2.38	2.26	2.21	2.21
	±0.14	±0.02	±0.05	±0.09	±0.05	±0.07	±0.08	±0.08
$H_2L(11)$	7.33	7.58	10.98	5.40	5.16	5.82	5.52	5.63
	±0.18	±0.09	±0.28	±0.20	±0.22	±0.19	±0.20	±0.21

$H_2L(10)$: $pk_1=4.40\pm0.06$, $pk_2=5.42\pm0.07$

$H_2L(11)$: $pk_1=2.90\pm0.10$, $pk_2=8.33\pm0.10$

Changing different substituted groups on N atoms of cryptand-[2,2] results in different sequence of complexing ability for metal ions. For cryptand-[2,2] amidocarboxylic acid $H_2L(10)$ the sequence is:

$$UO_2^{2+}>La^{3+}>Cu^{2+}>Ni^{2+},\ Co^{2+},\ Zn^{2+},\ Ca^{2+},\ Sr^{2+},\ Ba^{2+}$$

and for cryptand-[2,2] alkylcarboxylic acid $H_2L(11)$, it appears as:

$$Cu^{2+}>La^{3+},\ UO_2^{2+}>Zn^{2+},\ Sr^{2+},\ Ba^{2+},\ Ni^{2+},\ Co^{2+}>>Mg^{2+}$$

An important fact is that complexing ability of cryptand-[2,2] alkylcarboxylic acid is much stronger than that of crypand-[2,2] amidocarboxylic acid. It can be explained reasonably as the electronic cloud density of N atoms was drastically diminished by the attraction of adjacent carboxyl group and hence the complexing ability of donor N atoms of azacrown ether decreased. It also offers an indirect evidence of the occurrence of intramolecular synergism between carboxyl and azacrown ether portion.

Carrying further investigation on the influence of N-substituted group, cavity size and variety of donor atoms in crown ether will be valuable both in academic and practical respects.

Acknowledge

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POLYMERIZATION AND SOLVATION OF RARE-EARTH DI-(2-ETHYLHEXYL) PHOSPHATES

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ABSTRACT
Trifonov, Yu.I., Legin, E.K. and Suglobov, D.N. Polymerization and solvation of rare-earth di-(2-ethylhexyl) phosphates.

The results of investigation into the structure, solvation and coordination properties of RE di-(2-ethylhexyl) phosphates (LnA_3) are presented. According to X-ray and spectroscopic (IR, luminescent) data, the LnA_3 compounds have a structure of linear rigid-chain coordination polymers consisted of octahedral links connected by alkyl-phosphate bridges. The polymers in crystal lattice are placed parallel each other and interconnected by Van-der-Waals forces. In spite of the low coordination number (6) for Ln^{3+} in LnA_3, the LnA_3 compounds do not accept neutral organic donor ligands and therefore the polar liquids, for instance H_2O, ROH, R_3N, TBP, have adverse effect as solvents. LnA_3 is dissolved in some inert solvents (for example, in CCl_4) and forms liquid crystals. Phase diagram of the system EuA_3 - CCl_4 - $n\text{-}C_8H_{17}OH$ was studied. Unlike the neutral donors, the acid ligands (NO_3^-, Cl^-) are coordinated to Ln^{3+} ions in LnA_3 forming the mixed-ligand complexes. The investigation of spectra, molecular structure and some chemical reactions of these complexes (preferably Eu^{3+}) was performed.

INTRODUCTION

Di-(2-ethylhexyl) phosphoric acid (HA) is widely used in extraction chemistry of rare earth elements. There is a great body of data on distribution coefficients and chemical composition of extracted complexes (Martynov et al., 1978), kinetics and interphase processes (Yagodin et al., 1981). However some important problems on molecular structure and coordination properties of RE di-(2-ethylhexyl) phosphates (LnA_3) remain to be solved. These problems may be best approached by synthesis of complexes formed in extraction process and of related compounds containing A^--anion and by investigation of them. Such approach was mainly used in the present work for Eu^{3+} complexes, because in this case advantage may be taken of the relationship between luminescence spectrum and coordination sphere symmetry (Tsaryuk et al., 1989). However, the results obtained are common to all the series of rare earth elements.

2 EXPERIMENTAL PART

Di-(2-ethylhexyl) phosphoric acid was purified according to the procedure described by Trifonov et al., 1985 . Crystalline powders of LnA_3 (Ln = La, Eu) were synthesized by means of the method Trifonov et al., 1985 . The needle-like samples of LnA_3 crystals for X-ray investigations were grown from the solutions of LnA_3 (Ln = La, Eu) in mixed solvents (CCl_4 - 80 %, $n\text{-}C_8H_{17}OH$ - 20 %) by slow evaporation of CCl_4. The samples of LnA_3 were analyzed by adding 10 ml octane to the portion of ~ 1 g LnA_3 and by contacting with 10 ml HNO_3 (5 M). Then HA and Ln^{3+} were determined by titration in organic and aqueous phases respectively. According to the analytical data, the ratio of Ln^{3+}: A^- is 1 : 3 which corresponds to the formula LnA_3.

IR spectra were recorded on the IRS-29 spectrometer; luminescence spectra were registered on the SDL-2 spectrometer ($\lambda_{excitation}$ = 366 nm). X-ray patterns of the powder samples were registered on Dron - 1M diffractometer (CuK_α). X-ray patterns of crystal samples were recorded in Weissenberg chamber (CuK_α).

2.1 Molecular and crystal structure of LnA_3

X-ray investigation has shown that the crystals of LnA_3 exhibit axial textures. The presence of axial texture indicates that the molecules of LnA_3 and $Nd(O_2P(OC_2H_5)_2)_3$ (Lebedev et al., 1982) have identical structure type with configuration of a linear rigid-chain coordination polymer.

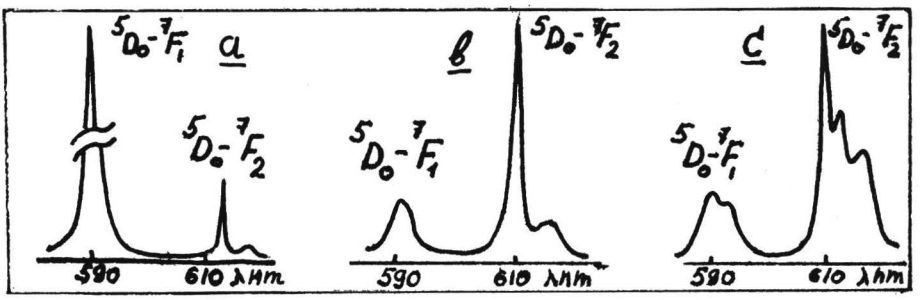


Fig. 1. The luminescence spectra of crystal pattern EuA_3 (a); solution $EuA_2(AHA)$ in octane, $C_{EuA_2(AHA)} = 10^{-2}$ mole/l (b); solution $Eu(AHA)_3$ in octane, $C_{Eu(AHA)_3} = 10^{-2}$ mole/l (c).

Identity period along the axis of texture of LnA_3 (5.3 Å) was determined on X-ray patterns. The character of splitting in luminescence spectra ($^5D_0$ — $^7F_{1,2}$) corresponds to octahedral coordination sphere of Eu^{3+} in EuA_3 (Fig. 1,a). In IR-spectra there are the bands ν_s (PO) = 1090 cm^{-1}, ν_{as} (PO) = 1180 cm^{-1} attributed to PO-vibrations of alkylphosphate in bridge bonds.

Model of the polymer molecule $(LnA_3)_n$ was constructed on the basis of X-ray and spectroscopy data (Fig. 2).

In compliance with the model, Ln^{3+} in LnA_3 ions have octahedral coordination sphere and the faces of neighbouring octahedral links are connected by alkylphosphate bridges. The distance Ln^{3+} - Ln^{3+} calculated from the model is in good agreement with the identity period of texture (5.3 Å). 2 - Ethylhexyl radicals are positioned perpendicular to the polymer axis. The elementary cell (hexagonal) of EuA_3 has the following parameters:

$a = 18.6$ Å; $c = 10.4$ Å; $Z = 2$; $\rho_{exp.} = 1.21$ g/cm^3; $\rho_{calc.} = 1.16$ g/cm^3.

In crystal lattice each molecule EuA_3 is surrounded by six neighbours at a distance of 18.6 Å and connected by Van-der-Waals forces.

2.2 Solvation and state of LnA_3 in non-aqueous solvents

So far as we know, Ln^{3+} ions in LnA_3 are not capable to coordinate the molecules of neutral donors (H_2O, ROH, R_3N, $OP(OR)_3$ etc.). As a result, the molecules of organic solvents can solvate only hydrocarbon radicals of LnA_3. The solvation of radicals is not accompanied by breaking the strong bridge bonds, but may

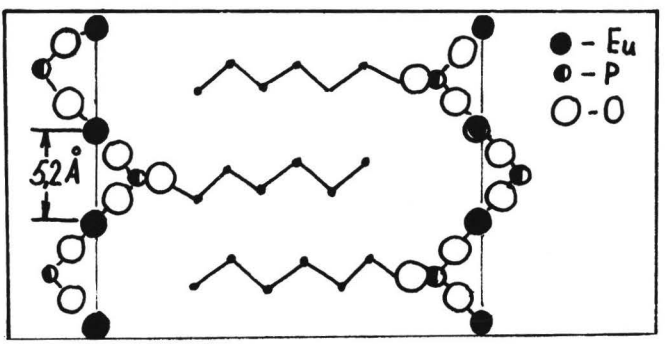


Fig. 2. Structure model of LnA_3 polymer.

disturb the molecular contacts between the chains. For instance, the addition of a very small portion of CCl_4 to LnA_3 crystal (CCl_4 : $LnA_3 \simeq 1 : 100$) leads to the destruction of crystal lattice and the formation of gel. The gel has optical anisotropy which is typical for liquid crystals. When adding CCl_4, the gels are converted to solution which retains anisotropy up to concentration of EuA_3 2 wt %. At lower concentration, the optical anisotropy disappears. When dissolving the polymer molecules of EuA_3, their structure remains unaffected; IR- and luminescence spectra are identical for solutions and crystals of EuA_3.

Polymer length may be evaluated according to theory Flory (Liquid crystal polymers, 1988). Taking into account that the diameter of polymer chain is equal to 26 Å, we obtain the length value of polymer 8000 Å. When polar component ($n\text{-}C_8H_{17}OH$) is added to two-component liquid crystal, three-component liquid crystal is formed, see Fig. 3, zone(M). In mixtures above the zone (M) there are present two phases: mesophase (M) and isotropic one (I). In the region of low concentration of EuA_3 and $n\text{-}C_8H_{17}OH$, the two-phase line passes to a narrow Flory corridor (F).

On addition of a polar component to the mixtures of EuA_3 - CCl_4, qualitative changes in optical textures and sharp decrease of viscosity were observed. As it is seen from IR- and luminescence spectra, these processes do not break the octahedral coordination of Eu^{3+} and bridge bonds.

2.3 Mixed-ligand complexes

We have found that acido-ligands (NO_3^-, Cl^-) can replace the

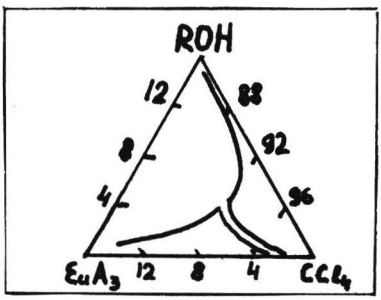


Fig. 3. Phase diagram of the system EuA_3 - CCl_4 - $n\text{-}C_8H_{17}OH$, T = 293 K.

part of A^- anions in LnA_3 to form mixed-ligand complexes. For instance, these reactions give rise to fast dissolution of LnA_3 (Ln = La, Eu) in acetone:

$$EuA_3\ (solid) + 2Eu(NO_3)_3 \cdot 6H_2O \longrightarrow \underset{(I)}{3EuA(NO_3)_2 \cdot 2H_2O} + 6H_2O$$

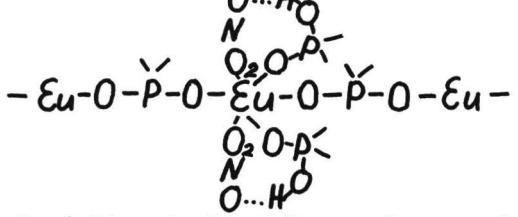
The reaction proceeds completely, and after evaporation of solvent a solid complex of $EuA(NO_3)_2 \cdot 2H_2O$ remains. The complex is dissolved in donor solvents and swells in inert solvents. IR-spectra have the bands of alkylphosphate bridges ($\nu_s(PO)$ = 1090 cm^{-1}; $\nu_{as}(PO)$ = 1170 cm^{-1}) bidentate coordinated NO_3^- anions (1275, 1507, 810 cm^{-1}) and the bands of coordinated H_2O (3400, 1620 cm^{-1}).

When adding the donors (n-octanol, tributyl phosphate, hexamethylphosphoramide etc.), the coordinated molecules H_2O are substituted by donor molecules, forming an anhydrous complex $EuA(NO_3)_2 \cdot 2TBP$ (II). This complex is a monomer; there is a band of bidentate coordinated POO groups as chelate on IR-spectra (1210 cm^{-1}); H_2O bands disappear and the bands of NO_3^- do not vary.

NO_3^- anions in the complex (I) are solvated by HA molecules to give an acid mixed-ligand complex (III):

$$EuA(NO_3)_2 \cdot 2H_2O + 2HA \longrightarrow \underset{(III)}{EuA(NO_3HA)_2}$$

The complex (III) can be also obtained by addition of 10-15 mole/l HNO_3 to suspension of LaA_3 in acetone up to complete dissolution. In IR-spectra of the complex (III) there are the bands of POH in coordinated bianions $(NO_3HA)^-$ (1030 cm^{-1}, 1190 cm^{-1}), bidentate coordinated NO_3^- (1275, 1507, 810 cm^{-1}) and POO bridge bonds (1170 cm^{-1}). These data are in compliance with coordination number Eu^{3+} - 8, as in the case of the complex I, but for an anhydrous one and are in agreement with molecular model



The acid mixed-ligand chloride complex can be obtained by addition of aqueous (10-11 mole/l) or gaseous HCl to suspension of

EuA_3 in acetone:

$$EuA_3 + HCl \longrightarrow \underset{(IV)}{EuA_2(ClHA)}$$

The anhydrous complex (IV)has a polymer structure. IR-spectra exhibit the bands of bianion $(ClHA)^-$ (1030, 1190 cm^{-1}) and the bands of alkylphosphate bridges ($\nu_s(PO)$ = 1090 cm^{-1}, ν_{as} = 1170 cm^{-1}). On luminescence spectra the coordination of Eu^{3+} is present as a deformed octahedron. By addition of water to solution of the complexes (I), (II), (III), (IV) in acetone, the complexes are decomposed with forming a precipitate of solid LnA_3. For instance:

$$EuA(NO_3)_2 \cdot 2H_2O \text{ (acetone)} \xrightarrow{(H_2O)} \underset{\downarrow}{EuA_3} + Eu(NO_3)_3 \cdot xH_2O$$

Interesting mixed-ligand complexes are formed on extraction of lanthanides by HA under conditions of deficient extractant. In it case extract is in equilibrium with precipitated LnA_3:

$EuA_3 + HA \longrightarrow EuA_2(AHA)$ and the ratio of HA : Eu = 5

The complex $EuA_2(AHA)$ is a polymer ($\nu_s(PO)$ = 1090 cm^{-1}; $\nu_{as}(PO)$ = 1180 cm^{-1}) and according to luminescence spectra (Fig. 1,b) Eu^{3+} ions have coordination sphere of a distorted octahedron. At the ratio of HA: $EuA_3 > 200$ monomer complexes of $Eu(AHA)_3$ are formed which according to luminescence spectra (Fig. 1,c), have a prismatic configuration with coordination number 6. Such complexes are formed on extraction of RE by low-loaded extractant.

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THE INFLUENCE OF EXTRACTANTS AND DILUENTS ON THE EXTRACTION OF ACTINOIDS IN THE SYSTEMS WITH HIGH CONTENT OF URANYL NITRATE

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ABSTRACT
Zilberman, B.Ya. and Fedorov, Yu.S., 1990. The influence of extractants and diluents on the extraction of actinoids in the systems with high content of uranyl nitrate.

As tributyl phosphate (TBP) is saturated with uranyl nitrate, the influence of diluent nature (CCl_4, $CHCl_3$, C_6H_6, C_6H_5Cl) on the extraction of tetravalent actinoids and nitric acid decreases; at maximum content of uranium in organic phase this effect is at a minimum.

Under the action of uranyl nitrate, changes in visible spectra of neptunium in organic phase are noted, while no such change occurs in aqueous phase.

The extraction of tetravalent actinoids and nitric acid into extractant saturated with uranyl nitrate at equilibrium with its salt increases for different extractants with increasing their basicity.

INTRODUCTION

The influence of diluents and extractants on the extraction of actinoids was investigated as a rule on systems practically non-saturated with metals (uranium) (Marcus and Kertes, 1969; Shevchenko et al., 1960). However, some works show that the extraction of actinoids and nitric acid by TBP saturated with uranium differs markedly from their extraction in the absence of uranium (Fedorov and Zilberman, 1986, 1988, 1989). This enables to expect changes in the character of the influence of diluents and extractants on the extraction of elements in the systems saturated with uranium.

2 EXPERIMENTAL

Twice-distilled TBP, recrystallized tetradecylammonium (TeDA) and trioctylphosphine oxide (TOPO) purified on anionite were used.

High pure diluents were used.

Concentration of HNO_3 in aqueous and organic phases was determined potentiometrically according to the procedure (Fedorov and Zilberman, 1986). Concentration of uranium was determined by means of vanadatometry, that of neptunium and plutonium - by radiometry or sometimes - by spectrophotometry.

The tests were conducted in separating funnels; phases were separated, centrifuged and then filtered for taking spectra. The tests were performed at 20 °C.

Estimate values of error for the determination of nitric acid are 10 %, uranium - 3 %, plutonium and neptunium - 7 %.

3 RESULTS AND DISCUSSION

On extraction of actinoids in small concentrations (~ 1 g) by TBP, a rather great difference in diluents is observed (Shevchenko et al., 1960), the nature of which is connected with the character of interaction between diluents and TBP. With loading the extractant by uranyl nitrate, the influence of diluent on the extraction of tetravalent Np and Pu decreases (Fig. 1) and disappears practically in the limiting case - equilibrium with solid salt of uranyl nitrate.

The character of diluent effect on the extraction of tetravalent elements (for example Np) by TBP for variable concentrations at saturation with uranyl nitrate is shown on Fig. 2. This figure shows the presence of three specific regions of extraction.

I. 100 - 60 % TBP. The region of sharp drop of Np (IV) distribution coefficients.

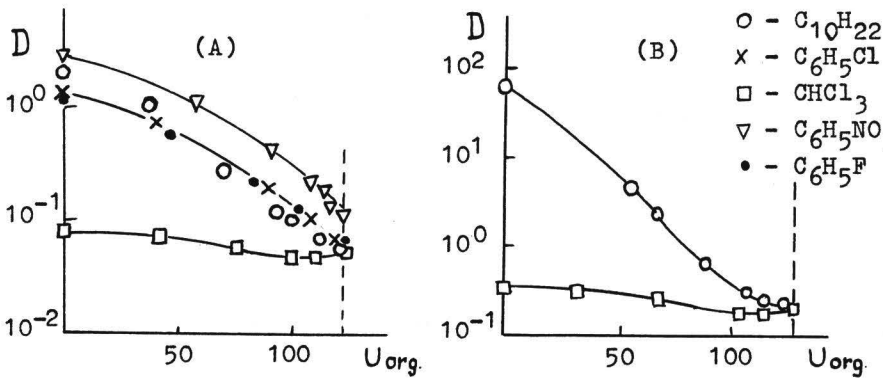


Fig. 1. Dependence of distribution coefficients of tetravalent neptunium (A) and plutonium (B) on extracting into 30 % TBP in different diluents on concentration of uranium in organic phase. Concentration of HNO_3 aq. - 2 M.

II. 60 - 15 % TBP. The region of linear decrease in Np (IV) distribution coefficients.

III. Below 15 % TBP. The region of diluent effect.

Each region seems to be connected with a specific role of diluent in extraction process.

The first region may be associated with the effect of short-range interactions between the molecules of $UO_2(NO_3)_2 \cdot 2TBP$. These forces affect also on the molecules of $Np(NO_3)_4 \cdot 2TBP$ and so its distribution coefficient increases. In this case a diluent plays merely mechanical part: the distance between molecules increases - the force of interaction decreases.

The second region is related to the action of long-range forces, as the main characteristics of Np (IV) extraction are determined by concentration of TBP saturated with uranium, while the diluent nature is unessential. This is true for less polar diluents than $UO_2(NO_3)_2 \cdot 2TBP$ with dipole moment 3.5 D (Michalczik and Hurwic, 1961). Among a series of diluents, nitrobenzene should be noted (4.2 D). Strong-polar nitrobenzene seems to counterbalance the decreased interaction between the molecules of $UO_2(NO_3)_2 \cdot 2TBP$.

In the third region the interaction between the molecules of $UO_2(NO_3)_2 \cdot 2TBP$ disappears and all molecular interactions are dictated by diluent properties.

It should be noted that the distribution coefficients of uranyl nitrate are equal in the region near to the complete saturation of TBP by uranium; this is also true for nitrobenzene.

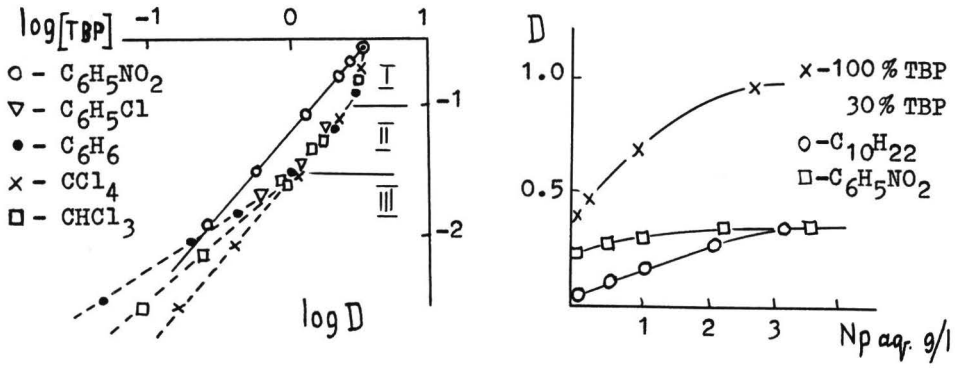


Fig. 2. Dependence of Np (IV) distribution on concentration of TBP saturated with uranium for different diluents. Concentration of HNO_3 aq. - 2 M.

Fig. 3. Concentration dependence of Np (IV) distribution coefficients. Concentration of HNO_3 aq. - 2 M, $U_{aq.}$ - 100 g/l.

Decane and nitrobenzene as diluents differently effect on extraction of actinoids in 30 % TBP from uranium solutions, that results in concentration dependence of distribution coefficients (Fig. 3). Such dependence for n-paraffines as diluents is one of distinctive features for the extraction process of tetravalent actinoids by TBP loaded with uranyl nitrate (Zilberman and Fedorov, 1989). "Anomal" effect of nitrobenzene in this case is difficult to explain by interaction of diluent with hydrated or solvated neptunium nitrate, as nitrobenzene by itself does not practically extract neptunium under the similar conditions. Hence, the diluent seems to act indirectly.

Fig. 4 presents visible spectra which exhibit the changes in spectra of tetravalent neptunium when loading the extract by uranium. Spectra of neptunium in organic phase in the absence of uranium are similar for decane and nitrobenzene, while at the loading with uranium the difference can be observed.

The main effect appears in intensity of a peak with 933 nm wavelength when decane is used. Spectra of neptunium in 100 % TBP saturated with uranium and without it are similar to those of Np in 30 % TBP in nitrobenzene. For aqueous solutions of tetravalent neptunium at a certain concentration of HNO_3, the increase of uranyl nitrate concentration causes no pronounced changes in Np spectra.

The changes in Np spectra in organic phase under the action of uranyl nitrate, as well as by using different diluents are not connected with anion forms of neptunium (because of the absence of corresponding peaks). The observed changes of spectra (Fig. 4) are likely to account for structural pecularities of

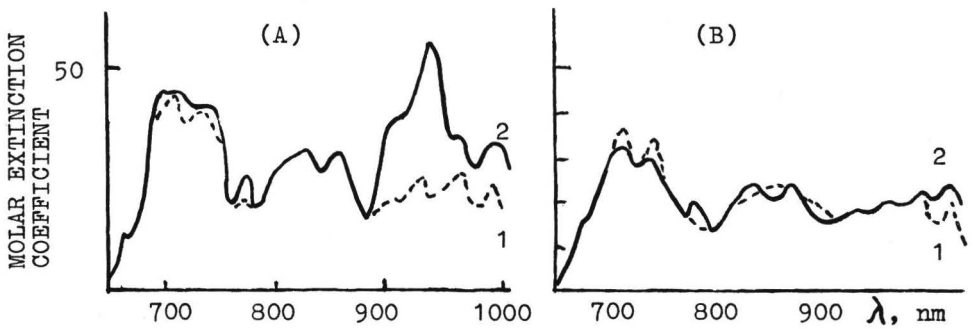


Fig. 4. Absorption spectrum of Np (IV) in 30 % TBP in decane (A) and nitrobenzene (B). Concentration of uranium in organic phase, g/l: 1 - 0; 2 - 120.

organic TBP solutions saturated with uranyl nitrate. Such ordered structure exerts a certain influence on the extraction of neptunium into organic solutions containing high concentrations of uranium, while the effect of diluent in these solutions is quite different from uranium-free systems.

On extracting HNO_3 into 30 % TBP saturated with uranyl nitrate, the most diluents have no effect.

Fig. 5 shows the extraction of nitric acid by different extractants saturated with uranyl nitrate up to equilibrium with solid salt. Concentrations of extractants are selected according to equal concentrations of uranyl nitrate in organic phase, i.e. the concentration of TeDA is one half as much as that of TBP and TOPO. In the absence of uranyl nitrate, these extractants in equal concentrations extract nitric acid in 5 - 10 M range nearly in equal measure (when filling the capacity of "free" extractant by one molecule of acid), i.e. the extraction is performed as if by monosolvates of nitric acid with extractants. The more unexpected high distribution coefficients of nitric acid in TeDA saturated with uranium proved to be; these values are rather higher than those for other extractants (TBP, TOPO) and higher by a factor of 4 than on extracting by TeDA of the same concentration, but in the absence of uranyl nitrate. For TOPO and TBP saturated with uranium, the distribution coefficients of nitric acid are one fourth as high as in the absence of uranium, i.e. a reverse effect is observed.

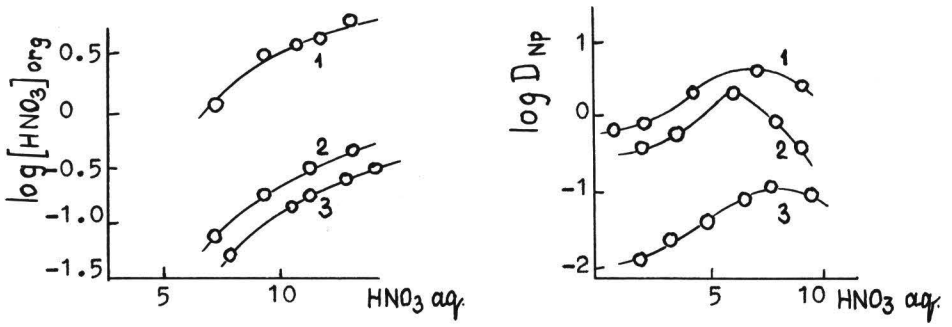


Fig. 5. Extraction of HNO_3 into different extractants saturated with uranium at equilibrium with its solid salt. Concentration of Uorg. - 60 g/l. Diluent CCl_4. 1 - TeDA (0.24 M); 2 - TOPO (0.53 M); 3 - TBP (0.53 M).

Fig. 6. Extraction of Np (IV) into different extractants saturated with uranium up to equilibrium with its solid salt. Concentration of Uorg. - 60 g/l. Diluent CCl_4. 1 - TOPO (0.53 M); 2 - TeDA (0.24 M); 3 - TBP (0.53 M).

In this case it is seen from IR-spectra that the state of nitric acid in TBP and TeDA saturated with uranium is similar and corresponds to the state of anhydrous nitric acid.

Such difference in extractability of nitric acid seems to be connected with uranyl form in organic phase. In the case of TBP and TOPO, uranium is present in the form of non-ionized disolvates, in the case of TeDA - as trinitrate (anion) complex of uranyl. It is evident that this form of uranyl has more affinity with nitric acid.

Fig. 6 shows the extraction of tetravalent neptunium into different extractants saturated with uranyl nitrate. At equal concentrations of nitric acid, the distribution coefficients of neptunium for different extractants saturated with uranium may be presented as follows: TBP : TeDA : TOPO $\approx$ 1 : 20 : 40; in the absence of uranyl nitrate these ratios for 2 M HNO_3 show the difference as the following: TBP : TeDA : TOPO $\approx$ 1 : 50 : 500.

So, when saturating the different extractants with uranyl nitrate, the difference in neptunium extractability decreases significantly. It should be noted that the concentrations of extractants, 0.53 M TBP and TOPO as well as 0.29 M TeDA, are established in accordance with uranium concentration in organic phase and therefore the distribution coefficients of uranium are the same for these concentrations of extractants.

The extraction of neptunium into extractants saturated with uranium (Fig. 6) is not correlated with the extraction of nitric acid in the same extractants under the similar conditions (Fig. 5).

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THERMODYNAMIC ASPECTS OF CHANGES IN ELECTRON-DONOR ABILITY OF HALOGENACETATE IONS AND EXTRACTION EQUILIBRIA

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ABSTRACT
Baluev, A.V., 1990. Thermodynamic aspects of changes in electron-donor ability of halogenacetate ions and extraction equilibria.

The results of calculations are presented for same thermodynamic characteristics of metal halogenacetates. Thermodynamic data have been analyzed for extraction parameters of the systems halogenacetate - water - TBP.

INTRODUCTION

In Baluev' works (1985, 1988) a thermochemical cycle was proposed and calculations were performed for thermodynamic characteristics of some halogenacetate ions and acetate ions, as well as lattice enthalpies of corresponding uranyl salts from experimental thermochemical data on standard formation enthalpies of salts ($\Delta H^{o}_{f,298}$), the data on gaseous uranyl ion (Marcus, 1975) and dissociation enthalpies of acids in gaseous state (ΔH^{o}_{D}) according to Cuming and Kibarle (1978). Near to linear character of dependencies for lattice enthalpies ($\Delta H_{lat.}$) of uranyl carboxylates and ΔH^{o}_{D} values of acids on Edwards parameter (H) (see Fig.), i.e. actually on logarithm of dissociation constants of acids in water, enables to suppose conservation of analogous dependencies for carboxylate of other metals. So, it is possible to calculate lattice enthalpies of halogenacetates, if the standard formation enthalpies of anhydrous nitrate and acetate of appropriate metal are available. The allowance for conservation of linear character of dependence under consideration for other crystalline carboxylates seems to be confirmed not only by the experimental dependencies mentioned-above but also by structural data on the coordination character of one-based carboxylate ions.

2 RESULTS AND DISCUSSION

Lattice enthalpy is defined as formation enthalpy of salts from gaseous ions under normal conditions, i.e. it can be expres-

sed as follows:

$$\Delta H_{lat.}^{MA_{n(c)}} = \Delta H_{f,298}^{o\,MA_{n(c)}} - \Delta H_{f,298}^{o\,M^{n+}_{(g)}} - n\Delta H_{f,298}^{o\,A^-_{(g)}} \quad (1)$$

where M^{n+} - cation, A^- - anion, c - crystalline state, g - gaseous state.

The equation (1) permits to carry out a reverse calculation of $\Delta H_{f,298}^{o\,MA_{n(c)}}$ from the known values of $\Delta H_{lat.}$. Since the uncertainty for $\Delta H_{f,298}^{o\,M^{n+}_{(g)}}$ given in reference books and scientific works is rather greater than for the values of formation enthalpies of cations in aqueous solutions in standard state ($\Delta H_{f,298}^{o\,M^{n+}_{sol.H_2O}}$), it is reasonable to introduce a function $\Delta H'_{f,298}{}^{MA_{n(c)}}$ as formation enthalpy of crystalline salt from cations which are present in aqueous solution in standard state and gaseous anions.

$$\Delta H'_{f,298}{}^{MA_{n(c)}} = \Delta H_{f,298}^{o\,MA_{n(c)}} - \Delta H_{f,298}^{o\,M^{n+}_{sol.H_2O}} - \Delta H_{f,298}^{o\,A^-_{(g)}} \quad (2)$$

The values of $\Delta H'_{f,298}$ for nitrates and acetates with the value of $\Delta H_{f,298}^{o}$ were calculated by equation (2). The initial data and calculation results are given in Tables 1 and 2. Then the values of $\Delta H'_{f,298}$ for halogenacetates of appropriate metals were determined by plotting (Fig.). The standard enthalpies for the formation of these compounds were calculated by using the transformed equation (2); by means of the equations (1) and (2) the lattice enthalpies of the compound under consideration were determined (Fig., Table 2). It should be noted that among the studied anions, besides the salts in the Table 2, the analogous values were obtained for compound of practically all alkaline metals, alkaline earth metals, some transition d-elements, as well as of tin, lead, europium, gadolinium and silver.

TABLE 1

Standard formation enthalpies of some cations in gaseous state at 0 K, at 298 K and in aqueous solution in standard state (kJ/mole). The data were taken from Glushko (1965-1982) or calculated from these data.

Cation	$\Delta H_{fo}^{o\,M^{n+}_{(g)}}$	$\Delta H_{f,298}^{o\,M^{n+}_{(g)}}$	$-\Delta H_{f,298}^{o\,M^{n+}_{sol.H_2O}}$
Na^+		609.6 ± 0.7	240.4 ± 0.1
Sr^{2+}	1775 ± 2	1781 ± 5	551.5 ± 0.6
Ba^{2+}	1648 ± 3	1654 ± 5	524 ± 2
Sm^{3+}	4075 ± 29	4083 ± 29	690 ± 3

TABLE 2

Standard formation enthalpies of salts, $\Delta H'_{f,298}$ functions and lattice enthalpies of some carboxylates and nitrates (kJ/mole).

Compound	$-\Delta H_{f,298}$	$\Delta H'_{f,298}$	$-\Delta H_{lat.}$
$NaNO_3$	468.2 ± 0.5[1]	101 ± 6	749 ± 6
$NaCF_3CO_2$	1328 ± 9	96 ± 9	754 ± 9
$NaCCl_3CO_2$	753 ± 9	89 ± 9	761 ± 9
$NaCH_2ClCO_2$	738 ± 9	65 ± 9	785 ± 9
$NaCH_3CO_2$	708.7 ± 0.5[1]	40 ± 9	810 ± 9
$Sr(NO_3)_2$	984 ± 1[1]	225 ± 9	2107 ± 10
$Sr(CF_3CO_2)_2$	2706 ± 13	213 ± 13	2120 ± 14
$Sr(CCl_3CO_2)_2$	1561 ± 13	195 ± 13	2138 ± 14
$Sr(CH_2ClCO_2)_2$	1543 ± 13	134 ± 13	2199 ± 14
$Sr(CH_3CO_2)_2$	1498 ± 4[1]		
$Ba(NO_3)_2$	979 ± 2[1]	203 ± 9	1975 ± 10
$Ba(CF_3CO_2)_2$	2699 ± 13	192 ± 13	1986 ± 14
$Ba(CCl_3CO_2)_2$	1552 ± 13	176 ± 13	2002 ± 14
$Ba(CH_2ClCO_2)_2$	1526 ± 13	123 ± 13	2055 ± 14
$Ba(CH_3CO_2)_2$	1473 ± 4[1]	68 ± 13	2110 ± 14
$Sm(NO_3)_2$	1210.8 ± 0.8[2]	464 ± 12	4308 ± 31
$Sm(CF_3CO_2)_2$	3802 ± 12	438 ± 12	4335 ± 31
$Sm(CCl_3CO_2)_2$	2096 ± 12	400 ± 12	4373 ± 32
$Sm(CH_2ClCO_2)_2$	2108 ± 14	268 ± 14	4505 ± 32
$Sm(CH_3CO_2)_2$	2086.2 ± 1.4[3]	129 ± 15	4643 ± 33

[1] Glushko (1965-1982).
[2] Del Pino et al. (1980).
[3] Batkibekova et al. (1978).

Table 3 presents hydration enthalpies (ΔH_h) of cations and anions under study. These values were defined as difference in formation enthalpy of ion in aqueous solution (in standard state) and of the same ion in gaseous state under the normal conditions taking into account the absolute value of $\Delta H^{o}_{f,298} H^{+}_{sol.H_2O}$ (Marcus, 1975) (445 ± 7 kJ/mole). Figure shows the ΔH_h dependence of ani-

TABLE 3

Hydration enthalpies of some anions and cations (kJ/mole).

Anions		Cations	
NO_3^-	324 ± 6[1]	UO_2^{2+}	1361 ± 23[1]
$CF_3CO_2^-$	348 [2]	Sr^{2+}	1442 ± 5
$CCl_3CO_2^-$	357 ± 9	Ba^{2+}	1288 ± 5
$CH_2ClCO_2^-$	384 ± 9	Sm^{3+}	3437 ± 29
$CH_3CO_2^-$	422 ± 9		

[1] Marcus (1975).
[2] Plotted (Fig.).

ons on Edwards parameter of corresponding acids. The linearity of this dependence permits to affirm that entropy effects of hydration in the investigated series are practically constant. For such extraction system as salt - water - TBP the following expression may be described:

$$\Delta G_{extr.} = -\Delta G_{sol.H_2O} + \Delta G_{solv.TBP} + \Delta G_{sol.TBP} + \Delta G_{dil.H_2O} \quad (3)$$

(where $\Delta G_{extr.}$ - free energy for extraction of salt into TBP; $\Delta G_{sol.H_2O}$ - as reffered to dissolution of salts in water, $\Delta G_{solv.TBP}$ - solvation of TBP salt, $\Delta G_{sol.TBP}$ - solution of solvated complex in TBP, $\Delta G_{dil.H_2O}$ - dilution of salt solution in aqueous phase). In rather diluted solutions the value of $\Delta G_{dil.H_2O}$ may be neglected. In the series of salts under study the value of $G_{sol.\ TBP}$ seems to be considered as a constant value. If solvation entropy is thought to vary little within carboxylate series (at least for cations of the same charge), so, taking into account the conclusions by Cuming and Kebarle (1978) and the data by Marcus (1973, 1975), the following expression may be described:

$$\delta\Delta G_{extr.} = -\delta\Delta H_h M^{n+} - \delta\Delta H_h A^{-} + \delta\Delta H_{lat.}{}^{MA_{n(c)}} + \delta\Delta H_{solv.TBP}{}^{MA_n} \quad (4)$$

(The sign δ denotes variation in value of transition to other cation or anion within the considered series).

The changes in values from expression (4) make allowance for variations in electron-donor ability of carboxylate ions under consideration. Tables 4 and 5 present concentration constants of

TABLE 4

Extraction systems of uranyl salt - water - TBP (maq = 0.01 mole/kg). Calculations from Baluev and Suglobova (1981) data.

Salt	$\tilde{K}_N$	$RT \cdot \ln \tilde{K}_N$, kJ/mole
$UO_2(NO_3)_2$	$1.08 \cdot 10^8$	46
$UO_2(CF_3COO)_2$	$2.81 \cdot 10^9$	54
$UO_2(CCl_3COO)_2$	$9.52 \cdot 10^9$	57
$UO_2(CH_2ClCOO)_2$	$2.04 \cdot 10^8$	47
$UO_2(CH_3COO)_2$	$3.64 \cdot 10^7$	43

TBP - tri-n-butylphosphate;
maq - molality of salt in aqueous phase;
$\tilde{K}_N$ - concentration extraction constant.

extraction which were calculated from the data by Baluev and Suglobova (1981) and then recalculated as $RT \cdot \ln K_N$ for convenient comparison with enthaply changes; this is an energetic expression of experimentally observed concentration constants and for the salts with cations of the same charge in TBP systems it takes likely account of changes in distribution coefficients as well. It should be noted that Marcus and Koloric (1973) have determined a true thermodynamic value of $\Delta G_{extr.}$ of uranyl nitrate into TBP (-41.0 ± 0.5 kJ/mole) what differs insignificantly from the value given in Table 4, with assumptions taken into consideration.

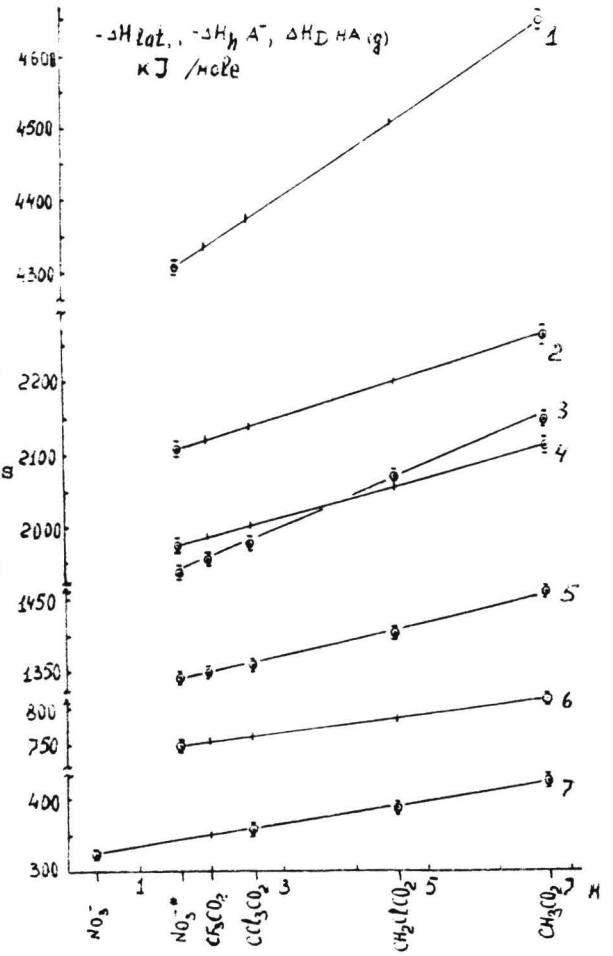


Fig. Lattice enthalpies of some saltes, hydration enthalpies of anions and dissociation enthalpies of corresponding acids in gaseous state as functions of Edwards parameter of acids. $-\Delta H_{lat.}$: 1 - SmA_3; 2 - SrA_2; 3 - UO_2A_2; 4 - BaA_2; 6 - NaA. ΔH_hA^- - 7; $\Delta H_DHA(g)$ - 5. * - corrected Edwards parameter for nitric acid (Baluev (1985, 1988)).

As it seen from the tables, when passing from barium trichloracetate to strontium trichloracetate, a gain in variation of $\Delta H_{lat.}$ (-136 ± 18 kJ/mole) (see equation (4)) is compensated by $\delta\Delta H_h$ (Ba^{2+} - Sr^{2+}) = (154 ± 7) kJ/mole. The circumstance that strontium trichloracetate has even so appreciable extraction constant, although a lesser one than in the case of analogous barium complexes, should be connected with increased negative value of $\Delta H_{solv.TBP}$ for strontium salt as compared with barium, what is in agreement with the known data on polarizing action of

TABLE 5

Extraction systems of trichloracetate - water - TBP at 25 °C.

Salt	α_m	$\tilde{K}_N$	RT·ln $\tilde{K}_N$, kJ/mole
$Ba(CCl_3CO_2)_2$ [1]	0.19	$1.9 \cdot 10^6$	36
$Sr(CCl_3CO_2)_2$ [1]	0.12	$1.2 \cdot 10^6$	35
$Sm(CCl_3CO_2)_3$ [1]	16	$1.6 \cdot 10^{11}$	63
$Sr(CCl_3CO_2)_2$ [2]	1.1	$5.8 \cdot 10^7$	39
$Ba(CCl_3CO_2)_2$ [2]	2.0	$1.1 \cdot 10^8$	40
$UO_2(CCl_3CO_2)_2$ [2]	35	$5.2 \cdot 10^8$	50

1) $m_{aq} = 0.034$.
2) $m_{aq} = 0.15$

cations. In passing from barium trichloracetate to uranyl trichloracetate, extraction constant increases sharply (Table 5). As it is seen from the tables, even taking into account the significant uncertainties, both $\delta_{\Delta H_{lat.}}$ and $\delta_{\Delta H_h} M^{2+}$ in the series of Ba^{2+} - UO_2^{2+} should decrease markedly the extraction constant. This fact is fairly explained by compensating change in solvatation enthalpy, what is supported by many works on the chemistry of uranyl compounds.

The presented examples for thermodynamic analysis of data on extraction do not exhaust a great body of thermodynamic information obtained and we hope to carry on further correlation of these data with investigations of extraction equilibria.

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2. EXTRACTANTS AND DILUENTS

Solvent Extraction 1990, T. Sekine (Editor)

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NEW EXTRACTANTS FOR THE NUCLEAR HYDRO-METALLURGY.

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ABSTRACT
This paper is a review of the features of some new extractants having a potential interest for the chemical separations of the nuclear industry. Extractants of actinides and lanthanides ; alkaline and alkaline earths as well as fission products platinoïds Ru, Rh, Pd, will be considered. Emphasis will be put on the extractants which generate the smaller amounts of non incinerable wastes.

INTRODUCTION

The development of the nuclear energy for electricity production is submitted to the proper management of the radioactive wastes. The spent fuels reprocessing and the others chemical separations performed for a best utilization of the fissile materials generate secondary wastes. In nowadays processes using liquid-liquid extraction, the solvent contributes strongly to the production of uncompressible nuclear wastes, because organophosphorus molecules such as tributylphosphate are used. Such spent extractants produces radioactive P_2O_5 when they are incinerated. In addition the restoration of the solvents, necessary because of the nature of the main degradation products ; dialkylphosphoric acid is another source of uncompressible wastes, because inorganic salts solutions are used to clean-up the degraded organic solutions.

New extractants could be also necessary because of changes in the goals of the spent fuels reprocessing. Nowadays only U and Pu are separated from the spent fuels and the rest of the fuels representing the majority of the radioactivity is stored (see figure 1.1). Another policy could be to recycle the long half-lives radionuclides in order to transmute then into shorter half lives radioisotopes. To do so, new chemical separations methods must be set up. An example of such fuels cycle is given figure 1.2.

The fission products of ^{235}U and ^{239}Pu contain highly valuable platinoïds (Ru, Rh, Pd). If these metals are recovered solvent extraction might play a role in the separations.

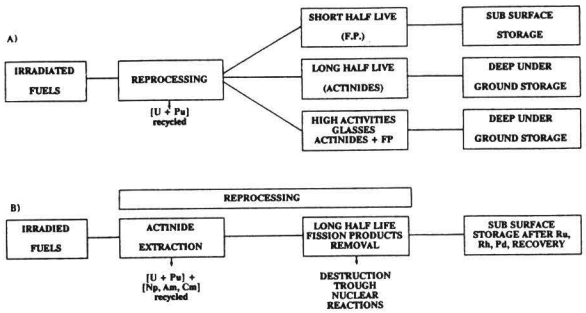


Fig. 1. Existing (A) and possible (B) future back-end of the nuclear fuels cycle

So this paper is a review of the extraction chemistry of the actinides and lanthanides ions by N,N-dialkylamides (R_2 N CO R')and by N,N'-tetraalkyle 2-propane diamides (($RR'N\ CO)_2$ CH R")which can help to limit the wastes in the existing nuclear plants.

The prospects for trivalent actinides-lanthanides group separation, use full for the advanced nuclear fuel cycles including the recycle of minor actinides (Am, Cm, Np) will be given. Cs^+ and Sr^{2+} separations by solvent extraction also suitable for complete reprocessing will be discussed. Finally the Ru, Rh and Pd removal from radioactive wastes and the possible application of solvent extraction for their separation will be described.

ACTINIDES AND LANTHANIDES EXTRACTANTS

The f series ions are "a" hard acceptors, so their stronger bonds are formed with the ligands possessing the higher electronegative donors. For comparable extractants the sequence of affinity is (O > N > S) ; for example the dialkylphosphoric acids ($(RO)_2POOH$) are better extractants than the dialkyldithiophosphoric acids ($(RO)_2PSSH$).Many organophosphorus molecules have been investigated as actinides or lanthanides extractants and it is out of the scope of this paper to review their properties. Tributylphosphate (TBP) is used for U purification from ores or from spent nuclear fuels. A rather new bifunctionnal extractant $C_8H_{17}\ C_6H_5\ PO\ CH_2\ CON(CH_2\ CH(CH_3)_2)$ (CMPO) developped by Horwitz et al. will be employed in the United States for military wastes declassification. However the phosphoryl moiety leads by radiolysis or hydrolysis to acidic extractants which precludes easy back-extraction of metals ions. The last step of these degradations is H_3PO_4 so the availability of completely incinerable extractants which do not form radiolytic or hydrolytic products disturbing the extraction or desextraction is suitable.

2. N,N-DIALKYLAMIDES (R_2 CONR")

Feder and short after Siddall proposed these extractants one alternative to TBP for the back-end of the nuclear fuel cycle. Gasparini et al. in Italy showed that N,N-dialkylamides were suitable extractants regarding their extraction chemistry and their physical properties for the spents nuclear fuels reprocessing. In the Soviet Union, many workers (Laskorin et al.) investigated the extractive properties of N,N-dialkylamides. However many advantages of N,N-dialkylamides such as : complete incinerability, no disturbing degradation products, better selectivity were balanced by the rather low solubility of dinitrato uranyle amides complexes into aliphatic hydrocarbons. Musikas et al. showed that β branched N substituents amides nitrato uranyle salts are highly soluble in hydrocarbons (see Table 1). This improved solubility has been attributed to the steric hindrance added in the proximity of the amide nitrogen ; because the easy splitting of the organic phases seems due to the interactions amide-nitrato uranyle amide complexe in the second coordination sphere of the complexes. This interaction prevails upon the second sphere diluent-metallic complex interaction.

TABLE 1.
Solubility of $UO_2(NO_3)_2$ in various N,N-dialkylamides solutions into TPH.

Amide	Organic solubility ($U\ g.l^{-1}$)	Aqueous acidity C^{aq}_3
$(C_4H_9)_2NCOC_{11}H_{23}$	80 71	0 4
$(C_2H_5CH(CH_3))_2NCOC_{11}H_{23}$	64 36	0 4
$(C_4H_9\underset{C_2H_5}{CH}-CH_2)_2NCOC_5H_{11}$	> 120	0 and 4
$(C_4H_9\underset{C_2H_5}{CH}-CH_2)NCOCH_3C(CH_3)_3$	> 120	0 and 4

2.1. Extraction chemistry of the N,N-dialkylamides

2.1.1. N,N-dialkylamides are stronger bases than TBP. They are titrated by $HClO_4$ in an acetic anhydride medium, unlike TBP. The solubility of water into amides hydrocarbon solutions is about ten times less than in equimolar TBP solutions. As, with TBP, HNO_3 is extracted by N,N-dialkylamides by forming the species $HNO_3.(Amide)_2$, $HNO_3.Amide$, $(HNO_3)_2Amide$. The infra-red spectra of $(Amide)_x.(HNO_3)_y$ adduct indicate that the HNO_3 and Amide are bond

by hydrogen bonds. In $(HNO_3)_x$.Amide where x > 1 ; the second and third molecule of HNO_3 are bond to the first HNO_3 attached to amide. Unlike TBP amides do not extract H_2SO_4, HCl or $HClO_4$; this has been correlated to the poorer affinity of amides for water which is coextracted with theses acids contrary to HNO_3 which is weaker and is transferred dehydrated (N. Condamines et al., 1988).

2.1.2 The actinides ions are extracted from diluted nitric acid solutions (0 to 2N) as they are extracted by TBP : U(VI) form the species : $UO_2(NO_3)_2(Amide)_2$. Amide representing either $(C_4H_9CHC_2H_5CH_2)_2NCOCH(CH_3)_2$ (DOiBA) or $(C_4H_9$ CH C_2H_5 $CH_2)_2$ N CO C_3H_7 (DOBA) a branched N,N-dioctylbutylamide or linear N,N-dioctyramide. For Pu^{4+} branched or linear chain amide form different species. One have : $Pu(NO_3)_4$ $(DOiBA)_3$ and $Pu(NO_3)_4$ $(DOBA)_2$. Extraction from more acidic solutions (C_{HNO3} > 2N) leads to : $UO_2(NO_3)_3H$.Amide and $Pu(NO_3)_6$ H_2.$(Amide)_2$ in which the metal is completely surrounded by nitrate ions.

The percentage of the anionic complexes of U(VI) and Pu(IV) in the organic phase as a function of the aqueous acidity are given Figure 2.

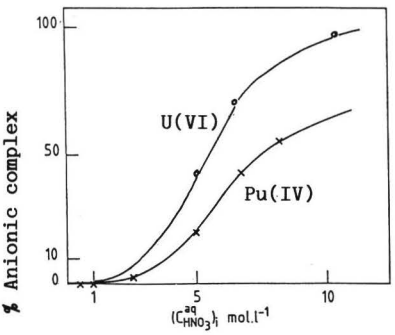


Fig. 2. % of $UO_2(NO_3)_3$ $H(DOBA)_x$ and $Pu(NO_3)_6$ H_2 $(DOBA)_y$ into 1.02 M DOBA in TPH as a function of the aqueous acidity.

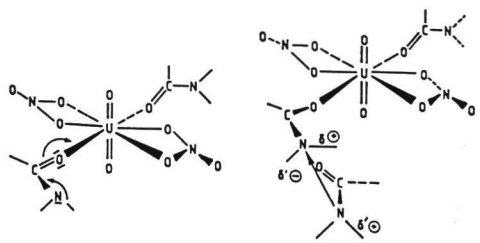


Fig. 3. Schematic representation of the $UO_2(NO_3)_2(Amide)_2$ complexe and $[UO_2(NO_3)_2(Amide)_2]$.Amide outer-sphere complexe.

Unlike TBP the slope of log D_M vs log C_{Amide} is very different from the number of solvate in the first coordination sphere of the organic complexes. Table 2 give some examples of the data obtained. This behaviour has been attributed by Condamines (1990) to non-oriented second sphere interactions between the CON groups binded to the metallic complexes and free amide as shown Figure 3. The π character of the amide moiety is responsible for this interaction due to higher transfer of electrons from N to O in the bonded amide, leaving a higher positive charge on nitrogen. The value of the slopes log D_M vs log C_{Amide} are lower for the N,N-dialkylamides with hindered nitrogens.

TABLE 2.

Slopes of log $D_{U(VI)}$ vs log C^{org}_{Amide}

Extractant	Diluent	Organic complexe	Slope
$(C_4H_9)_2$ NCO $C_{11}H_{23}$	t-butylbenzene	$UO_2(NO_3)_2(Amide)_2$	2.67
$(C_4H_9)_2$ NCO C_3H_7	decane	$UO_2(NO_3)_2(Amide)_2$	2.7
$[C_2H_5-CH(CH_3)_2]_2NCO$ $C11H_{23}$	t-butylbenzene	$UO_2(NO_3)_2(Amide)_2$	2.15
$[C_4H_9$ CH - $CH_2]_2NCO$ C_5H_{11} C_2H_5	dodecane	$UO_2(NO_3)_2(Amide)_2$	2.35

The achievement in the way of an eventual replacement of TBP by amides in France is illustrated by the results presented by Musikas et al. in a poster in session 3 of this meeting.

3. N,N-TETRAALKYLE PROPANE DIAMIDES

Many liquid radioactive wastes belong to the transuranium wastes category which must be stored in deep geogical repositories because they contain more than 3.7 10^3 Bq of α activity per gram. It is interesting to convert these wastes into wastes storable in near surface disposals. The TRUEX process developped by Horwitz and Schulz will be used for this purpose in the United States. The N,N-tetraalkyle alkyle propane diamides $(RR'NCO)_2$ CHR" (DIAM) have been investigated by Musikas et al. as actinides extractants included the trivalent ones. These last ones are the more difficult to extract from acidic nitrate solutions, also the substituents R, R', R" have been choosen as a function of Am(III) extraction (see Table 3). The extraction chemistry of DIAM has been investigated for Ln(III) or Am(III) for U(VI) and for HNO_3. The trivalent ions are extracted by diamides under the complexes : $M(HNO_3)_3$.DIAM (I) $M(NO_3)_3$ $(DIAM)_2$ (II). In the lanthanide serie the proportion of complex I/II varies inversely with the ionic radius. UO_2 is extracted as $UO_2(NO_3)_2$.DIAM. The acidic complex $UO_2(NO_3)_3H$ (DIAM) has not been observed probably because of the unfavorable competition DIAM-NO_3^- to occupy the first coordination sphere of UO_2^{2+} for the third NO_{3-}.

As for the monoamides the species $(DIAM)_2.HNO_3$, DIAM-HNO_3 and DIAM $(HNO_3)_2$ have been observed. IR evidence for this feature is shown figure 4. The larger low wave number shift and the fact that IR spectrum of extracted $HClO_4$, a stronger acid, than HNO_3 shows up the 1510 cm^{-1} band attributed to $-COH^+$ stretch in $(HNO_3)_2$.DIAM support this interpretation. The degre of development achieved for the diamide extractant from the practical point of view is

illustrated by the results given in the poster of Musikas et al. of session 3 of this conference.

TABLE 3.
Influence of the substituents R, R', R" of (R R' NCO)$_2$ CHR"(DIAMIDES) upon the distribution ratios of Am(III) between nitric acid solutions and 0.5M diamide into t-butylbenzene or benzene.

R"	R	R'	$D^{*}_{Am^{3+}}$	Diluent	C $^{aq*}_{HNO_3}$
H	C_6H_{13}	C_2H_5	0.11	benzene	2 to 3
H	C_4H_9	C_4H_9	0.18	benzene	2 to 3
H	C_3H_7	C_8H_{17}	0.45	benzene	2 to 3
H	CH_3	C_4H_9	0.55	benzene	2 to 3
H	CH_3	C_8H_{17}	1.18	benzene	2 to 3
C_6H_{13}	CH_3	C_4H_9	1.16	t-butylbenzene	5
C_2H_4 O C_2H_5	CH_3	C_4H_9	3.28	t-butylbenzene	5
C_2H_4 O C_6H_{13}	CH_3	C_4H_9	7.55	t-butylbenzene	5
C_2H_4 O C_2H_4 O C_8H_{17}	CH_3	C_4H_9	9.43	t-butylbenzene	5
$C_2H_4OC_2H_4OCH(C_2H_5)CH_2C(CH_3)_3$	CH_3	C_4H_9	10.4	t-butylbenzene	5

* D^{3+}_{Am} for R" = H serie are those at the maximum of the curve $D^{aq}_{Am^{3+}}$ vs $C^{aq}_{HNO_3}$. At the maximum $2N < C^{aq}_{HNO_3} < 3N$.

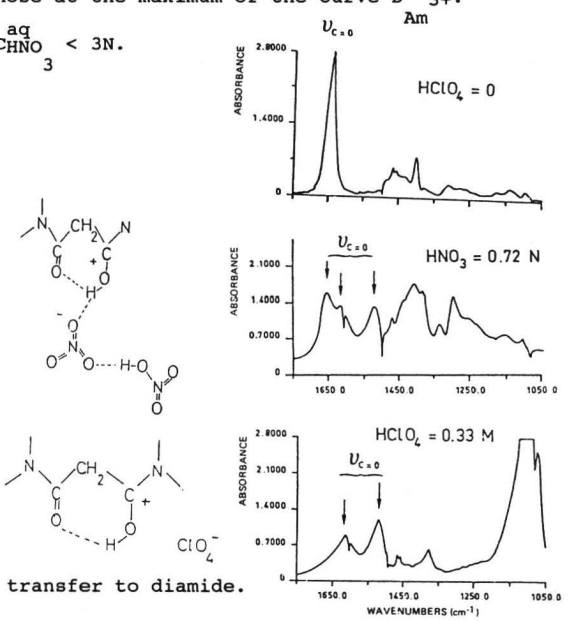


Fig. 4. IR evidence for proton transfer to diamide.

4. EXTRACTANTS FOR ACTINIDES-LANTHANIDES GROUP SEPARATIONS

The ideal solvent extraction process for the spent nuclear fuels reprocessing with minor actinides partionning comprises a selective extraction step of the actinide (III, IV, VI) which leaves the trivalent lanthanides in the aqueous phase with the other fission products. With such extractant only

one extraction step needs heavy shielding for biological protection. Unfortunately such extractant is not known because trivalent actinides and lanthanides have very close chemical properties. Soo research in actinides (III)-lanthanides (III) group separation is crucial for advanced reprocessing. Musikas et al. (1984) showed that the soft donor ligands complexes selectively the trivalent actinides (see Table 4). Taking into account these results several solvent extraction systems have been proposed for the 5f - 4f trivalent ions group separations.

TABLE 4.
S* values for selected donors for the Am-Nd and Am-Eu couple. (Ionic radius : Am^{3+} 0.99 Å, Nd^{3+} 0.99 Å, Eu^{3+} 0.96 Å)

Ligand	Complexe	S_{Am-Nd}	S_{Am-Eu}	Donor Electronegativity
F^-	MF^{2+}	- 0.05	- 0.084	4
$CH_3CO_2^-$	MCH_3COO^{2+}	0.074	0.03	3.5
N_3^-	MN_3^{2+}	0.95	0.93	3.0
Phen	$MPhen^{3+}$	0.84	0.69	3.0
DEHDTP***	$M(DEHDTP)_3.TBP$		4.6	2.5 (6)** 3.5 (1)

*$S = 2\ (\Delta G_{Ac} - \Delta G_{Ln})/\Delta G_{Ac} + \Delta G_{Ln}$
** numbers indicate the number of atom donor in the complex
*** DEHDTP = $(C_4H_9\ CH(C_2H_5)CH_2O)_2\ PSS^-$.

Figure 5A shows the variation of Am(III) and Eu(III) distribution ratios as a function of the proportion of tris 2-pyridyl 1,3,5-triazine (TPTZ) mixed with dinonylsulfonic acid (HDNNS). It can be seen that the nitrogen donor (TPTZ) is responsible for the Am(III)-Eu(III) separation. All the lanthanides (III) behave like Eu(III) and Cm(III) as Am(III). Figure 5B shows the Am(III)-Eu(III) separation obtained with the use of a sulfur donor di(2-ethyl)hexyl dithiophosphoric acid (HDEHDTP) in synergy with TBP. Here again Cm(III) behaves like Am(III) and the lanthanides (III) like Eu(III). Smith, B.F. et al. (1987) and Ensor, D.D. and al. (1988) showed that other synergistic extraction systems containing soft nitrogen or sulfur donor are proper for actinides (III)-lanthanides (III) group separation. Smith, B.F. et al. measured a Am(III)-Eu(III) separations factor as high as 70 for the mixture BMPPT-(acidic sulfur donor)-TOPO from $HClO_4$ solutions, Ensor, D.D. found separation factors close to 200 by replacing TOPO by 4,7-diphenyl 1-10 orthophenanthroline. The results obtained by Musikas et al. in a counter current separation using TPTZ-HDNNS into $CClO_4$ as solvent are given in a **poster of session 3 of this meeting.**

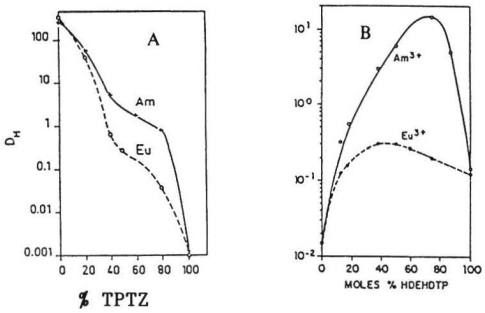


Fig. 5. Am(III)-Eu(III) separations
A : Solvent : 0.01M (HDNNS + TPTZ) into t-butylbenzene - Aqueous : 0.1M HNO_3
B : Solvent : 1M (TBP + HDEHDTP) into dodecane - Aqueous : 0.05N HNO_3 (0.05M Eu(III).

However it appears that an extraction system easily usable at the industrial scale is not yet available. All of the system described have drawbacks, these are contained Table 5. Two kinds of actinides-lanthanides group separation extractants would be usefull ; those which are able to perform the separation from a separated actinides-lanthanides fraction obtained with other solvents (CMPO or DIAMIDES) for example and those which will be able to separate all the actinides ((III), (IV) plus (VI)) from the nitric acid dissolution liquors containing high concentrations of U(VI) (~ 1 $mole.l^{-1}$).

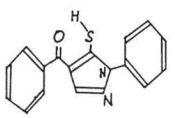
5. Cs^+ AND Sr^{2+} SEPARATION BY SOLVENT EXTRACTION

^{137}Cs and $^{90}Sr^{2+}$ have been separated from many nuclear wastes because of beneficial uses such as food preservation by irradiation, sterilization of medical supplies, remote emergency power, heat source applications .... However if the concept of closed nuclear fuel cycle is adopted the separation of Cs and Sr from the wastes and their further use or elimination through nuclear reactions will be an interesting option. In this paragraph the possibilities offered by solvent extraction will be reviewed. Because the problem of waste limitations the most interesting process are those working in acidic media. They can be achieved after the actinides separation shown figure 1b. Two solvent extraction procedures have been proposed. The first by Rais et al. the ion pair H^+ $[[¶ - (3) - 1,2\ B_9\ C_2H_{11}]_2Co]^-$ (dicarbollide) see figure 6 in which H^+ can be replaced by Cs^+ or Sr^{2+}. The diluent of such system is nitrobenzene and is probably one of the major drawbacks. Addition of polyxoethylene to the aqueous solutions increase the distribution ratios of Sr^{2+}. This has been attributed to the extraction of species such as SrBL in which B is the dicarbollide and L the polyoxoethylene. The conditions of extraction and back extraction of Cs^+ and Sr^{2+} are given Table 6.

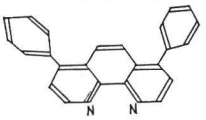
TABLE 5
Comparison of the extraction system proposed for the trivalent actinide-lanthanide group separations.

Solvent	Aqueous phase	$D_{Am(III)}/D_{Eu(III)}$	Drawbacks
0.6 M Alamine 336.HCl into diethylbenzene	10 to 12 M LiCl pH 1.0 to 2	150	High salt concentration pH difficult to maintain-diluent
0.3 M HDEHP in diisopropylbenzene	1 M lactic acid 0.005M DTPA pH 20	0.0167	Lanthanide more extracted pH difficult to maintain slow kinetics-diluent
0.05 M HDNNS + 0.03 M TPTZ into CCl_4	0.125 N HNO_3	10	Slow phases disengagement partial solubility of TPTZ into the aqueous phase-diluent
HDEHDTP 0.75 M TBP 0.25 M into dodecane	0.05 N HNO_3	40	Low chemical stability of HDEHDTP in the presence of HNO_3
0.3 M BMPPT* 0.01 M TOPO benzene	$HClO_4$ pH 3.0 $NaClO_4$	68	Perchlorate medium. Too high pH-diluent
BMPPT 0.03 DPPHEN** 0.0027 toluene	$HClO_4$ pH 3.7 $NaClO_4$	190	Perchlorate medium. Too high pH-diluent

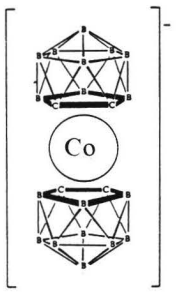
*BMPPT



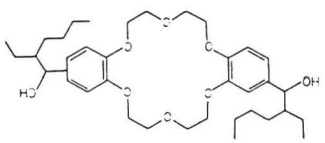
** DPPHEN



A (Cs^+, Sr^{2})

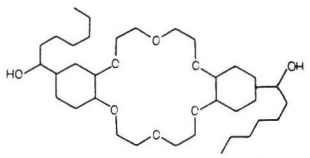


B (Cs^+)



Crown XVII
Bis 4,4'(5')[1-hydroxy 2-ethylhexyl]benzo 18-crown-6

C (Sr^{2+})



Crown XVI
Bis 4,4'(5')[1-hydroxyheptyl] cyclohexo 18-crown-6

Fig. 6. Structure of the reagents used for Cs^+ and Sr^{2+} extraction from acidic solutions. A) Co dicarbollide - B) Crown XVII - C) Crown XVI

Table 6.
Distribution ratios of Cs^+ and Sr^{2+}

Solvent	Aqueous phase	$D_{Sr^{2+}}$	D_{Cs^+}
0.01 M dicarbollide - nitrobenzene	0.1 N HNO_3 0.003 M polyethylenglycol	569	
0.01 M dicarbollide - nitrobenzene	1 N HNO_3 0.003 M polyethylenglycol	15,3	
0.01 M dicarbollide - nitrobenzene	0.1 N HNO_3		102.6
" "	0.5 N HNO_3		22
0.98 M TBP 0.1 M HDNNS 0.05 M crown XVII kerosene (68 %)	3 N HNO_3	0.06	1.59
" "	0.5 N HNO_3		1
0.98 M TBP 0.1 M HDNNS 0.02 M crown XVI kerosene (68 %)	3 N HNO_3	1.98	0.00
" "	0.5 N HNO_3	2.57	

The crown ethers are known as size selective complexants. Kinard and Mc Dowell showed that the distribution ratios of alkaline and alkaline earths crown ethers complexes increased in the presence of lipophilic acidic extractants such as di 2-ethylhexylphosphoric acid (HDEHP) or didodecyl-naphatalene sulfonic acide (HDDNS). Shuler et al. selected two crown ethers for the extraction of Cs^+ and Sr^{2+} from 3 N HNO_3 solutions mimicking the fission products solutions. Their formula are given figure 6. The solvent 68 % kerosene, 27 % TBP and 5 % HDDNS was choosen to solubilize the crown ethers complexes. Illustrating distribution ratios are given in Table 6. However the drawbacks of these 4 components solvents were the incomplete back extraction of Cs^+ ans Sr^{2+} by 0.5 N HNO_3 solutions.

6. FISSION PRECIOUS METAL RECOVERY

The amounts of Pd, Rh, Ru containd in the fission products match favorably with several national production from natural resources. This is the case for France and United States which have large sources of fission products from their installed nuclear plants power.

It is out of the scope of this paper to discuss the different possible strategies for platinoïdes recovery from fission products and the chemical processes involved : A short point about the solvent extraction of Ru, Pd, Rh from acidic nitrate solutions is given.

In the PUREX process using Pd, Ru and Rh stay in the effluent solutions of the first cycle U, Pu extraction because of the low affinity of Ru, Pd, Rh, rather soft acceptors for the oxygen donors extractants.

Fitoussi et al. showed that Ru and Pd can be readily extracted from HNO_3 solutions by di 2-ethylhexyldithiophosphoric acid. Rhodium is one of the less extractible metals. However Patel et al. proposed to extract Rh from nitric (0.1-1 N HNO_3) solutions by HDNNS (dinonylnaphtalene sulfonic acid) in kerosene. The advantage of this extractant is its inverted micelle form in kerosene so hydrated species such as $Rh(H_2O_6)_6^{3+}$ and $Rh(H_2O)_5NO_2^{2+}$ are extracted rapidly. However HDNNS is not a selective extractant and others metallic species are carried in the organic phase. Sulfur donor like sulfur phosphine R_3PS have been proposed as Rh extractants from 3 N HNO_3 solutions by Longden et al. The best extractant was N,N,N"-tri-n-hexylphosphorothioïc-triamide $(C_6H_{13}\ NH)_3\ P = S$, THPS, diluted in heptanol. Slow kinetics of extraction is a major drawback for this system.

7. CONCLUSION

The development of nuclear fission energy depends of the public acceptance. So the nuclear wastes management is increasingly important. Others solutions than the deep ground storage night be proposed. To do so several gaps must be overcomed especially in the chemical separations.

To limit the amounts of wastes coming from the solvent extraction processes, completely incinerable extractants and diluents must be preferred. Within the nowadys reprocessing strategy which has for goals the recovery of fissionable U and Pu isotopes it is possible to limit the amount of wastes by replacing the TBP by N,N-dialkylamides for which a limited amount of research and development is still necessary. The underground storable wastes can be limited by removing. 1) The α emitters, actinides. 2) The longes lived fission products such as Cs^+ and Sr^{2+}. For the first goal N,N'-tetralkylpropane diamides are good alternate to polyfunctionnal organo phosphorus molecules. Here the amount of research and development necessary to design successful industrial processes depends of the kind of wastes. For $^{137}Cs^+$ and $^{90}Sr^{2+}$ separation from HNO_3 solutions solvent extraction processes have been proposed, however the possibilities of industrial applications seems limited because of major drawbacks such as the type of diluent (carbollide process) or the type of extractant (crown-ether). Finally some fission products are valuable (Pd, Ru, Rh), if an advanced reprocessing is set up there is a good opportunity to recover such metals. The solvent extraction of Ru, Pd and especially Rh has not been extensively investigated and large scale applications need surely others processes than those suggested by the data presented here.

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ADDUCT FORMATION PROPERTIES OF SOME POLYDENTATE PHOSPHINE OXIDES IN THE SYNERGISTIC EXTRACTION OF METALS WITH 4-ACYL-5-PYRAZOLONE DERIVATIVES

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ABSTRACT

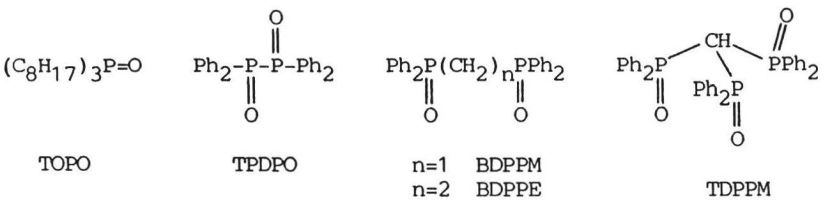
Some bi- and tridentate phosphine oxide compounds were synthesized and the liquid-liquid extraction equilibria of metal ions with 4-acyl-5-pyrazolone derivatives and the neutral phosphine oxide compounds were investigated. Bis(diphenylphosphinyl)methane was found to be a very powerful ligand in the synergistic extraction of rare earths, alkaline earths and the divalent metals such as Co(II), Ni(II), Zn(II) and Cd(II). The composition of the extracted species were determined by a graphical method. The adduct formation constants between the acylpyrazolone chelates and the neutral ligands were determined and discussed in terms of the molecular structure.

1. INTRODUCTION

The utilization of a Lewis base in the solvent extraction of metal ions has been well-known as so-called synerism [1,2]. The addition of a Lewis base not only enhances the extraction of metal ions but also makes it possible to extract even alkali and alkaline earth metals which are usually unextractable owing to the low stability of the chelate and the remaining water molecules in the chelate [3-5].

Many investigations have been made on the monodentate neutral ligands such as tri-n-octylphosphine oxide, tributylphosphate or pyridine but a little has been done on the bidentate neutral ligands such as phenanthroline or bipyridine [6-11]. In particular, little attention has been paid to the polydentate phosphine oxide compounds [12-17], although they are expected to be more powerful than the monodentate neutral ligands and to exhibit specific adduct formation reactions.

In the present work, some polydentate phosphine oxides (Fig. 1) are synthesized and the adduct formation properties are elucidated through the synergistic extraction of metals with 4-acyl-5-pyrazolone derivatives.



2. EXPERIMENTAL

2.1 Materials

1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) and 1-phenyl-3-methyl-4-trifluoroacetyl-5-pyrazolone (HPMTFP) were synthesized according to the literature [18]. The crude compounds were recrystallized from dioxane-water and dried under reduced pressure.

Bis(diphenylphosphino)methane and ethane were prepared according to the literature [19]. These compounds were suspended in water and oxidized with an excess of hydrogen peroxide solution yielding bis(diphenylphosphinyl)methane (BDPPM) and -ethane (BDPPE).

Tris(diphenylphosphinyl)methane (TDPPM) and tetraphenyldiphosphine dioxide (TPDPDO) were prepared according to the literatures [20,21], respectively.

2.2 Procedure

The extraction procedures are almost the same as described previously [3-5]. Benzene was employed for the extraction of alkaline earths, Co, Ni, Zn and Cd, and chloroform for rare earths.

3. RESULTS AND DISCUSSION

The overall extraction equilibrium in the presence or in the absence of a neutral ligand can be written as eqns. (1) and (2). M, HA and L stand for metal ion, acylpyrazolone and a neutral ligand, respectively. Subscript o denotes the species in the organic phase.

$$M^{n+} + nHA_o \rightleftharpoons MA_{n,o} + nH^+ \quad (1)$$

$$M^{n+} + nHA_o + sL_o \rightleftharpoons MA_nL_{s,o} + nH^+ \quad (2)$$

The extraction constant, K_{ex} and $K_{ex,s}$, can be written as eqns. (3) and (4).

$$K_{ex} = [MA_n]_o[H^+]^n/[M^{n+}][HA]_o^n \quad (3)$$

$$K_{ex,s} = [MA_nL_s]_o[H^+]^n/[M^{n+}][HA]_o^n[L]_o^s \quad (4)$$

The adduct formation equilibrium in the organic phase and its stability constant, β_s, are written as eqns. (5) and (6).

$$MA_{n,o} + sL_o \rightleftharpoons MA_nL_{s,o} \quad (5)$$

$$\beta_s = [MA_nL_s]_o/[MA_n]_o[L]_o^s \quad (6)$$

Dividing the distribution ratio of metal ion in the presence of a neutral ligand, D^*, by the distribution ratio in the absence of a neutral ligand, D, gives the relationship in eqn. (7).

$$D^*/D = 1 + \Sigma\beta_s[L]_o^s \quad (7)$$

Owing to the strong basicity and the large hydrophobicity, metal ions are extractable when an appropriate anion such as picrate or perchlorate is present in the aqueous phase [22] as seen in eqn. (8).

$$M^{n+} + nX^- + nL_o \rightleftharpoons MX_nL_{n,o} \quad (8)$$

Consequently, the extraction experiments were performed without any salt which is often added in order to keep the ionic strength constant.

The effect of the neutral ligand concentration was examined in the synergistic extraction of Cd. As seen in Fig. 1(a), the plots for BDPPM and BDPPE are straight lines with a slope of unity, whereas the plots for TOPO is a curve with an increasing slope. The slope of the straight portion in the higher TOPO concentration region is almost two. Considering the coordination number and the large adduct formation constant, one can safely conclude that BDPPM works as a bidentate ligand. The adduct formation constant for BDPPE is much smaller than that for BDPPM. BDPPM is expected to form a six-membered ring when it attaches to a metal ion, whereas BDPPE is expected a seven-membered ring. It is well known that six-membered ring is more stable than seven-membered ring. The stable adduct formation reaction of BDPPM could be attributed to this ring stability.

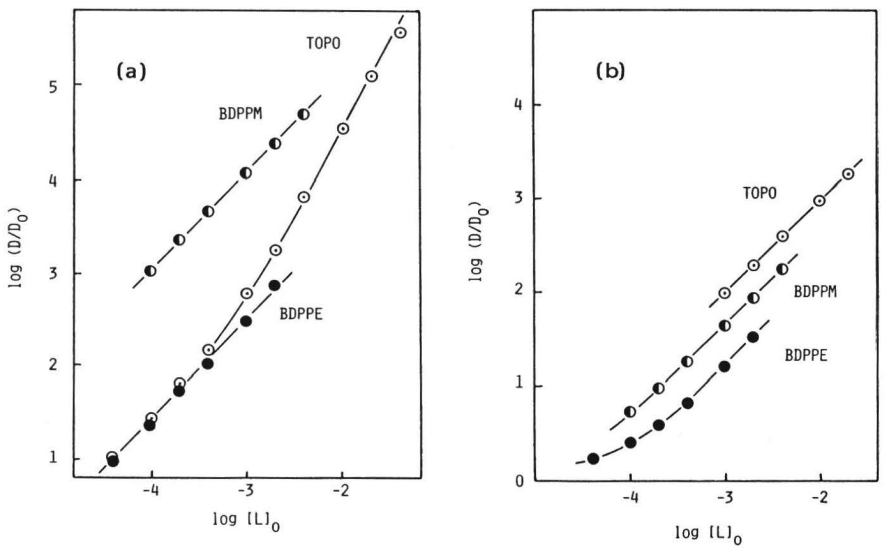


Fig. 1 Comparison of mono- and bidentate phosphine oxide compounds on the synergistic extraction of (a) Cd(II) and (b) Zn(II) with HPMBP.

The effect of the neutral ligand concentration was also examined in the synergistic extraction of Zn. As can be seen in Fig. 1(b), the plots for TOPO, BDPPM and BDPPE are all straight lines with a slope of unity, indicating that the number of the neutral ligand in the extracted species is one. In the case of Zn extraction, the coordination number is five, and it could be considered that BDPPM and BDPPE work as a monodentate ligand. A steric hindrance caused by the free phosphoryl group would result in the lower stability for BDPPM and BDPPE.

The extraction parameters for Co, Ni, Zn and Cd are summarized in Table 1. In the extraction of Co and Ni, as well as Cd, BDPPM works as a bidentate ligand. Its β_1 values are much larger than those for TOPO and BDPPE.

Table 1

Extraction parameters for MA_2L_s

Neutral		BDPPM		BDPPE		TOPO		
ligand	log K_{ex}	log $K_{ex,1}$	log $\beta_{a,1}$	log $K_{ex,1}$	log $\beta_{a,1}$	log $K_{ex,s}$	log $\beta_{a,1}$	log $\beta_{a,2}$
Co(II)	-7.10	-0.28	6.82	-2.04	5.06	0.13	5.28	7.23
Ni(II)	-7.00	-0.34	6.66	-2.10	4.90	0.06	4.63	7.06
Zn(II)	-5.36	-0.66	4.70	-1.08	4.28	-0.30	5.06	—
Cd(II)	-8.90	-1.88	7.02	-3.22	5.68	-0.39	5.35	8.51

The advantage of BDPPM over TOPO can be seen (Table 2) in the synergistic extraction of rare earths with HPMTFP [17]. The extracted species is $Ln(PMTFP)_3(TOPO)_s$ (s=1,2) and $Ln(PMTFP)_3(BDPPM)$. BDPPM was found to be more powerful than n-octylphenyl(N,N-diisobutylcarbamoylmethyl)phosphine oxide (CMPO) which is also a bidentate ligand having P=O and C=O as donating groups.

Table 2

Extraction parameters for $Ln(PMTFP)_3L_s$

neutral		BDPPM		CMPO		TOPO		
ligand	log K_{ex}	log $K_{ex,s}$	log β_1	log $K_{ex,s}$	log β_1	log $K_{ex,s}$	log β_1	log β_2
La(III)	-6.18	3.81	9.99	1.47	7.65	4.20	—	10.38
Pr(III)	-4.98	4.89	9.87	2.61	7.59	5.19	—	10.17
Eu(III)	-3.78	5.64	9.42	3.45	7.23	6.06	5.88	9.84
Ho(III)	-3.36	5.52	8.88	3.54	6.90	6.08	5.90	9.44
Yb(III)	-3.15	5.34	8.49	3.42	6.57	5.68	6.31	8.70

Adduct formation properties of polydentate phosphine oxides have been examined in the synergistic extraction of alkaline earth metals. The synergistic extraction constants, $K_{ex,s}$, of alkaline earth metals are plotted for polydentate ligands in Fig. 2. The number in the parenthesis is the number of the neutral ligand in the extracted species. When the number in the parenthesis is the same, then it is possible to compare the adduct formation reaction.

Taking strontium as an example, it was found that the $K_{ex,s}$ value for BDPPM is much larger than that for TOPO. Considering that the number of the neutral ligand in the extracted species for TOPO and BDPPM is equal and the extraction constant for BDPPM is remarkably larger than that for TOPO, it could be concluded that BDPPM works as a bidentate ligand. The extraction constant for BDPPE is smaller than that for BDPPM and is close to that for TOPO. The difference between BDPPM and BDPPE could be interpreted by the ring stability.

The number of the tridentate ligand, TDPPM, in the extracted species was found to be one for magnesium and two for calcium, strontium and barium. The extraction constants are smaller than those for BDPPM and BDPPE except for barium. If TDPPM works as a tridentate ligand, the coordination number is ten, and this should be abnormally large. It could be considered that TDPPM might work as a bidentate ligand like BDPPM and the free diphenylphosphoryl group would cause a steric hindrance resulting in a small extraction constant. In the synergistic extraction with tridentate neutral ligand, there would be two factors governing the adduct formation reaction. One is a ring stability and the another one is a steric hindrance. TDPPM forms a stable six-membered ring like BDPPM, however, causes a large steric hindrance especially when the ionic radius of the central metal is small.

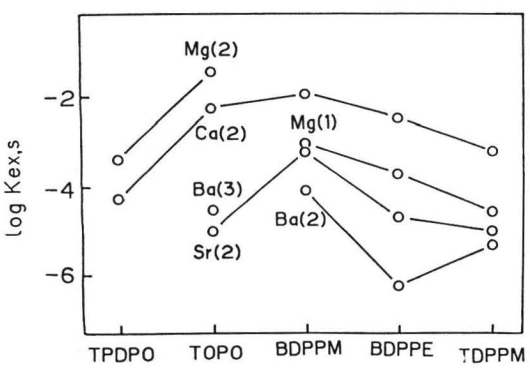


Fig. 2 log $K_{ex,s}$ for HPMBP system

Although tetraphenyldiphosphine dioxide is a bidentate ligand and is expected to form a five-membered ring which is usually more stable than a six-membered ring, the extraction constants are much smaller than those for even monodentate ligand. The extraction of strontium and barium was negligibly low. According to IR data, the basicity of the P=O group of TPDPO is similar to other

phosphine oxides. There is much difficulty in recognizing the adduct formation property of TPDPO. This ligand seems to work not as a bidentate ligand but a monodentate ligand with a steric hindrance caused by the free phosphoryl group.

4. CONCLUSIONS

Among the polydentate phosphine oxides in the present work, bis(diphenylphosphinyl)methane was found to be the most promising ligand when it can work as a bidentate ligand. Tridentate ligand seems to work as a bidentate ligand in the synergistic extraction of divalent metals.

It is notable that besides the unique reactivity, polydentate phosphine oxides have another advantage over the nitrogen-containing bidentate ligand such as phenanthroline or bipyridine. It is able to employ these ligands in the acidic media, for the distribution of these ligands does not depend on a pH.

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EXTRACTION AND SEPARATION OF METAL IONS WITH N-ALKYLCARBONYL-N-PHENYLHYDROXYLAMINES

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ABSTRACT

A series of N-alkylcarbonyl- substituted N-phenylhydroxylamines (R-PHAs) were synthesized and applied to the extraction of several divalent metal ions and tervalent lanthanoid ions from aqueous solutions into carbon tetrachloride. The distribution constants of these extractants increased with an increase in the carbon number in the substituent. Stoichiometries of the extracted species were determined for the extraction of individual metal ions with R-PHAs and the extraction constants for the chelates were evaluated. Among the R-PHAs studied, N-(2-hexyldecanoyl)-N-phenylhydroxylamine was an excellent extractant for the separation of heavy lanthanoids. The effects of the substituents on the extractability and selectivity of metal ions are discussed.

INTRODUCTION

N-Benzoyl-N-phenylhydroxylamine (BPHA) and its analogues have been employed as gravimetric, spectrophotometric and extracting reagents for a wide variety of metal ions (Majumdar, 1972). Recently, attention is paid to hydrophobic chelating extractants having long-chain alkyl substituents, because of their successful applications in the extraction of various metal ions. In this respect, we have reported that certain N-alkylcarbonyl- derivatives of N-phenylhydroxylamines (R-PHAs), such as N-octanoyl- (C8-PHA) and N-hexanoyl-N-phenylhydroxylamine (C6-PHA) are promising extractants for some divalent metal ions (Haraguchi, et al., 1989). The present paper describes the synthesis and properties of some new R-PHAs and the extraction equilibria of several divalent metal ions and tervalent lanthanoid ions from aqueous solutions into carbon tetrachloride with these R-PHAs. The effects of the substituents on the extractability and selectivity of metal ions are also discussed.

EXPERIMENTAL

Reagents

R-PHAs were synthesized from N-phenylhydroxylamine and corresponding acid chlorides accroding to the reported procedure (Agrawal and Tandon, 1971) with some modifications. The confirmation of white crysalline products was carried out by melting-point measurements, elemental analysis and measurements of H-NMR, IR and mass spectra.The R-PHAs thus obtained are listed in Table 1. Stock

TABLE 1. Alkylcarbonyl- substituted N-phenylhydroxylamines, R-C(=O)-N(OH)-C$_6$H$_5$

Acronym	Substituent (R-)	Acronym	Substituent (R-)
C4-PHA	$CH_3(CH_2)_2$-	PP-PHA	$(CH_3(CH_2)_2)_2CH$-
C12-PHA	$CH_3(CH_2)_{10}$-	HD-PHA	$CH_3(CH_2)_7CH(CH_2)_5CH_3$-
tC5-PHA	$(CH_3)_3C$-		
tC9-PHA	$(CH_3)_3CCH_2CH(CH_3)CH_2$-	C4Hx-PHA	$CH_3(CH_2)_3$-C$_6$H$_{11}$-
		C4Ph-PHA	$CH_3(CH_2)_3$-C$_6$H$_5$-

solutions of metal ions were prepared by dissolving the metal nitrates in 10^{-3} mol dm^{-3} nitric acid. Their metal ion concentrations were determined by EDTA titrations. All the chemicals were of analytical grade. Distilled-deionized water was used throughout the experiments.

Apparatus

R-PHAs extracted into the organic phase were determined with a Hitachi 320 spectrophotometer with 1-cm qualtz cells. The concentration of divalent metals in the aqueous phase were measured with a Varian SpectrAA-40 atomic absorption spectrometer. The concentration of lanthanoids(III) in the aqueous phase were determined by a Shimadzu GVM-1000P inductively coupled plasma atomic emission spectrometer. A Toa HM-15A pH meter was employed for measuring pH values. A Yamato SA-31 mechanical shaker was used for mixing the two phases. A Kokusan H-200 centrifuge was also used for rapid and complete phase separation.

Procedure for distribution of R-PHAs

A 25.0-cm^3 portion of an aqueous phase and 5.0-cm^3 portion of carbon tetrachloride containing 1.00×10^{-4} mol dm^{-3} R-PHA were shaken in a 60-cm^3 glass vial for 1 h at 298 $\pm$ 1 K. The pH of the aqueous phase was adjusted by addition of a buffer component (phosphate: 2×10^{-2} mol dm^{-3}) or sodium hydroxide. The ionic strength was kept at 0.1 with sodium nitrate. The concentration of the R-PHA in the organic phase was determined by measuring the absorbance at 260 nm. The concentration of the R-PHA in the aqueous phase was calculated on the basis of the material balance.

Procedure for the extraction of metal ions

A 20.0-cm^3 portion of an aqueous solution containing a specified metal ion (5.0×10^{-5} or 1.0×10^{-4} mol dm^{-3}) was shaken with an equal volume of carbon tetrachloride containing a definite amount of a R-PHA for a sufficient time for equilibration at 298 $\pm$ 1 K. The pH of the aqueous phase was controlled with an appropriate buffer agent and the ionic strength was adjusted to 0.1 with sodium

nitrate. After phase separation, the metal concentration in the aqueous phase was determined by atomic absorption spectrometry or ICP atomic emission spectrometry. The concentration of the metal in the organic phase was determined by the material balance.

RESULTS AND DISCUSSION

Distribution of R-PHAs

The distribution ratio, D_L, of a specified R-PHA (HL) between the aqueous and the organic phases can be given by Eq. (1) where the subscript (o) refers to the concentration in the organic phase.

$$D_L = [HL]_{(o)} / ([HL] + [L^-]) \quad (1)$$

Eq. (1) is rewritten as Eq. (2) by employing two equilibrium constants; acid dissociation constant, K_a, and distribution constant, K_d, of the R-PHA.

$$\log D_L = \log K_d - \log (1 + K_a[H^+]^{-1}) \quad (2)$$

A curve-fitting method has been applied for the plots of log D_L against the pH to determine a set of K_a and K_d values of respective R-PHA. The equilibrium constants thus obtained are summerized in Table 2.

TABLE 2. log K_d and pK_a values of R-PHAs

R-PHA	log K_d	pK_a	R-PHA	log K_d	pK_a
C4-PHA	0.39	8.57	tC5-PHA	0.77	9.71
C5-PHA	1.14	8.60	tC9-PHA	2.00	9.90
C6-PHA	1.89	8.63	PP-PHA	2.46	9.26
C8-PHA	2.88	8.76	HD-PHA	4.00	9.74
C9-PHA	3.42	8.75	C4Hx-PHA	2.30	8.42
C10-PHA	3.79	8.52	C4Ph-PHA	2.59	9.25

The K_d value increases with an increase in the carbon number of the alkyl substituent of the R-PHA with a linear alkyl chain. The increment of log K_d is about 0.5 per carbon atom. This should be ascribed to an increase in hydrophobisity. The K_d value for a R-PHA with a linear alkyl chain is larger than that of a R-PHA with a branched alkyl group having the same carbon number. On the other hand, a progressive increase in the carbon number of the alkyl chain brought only a slight change in the pK_a value. The pK_a values of R-PHAs with a linear alkyl chain are in the range from 8.5 to 8.8 whereas those of R-PHAs with a branched chain are from 9.3 to 9.9, which suggests that the +I effect of the branched chain is greater than that of the linear chain.

Extraction equilibrium of metal ion

The extraction of a metal ion (M^{n+}) with a R-PHA can be described in general according to Eq. (3), by assuming that a free metal ion is predominant in the aqueous phase.

$$M^{n+} + (n + m)HL_{(o)} \rightleftharpoons ML_n(HL)_m + nH^+ \quad (3)$$

The extraction constant, K_{ex}, is thus defined as Eq. (4).

$$K_{ex} = [ML_n(HL)_m]_{(o)}[H^+]^n / [M^{n+}][HL]_{(o)}^{(n+m)} \quad (4)$$

Therefore, the distribution ratio of metal ion, D_M, between the two phases can be given by Eq. (5).

$$\log D_M = \log K_{ex} + (n + m)\log [HL]_{(o)} + npH \quad (5)$$

Accordingly, stoichiometries of the extracted species and the extraction constants can be obtained from the relationships of log D_M vs. pH at constant $[HL]_{(o)}$ and log D_M vs. log $[HL]_{(o)}$ at constant pH. Table 3 summerizes the results of the slope analysis of the extraction of several divalent metal ions with C8-PHA along with the extracted species and their extraction constants. The values of log K_{ex} for C6-PHA chelates were almost the same as those for C8-PHA in the extraction of respective divalent metal ion.

TABLE 3. Equilibrium data for the extraction of divalent metal ions with C8-PHA

Metal ion	Slope of log D_M vs. pH / vs. log$[HL]_{(o)}$		Extracted species	log K_{ex}
Cu(II)	2.1	1.9	CuL_2	-2.01
Co(II)	1.9	2.0	CoL_2	-10.63
Ni(II)	2.0	2.9	$NiL_2(HL)$	-7.27
Zn(II)	2.0	2.9	$ZnL_2(HL)$	-8.02
Pb(II)	2.2	1.9	PbL_2	-6.82

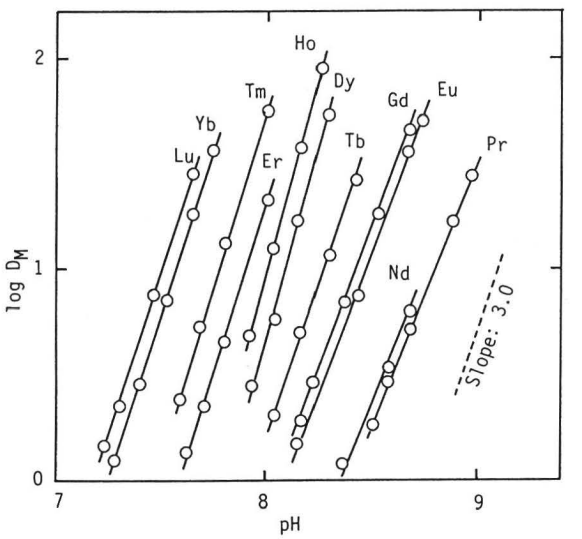


Fig. 1. Relationships between log D_M vs. pH for the extraction of lanthanoids(III) with HD-PHA. $[M^{3+}] = 5.0 \times 10^{-5}$ mol dm^{-3}, $[HL]_{(o)} = 1.0 \times 10^{-2}$ mol dm^{-3}

TABLE 4. log K_{ex} values for the extraction of lanthanoids(III) with various R-PHAs

	C8-PHA	tC9-PHA	PP-PHA	HD-PHA	C4Hx-PHA	C4Ph-PHA
Pr	-12.19	-12.70	-14.44	-15.40	-12.10	-11.26
Nd	-12.10	-12.55	-14.20	-15.31	-12.85	-11.14
Eu	-10.96	-11.50	-13.30	-14.38	-11.89	-10.33
Gd	-10.87			-14.29		
Tb	-10.15			-13.81		
Dy	-9.73			-13.27		
Ho	-9.58			-13.03		-9.07
Er	-9.49			-12.73		
Tm	-9.34			-12.34		
Yb	-9.25	-9.94	-11.20	-11.74	-10.54	-8.74
Lu	-9.13			-11.53		

The relationships of log D_M vs. pH at constant R-PHA concentration and (log D_M - 3pH) vs. log $[HL]_{(o)}$ at constant pH for the extraction of tervalent lanthanoids with N-(2-hexyldecanoyl)-N-phenylhydroxylamine (HD-PHA) are shown in Figs. (1) and (2). From these figures, slopes of 3 with respect to pH and 5 with respect to log $[HL]_{(o)}$ were obtained within the experimental error for all the lanthanoids studied. Similar results were obtained in the extraction with other R-PHAs. Thus, it is concluded that the lanthanoids are extracted as a self-adducted chelate, $ML_3(HL)_2$. The evaluated K_{ex} values for the extraction of lanthanoids(III) with various R-PHAs are summerized in Table 4. The log K_{ex} value for a specified lanthanoid with HD-PHA is smaller than that with C8-PHA as shown in Table 4. This indicates that the higher extractability of C8-PHA over HD-PHA for the extraction of lanthanoids. However, in the extraction of heavier lanthanoids from Ho(III) to Lu(III), the differences in the log K_{ex} values between two adjacent lanthanoids are greater than those of C8-PHA, which suggests that HD-PHA is superior to C8-PHA for separation of heavy lanthanoids.

Separation factors (SF) for Eu/Pr and Yb/Eu pairs were compared for further elucidation of the selectivity of R-PHAs. Separation factor is defined as the ratio of K_{ex} values for a pair of lanthanoids. In Table 5, the log SF values for R-PHAs are shown along with those for other extractants which are already known (Freiser, 1988). The log SF value of C8-PHA for a pair of Eu/Pr (1.23) is very close to that of di-(2-ethylhexyl)phosphoric acid (D2EHPA) (1.26) which is currently used for the intragroup separation of lanthanoids. For a pair of Yb/Eu the log SF value of C8-PHA (1.71) is considerably smaller than that of D2EHPA (2.70), but that of HD-PHA (2.64) is comparable to D2EHPA. Thus, it can be concluded that HD-PHA is a very promising extractant for the separation of heavy lanthanoids(III). The branching at the α-position of the alkyl chain in the substituent seems to transmit to R-PHAs different chemical properties with respect to the straight chain R-PHAs. However, if this improvement of the selectivity is caused by the steric hindrance of the branched chain, the

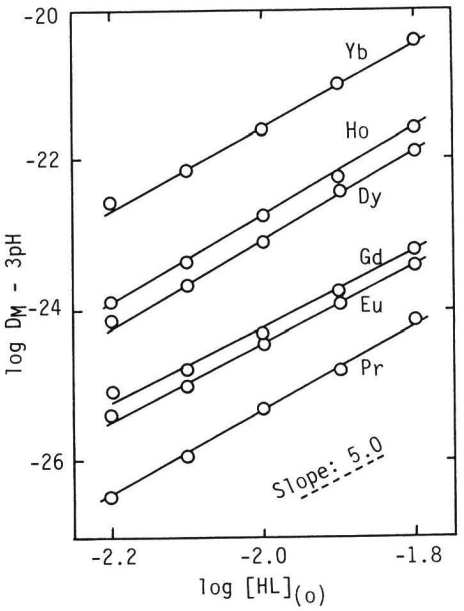


Fig. 2. Plots of (log D_M - 3pH) vs. log $[HL]_{(o)}$ for the extraction of lanthanoids(III) with HD-PHA

TABLE 5. log SF for Eu/Pr and Yb/Eu with various extractants

Extractant	Extracted Species	log SF Eu/Pr	log SF Yb/Eu
C8-PHA	$ML_3(HL)_2$	1.23	1.71
tC9-PHA	$ML_3(HL)_2$	1.20	1.56
PP-PHA	$ML_3(HL)_2$	1.14	2.10
HD-PHA	$ML_3(HL)_2$	1.02	2.64
C4Hx-PHA	$ML_3(HL)_2$	0.21	1.35
C4Ph-PHA	$ML_3(HL)_2$	0.93	1.59
BPHA*	$ML_3(HL)$	1.24	0.68
PBBPHA*	$ML_3(HL)_2$	0.88	1.05
HQ*	$ML_3(HL)_3$	2.0	1.9
diBr-HQ*	$ML_3(HL)$	0.94	2.01
Kelex 100*	ML_3	1.58	2.10
D2EHPA	$M(LHL)_3$	1.26	2.70

PBBPHA: p-tert-butyl-BPHA
HQ: 8-quinolinol
diBr-HQ: 5,7-dibromo-HQ
*Data from (Freiser, 1988)

extractability should be weaker with decreasing the ionic radii of lanthanoids, or with increasing the atomic number. This does not agree with the findings in the present study. The effect of a branched alkyl group on the extraction of lanthanoids(III) seems to be different from that of the 2-methyl group in 8-quinolinol which is well known as a sterically hindered ligand.

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RATIONAL DESIGN OF ORGANIC SOLVENT EXTRACTANTS

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ABSTRACT
Various approaches leading to the rational design of solvent extractants are reported. Qualitative evaluation of the performance of organic ligands in metal extraction was achieved by Pearson's HSAB principle, quantum mechanical calculation and computational multivariation analysis. Quantitative estimation of the reactivity of organic ligands, the basis for the molecular design of solvent extractant, was discussed. Two new sets of substituent steric parameters of extractant, the most important term in such treatment, were introduced by us based on the spectroscopic investigation and molecular mechanics calculation.

INTRODUCTION

The technological and economic feature of a solvent extraction process are determined chiefly by the basic characteristics of organic extractant. The structure-reactivity studies of solvent extractant has been the subject of our lectures on the ISEC during last decade (Yuan et al. 1980, 1983, 1985, 1988). In this paper the state of art and future of structure-reactivity relatioship (SAR) and quantitative structure-activity relationship (QSAR) problems are discussed in addition to a historic review of this investigation.

1 QUALITATIVE EVALUATION

1.1 Pearson's HSAB principle

Solvent extraction of metal may be considered simply as the replacement reaction of molecule in the hydration shells of metal ion in the aqueous solution by organic ligand. Both metals (acceptor) and coordinating atoms (donor) can be classified as hard, soft and borderline acids and bases according to the Pearson's scale. Oxygen-based ligands are referred to hard bases, which prefer to coordinate with hard acids such as lanthanides, actinides, Nb, Ta, Zr or Hf. As soft base, sulfur-containing ligands are preferred to combine with soft acid type metals such as Cu, Au, Ag, Pd, Pt or Hg. Being a borderline base, aniline or pyridine reacts smoothly with borderline acid type metals, such as Fe, Co, Ni, Ru or Rh. The hardness of donor atoms can be modified by the inductive or conjugative effect of the neighbouring group or radical. This opens a broad prospect for synthetic chemists to design new extractants.(Yuan, 1980)

1.2 Quantum mechanical calculation

The reactivity of coordinating atom or group, as represented by charge density or bond order, can be evaluated by quantum mechanical calculation. We applied

perturbational molecular orbital (PMO) method for the study of correlation between the ionization constant and distribution of π-electrons in some aromatic bases and acids (Li & Yuan, 1981). PMO method was also used for the investigation of intramolecular hydrogen bonding of chelating agents. (Li & Yuan, 1982). Later on we introduced the Huckel molecular orbital (HMO) method and its extented variation (EHMO) in structure-reactivity studies of various types extractants. (Yuan et al 1981,1983,1989) Rozen and his colleagues (1986) used the modified neglet of diatomic overlap (MNDO) method, the best semi-empirical quantum mechanical calculation method, for the predition of extraction ability of organic molecules. By combination of MNDO and molecular mechanical treatments, we are successful in evaluation of phosphorus-based extractants.

1.3 Computational multivariation analysis.

Since the metal extraction, which is based on the formation of complexes by organic ligand with metal ion or corresponding ionic species, may be regarded as a multi-componental coordination process between heterogeneous phases, it is therefore reasonable to understand the limitation of structure-reactivity studies based on univariate analysis. In order to overcome this imperfection, the application of pattern recognition (Hui et al. 1981) gave, however, some promising results. Meanwhile, various methods of multivariate analysis were developed rapidly in recent years as an effective way to extract valuable information from multi-dimensional data and applied extensively to chemistry. As one of the new approaches to the molecular design of extractants, the application of cluster analysis and factor analysis to structure-reactivity studies of acidic phosphorus esters in extraction of rare earth was reported (Yuan S.G. et al. 1987). In this work two of the most common methods of cluster analysis, i.e. Hierarchical Cluster and Minimal Spanning Tree were used. (Figure 1 and 2)

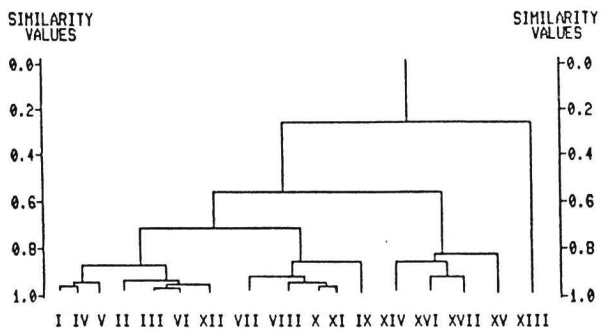


Fig. 1 Hierarchical Cluster

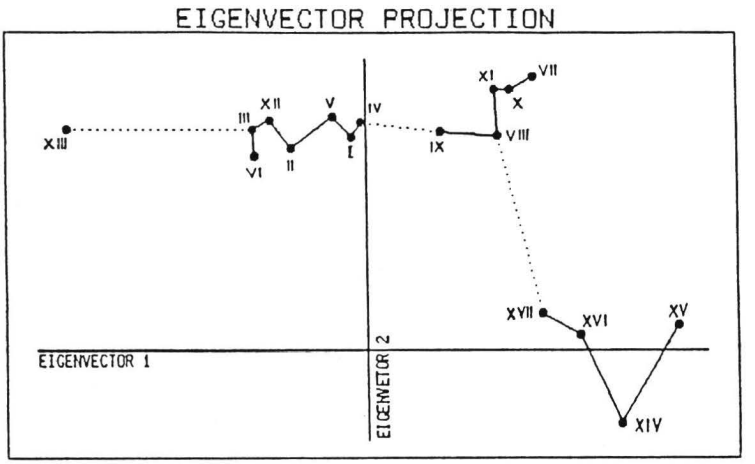


Fig. 2 Minimal Spanning Tree

Roman numerals in the Figures represent acidic phosphorus esters with various structures: I, $(i\text{-OctO})_2P(O)OH$; II, $(s\text{-OctO})_2P(O)OH$; III, i-OctP(O)OOct-i(OH); IV, cycHexP(O)OOct-n(OH); V, cycHexP(O)OOct-i(OH); VI, cycHexP(O)OOct-s(OH); VII, $C_6H_5P(O)OOct\text{-}n(OH)$; VIII, $C_6H_5P(O)OOct\text{-}i(OH)$; IX, $C_6H_5P(O)OOct\text{-}s(OH)$; X, $o\text{-}MeC_6H_4P(O)OOct\text{-}n(OH)$; XI, $o\text{-}MeC_6H_4P(O)OOct\text{-}i(OH)$; XII, $o\text{-}MeC_6H_4P(O)OOct\text{-}s(OH)$; XIII, $i\text{-}Oct_2P(O)OH$; XIV, $i\text{-}OctOP(O)(OH)_2$; XV, $NonCH(Hept)CH_2OP(O)(OH)_2$; XVI, $i\text{-}OctP(O)(OH)_2$; XVII, $NonCH(Hept)CH_2P(O)(OH)_2$.

On the basis of the above studies further investigation was made by factor analysis. Since the two abstract factors directly obtained by factor analysis have no chemical significance, trial has been made by rotating the principal factors to a series of target factors, in order to get the real factors. After the target rotation we got a series of combinations of typical factors by which to describe the original data. The five best combinations in the descending order are: VI and X, VI and IX, II and IX, X and XV as well as V and IX.

If M designates the different rare earth metal, $(\log Kex)_{M,VI}$ and $(\log Kex)_{M,X}$ represent the logarithm of extraction equilibrium constant of compound VI and X to the metal respectively, we have the general equation:

$$(\log Kex)_{M,i} = f_{1,i}(\log Kex)_{M,VI} + f_{2,i}(\log Kex)_{M,X} \qquad (1)$$

This equation can clearly and quantitatively describe the behaviour of different phosphorus compounds in lanthanide extraction. It is more interesting that as long as we get the Kex of VI and X to other metal ions, we can predict the Kex value of the residual fifteen phosphorus compounds with a satisfactory precision using this model and the corresponding $f_{1,i}$ and $f_{2,i}$ reported by us(YuanS.G.1987).

2 QUANTITATIVE ESTIMATION

For the QSAR study of organic ligands in metal extraction, we proposed a principle mathmatical model early sixties.(Yuan, 1980)

$$\log Kex = \rho \Sigma\sigma + \delta \Sigma Es + \gamma C \qquad (2)$$

Where σ , Es and C represent substituent polar, steric parameter and total carbon number of ligand. The relative coefficients ρ, δ and γ indicate the contribution of the corresponding term to Kex value. The term C is equivalent to Kd, the distribution ratio of ligand between kerosene and water, and which is determined by the molecular weight of ligand.

As shown by us, the term C or Kd may be neglected if similar types of compounds with approximate molecular weight are applied. In such case the problem turns to the selection or establishment of substituent parameters suitable for metal extraction.

2.1 Substituent polar parameter.

In the chemistry of carbon compounds there are several sets of parameters representing polar or field effect of the substituents directly bonded to the reaction center including Hammett $\sigma$and Taft σ. In organophosphorus chemistry, Kabachnik introduced a new scale (σ_ϕ) for the polarity of substituent based on the pKa measurements of various kinds of phosphorus acids.(Kabachnick 1971). In recent years we extended this method for the evaluation of the substituent effect of alkyl and alkoxyl group with carbon number up to ten. (Yuan et al.1986) As an empirical parameter,σ^P is useful in correlation analysis of QSAR study of phosphorus-based ligands in metal extraction. (Yuan et al, 1987, 1988) However, the σ^P parameters reflect not only polar but also other substituent effects, since the contribution of steric effect could not be excluded in such treatment. As the result of our systematic study of 4-substituted-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane-1-oxide and p-substituted phenylphosphonic acid mono-hexyl-ester by ^{31}P NMR spectroscopy, it revealed that both Taft,s and Hammett's parameters widely used in carbon chemistry are applicable to correlation analysis of organophosphorus compounds. Consequently, it seems unnecessary to define a new set of polar substituent parameters in organophosphorus chemistry.(Yuan1990)

2.2 Substituent steric parameter.

A significant difference of the substituent steric parameters of organophosphorus esters from carbon carbons was evidenced by poor results in correlation analysis using Taft's Es or Charton's ν in the alkaline hydrolysis of alkylphosphonates. This is because of the larger steric influence of the substituents for phosphonates than that for carboxylates. It may be rationalized by the fact that the structural change between ground state and transition state in the carboxylate hydrolysis is completely different from the phosphonate hydrolysis. The steric influence of substituent on phosphorus must be quite different too.

By careful examination of pKa of mono-hexyl alkylphosphonate and $\delta\Delta$ ^{31}P NMR of di-n-hexyl alkylphosphonates in MeOH and CCl_4, compounds with substituents directly bonded to phosphorus, we succeeded in establishing a new set of substituent steric parameters for organophosphorus compounds $E_s^P(R)$, from which corresponding parameters for alkoxyl group $E_s^P(RO)$ can also derived. (Table 1) (Yuan, Li 1990)

TABLE 1

Substituent Steric Parameters

Group	$E_s^P(R)$	$E_s^P(RO)$	$E_{s,ex}(R)$	$E_{s,ex}(RO)$	ν	E_s
Me	0.50	0.38	-0.037	0.0	0.52	-1.24
Et	0.75	0.62	0.0	0.003	0.56	-1.31
n-Pr	0.85	0.72	0.007	0.003	0.68	-1.60
i-Pr	1.12	0.98	0.216	0.021	0.76	-1.71
n-Bu	0.91	0.77	0.010	0.003	0.68	--
i-Bu	1.05	0.91	0.053	0.015	0.98	--
s-Bu	1.17	1.02	0.246	0.102	1.02	-2.37
t-Bu	1.36	1.21	0.545	--	1.24	-2.78
n-Am	0.91	0.77	0.010	0.010	0.68	--
i-Am	0.92	0.78	--	--	0.68	--
cyc-Hex	1.07	0.93	0.218	--	6.87	-1.01
n-Oct	0.90	0.76	0.011	0.012	0.68	--
i-Oct	1.10	0.96	0.068	0.023	1.01	--
s-Oct	1.25	1.05	0.277	0.169	1.05	--

Abbreviation i-Oct and s-Oct denotes $BuCHEtCH_2$- and HeptCHMe- respectively.

With the aid of molecular mechanical calculation (MM) method, we are able to introduce another set of substituent steric parameters for phosphorus-ligands in metal extraction $E_{s,ex}(R)$ and $E_{s,ex}(RO)$. (Li, Yuan,1989) (Table 1)

2.3 Multiple regression analysis.

The applicability of the substituent parameters thus obtained is checked by multiple regression analysis in extraction reactions of rare earths, cobalt and nickel. (Li, Yuan 1989; Yuan, Li, Hu 1990)

(i) Correlation analysis in lanthanides extraction.

Based on the Kex values for lanthanides extraction by series of acidic phosphorus esters using Equation 2 we got:

$$\log K_{ex}^{La} = 8.43\Sigma\sigma_I - 3.84\ \Sigma E_s^P + 3.27 \qquad (3)$$

and

$$\log K_{ex}^{Nd} = 9.02\Sigma\sigma_I - 3.54\ \Sigma E_s^P + 3.50 \qquad (4)$$

The results of the multiple regression analyses are as follows:

	r	S	n	S_ρ	S_δ	S_c	T_ρ	T_δ	T_c
For Eq. 3	0.994	0.195	23	0.60	0.14	0.36	14.08	-26.89	9.00
For Eq. 4	0.989	0.247	23	0.76	0.18	0.46	11.93	-19.52	7.61

Therefore,

$$\log Nd/La = 0.59\Sigma\sigma_I + 3.0\ \Sigma E_s^P + 0.23 \qquad (5)$$

The calculated value is well supported by the experimental data.

(ii) Correlation analysis in extraction of cobalt and nickel.

Since extraction of Co and Ni by mono-basic phosphorus ester proceeds with the formation of different configuration of complexes, the steric effect is most important. It is necessary to establish specific steric parameters.(Yuan,1987,88)

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EXPERIMENTAL STUDY OF THE INFLUENCE OF DILUENT CHARACTERISTICS ON PERFORMANCE IN METAL EXTRACTION.

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ABSTRACT

Experimental work carried out recently by Exxon Chemical on copper extraction in Australia have confirmed that low aromatic diluents give an overall better performance than regular grades. In particular, a linear paraffin-rich diluent was shown to give significant advantages in terms of metal extraction rate, loading and phase separation time. As this study was being carried out on fresh diluent/extractant systems in Australia, work was going on in Exxon Chemical laboratories in Canada in order to establish whether the advantages exhibited would be maintained after the organic solutions have been aged. The results obtained indicate that low aromatic diluents continue to give superior performance, even when oxidized. The best system was again based on Escaid 300, a linear paraffin-based diluent.

INTRODUCTION

The recovery of metal values by solvent extraction is now a well established industry. Over the years, operators have been striving to optimize plant performance through a variety of ways: more efficient equipment has been developed, better extractants were brought to the market,new modifiers were introduced, etc... The area of diluent, or carrier, has also received attention. There is now in the literature a considerable number of articles dealing with the effect of the composition of the diluent on the solvent extraction process,(see forinstance refs.1 to 8). It is indeed recognized that the very different needs of the modern metal extraction industry cannot be met with a single diluent such as kerosene, however refined it may be.
Exxon Chemical has been pioneering the development of grades better suited to that Industry for many years. In particular, they have been the first to promote the concept of low aromatic carriers. Today an extensive range of such grades are marketed by Exxon Chemical worldwide.

Further studies have been carried out recently in order to reassess the value for the user of low aromatic carriers.

EXPERIMENTAL

Carrier optimization studies were carried out locally. Two case studies are reported below:
The first case involved the recovery of copper from a solution containing 3.85 g/l copper. pH was 2.3. Extraction isotherms and phase separation times were measured on three organic phases containing Acorga M.5640 as the extractant and Escaid 100,110 and 300 resp.as the carrier. Temperature was 30^{o}C in all cases.

The isotherm curves are presented in Fig.1. In this particular case, Escaid 300 gave a much more favourable isotherm than the other two carriers,that performed practically on a par. Escaid 300 came on top as well as far as phase separation rate is concerned.

This study concentrated on the following aspects:

- oxidation stability
- kinetics of metal transfer
- stripping efficiency
- equilibrium characteristics

Each diluent, to which 5 vol% of LIX 984 has been added, was loaded twice with an equal volume of leach liquor. This resulted in organic phases containing 2100-2200 mg/l.copper. Each organic phase was split in two portions: one would be stripped and save for later use. The other part would be blended with 3 times its volume of leach liquor and oxidized for 48 hours at a pressure of 1135-1340 kPa of pure oxygen. Temperature was normally kept at 50°C but a few runs were also carried out at 65 and 80°C. During these runs, oxygen pressure would be monitored and the amount consumed during each experiment calculated.

Oxygen Consumption

The results obtained are shown in Table 2. The average oxygen consumption for the tests carried out at 50°C is 18.3 mM/l. There is no significant difference between aromatic-containing and aromatic-free grades. A simple calculation shows that the oxygen consumption measured corresponds to less than 1% of material oxidized. In a test carried out on pure diluent, oxygen consumption was 17.4 mM, confirming that extractant oxidation was apparently negligible. Considering the extreme severity of the oxidation carried out here one can thus conclude that all the organic phases tested are extremely resistant to oxidation. When oxidation conditions are rendered even more severe by increaqsing temperature to 65 or even 80°C, the consumption of oxygen tends to increase slightly. At this stage however, it was not clear whether the increase corresponds to further degradation of the diluent, or to incipient degradation of the extractant. We will come back to this point.

Measurement of performances

The hydrometallurgical performance of batches of oxidized phases was compared side by side with their non-oxidized equivalent: the amount of copper that could be stripped from all systems was measured and then kinetic extraction measurements were carried out.

Finally, metal loading capacity was determined. Extensive analytical work was also done in order to identify the chemical changes that could have occurred.

- Stripping
  For all practical purposes, metal stripping was essentially complete in all cases, which seems to indicate that the nature of the metal-extractant bond had not been affected during the oxidation step.
- Kinetics and loading
  All stripped organic phases were loaded again with fresh pregnant liquor in a series of experiments where the rate at which copper was transferred was followed as a function of time.

Measurement of Performances - Non-oxidized systems

The results are presented in Table 3. Some difference in metal transfer rate can be observed between diluents. Among the aromatic-free carriers, Escaid 300 and Escaid 110 were the best performers. After 30 seconds, these systems had extracted 89 and 83% resp. of the copper, against 74% for the aromatic-containing systems.

At the one minute mark, the difference is still of the order of 9%. After two minutes, close to equilibrium, there is a 5% delta between the two extreme cases. At the end of the kinetic experiments, each organic phase was separated from the aqueous raffinate and submitted to a second loading with fresh pregnant liquor. No kinetic measurements were made. The amount of metal transferred was simply measured after another 2 minutes contact time.

The results of these tests are presented in the last column of Table 3. The highest loading was obtained with Escaid 300 as the carrier: 64% of copper transferred. The lowest result was obtained with mining kerosene: 48.5%.

Measurement of Performances - Oxidized systems

The data obtained on oxidized systems are presented in Table 4. They indicate that provided the oxidation temperature did not exceed 50°C, the oxidized phases performed generally very similarly to the non-oxidized ones both from the kinetic standpoint and from a loading standpoint (last column of the table). Again the performance of Escaid 300 was significantly above the others. However, when oxidation conditions were rendered more severe by raising temperature to 65 or 80°C, metal transfer rate decreased substantially. This appears very clearly on plotting the data as has been done for Escaid 100 in Fig.4. Also, the amount of metal that could be loaded was found to be significantly inferior.

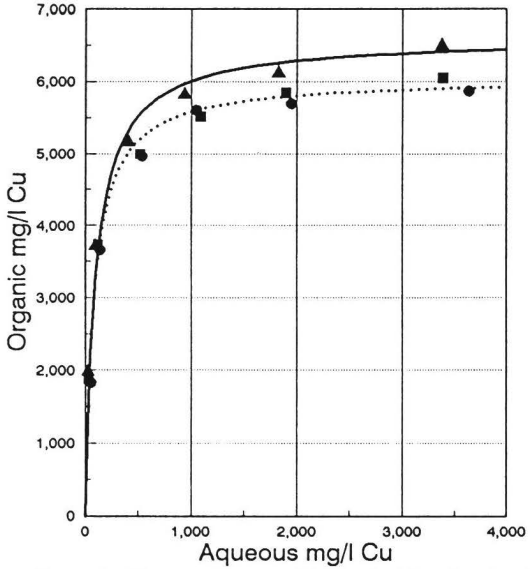
This indicates that a portion of the extractant has been rendered unavailable for copper uptake during the oxidation process. Extensive analytical measurements were carried out in order to identify the nature of the products formed but the results so far have been inconclusive. It is noteworthy that in all the work reported here, copper/iron selectivity was never a problem as iron content stayed in the 1-2 ppm range in all organic phases.

CONCLUSIONS

The data obtained indicate that whether exposed to oxidation conditions or not, different organic phases exhibit different performances. In general, low aromatic systems performed better than the non-dearomatized versions when fresh. The same trend was observed on laboratory aged systems. However, the composition of the diluent - other than aromatic content - plays a role too: the linear paraffin-rich Escaid 300 grade exhibited a definite advantage when compared with other low aromatic grades, even Escaid 110. It provided faster metal transfer rate and better loading, two key elements in commercial operation. Also of significance is the observation that the use of mining kerosene consistently gave lower loading values than the Escaid grade with a comparable aromatic content, Escaid 100. A possible explanation is that the unsaturated components present in the kerosene in greater amount than in the other grades tested would reduce the availability of the extractant for metal. This hypothesis is being currently checked in the laboratory.

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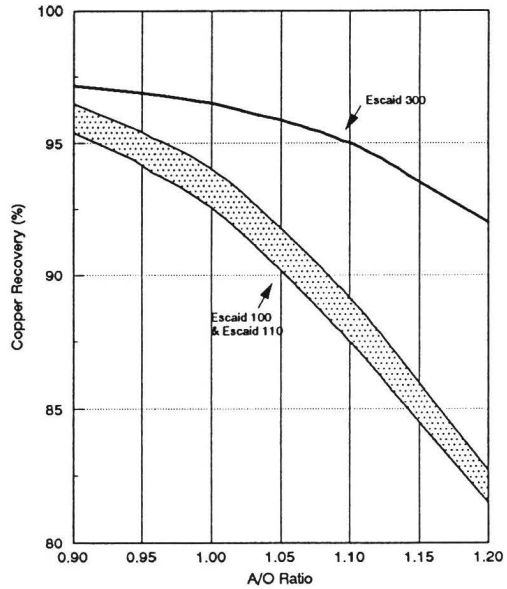


Organic Phase: Acorga M.5640, 11 vol % in diluent
Aqueous: 3.85 g/l Cu.

Escaid 300 Escaid 100 Escaid 110

Figure 1

Extraction Isotherms



Extractant: Acorga M.5640, 11 vol %
Overall Stage Efficiency: 95%

Figure 2

Comparative Performance of Carriers For the Extraction of Copper

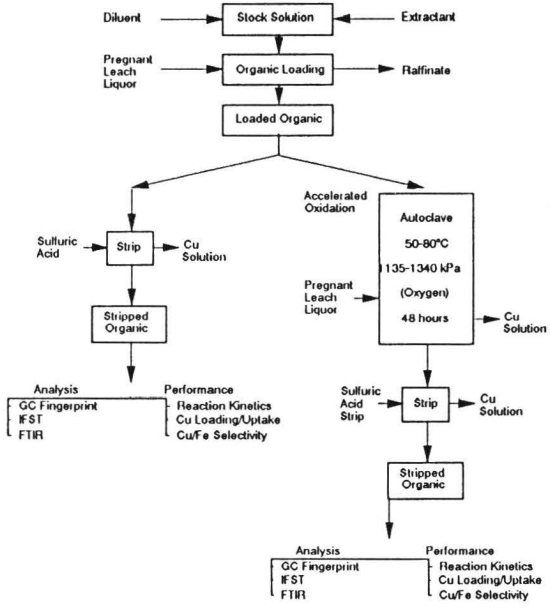


Figure 3

Oxidation Stability Studies

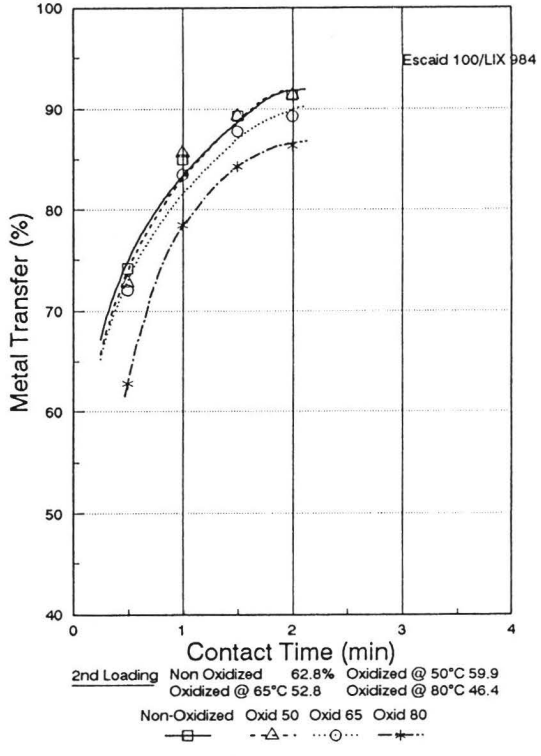


Figure 4

Effect of Oxidation on Metal Transfer Rate

TABLE 1

Physical Properties Of The Carriers

ESCAID	100	110	111	115	300	MINING KEROSENE
Flash Point (°C)	78	82	76	101	95	69
Aromatic Content (wt%)	23	1.0	0.4	6.2	0.5	25
Bromine Index (mg/100g)	360	5	12	276	<3	1150
Density (15°C)	0.81	0.79	0.82	0.82	0.76	0.82
Viscosity (25°C) (cSt)	1.8	2.1	2.1	2.9	2.3	2.0
Aniline Point (°C)	63	79	70	76	89	62
K-B Value	34	27	35	30	21	35
Surface Tension @ 25°C (mN/m)	27.1	26.8	27.5	28.0	26.4	27.4

TABLE 2

Oxidation Stability Study
Oxygen Consumption Data

ESCAID	Temperature (°C)	O_2 Consumption (mM/l)
Mining Kerosene	50	20.8
100	50	16.8-18.5
110	50	18.7
111	50	19.3
300	50	17.0
115	50	20.8
100	65	22.6
100	80	23.0
110 (*)	50	17.4

(*) No extractant

Experimental Conditions:

- o Feed Metal Content : Copper : 1400 wt ppm
  : Iron : 1380 wt ppm
- o pH : 1.63
- o Extractant : LIX 984, 5 vol %
- o Time : 48 hours
- o Oxygen Pressure : 1135-1340 kPa

TABLE 3

Kinetic Tests
Non-Oxidized Systems
Copper Transfer (%)

Contact Time (min)	0.5	1.0	1.5	2.0	2.0 *
Mining Kerosene	74.2	85.0	88.6	90.0	48.5
Escaid 100	74.2	84.3	89.3	91.4	62.8
110	82.8	90.0	92.1	92.1	60.7
111	75.7	86.4	90.7	92.1	61.4
300	89.3	93.1	93.8	94.1	64.2
115	78.5	88.6	90.0	89.3	54.2

* 2nd Loading

Conditions:

- o Feed Copper Content 1400 wt ppm
- o Extractant LIX 984, 5 vol %
- o Temperature 25°C

TABLE 4

Kinetic Tests
Oxidized Systems
Copper Transfer (%)

T(°C)	Contact Time (Min)	0.5	1.0	1.5	2.0	2.0 *
50	Mining Kerosene	70.7	85.0	88.6	89.3	49.9
50	Escaid 100	72.8	85.7	89.3	91.4	59.9
50	110	87.8	92.1	92.8	92.8	59.2
50	111	80.7	90.0	92.1	92.1	59.9
50	300	87.8	93.3	93.8	94.0	64.2
50	115	81.4	89.3	90.7	91.4	60.7
65	100	72.1	83.5	87.8	89.3	52.8
80	100	62.8	78.5	84.3	86.4	46.4

* 2nd Loading

Conditions:

- o Feed Copper Content : 1400 wt ppm
- o Extractant : LIX 984, 5 vol %
- o Temperature : 25°C

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NEW ASPECTS IN EXTRACTION BY ACID-BASE COUPLE EXTRACTANTS

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ABSTRACT

Reversible extraction of mineral acids and of their salts by acid-base couple extractants (mixed ionic solvents) provided the basis for several processes developed for the fertilizer industry and for treating industrial effluents. Extraction properties of couple extractants are strongly dependent on the acidity/basicity of their components. pH_{HN} values, (pH of half-neutralization) measured by contacting the extractant with HCl solution, were found to provide a convenient tool for tailoring extractant composition for various industrial uses.

1. INTRODUCTION

Acid - base couple extractants (also denoted "mixed extractants") are composed of an amine, an organic acid and a diluent, all of them water immiscible.

Our group in the Casali Institute had thoroughly investigated acid extraction by these extractants and found that they form a "new generation" of acid extractants, providing some very important advantages. Couple extractants combine the selectivity, efficiency and water immiscibility of strong extractants such as long chain amines, with reversibility similar to that of weak extractants such as alcohols. As a result, extracted acids can be recovered by back - extraction with water. Concentrations of the recovered acids approach those of the feed to extraction (Eyal and Baniel 1982).

These properties of couple extractants make them highly suitable for acid purification (e.g. upgrading of wet process phosphoric acid (Eyal and Baniel 1984)) and for recovery of acids from waste streams (Eyal et al. 1990). They also open new possibilities in process development as shown by the processes for KNO_3 production (Eyal et al. 1985) and for recovery of sulfuric acid from gypsum (Eyal et al. 1986).

In addition to recovery of pure, concentrated mineral acids from waste streams, acid extraction by couple extractants greatly facilitates further treatments, such as recovery of other valuable components from waste solution. It can be advantageously integrated into tailor - made flowsheets with other operations such as evaporation or crystallization.

Couple extractants also extract reversibly salts of mineral acids providing for extraction of both acid and salt sequentially by the same extractant. Thus a process was developed for recovery of sulfuric acid and zinc sulfate from effluents of zinc electrowinning plants (Eyal

et al. 1990a). For zinc electrowinning plants, using alkali sulfate for jarosite precipitation, the unique properties of the extractant provide for recovery of $ZnSO_4$ in concentrations above 30% (compared to about 16% in the effluent).

Acid - base couple extractants are simply prepared by mixing amines with organic acids and diluents. The large variety of commercially available amines and organic acids allows the tailoring of extractant properties by derivation from component properties. Although extraction by couple extractants has already been studied for about 20 years (mainly extraction of alkali and alkali earth salts), several aspects still need clarification.

We have studied the effect of acid/base properties of extractant components on extraction of acids and of salts.

2. EXPERIMENTAL

Extractants were prepared by mixing desired amine and organic acid (molar ratio of 1:1) and diluting them in an aromatic free kerosene to 0.5 mole/Kg each. Extractants containing MTCA (methyltricaprylyl amine) were prepared by mixing the desired acid and diluent with methyltricaprylyl amine and washing with water in order to remove HCl.

Extraction experiments were performed at ambient temperature. Experimental procedures and analytical methods were previously described (Eyal et al. 1990). pH_{HN} (pH of half-neutralization) was measured by the procedure described by Grinstead (1967). pH values in $ZnSO_4$ solutions were measured after equilibration with extractants at aqueous to organic weight ratio of 10:1.

3. RESULTS AND DISCUSSION

3.1 Extraction of acids

Figures 1 shows distribution curves for extraction of HCl and H_3PO_4 by two couple extractants composed of tricaprylyl amine (TCA) and organic acids.

Amines extract HCl very efficiently and acid/amine molar ratio (Z) of 1 is reached in equilibrium with dilute aqueous solutions. An ion pair is formed:

$$R_3N_{(org)} + HCl_{(aq)} \dashrightarrow R_3NHCl_{(org)} \qquad (1)$$

Above-stoichiometric extraction through H-bonding to the salt, is however observed only in equilibrium with highly concentrated aqueous solutions:

$$R_3NHCl_{(org)} + HCl_{(aq)} \dashrightarrow R_3NHCl\text{-}HCl_{(org)} \qquad (2)$$

This phenomenon has been extensively described and discussed (Frolov and Sergievskii 1966, Mrnka et al 1974).

In extraction by couple extractants the picture is complicated by the presence of organic acid, which competes with HCl on binding both to the amine (Z<1, sub-stoichiometric extraction) and to the salt formed.

Previous studies show that stronger acids are preferred by amines. Consequently, up to Z=1, stronger organic acids in the couple extractant better compete with the mineral acid and decrease its extraction (see Fig. 2).

In the region of Z>1 extraction by TCA-DEHPA (di-(2-ethylhexyl)phosphoric acid) exceeds extraction by TCA-ABL (α-bromolauric acid). Here again an analogy to extraction of mineral acid exists. In extraction by amine salt weaker acids are preferred (Shmidt and Rybakov 1977). ABL better competes therefor with H_3PO_4 than DEHPA.

Effects of relative strengths of acids are even more pronounced in extraction of a weaker mineral acid such as H_3PO_4. In extraction up to Z=1, distributions coefficients for of H_3PO_4 are lower than those for HCl and are more strongly affected by presence of the organic acid. However, its extraction by the salt formed is considerably higher than that of HCl, due to higher tendency of the weaker acids to form H-bonds. Similar behavior was found in HF extraction (Eyal 1989).

Grinstead (1967, Grinstead and Davis 1968) measured pKa values of water insoluble amines by equilibrating them with aqueous HCl solutions containing 0.5 mole acid per mole of amine and measuring pH values in the aqueous phase (denoted pH_{HN}). We adopted this method as a tool for characterizing acid-base properties of couple extractants.

As shown in Fig. 3, although pH_{HN} is measured in equilibrium with very dilute HCl solutions, it shows a very good correlation with H_3PO_4 extraction at high concentration. The concentration of the aqueous phase, at which Z=1 is reached (Z*), linearly decreases with increasing pH_{HN} (decreasing effect of the organic acid in the extractant).

3.2 Extraction of salts

Figure 4 shows pH values measured in $ZnSO_4$ solutions equilibrated with an organic acid and with couple extractants. Figure 5 summarizes distribution of $ZnSO_4$ between aqueous solutions and couple extractants.

Metal ion extraction by organic acids proceeds through cation exchange:

$$ZnSO_{4\,(aq)} + 2HA_{(org)} \quad <---> \quad ZnA_{2\,(org)} + H_2SO_{4\,(aq)} \qquad (3)$$

(where HA denotes an organic acid).

Acidity in the aqueous phase increases and a base should be added to facilitate further extraction.

Extraction by couple extractants avoids the need for neutralization as acid formed binds to the amine:

$$ZnSO_4\ (aq) + 2R_3NHA\ (org) \leftrightarrow ZnA_2\ (org) + (R_3NH)_2SO_4\ (org) \quad (4)$$

Figure 4 demonstrates the effect of amine basicity on pH of the aqueous phase in equilibrium. pH values decrease with $ZnSO_4$ concentration due to $ZnSO_4$ hydrolysis. At a given concentration it is lowest for solutions equilibrated with the acid and then increases with the basicity of the amine: branched chain tertiary amine < straight chain tertiary amine < primary amine.

Extraction by weak acids such as LA is very sensitive to pH and thus extraction by couple extractants containing LA with relatively weak bases, such as tris-(2-ethyhexyl)amine (TEHA) and TCA is very low. Replacing the weak amines by stronger ones, however, enhances extraction considerably (see Fig. 5).

pH_{HN} of couple extractants were shown above to correlate with acid extraction. As pH_{HN} is affected by the acid-base properties of the organic acid and of the amine, one may also expect some correlation with metal salts extraction.

$ZnSO_4$ concentration in DEHPA containing couple extractants in equilibrium with $ZnSO_4$ saturated aqueous solutions are drawn in Fig. 6 against pH_{HN} values of these extractants (pH_{HN} increases with increasing basicity of the amine).

Here too, although pH_{HN} measures HCl extraction from very dilute aqueous solutions it shows correlation with $ZnSO_4$ extraction from concentrated solutions. A curve with a minimum is observed rather than the linear correlation found for acid extraction. A combination of two opposite effects is indicated.

Grinstead et al. (1969) explained extraction enhancement with amine basicity by increasing interaction with the anion of the extracted salt. It however seems that for couple extractants containing weak organic acids, acidity regulation is the determining factor in agreement with Nishimura and Watanabe (1975). Amines however may compete with the metal ion on the organic acid and thereby hinder salt extraction. The results presented in Fig. 6 indicate that for couple extractants composed of DEHPA (stronger acid than LA) and relatively weak amines, this effect overrides the effect of acidity control.

4. CONCLUSIONS

Acid-base couple extractants extract both acids and salts efficiently, selectively and reversibly. Their extraction properties are strongly dependent on the acidity/basicity of their components. pH_{HN} values measured in a simple, single experiment were found to correlate with extraction data of both acids and salts. It therefore provides an important tool for tailoring acid-base couple extractants for various industrial uses.

5. ACKNOWLEDGEMENTS

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The proprietary know-how and patents relevant to the use of couple extractants have been assigned to SEPROS Separation Processes LTD., Kibbutz Ramat Rachel, 90900 Israel.

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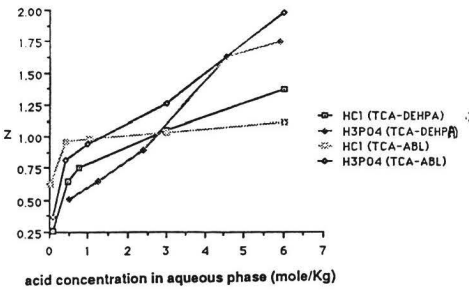


Figure 1. Distribution curves for extraction of HCl and H_3PO_4 by couple extractants. composed of tricaprylyl amine+alpha bromo lauric acid and tricaprylyl amine+di-(2-ethylhexyl)phosphoric acid. Z denotes acid/amine molar ratio.

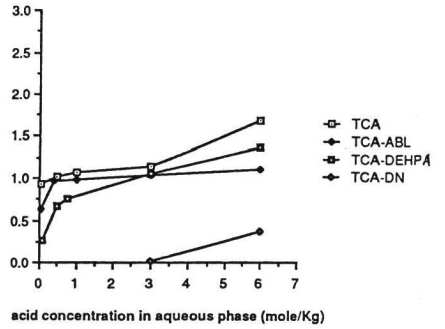


Figure 2. Distribution curves for extraction of HCl by an amine and by couple extractants. Z denotes acid/amine molar ratio.

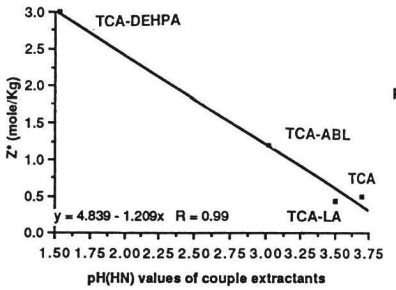


Figure 3. Concentrations of H_3PO_4 aqueous phases at which Z=1 is obtained (Z*) vs. pH_{HN} values for the corresponding couple extractant.

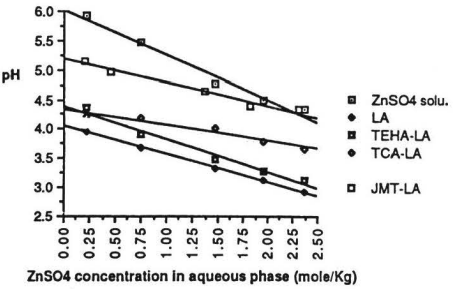


Figure 4. pH values of $ZnSO_4$ solutions equilibrated with an organic acid and with couple extractants.

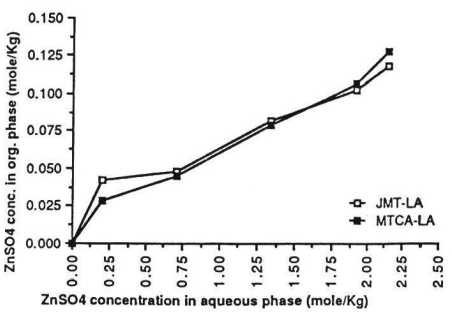


Figure 5. Distribution curves for $ZnSO_4$ extraction.

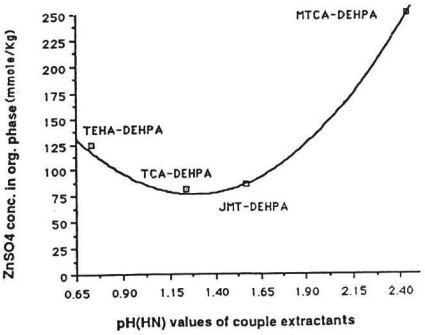


Figure 6. $ZnSO_4$ concentrations in couple extractants in equilibrium with saturated aqueous solutions vs. pH_{HN} values for the extractants.

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EFFECT OF TEMPERATURE AND ACIDITY ON VARIOUS PHOSPHORUS CONTAINING EXTRACTANTS

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Albright & Wilson Americas, P. O. Box 26229, Richmond, VA 23260 (USA)

ABSTRACT

The hydrolytic stability of several organophosphorus extractants has been measured at different acidity and temperature conditions. The extractants studied were DEHPA® Extractant, IONQUEST® 801, and Dibutyl Butylphosphonate. The stability tests were carried out with 20% by volume extractant in a refined kerosine. The extractant/diluent blends were contacted with 4 and 10 Normal Hydrochloric, Sulfuric and Nitric Acid solutions. Hydrolytic degradation was measured as a function of time.

INTRODUCTION

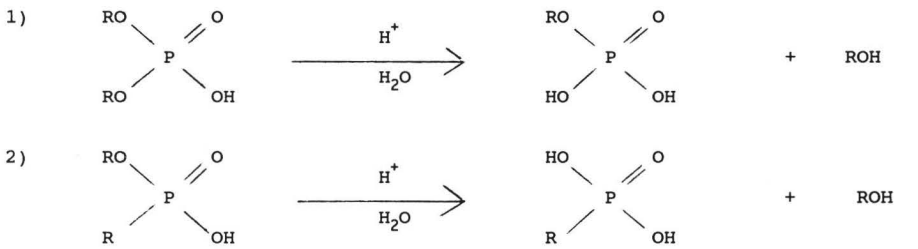
Phosphorus compounds have been used in solvent extraction for over 50 years. In the past 15 years, commercialization of new solvent extraction technology has accelerated, spurring commercial development of phosphorus-based extractants. DEHPA Extractant, IONQUEST 801 Extractant and DBBP are three extractants which have been commercialized for this purpose.

DEHPA® Extractant, IONQUEST® 801, and DBBP are a family of the phosphorus liquid-liquid ion exchange resins developed for those needs.

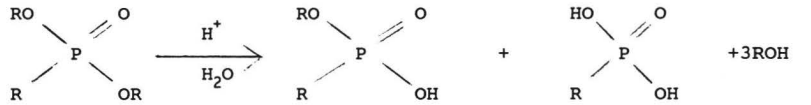
Processes for recovery of uranium from wet-process phosphoric acid, which were commercialized in the late 1970's were the first major use for DEHPA[1]. Rhone Poulenc's use of DBBP extractant to purify wet process phosphoric acid followed in the early 1980's[2].
2-Ethylhexyl Phosphoric Acid, Mono-2-ethylhexyl Ester (IONQUEST 801) has now become[3] the extractant of choice for difficult separations involving rare earths.

Extractant losses frequently are observed in commercial extraction systems. These losses are usually due to solubility or microemulsion formation in the aqueous phase, third phase formation or hydrolytic decomposition. This study was directed at measuring extractant stability with respect to hydrolytic decomposition.

Decomposition products formed in hydrolysis of the organophosphorus extractants in this study are shown below:



DEHPA is a U.S. registered trademark of Albright & Wilson.
IONQUEST is a U.S. registered trademark of Albright & Wilson.

3) 

Hydrolysis of the extractants produces products with significantly higher water solubility. These can also complex with metal ions; however, they are usually removed by the aqueous stream, leaving lower levels of extractants and reduced extraction coefficients.

Hydrolysis rates are expected to be a function of the inherent stability of the extractant, the temperature, the type of acid used and the acid concentration. In this study, the hydrolytic stability of DEHPA, IONQUEST 801 and DBBP were evaluated as a function of acid concentration, temperature and time.

EXPERIMENTAL

For this testing, 4 Normal and 10 Normal solutions of sulfuric acid, nitric acid and hydrochloric acid were prepared using technical grade acids and distilled water. DEHPA® Extractant, DBBP, and IONQUEST 801, supplied by Albright & Wilson Americas, were diluted to 20.0% by volume solutions using Kermac 400-500 refined kerosene.

Fifty gram aliquots of acid and extractant were weighed out in 4 ounce glass bottles and sealed with lids containing teflon gaskets. The bottles were tumbled in a rotary oven at 22° and 50°C for periods of 1 day, 7 days, and 28 days. After the period of time, the bottles were removed from the oven and the solutions placed in separatory funnels for phase separation. Each phase was removed and stored separately. Analyses were conducted on the organic phases.

ANALYTICAL PROCEDURE

Gas chromatographic analyses of the organic layer were carried out on a Hewlett Packard Model 5890A gas chromatograph equipped with a Model 7673A auto-injector, a split/splitless capillary injection port, a flame ionization detector (FID) and a Model 3396A integrator. The gas chromatograph was operated in the split mode using a 10 meter by 0.53mM diameter bonded FSOT fused silica capillary column coated with polyphenylmethylsiloxane at 2.0uM, i.e. Alltech RSL-300 NON-PAKD.

The samples were analyzed using an internal standard method with triphenyl phosphate as the internal standard and the starting extractants in kerosine as standards. A four or five point standard curve was generated. Linear regression analyses gave correlation coefficients >.99. The response of the FID was checked periodically by injecting standards.

In the case of DEHPA and IONQUEST 801, the samples had to be derivatized by silyation using N-methyl-N-(tert-butyldimethylsilyl)trifluoroacetamide (Pierce Chemical Co.) before analysis.

DISCUSSION OF RESULTS

All three extractants showed very good hydrolytic stability. No useful data were generated with the 50°C nitric acid samples. These runs were aborted after one day, due to pressure build-up in the bottles, which caused leakage.

DBBP

The DBBP data, at first look, suggest that this extractant has poor stability in sulfuric and hydrochloric acid, with weight losses up to 100% (figures 1 & 2). However, third phases were formed, which appeared to contain all of the missing DBBP.

DEHPA

DEHPA Extractant showed excellent hydrolytic stability in all cases (figures 4, 5, 6). No third phase formation was observed.

IONQUEST 801

IONQUEST 801 showed good stability with all of the acid solutions tested (figures 7, 8, 9).

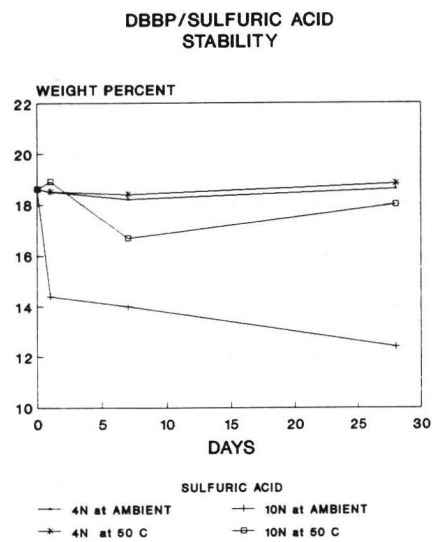


FIGURE 1

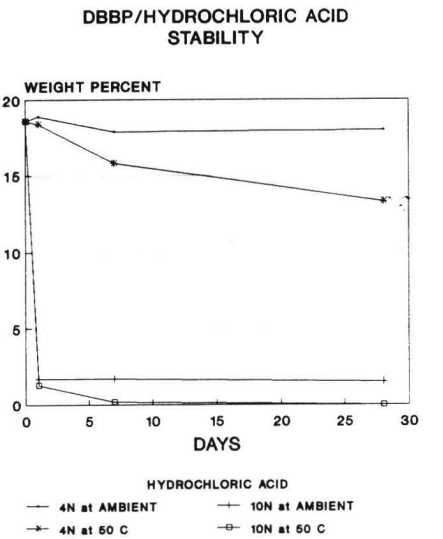


FIGURE 2

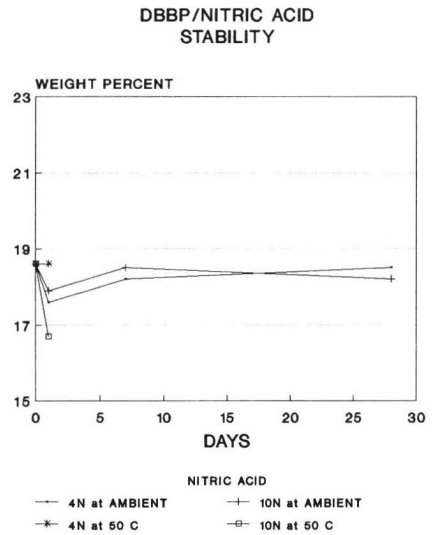


FIGURE 3

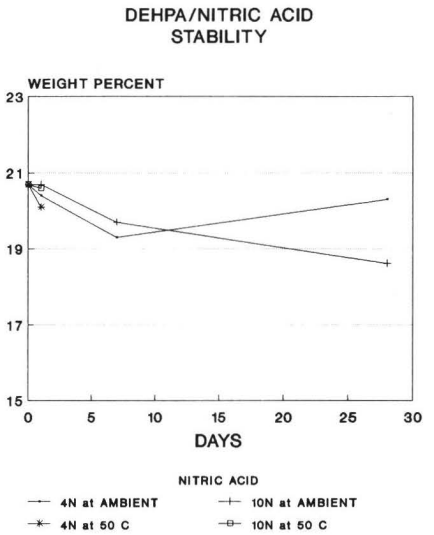


FIGURE 4

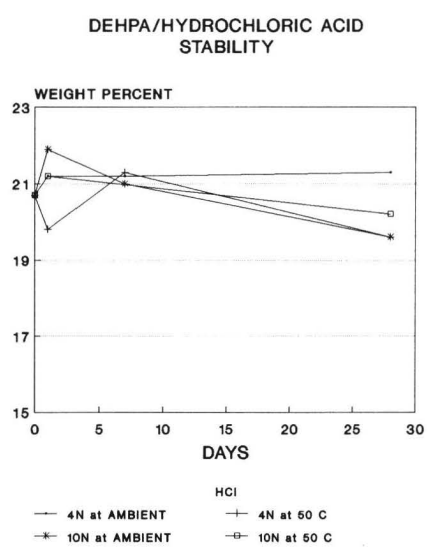


FIGURE 5

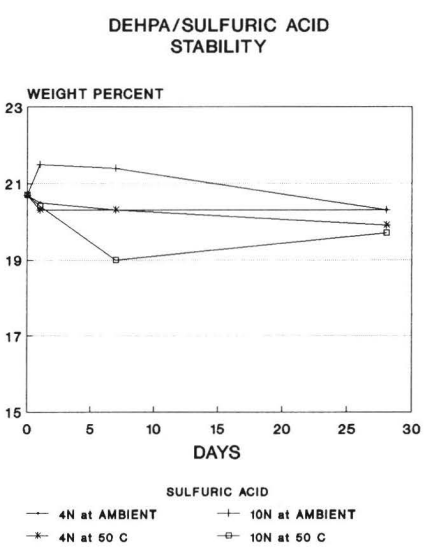


FIGURE 6

IONQUEST 801/HYDROCHLORIC ACID
STABILITY

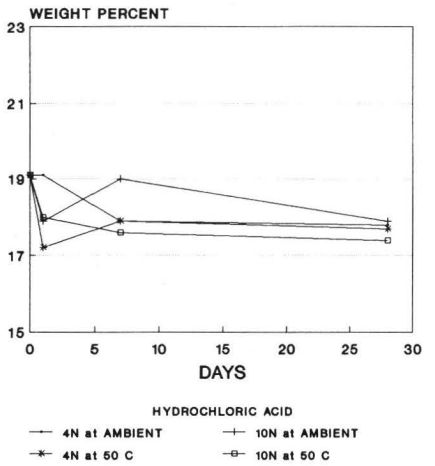


FIGURE 7

IONQUEST 801/SULFURIC ACID
STABILITY

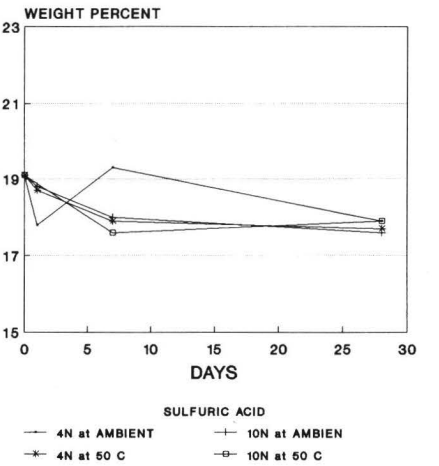


FIGURE 8

IONQUEST 801 / NITRIC ACID
STABILITY

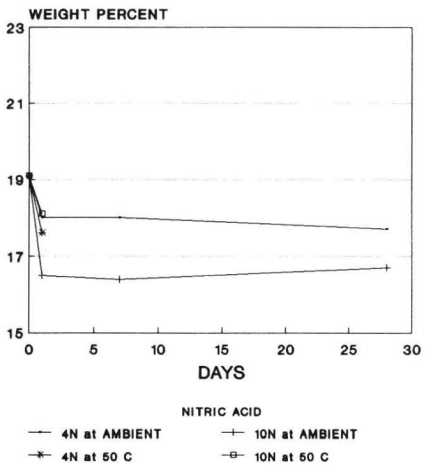


FIGURE 9

CONCLUSIONS

DEHPA Extractant, IONQUEST 801, and DBBP showed very good stability with sulfuric, hydrochloric and nitric acids. Third phase formation was observed with DBBP, especially at high hydrochloric acid concentrations. No third phase formation was observed with DEHPA or IONQUEST 801.

FROM THE AUTHORS

Special appreciation to Bradley J. Balint for setting up and carrying out the experimental work.

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3) "Extraction Separation of Rare Earth Elements, Scandium and Thorium with Mono (2-Ethylhexyl) 2-Ethylhexyl Phosphonate". Li, D. et al., ISEC, (Proc.) Vol. 3 Paper 80-202, 1980.

Solvent Extraction 1990, T. Sekine (Editor)

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EXTRACTION OF ANIONIC METAL COMPLEXES AND ORGANIC ANIONS BY USE OF DICATIONIC ANION-EXCHANGE EXTRACTANTS

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ABSTRACT

A series of lipophilic diphosphonium ions ($R_3P^+-(CH_2)_n-P^+R_3$; R = octyl; n = 2 - 12; abbreviated as C_nBP) were prepared as anion-exchange extractants. The extraction of anionic metal complexes was investigated. In the extraction of dianionic species such as $M^{II}X_4^{2-}$ and $M^{II}(C_2O_4)_2^{2-}$ (M^{II}: Zn^{2+}, Cd^{2+}; X^-: Cl^-, Br^-, CN^-), the dicationic extractants (C_nBPs) exhibited much higher extraction ability than monocationic extractants ($R_3N^+-CH_3$ (Capriquat) and $R_3P^+-C_4H_9$), and the extraction ability of C_nBPs is remarkably dependent on their methylene-chain length (n) between two phosphonium cationic centers. Further, the extraction of organic dianions, such as phthalates, naphthalenedisulfonates, and dansyl-amino acids, was investigated. Similarly to the extraction of anionic metal complexes, the extraction ability of C_nBPs largely surpassed that of the monocationic extractants. The compatibility between the ionic center distance of C_nBPs and that of the dianionic species proved to play an important role on the extractability. The concepts, "multiple charge compatibility" and "geometrical charge distribution compatibility", are discussed.

1 INTRODUCTION

The extraction of anionic species by anion-exchange extractants (ion-pair extractants) is widely used in analytical and separation chemistry. Anionic metal complexes (Green, 1973) and organic anions (Kertes et al., 1986) are extracted. As for such extractants, long-chain quaternary ammonium ions and protonated long-chain tertiary amines are most frequently used. Only a few study have concerned with the extractants having multiple cationic centers in a molecule (Tabushi et al., 1981, Preez et al., 1984).

We have prepared novel type extractants having the structure in which two of the conventional monocationic extractants above mentioned are connected by appropriate bridging chains; these will be called "dicationic (anion-exchange) extractants", and thus the conventional extractants are called "monocationic extractants". By use of such dicationic extractants, we have studied the extractions of anionic metal complexes (Ohki et al., 1984, Ide et al., 1985, Ohki et al., 1989) and of organic anions (Xiao et al., 1985, Ohki et al., 1990). As results of these studies, it is found that (i) as for the extraction of dianionic species, the dicationic extractants are much superior to the monocationic extractants, and (ii) the extraction ability of the dicationic

extractants is greatly dependent on the "bridge-chain length" which is defined as the length of the bridging methylene chain connecting the two phosphonium cationic centers within the extractants.

In this study, we investigated the extraction of various dianionic species including anionic metal complexes and organic anions by the dicationic extractants in detail, and proved the concepts, "multiple charge compatibility" and "geometrical charge distribution compatibility".

2 EXPERIMENTAL

2.1 Materials

The syntheses of the dicationic extractants, polymethylenebis(trioctylphosphonium) dibromides (abbreviated as C_nBP (n = 2 - 12); Fig. 1) as well as a monocationic extractant, butyltrioctylphosphonium bromide (BuMP) were described in our previous papers (Ohki et al., 1984, Ohki et al., 1989). "Capriquat" (methyltrioctylammonium chloride) was a commercial product (Dojindo Lab., Japan). The counter anion of these extractants was converted to other anion if necessary. Other chemicals were of reagent grade and used without further purification. The structures of these extractants as well as extracted anions are indicated in Fig. 1.

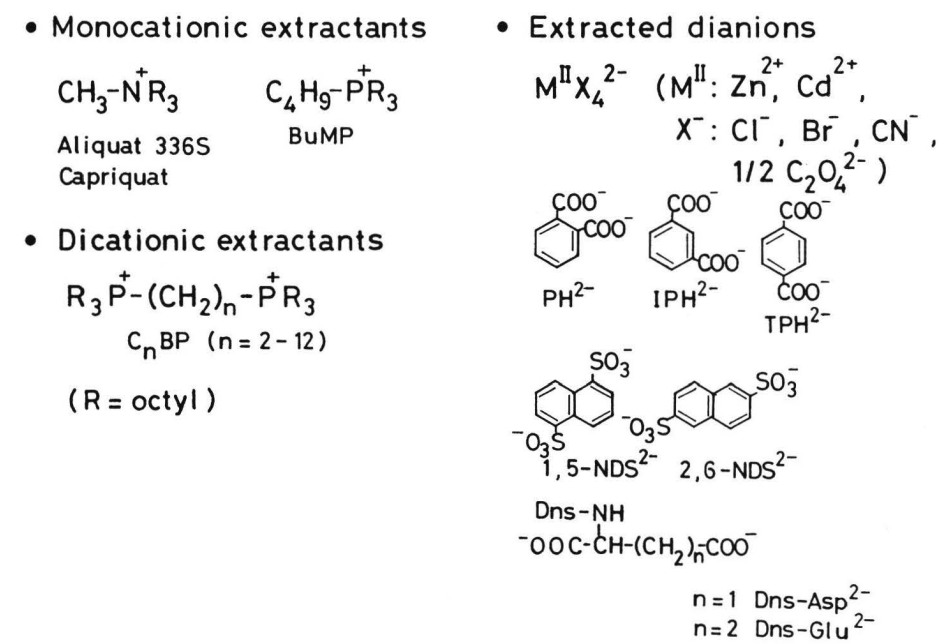


Fig. 1 Anion-exchange extractants and extracted anions.

2.2 Extraction of anionic metal complexes

An aqueous solution (10 ml) containing zinc(II) or cadmium(II) salt was shaken with an organic solution (10 ml) containing an anion-exchange extractant in a stoppered centrifuge tube at 25°C for 20 min. After phase separation, the concentration of metal ion in the aqueous phase was determined by atomic absorption spectrophotometry with a Nippon Jarrel Ash AA-855 instrument.

2.3 Extraction of organic anions

An aqueous phase (10 ml) containing an organic anion and a buffer was shaken with an organic solution (10 ml) containing an extractant in the tube at 25°C for 30 min. After phase separation, the concentration of the organic anion in the aqueous phase was determined by spectrophotometry with a Hitachi 228 or by HPLC using a Shimadzu LC-6AD with an ODS column and a UV detector.

3 RESULTS AND DISCUSSION

3.1 Extraction of anionic metal complexes

The most lipophilic and the most extractable zinc(II)-chloride complex is $ZnCl_4^{2-}$. One can therefore assume that the extraction reaction involves the formation of 1:1 ion-pair between the dicationic extractant (Q^{2+}) and the metal complex:

$$(Q\cdot Cl_2)_o + (Zn^{2+})_w + 2(Cl^-)_w \rightleftharpoons (Q\cdot ZnCl_4)_o \quad (1)$$

$$K_{ex} = [Q\cdot ZnCl_4]_o/[Q\cdot Cl_2]_o[Zn^{2+}]_w[Cl^-]_w^2 \quad (2)$$

where subscripts w and o denote the aqueous and organic phases, respectively. The log - log plots gave straight lines with the theoretical slope in all cases of the dicationic and monocationic extractants. With the monocationic extractants, calculations were performed in such a way that $[Q\cdot Cl_2]_o$ and $[Q\cdot ZnCl_4]_o$ were taken as 2 X $[Q'\cdot Cl]_o$ and $[Q'_2\cdot ZnCl_4]_o$, respectively (Q'^+: monocationic extractant).

In the extraction of zinc(II)-oxalate complex, the following reaction is considered:

$$(Q\cdot Ox)_o + (ZnOx_2^{2-})_w \rightleftharpoons (Q\cdot ZnOx_2)_o + (Ox^{2-})_w \quad (Ox^{2-}: C_2O_4^{2-}) \quad (3)$$

$$K_{ex} = [Q\cdot ZnOx_2]_o[Ox^{2-}]_w/[Q\cdot Ox]_o[ZnOx_2^{2-}]_w \quad (4)$$

The log - log plots gave straight line with the theoretical slope. When cadmium(II) was used, similar extraction equilibria were observed in both extractions of chloro- and oxalate-complexes.

Figure 2 (a) and (b) show the plots of log K_{ex} against the bridge-chain length (n) in C_nBPs in the extractions of zinc(II) and cadmium(II), respectively. The chloro-complexes were favorably extracted by the long bridge-chain extractants such as C_{8-12}BPs, whereas conversely the oxalato-complexes, by the short bridge-chain extractants such as C_2BP. When the bromo- and cyano-complexes of these metal ions were extracted, similar extraction

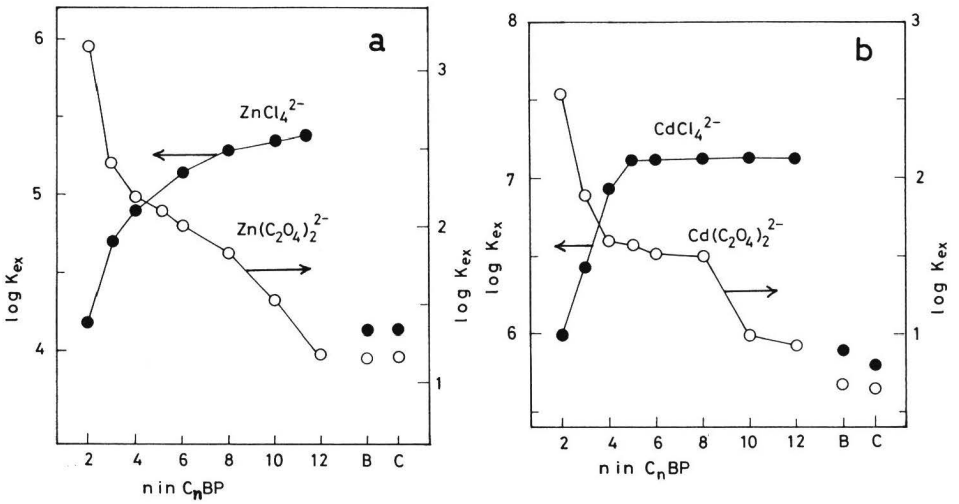


Fig. 2 (a) Extraction of zinc(II) complexes. Initial conditions. Aqueous phase (Aq.): 0.2 mM (1 M = 1 mol/dm^3) $ZnSO_4$ + 0.05 M - 0.4 M HCl (or 0.05 M - 0.4 M $K_2C_2O_4$); Organic phase (Org.) (1,2-dichloroethane): 0.75 mM extractant. (b) Extraction of cadmium(II) complexes. Initial conditions were the same as those in (a) except that $CdSO_4$ was used. B: BuMP; C: Capriquat.

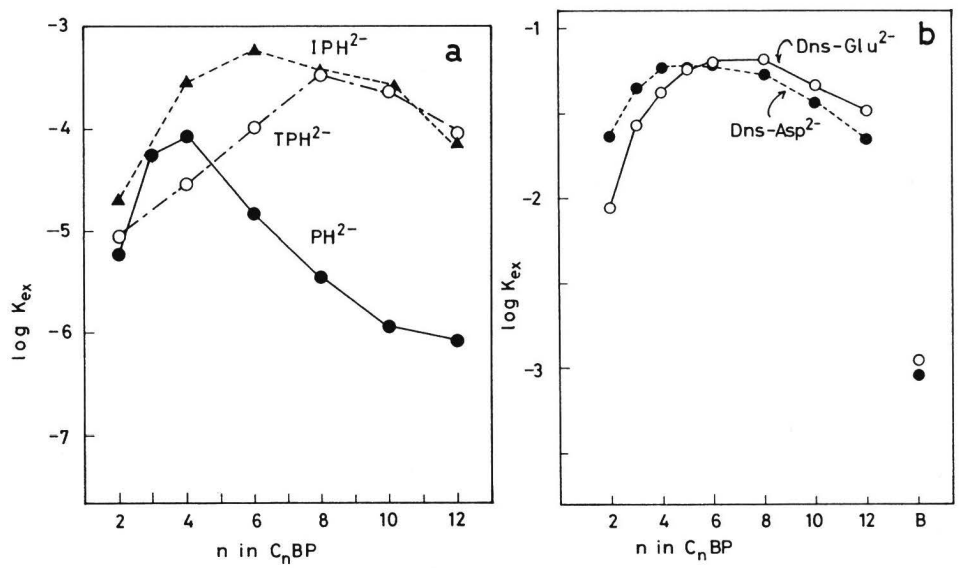


Fig. 3 (a) Extraction of phthalates. Initial conditions. Aq.: 1 mM phthalates + 0 - 4 mM NaBr + 20 mM NaOH (pH > 11); Org. (1-octanol): 1.5 mM extractant. (b) Extraction of dansyl amino-acids. Initial conditions. Aq.: 0.1 mM dansyl-amino acid + 0.3 - 3 mM NaBr + 10 mM $Na_2B_4O_7$-NaOH buffer (pH 10); Org. (1-octanol): 0.2 mM extractant. B: BuMP.

behaviors to those of the chloro-complexes were observed; the long bridge-chain extractants exhibited higher extraction ability.

3.2 Extraction of organic anions

One can assume that the extraction reaction of organic dianion (A^{2-}) by the dicationic extractants occurs via the formation of 1:1 ion-pair between Q^{2+} and A^{2-} as follows:

$$(Q\cdot Br_2)_o + (A^{2-})_w \rightleftharpoons (Q\cdot A)_o + 2\,(Br^-)_w \quad (6)$$

$$K_{ex} = [Q\cdot A]_o[Br^-]_w^2/[Q\cdot Br_2]_o[A^{2-}]_w \quad (7)$$

The log - log plots gave straight lines with the theoretical slope in the extractions of phthalates, naphthalenedisulfonates, and dansyl-amino acids.

Figure 2 (a) and (b) show the extractions of phthalates and dansyl-amino acids, respectively. Since the distance of anionic center within the phthalate isomers was longer ($PH^{2-} \rightarrow IPH^{2-} \rightarrow TPH^{2-}$), the bridge-chain length of the most efficient C_nBP was longer. Such a tendency was observed as well in the extraction of dansyl-amino acids.

3.3 Extraction by dicationic extractants

Table 1 summarizes the most efficient C_nBP in each extraction case and the difference between the extraction constant (log K_{ex}) of the C_nBP and that of BuMP (Δ log K_{ex}).

TABLE 1

The most efficient C_nBP and Δ log K_{ex} value

Extracted anion	n[a]	Δ log K_{ex}[b]	Extracted anion	n[a]	Δ log K_{ex}[b]
$ZnCl_4^{2-}$	12	1.2	PH^{2-}	4	1.2
			IPH^{2-}	6	1.2
$Zn(C_2O_4)_2^{2-}$	2	1.4	TPH^{2-}	8	1.1
			$1,5\text{-}NDS^{2-}$	6	c
$CdCl_4^{2-}$	8-12	1.2	$2,6\text{-}NDS^{2-}$	10	c
			$Dns\text{-}Asp^{2-}$	4-6	1.8
$Cd(C_2O_4)^{2-}$	2	1.9	$Dns\text{-}Glu^{2-}$	8	1.8

[a]The bridge-chain length of the most efficient C_nBP.
[b]The difference between the log K_{ex} value of the C_nBP and that of BuMP.
[c]The log K_{ex} value of BuMP was not measured.

All dianionic species indicated in Table 1 were preferably extracted to a great extent by the dicationic extractants compared to the extractions by the monocationic extractant (BuMP); the extraction constants (log K_{ex}) of C_nBP are higher by 1.1 - 1.9 than those of BuMP. However, in the extraction of monoanionic species such as FeX_4^-, InX_4^- (X^-: Cl^-, Br^-), naphthalenemono-

sulfonates, Dns-Ser$^-$, and Dns-Phe$^-$, C_nBPs exhibited similar extraction abilities to those of the monocationic extractants (Ide et al., 1985). The concept "multiple charge compatibility" is generally found in the extractions by the dicationic extractants. It is considered that dication-dianion interaction enhances the extractability via chelation-like mechanism.

The metal complexes in Table 1 are essentially the same in the coordination structure (regular tetrahedral structure). However, the chloro-complexes and the oxalato-complexes are quite different each other in their extraction behaviors; the former complexes are favorably extracted by the long bridge-chain extractants, whereas the latters, by the short bridge-chain extractants. Presumably, such difference is ascribed to the size and charge distribution about the complexes.

The organic dianions shown in Table 1 have two anionic centers which are separately present within the ions. The compatibility between the anionic center distance and the cationic center distance proved to play an important role in the determination of the extractability. The concept "geometrical charge distribution compatibility" is also generally found in the extractions by the dicationic extractants.

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SOLVENT EXTRACTION OF MERCURY(II) WITH THE NOVEL TYPES OF SULFUR-CONTAINING EXTRACTANTS

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ABSTRACT
Yoshinari Baba, Katsutoshi Inoue, Kazuharu Yoshizuka, Ritsu Yasukawa and Masato Tazaki, 1990
Solvent extraction of mercury(II) with novel types of sulfur-containing extractants

Distribution equilibria of mercury(II) from acidic chloride media with 3,3-diethylthietane(=DETE), 3,3-dibutylthietane(=DBTE) and 2-ethyl-2-(isobutylthiomethyl)butanethiol(=EIBT) in 1,2-dichloroethane were investigated to elucidate the extraction reactions. Mercury was found to be extracted as monomeric species with the composition of 1:2 metal:reagent for these extractants. The extraction reactions with alkylthietanes(=$\overline{S}$) and alkylthiol(=$\overline{HS}$) are shown as follows, respectively.

$$HgCl_4^{2-} + 2\overline{S} \rightleftharpoons \overline{HgCl_2S_2} + 2Cl^- \quad ;K_e$$

$$HgCl_4^{2-} + 2\overline{HS} \rightleftharpoons \overline{HgS_2} + 2H^+ + 4Cl^- \quad ;K'_e$$

The equilibrium constants were evaluated as $_6K_e$= 2.2 and 2.4 for DETE and DBTE, respectively and K'_e= 5.4 x 10^6(mol/dm^3)^4.

1. INTRODUCTION

The solvent extraction of mercury(II) has been investigated using the extractants containing nitrogen or oxygen as a donor atom. However, these extractants have only poor selectivities to mercury (II) over other metals. On the other hand, it is well-known that the extractants containing sulfur-atoms are very powerful and selective extractants for mercury(II)(Handley, 1960;Mojski, 1975). So far, the authors investigated the extraction equilibria of mercury(II) from acidic chloride media with the sulfur-containing extractants such as sulfur-containing carboxylic acid, 1,2-bis-(hexylthio)ethane, dihexyl sulfide and triisobutylphosphine sulfide(Baba et al, 1985, 1986). It was concluded that these extraction reactions were expressed in terms of the solvation reaction mechanism.

In the present paper, using thietanes with chemical structure having a forcedly exposed sulfur atom and a thiol compound with a sulfur atom and thiol group as donor atoms which are expected as the

excellent extractants for mercury(II), the quantitative investigation on the extraction equilibrium of mercury(II) from acidic chloride media was carried out at 303 K using 1,2-dichloroethane as a diluent. In order to elucidate the composition of the extracted species and to evaluate the extraction equilibrium constants, the concentration dependencies of the reactant species on the distribution ratio were examined using each extractant.

2.EXPERIMENTAL

2.1 Reagents

3,3-Diethylthietane(=DETE), 3,3-dibutylthietane(=DBTE) and 2-ethyl-2-(isobutylthiomethyl)butanethiol(=EIBT) were used as the extractants. The structures of these reagents are shown in **Fig.1.**

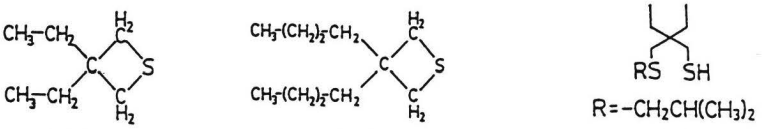
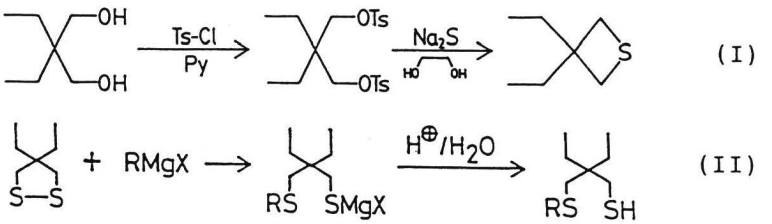


Fig.1. Structures of DETE, DBTE and EIBT

DETE and DBTE were synthesized from 2,2-diethyl-1,3-propanediol and 2,2-dibutyl-1.3-propanediol, respectively, according to the reaction of Eq.(I). EIBT was synthesized from diethylditiolane according to the reaction of Eq.(II)(Tazaki, 1988).



The purities of these reagents are 99.95%, 99.9% and 99.6% respectively. An organic phase was prepared by diluting these extractants with analytical grade of 1,2-dichloroethane on a gravimetric basis. An aqueous phase was prepared by dissolving mercury(II) chloride in hydrochloric acid and acidic sodium chloride solution in the extraction using the thietanes and EIBT, respectively. The initial concentration of mercury(II) was 1 x 10^{-3} mol/dm^3.

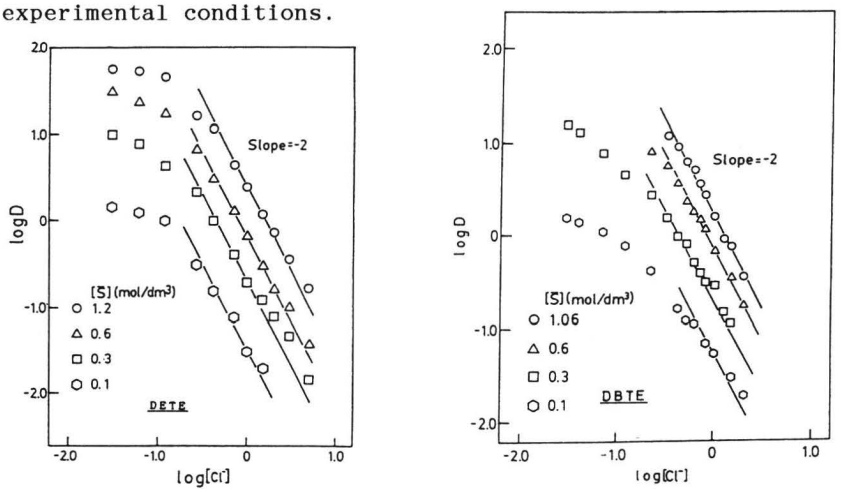
2.2 Procedure

Equal volumes of the aqueous and organic phases were shaken in a

stoppered glass flask immersed in a thermostated water bath maintained at 303 K overnight to attain equilibrium. The concentration of mercury(II) in the aqueous phase was determined by titration with EDTA in the presence of an excess Mg-EDTA using eriochrome black T (BT) as an indicator or by atomic absorption spectrochemical analysis using Nippon Jarrell-Ash model AA-782 spectrophotometer. In the range of low loading ratio, the concentration of mercury(II) in the organic phase was determined by the same methods mentioned above after stripping with a 1 mol/dm^3 aqueous ammonium thiocyanate solution.

3.RESULTS AND DISCUSSION

Figures 2 and 3 show the effects of the concentration of chloride ion on the distribution ratio of mercury(II) from hydrochloric acid solutions with various concentrations of DETE and DBTE, respectively which have the different alkyl-chain length. It was found from a comparison of these results that the extraction of mercury(II) with DETE and DBTE is not almost affected by the alkyl-chain length under the experimental conditions.



Figs. 2 and 3. Effect of chloride ion concentration on distribution ratio (Fig.2:DETE, Fig.3:DBTE).

As is evident from Figs.2 and 3 the distribution ratio, D, decrease with the increase in the hydrochloric acid concentration for all extractant concentrations, suggesting that mercury(II) is extracted according to the following solvation reaction:

$$HgCl_4^{2-} + n\overline{S} \rightleftharpoons \overline{HgCl_2S_n} + 2Cl^- \quad ;K_e \qquad (1)$$

where $\overline{S}$ denotes the extractant species, and overline represents the species in the organic phase. The equilibrium constant, K_e, for the above reaction is given by Eq.(2).

$$K_e = \frac{[\overline{HgCl_2S_n}][Cl^-]^2}{[HgCl_4^{2-}][\overline{S}]^n} \tag{2}$$

In the aqueous chloride solution, mercury(II) give rise to chloro complexes as follows:

$$Hg^{2+} + iCl^- \rightleftharpoons HgCl_i^{(i-2)-} \quad ;\beta_i \tag{3}$$

$$\beta_i = \frac{[HgCl_i^{(i-2)-}]}{[Hg^{2+}][Cl^-]^i} \tag{4}$$

where β_i denotes the stability constants of the i-th chloro complex of mercury(II). The concentration of the tetrachloro complex anion, $[HgCl_4^{2-}]$, is expressed as follows:

$$[HgCl_4^{2-}] = \alpha_4 C_{Hgw} \tag{5}$$

where $$\alpha_4 = \beta_4[Cl^-]^4/(1 + \sum \beta_i[Cl^-]^i) \tag{6}$$

In the region of high chloride ion concentration($[Cl^-]>1$ mol/dm^3), it can approximated by Eq.(7)

$$[HgCl_4^{2-}] \simeq C_{Hgw} \tag{7}$$

By substituting Eq.(7) into Eq.(2), the distribution ratio is approximately expressed by Eq.(8) in the high concentration region of chloride ion.

$$D = \frac{[\overline{HgCl_2S_n}]}{C_{Hgw}} = K_e[Cl^-]^{-2}[\overline{S}]^n \tag{8}$$

where C_{Hgw} denotes the total concentration of mercury in the aqueous phase.

The logarithm of the distribution ratio is approximately expressed by Eq.(9) from Eq.(8) in the region of low loading ratio since the concentration of the unreacted extractant, $[\overline{S}]$, is nearly equal to its initial concentration, C_{B0},

$$\log D = -2\log[Cl^-] + \alpha \tag{9}$$

where $$\alpha = n\log C_{B0} + \log K_e \tag{10}$$

As seen from Figs.2 and 3, the plotted points lie on straight lines of slope -2 in the high concentration range of hydrochloric

acid as expected from Eq.(9). The values of α, defined by Eq.(10), were obtained from the intercepts of these straight lines with the ordinate for each C_{B0} in Figs.2 and 3, and plotted against $\log C_{B0}$ in **Fig.4** to evaluate n and K_e. As is evident from Fig.4, the plotted points lie on straight lines of slope 2, which suggests that n=2 in Eq.(10); that is, mercury(II) is coordinately solvated by two molecules of thietanes in the organic phase. Therefore, the stoichiometric relation of this extraction reaction is expressed as follows:

$$HgCl_4^{2-} + 2\overline{S} \rightleftharpoons \overline{HgCl_2S_2} + 2Cl^- \quad ;K_e \qquad (11)$$

The extraction equilibrium constants, K_e, were evaluated as K_e=2.2 for DETE and K_e=2.4 for DBTE from the intercepts of the straight lines with the ordinate in Fig.4 according to Eq.(10).

Consequently, the difference of extraction equilibrium constants between two kinds of thietanes with different length of alkyl radicals was not almost observed under conditions.

Meanwhile in the extraction using EIBT, the effect of hydrogen ion concentration on the distribution ratio, D, was examined as shown in **Fig.5.** In the high concentration region of the hydrogen ion, the plots are lying on a straight line with the slope -2. This suggests that two hydrogen ions were released when one mercury(II) ion is extracted with EIBT.

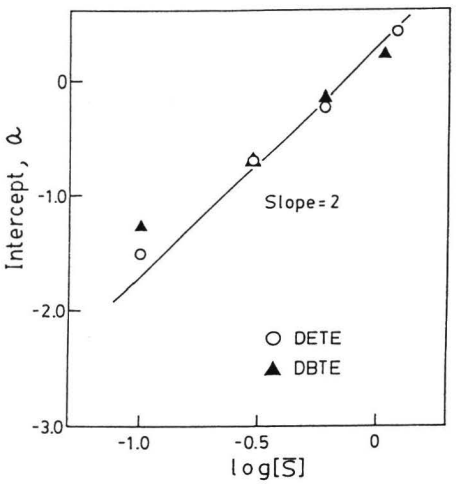


Fig.4 Relation of α and $\log[\overline{S}]$.

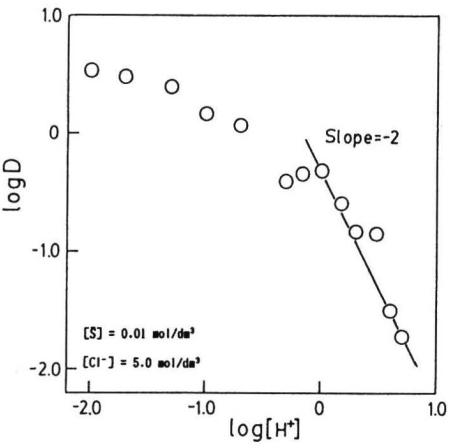


Fig.5 Effect of hydrogen ion concentration on distribution ratio (EIBT).

At a constant hydrogen ion concentration([H+]=2 mol/dm3), the effect of chloride ion concentration on the distribution ratio was examined as plotted in **Fig.6**. The distribution ratio decreases with increasing concentration of chloride ion. The plotted points lie on a straight line of slope -4. **Figure 7** shows the effect of the extractant concentration on the distribution ratio. The plots are lying a straight line with slope 2, which indicates that two extractant molecules participate in the extraction reaction. Consequently, the extraction reaction with EIBT is expressed as follows.

$$HgCl_4^{2-} + 2\overline{HS} \rightleftharpoons \overline{HgS_2} + 2H^+ + 4Cl^- \quad ;K'_e \qquad (12)$$

The equilibrium constant was evaluated as $K'_e=5.4 \times 10^6$ $(mol/dm^3)^4$.

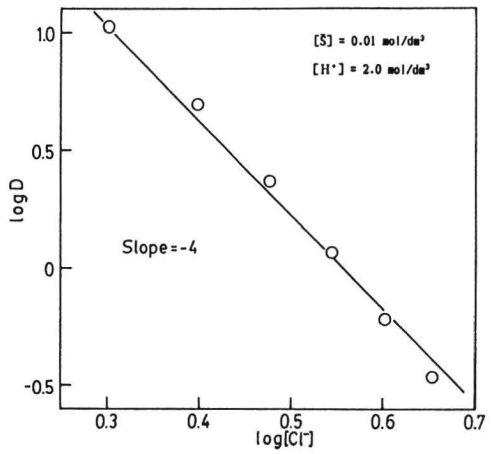


Fig.6 Effect of chloride ion concentration on distribution ratio (EIBT)

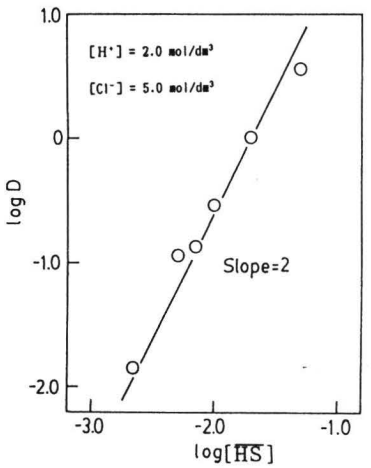


Fig.7 Effect of EIBT concentration on distribution ratio.

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TUCS: A NEW CLASS OF AQUEOUS COMPLEXING AGENTS FOR USE IN SOLVENT EXTRACTION PROCESSES*

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ABSTRACT

The 1-hydroxyethyl-1,1-diphosphonic (HEDPA) and vinylidene-1,1-diphosphonic (VDPA) acids have been studied as stripping agents for Am, Pu, and U from TRUEX process solvent (0.2 M CMPO-1.2 M TBP-dodecane). Both diphosphonic acids have been shown to be highly effective stripping agents using pristine process solvent as well as radiolytically degraded solvent. The actinide-HEDPA and -VDPA complexes are more soluble than the corresponding oxalate complexes and are readily destroyed by metal-catalyzed H_2O_2 oxidation.

INTRODUCTION

During the course of separations by solvent extraction, it sometimes becomes necessary to use supplementary, aqueous soluble, complexing agents to enhance the selectivity of the extractant or to aid in back-extraction or stripping. Despite the usefulness of aqueous complexants in solvent extraction processes, they sometimes have some major drawbacks. First, the complexants that are available will frequently not function effectively at high acidities, e.g. $[H^+] > 0.1$ M. Second, the complexes formed between metal ions and the complexants are sometimes insoluble, which creates a solids problem in solvent extraction equipment. Third, the complexants are not readily degradable and, therefore, they create serious environmental or waste disposal problems. Of the three drawbacks, the last is becoming the most serious in todays climate of environmental constraints.

We have recently been studying a class of complexants which overcome the problems listed above (Nash and Horwitz, 1990, Gatrone et al., in Press). The new class of complexants must meet three criteria: (1) they form highly stable complexes with metal ions in the III, IV, and VI oxidation states in very acidic media (pH < 1 to 7 M strong acid); (2) their complexes with metal ions are water soluble; and (3) the metal ion-complexes and the uncomplexed reagent readily decompose to innocuous substances either spontaneously or in the presence of moderate oxidizing agents. We call this new class of complexants TUCS, which is an acronym for thermally unstable complexants.

We have focused our studies on substituted methane diphosphonic acids for reasons elaborated in (Nash and Horwitz, 1990). Although complexes containing phosphonate ligands have been extensively studied (Rizkalla, 1983), particularly by Soviet Chemists (Kabachnik

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et al., 1974, Kochethova et al., 1983), diphosphonic acids possessing the three properties of TUCS is an innovation (Horwitz et al., 1988).

Three diphosphonic acids in particular, namely, 1-hydroxyethane-1,1-diphosphonic acid (HEDPA), vinylidene-1,1-diphosphonic acid (VDPA) and 1,2-dihydroxyethane-1,1-diphosphonic acid (DHEDPA), meet the three criteria of a TUC. The DHEDPA is a unique TUC because it is stable as its tetrasodium salt but decomposes spontaneously in acid solution with a half-life of approximately 15 days at room temperature (Gatrone, 1989). The objective of this study was to demonstrate the effectiveness of HEDPA and VDPA as stripping agents for actinides from TRUEX process solvent [0.2 M n-octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO)-1.2 M tri-n-butyl phosphate (TBP)-dodecane]. DHEDPA was not included in the actinide stripping studies because of its instability in acidic media. Nevertheless, its complexing strength for Eu(III) was compared to the other complexants. Based on the data obtained with TRUEX process solvent the application of these reagents to other solvent extraction processes may be deduced.

2. EXPERIMENTAL

HEDPA was obtained from Albright and Wilson Americas, Inc., Richmond, VA, 26229, USA, as a 65 weight percent solution. The HEDPA was purified by crystallization from acetic acid (Merck Index, 1983). VDPA and DHEDPA were synthesized by a procedure described in (Gatrone et al., in Press). Stock solutions of VDPA, HEDPA and DHEDPA were prepared by dissolving the solid in water and standardizing by titration (Nash and Horwitz, 1990). The properties of DHEDPA, VDPA and HEDPA are described in (Gatrone, 1989), (Nash and Horwitz, 1990) and (Gatrone et al. in Press).

The CMPO used in this study was obtained from Atochem North America, Inc., Parkway, Philadelphia, PA 19102, as a solvent extraction grade (95-98%) product, and was purified by double crystallization from hexane. TBP (> 98%) was obtained from Eastman Chemical Company and was distilled from calcium hydride at reduced pressure. A stock solution of the TRUEX process solvent was prepared by dissolving weighed amounts of CMPO and TBP in n-dodecane (99%, Aldrich).

Distribution ratios, D, were measured radiometrically using standard gamma counting (241Am) or scintillation counting (233U, 239Pu, and 242Pu) techniques. Prior to each measurement, the organic phase was preconditioned three times (org. to aq. phase ratio = 0.5) with the appropriate nitric acid solution. Phases were mixed for one minute at room temperature. Since D_U and D_{Pu} were measured by scintillation counting, it was necessary to ensure that no interfering activity was present by purifying the stock solutions of these isotopes. Pu(IV) was obtained by adding small portions of hydrogen peroxide to concentrated nitric acid solution of Pu and evaporating to dryness.

Mock stripping experiments were conducted by extracting the appropriate actinide into the organic phase from 1 to 3 M HNO_3 and subjecting it to successive equilibrations with small volumes of fresh aqueous strip solution.

3. RESULTS AND DISCUSSION

A comparison of the complexing ability of HEDPA, VDPA, and DHEDPA with oxalic acid and EDTA for Eu(III) as a function of pH (0.0 to 2.0) is shown in Fig. 1. The formation constants for Eu(III) are from (Nash and Horwitz, 1990); the oxalic acid and EDTA data are from (Martell and Smith, 1977). (Europium was selected as a standin for Am(III) because of its similar chemical properties and the need to apply instrumental methods without danger of contamination or concern for radiolytic effects.) The complexing ability of the ligands is expressed as the stripping factor (D_o/D), which is defined by the equations below. The higher D_o/D, the more effectively the complexant lowers the distribution ratio. The data in Fig. 1 were obtained using bis 2-ethylhexyl phosphonic acid (HDEHP), however, D_o/D is independent of the extractant. HDEHP was used because D_{Eu} is easily adjusted over the pH range of 0 to 2 by changing extractant concentration. The data in Fig. 1 show clearly the superiority of HEDPA, DHEDPA, and VDPA as stripping agents over oxalic acid and EDTA, especially at pH < 1.

The effectiveness of HEDPA and VDPA in reducing the distribution ratios of U(VI), Pu(IV) and Am(III) from a strong neutral organophosphorus extractant is shown in Figs. 2, 3, and 4, respectively. The extractant used was TRUEX process solvent (0.2 M CMPO-1.2 M TBP-dodecane). The lowering of D is most impressive, especially in the case of Pu. D_{Pu} is reduced by > 10^4 even from 6 M HNO_3; in 1 M HNO_3 the reduction is 10^6. Both diphosphonic acids are also very effective in reducing D_U and D_{Am} from the same process solvent. Thus, HEDPA and VDPA are ideal actinide stripping agents in the TRUEX process if all of the actinides are to be routed to vitrification as opposed to recovery.

No Aqueous Complexes

$$D = \frac{[M(EHE)_3]}{[M^{3+}]} = D_o$$

Aqueous Complexes Formed

$$D = \frac{[M(EHE)_3]}{[M^{3+}] + \Sigma\Sigma\Sigma[M_m H_l L_l]}$$

$$D = \frac{D_o}{1 + \Sigma\Sigma\Sigma\beta_{mnl}\,[M]^{m-1}\,[H]^n\,[L]^l}$$

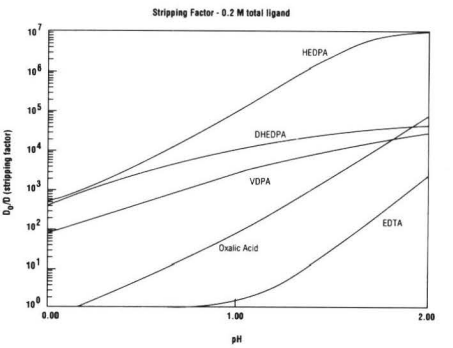
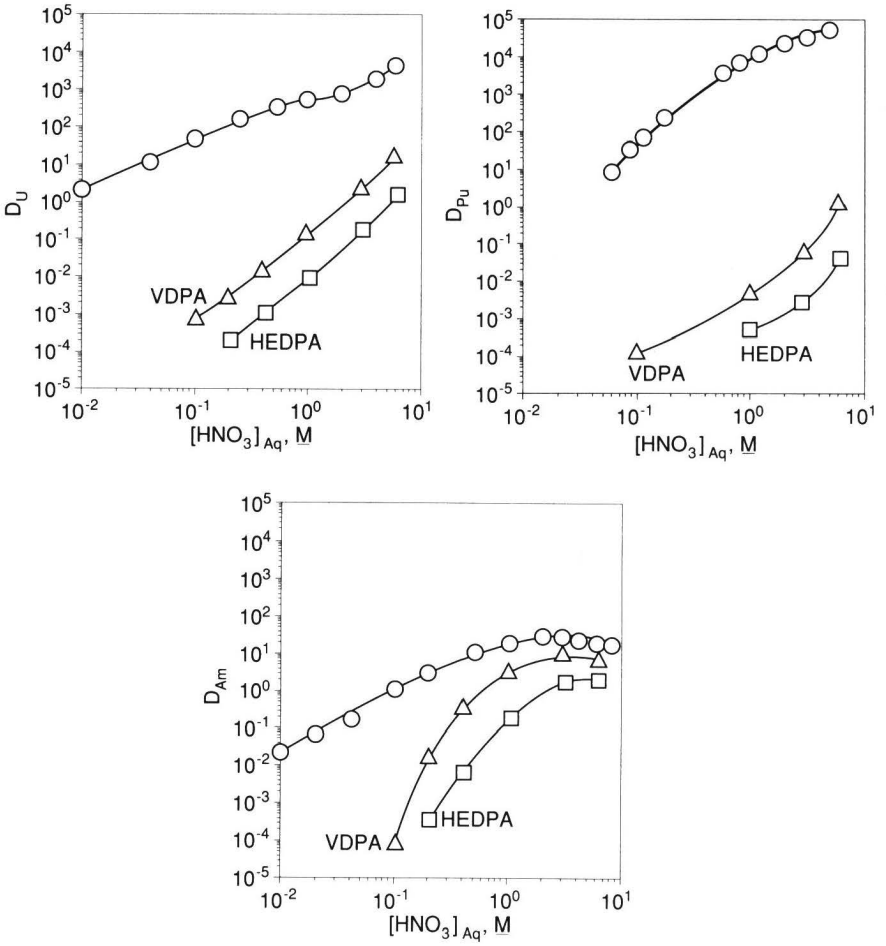


Fig. 1. The effect of aqueous complexes on the metal ion distribution ratios of Eu(III) as predicted from stability constants.



Figs. 2, 3 and 4. Comparison of the acid dependencies of D_U, D_{Pu}, and D_{Am} in the presence and absence of VDPA and HEDPA. Organic phase 0.20 M CMPO-1.2 M TBP-dodecane. HEDPA and VDPA = 0.25 M.

The D_{Am}, on successive stripping of TRUEX process solvent with different concentrations of VDPA is shown in Table 1. The data again show the extreme effectiveness of the TUCS reagent. The higher D_{Am} values obtained on the first contact are due to the extraction of excess nitric acid from the solvent which lowers the pH.*

TABLE 1

Stripping TRUEX-NPH Process Solvent * with VDPA.

	D_{Am}, O/A = 2		
VDPA, M	1st Strip	2nd Strip	
0.50 M	8.1×10^{-4}	-	
0.25 M	2.1×10^{-3}	1.6×10^{-4}	
0.10 M	7.8×10^{-3}	1.9×10^{-4}	
	D_{Am}, O/A = 5		
VDPA, M	1st Strip	2nd Strip	3rd Strip
0.25 M	9.3×10^{-3}	2.3×10^{-3}	1.4×10^{-3}

*Am extracted from 1 M HNO_3 and scrubbed twice with 0.1 M HNO_3, O/A = 2.

In addition to being effective stripping agents, the solubility of the UO_2^{2+}, Eu^{3+}, and Th^{4+} complexes with HEDPA and VDPA are at least an order of magnitude greater than the corresponding oxalate complexes. (Eu^{3+} and Th^{4+} were used as standins for Am^{3+} and Pu^{4+}, respectively.)

The ability to readily decompose TUCS and their metal ion complexes is an important property of these reagents. HEDPA, VDPA, and DHEDPA may be decomposed in < 5 hrs by metal catalyzed oxidation with H_2O_2 at 80 °C. The solution to be decomposed is made 2 to 3 M in H_2O_2 and 10^{-3} M in Na_3VO_4. Identified decomposition products are phosphoric acid and CO_2 with lesser amounts of acetic and formic acids (McEwen and Meisinger, Personal Communication). VDPA and DHEDPA (but not HEDPA) may be completely decomposed in < 3 hrs. in 8 M HNO_3 at 100 °C. Decomposition of VDPA and HEDPA in the presence of macro-concentrations of actinides and lanthanides yields granular precipitates which are believed to be insoluble phosphates. In the case of Nd(III) the precipitate has been identified as hexagonal $NdPO_4 \cdot 0.5H_2O$ (Morss, Personal Communication).

The effectiveness of HEDPA and VDPA in complexing actinides at low pH's may also be exploited in stripping hydrolytically and radiolytically degraded solvent. Radiolytic and hydrolytic degradation of a neutral extractant such as CMPO or TBP is manifested by an increase in the distribution ratio of e.g., Am(III), at low acidity because of the the generation of acidic extractants. (Acidic extractants are very effective at low acid concentration, whereas neutral extractants have very low D's under the same condition.) For example, the footnote in Table 2 compares D_{Am} at 0.04 M HNO_3 for pristine and degraded TRUEX process solvent. The presence of acidic extractants is responsible for the 8-fold increase in D_{Am}. Table 2 shows the reduction in D for Am(III), Pu(IV), and U(VI) by using 0.25 M HEDPA and an organic-to-aqueous phase ratio (O/A) equal to five on degraded TRUEX process solvent. For each transuranic element the reduction is over 10^4 in three successive contacts.

Very large reductions in alpha activity from process solvents are very important in nuclear waste processing. To reduce the level of toxicity of TRU or high-level waste, very large decontamination factors for all transuranic elements are required. These large decontamination factors require the recycling of the process solvent with negligible levels of alpha

activity. The HEDPA and VDPA are far superior to any chemical reagent for stripping actinides and Zr and rare earth fission products. By preceding the alkaline (Na_2CO_3) solvent wash step (which is used to remove organic degradation products) with a TUCS strip, one can avoid generating an alkaline TRU waste stream. The TUCS strip reagent may be recycled a number of times before decomposing the diphosphonic acid by oxidation. Since only very low concentrations of actinides are involved in solvent cleanup and, thus, no precipitate will be formed, the decomposed TUCS solution may be recycled to the feed. This procedure avoids generating additional TRU waste streams in solvent cleanup operations.

TABLE 2

Stripping of Degraded* TRUEX Process Solvent (0.2 M CMPO - 1.2 M TBP in Dodecane) Aqueous Strip: 0.25 M HEDPA, O/A = 5.

Strip No.	D_{Am}	D_{Pu}	D_U
1	4.3×10^{-3}	1.6×10^{-4}	1.6×10^{-3}
2	1.8×10^{-3}	$\sim 9 \times 10^{-3}$	$\sim 9 \times 10^{-3}$
3	$\sim 4 \times 10^{-3}$	---	$\sim 2 \times 10^{-3}$
Overall reduction in nuclide conc.	2.8×10^{5}	3.9×10^{4}	3.6×10^{4}

*Hydrolytic and Radiolytic Degradation

$D_{Am} = 1.6$ at 0.4 M HNO_3

$D_{Am}^{ref} = 0.2$ at 0.4 M HNO_3

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SOLVENT EXTRACTION OF AQUEOUS METAL PICRATES WITH (3*m*+*n*)-CROWN-*m* (*m*=4-12, *n*=0-4) AND THE RELATED GLYMES

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ABSTRACT

The solvent extraction of aqueous alkali and heavy metal picrates with a series of symmetrical 3m-crown-m ethers (*m*=4-12), ring-enlarged (3*m*+*n*)-crown-*m* (*m*=4-12, *n*=1-4), and the related glymes has been carried out. Their cation binding ability and cation selectivity are discussed in terms of cavity size, conformation, and molecular symmetry of the crown ethers.

INTRODUCTION

Most works on the cation binding ability of crown ethers have been focused on 12- to 18-membered symmetrical crown ethers, while no systematic studies have been reported on the effects of ring size and symmetry upon complexation behavior of crown ethers. The cation binding abilities of the related oligoglymes have scarcely explored systematically. Furthermore, little attention has been paid so far to the larger crown ethers with more than 21-membered rings (Son *et al.*, 1984; Grootenhuis *et al.*, 1987).

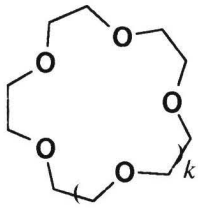
In this paper we report the synthetic feasibility of a series of (3*m*+*n*)-Crown-m (*m*=4-12, *n*=0-4), and the related long-chain oligoglymes, and evaluate their cation-binding abilities by means of the solvent extraction of aqueous metal picrates.

RESULTS and DISCUSSION

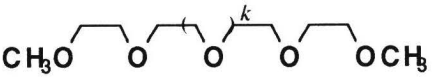
Synthesis. 12-crown-4, 15-crown-5, and 18-crown-6 were commercially available and were used as received. (3*m*+*n*)-Crown-m (*m*=4-12, *n*=0-4) were synthesized in 8-36 % isolated yields by reactions of appropriate combinations of oligoethylene glycol with oligoethylene glycol ditosylate in the presence of metal hydroxide in THF. The penta- to undecaglymes were synthesized in 30-80 % isolated yields by reactions of the corresponding oligoethylene glycol monomethyl ether with oligoethylene glycol ditosylate in THF.

Solvent Extraction. *1. Symmetrical crown ethers and oligoglymes.* The solvent extractions of aqueous solutions of metal picrates (3 mM) were performed at

Symmetrical Crown Ethers and Oligoglymes

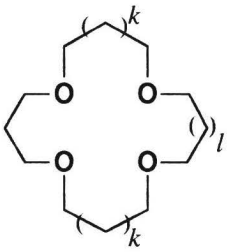


k = 1-8



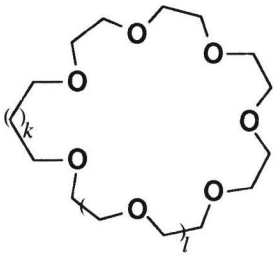
k = 1-9

Less Symmetrical Crown-4



13-Crown-4: k=0, l=0
14-Crown-4: k=0, l=1
15-Crown-4: k=1, l=0
16-Crown-4: k=1, l=1

Large Ring Crown-7 and Crown-8



21-Crown-7: k=0, l=1
22-Crown-7: k=1, l=1
23-Crown-7: k=2, l=1
24-Crown-8: k=0, l=2
26-Crown-8: k=2, l=2

25°C with dichloromethane solutions of a ligand (3 mM; 3*m*-crown-*m*, *m*=4-12, and glyme) according to the procedures reported (Ouchi *et al.*, 1984). In Figure 1, the distribution ratios of cations between the two phases, *i.e.* $D_M=[M^+]_{org}/[M^+]_{aq}$, are plotted as a function of the number (*m*) of oxygens in ligand.

With the symmetrical crown ethers 3m-crown-m , it is noted that each cation exhibits two peak(s)/shoulder(s) in the metal distribution, D_M. The global maximum in D_M is obtained in general with the crown ether size-fitted to the cation employed; the first peak for Na^+ at the ring size 15 (*m*=5), for K^+, Rb^+, Ag^+, and Tl^+ at 18 (*m*=6), and for Cs^+ at 21 (*m*=7). Therefore the favorable 1:1 complexation of a cation with a ligand must be responsible for the first peak. The second peak/shoulder appears at larger ring size with lower D_M. Again peak position is closely related to the cation diameter; for Na^+ and Ag^+ at 24 (*m*=8) (very weak) for K^+, Rb^+, and Tl^+ at 30 (*m*=10), and for Cs^+ at 33 (*m*=11). The second peaks may be accounted for in terms of the encapsulating complexation of the cations.

With oligoglymes, the cation binding ability increased with increasing number of the donor oxygen atoms in the chain. It should be noted that the D_M values reach the plateau; for the small cations, Na^+ and Ag^+, at m>8, and for K^+, Rb^+, and Cs^+ at m>9 or 10. The results may indicate that some of the oxygens in the oligoglymes with too long chain do not act as an effective donor atom.

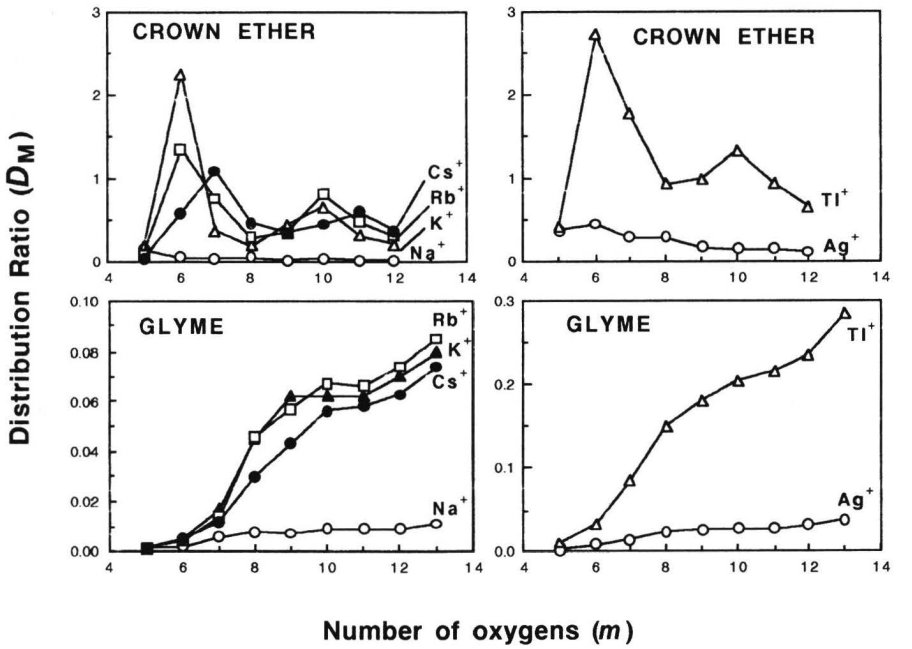


Figure 1. Plots of distribution ratio (D_M) *vs.* number of oxygens in crown ether (top) or glyme (bottom): temperature 25°C; [ligand] = 3 mM in CH_2Cl_2; [picrate] = 3 mM in H_2O.

2. Less symmetrical crown-4 ethers. It has been reported that, in general, the 14-crown-4 derivatives have the highest cation-binding abilities and selectivities for Li^+ based on the size-fit concept (Czech *et al.*, 1984; Kimura *et al.*, 1986), although the other crown-4 derivatives have not extensively been surveyed systematically. As can be seen from Table 1, unsubstituted 14-crown-4 clearly shows the highest extractability and selectivity for Li^+. It should also be noted that 12-crown-4 showed the highest extractability for Na^+, while 13- to 16-crown-4 showed only low or almost negligible extractabilities for the larger cations.

Table 1. Solvent Extraction of Aqueous Metal Picrates with 12- to 16-Crown-4[a]

	% Extractability[b]						
Ligand	Li^+	Na^+	K^+	Rb^+	Cs^+	Ag^+	Tl^+
12-Crown-4	2.7	14.4	3.5	3.5	3.1	13.3	15.3
13-Crown-4	0.8	3.8	1.2	0.8	0.6	8.7	6.1
14-Crown-4	13.9	1.0	0.6	0.2	0.2	4.6	2.5
15-Crown-4	1.7	1.2	0.2	0.2	0.1	6.4	0.9
16-Crown-4	0.3	0.2	0.1	*c*	*c*	1.2	0.3

[a]Temperarure 25°C; aqueous phase (10 mL): [picrate] = 3 mM; organic phase (CH_2Cl_2, 10 mL): [ligand] = 30 mM. [b]Defined as % picrate extracted into the organic phase. Average of two or three independent runs; error <0.7. [c]Extractability not determined.

Table 2. Solvent Extraction of Metal Picrates with 21- to 23-Crown-7 and 24- to 26-Crown-8[a]

	% Extractability[b]					
Ligand	Na^+	K^+	Rb^+	Cs^+	Ag^+	Tl^+
21-Crown-7	3.2	26.8	43.1	52.2	22.4	63.9
22-Crown-7	2.6	24.6	27.7	25.0	17.2	47.1
23-Crown-7	1.4	4.3	6.1	9.0	8.2	24.0
24-Crown-8	5.1	16.2	22.4	32.4	20.0	48.4
26-Crown-8	1.4	7.8	10.5	12.8	8.9	26.9

[a]Temperature 25°C; aqueous phase (10 mL): [picrate] = 3 mM; organic phase (CH_2Cl_2, 10 mL): [ligand] = 3 mM. [b]Defined as % picrate extracted into the organic phase. Average of two independent runs: error <1.0.

3. Less symmetrical (3m+n)-crown-m ethers (m=5-8, n=1,2). We have reported that less symmetrical crown-5, and crown-6 show lower extractabilities in general, but exhibit drastically different and, in some cases, higher selectivities for specific cations (Ouchi *et al.*, 1984). Compared with that of 18-crown-6, the cation selectivity of 20-crown-6 and 22-crown-6 showed a significant shift probably due to the enlarged cavity size. 16-Crown-5, in particular, shows much higher cation selectivity for Na^+ and Ag^+ than any other crown-5. This behavior prompted us to evaluate the cation-binding ability of the larger, less-symmetrical crown-7 and crown-8. However, as can be seen from Table 2, 22-crown-7, 23-crown-7, and 26-crown-8 showed lower extractabilities than 21-crown-7 and 24-crown-8, respectively, and no significant shift in cation selectivity was observed.

In conclusion, this report deals with the systematic study of the cation binding ability and cation selectivity of unsubstituted crown ethers in view of the ring size and symmetry of ligands. These ligands can be modified for further complexation study which would develop the crown ether chemistry.

ACKNOWLEDGMENT

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THE SOLVENT EXTRACTION OF SOME DIVALENT TRANSITION METALS WITH N-PENTAFLUOROBENZOYLPHENYLHYDROXYLAMINE

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ABSTRACT

A study of the extraction behavior of representative transition metals, Zn, Ni, Co, and Mn, was carried out with chloroform solution containing N-pentafluorobenzoylphenylhydroxylamine (PFBPHA). The results demonstrate that the metals are extracted as a simple chelate MR_2, whereas these metals can not be extracted with N-benzoylphenylhydroxylamine(BPHA) under the same experimental condition.

1 INTRODUCTION

It is expected that fluorine substitution of chelating agent would result in the increasing of its acidity without decreasing hydrophobicity and, consequently, in the improvement of extractability of chelating agent. N-Benzoylphenylhydroxylamine analogue was chosen to prove this hypothesis because of ease of synthesis. Many analogues of BPHA have been synthesized and studied for the extraction of metals,[1] however, polyfluorinated derivative is not known other than N-trifluoromethylbenzoylphenylhydroxylamine.[2]

In this study, N-pentafluorobenzoylphenylhydroxylamine was newly synthesized and was examined to compare chemical properties and extractability with BPHA. PFBPHA is more acidic(pKa=7.05 for PFBPHA, pKa=8.30 for BPHA) and is also lipophilic(log K_{DR}=2.56 for PFBPHA, log K_{DR}=2.33 for BPHA). Extractability of PFBPHA was also studied for some divalent transition metals.

2 Experimental

2.1 Reagents

Metals of zinc, cobalt, nickel, and manganese, having a purity of 99.9% or more, were dissolved with nitric acid and fumed with sulfuric acid to almost dryness, followed by dissolving the residue with 0.05M sulfuric acid. These solutions were stored in polyethylene bottles and properly diluted for use. A buffer

solution including 0.066M ammonia and 0.033M ammonium sulfate(pH = 9.5) was prepared to cover the pH range of 7-9. Masking reagents were not used since organic hydroxycarboxylic acids such as tartaric acid disturb the metal extraction with BPHA and could not be used for masking of metal ions.

To prepare a series of extracting solutions including PFBPHA, calculated amounts of 0.025M PFBPHA solution were taken into volumetric flask and diluted to the mark with washed chloroform. Chloroform(Analytical reagent grade) was washed with deionized water prior to use. All other reagents were of analytical grade and used without purification.

2.2 Synthesis

N-Pentafluorobenzoylphenylhydroxylamine was synthesized by reaction between pentafluorobenzoylchloride and phenylhydroxylamine.[1] Phenylhydroxylamine was prepared according to the method described by Kamm.[3] PFBPHA is a white needle-like crystalline solid, with melting point 166-167° C. Its solubility in water 25 ± 1.0° C is 0.003g per 100ml. UV spectrum in 50% ethanol; λ_{max} 260nm(ε = 6400); isosbestic point 247nm and 288nm. Elemental Analysis; Calcd. for $C_{13}F_5H_6NO_2$; C, 51.45; H, 1.77; N,4.65; Found C, 51.50; H, 1.99; N, 4.62.

2.3 Extraction Procedure

A 10ml portion of buffered metal ion solution and an equal volume of the reagent chloroform solution were equilibrated in a 30ml extraction vial by vigorously shaking for one hour at 25±1° C. It was found that the extraction equilibrium with PFBPHA was attained within one minute, however, shaking time was placed one hour just to make sure. After phase separation by using centrifuge, the pH value of the aqueous phase was taken as the equilibrium pH value and metal ion concentration in aqueous phase was determined by AAS method. The distribution ratio, D, was calculated from the known total concentration of metal ion and from the determined concentration in the aqueous phase.

2.4 Acid Dissociation Constant

The pKa value of PFBPHA was determined spectrophotometrically in an aqueous medium of ionic strength 0.1 with 0.033M potassium

sulfate at 25±1.0°C. Solutions of PFBPHA(7.35×10^{-5}M) were prepared in aqueous solution at pH values ranging from 3.97 to 10.39. The absorbance of the 233nm band, which increases 0.595 to 0.812 with increasing pH, was measured. The pKa value was determined from the plots of absorbance vs. pH.

2.5 Distribution Constant

A 10ml portion of 10^{-2}M chloroform solution of ligand was shaken vigorously with 10ml of an aqueous solution of pH 3.87-8.86 containing 0.033M K_2SO_4 in a 30ml extraction vial for one hour at 25±1.0°C. After phase separation, the concentration of ligand in aqueous phase was determined spectrophotometrically. Thus, the distribution constant of undissociated PFBPHA between chloroform and water, K_{DR}, was calculated from the known total concentration of ligand in chloroform solution and the determined concentration of ligand in aqueous phase.

3 Results and Discussion

The dissociation constant, pK_a and distribution constant, K_{DR} of PFBPHA are given in Table 1 together with its solubility in water, compared with those of BPHA and N-m-trifluoromethylbenzoylphenylhydroxylamine. As shown in Table 1, the pK_a value for PFBPHA is the least among the cited BPHA derivatives, because of the electron-withdrawing nature of the $-C_6F_5$ group.

TABLE 1 Physical properties of hydroxylamine derivatives

Substituted hydroxylamines	m.p. (°C)	Solubility in H_2O, g/100ml	pKa value	log K_{DR} [3]
N-Pentafluoro-benzoylphenyl	166-167	0.003[1]	7.05±0.10[1]	2.56±0.02
N-m-Trifluoro-methylbenzolyphenyl	80-81	0.03	7.96±0.02	2.93±0.02
N-Benzoylphenyl	122-122	0.040	8.30±0.04[2]	2.33±0.01

1) at 25°C, 2) at 22.5°C, 3) Distribution between $CHCl_3$ and H_2O

The composition of extracted metal chelate species by PFBPHA and equilibrium constant of examined extraction process were

determined on the basis of "slope analysis", in which the extraction data were plotted in the form of log D vs. different experimental variables such as pH of the aqueous phase and logarithm of the concentration of PFBPHA for representative transition metals Co, Ni, Mn, and Zn.

The chelate extraction equilibrium of metals with PFBPHA, symbolized by HR, can be represented by Eqs. 1 and 2.

$$M^{2+} + 2HR_{(o)} \overset{\beta}{\rightleftharpoons} MR_{2(aq)} \qquad (1)$$

$$MR_{2(aq)} \overset{K_{DC}}{\rightleftharpoons} MR_{2(o)} \qquad (2)$$

where β and K_{DC} are the overall aqueous phase formation constant and the distribution constant of the chelate, MR_2, respectively. Taking into account the fact that metal is present as mixture of intermediate amine complexes, the distribution ratio, D, of metals for Eqs. 1 and 2 is given by

$$D = \frac{C_{M(o)}}{C_{M(aq)}} = \frac{[MR_2]_{(o)}}{[M^{2+}] + [ML^{2+}] + \cdots\cdots [ML_n^{2+}]}$$

$$= \frac{[MR_2]_{(o)}}{[M^{2+}]\{1 + k_1[L] + \cdots\cdots k_1k_2\ k_n[L]^n\}} \qquad (3)$$

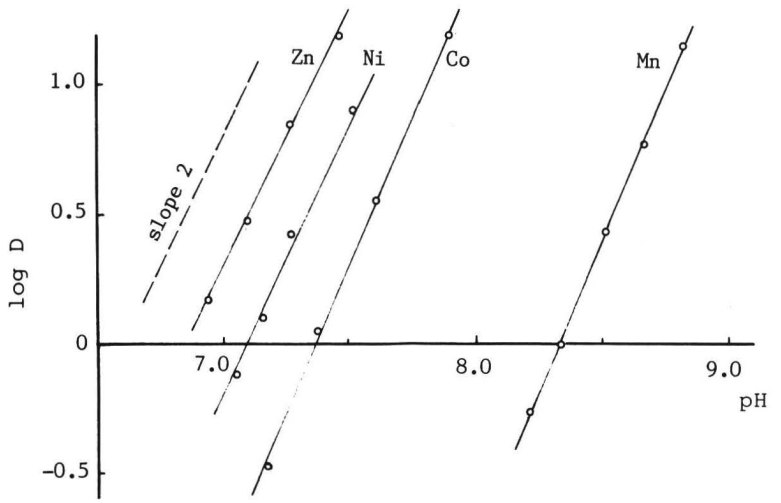


Fig. 1. Distribution of metals in the presence of PFBPHA as a function of pH. $[M^{2+}]=1\times10^{-4}$M in an aqueous phase, [PFBPHA]=0.01M in $CHCl_3$, $[K_2SO_4]=0.033$M.

where L is ammonia and subscript (o) and (aq) refer to the species in the organic and aqueous phase, respectively. The calculated values of [L] at $pH_{1/2}$ and the stepwise formation constants for ammine complexes[4], k_1 through k_n, were substituted into the Eq.3. All the values of the second terms in the denominator of Eq.3, $k_1[L]$, are smaller than 1, e.g., 5.99×10^{-2} for Ni, 1.58×10^{-2} for Zn, 9.12×10^{-3} for Mn, and 2.16×10^{-2} for Co, and those of the later terms in the denominator are all smaller than the values of the second terms. Therefore, Eq. 3 is simplified as

$$D = \frac{[MR_2](o)}{[M^{2}]} = \frac{K_{DC} K_a^{2} [HR]_{(o)}^{2}}{K_{DR}^{2} [H^+]^2} = \frac{[HR]_{(o)}^{2}}{[H^+]^2} \qquad (4)$$

where K_a and K_{DR} are the acid dissociation constant, $10^{-7.05}$ and distribution constant, $10^{2.56}$, of HR, respectively.

As shown in Fig.1, all slopes of log D vs. pH are close to two, e.g., 2.4 for Ni, 2.1 for Zn, 2.3 for Co, and 2.3 for Mn, which indicates that two hydrogen ions are released in their formation. Figure 2 is the relationship between log D - 2pH vs. $\log[PFBPHA]_{(o)}$. The plots exhibit a slope of two for all of the ions, e.g., 2.1 for Ni, 2.3 for Zn, 1.9 for Co, and 2.3 for Mn, respectively. This means that the extracted species contain two R^- ions. From these extraction data, the values of log K_{ex} can be calculated by using Eq.4, and are listed in Table 2, together with $pH_{1/2}$ values.

Extraction of metals were carried out by using 0.01M BPHA chloroform solution in order to compare the extractability of PFBPHA with that of BPHA. However, in the BPHA system, it

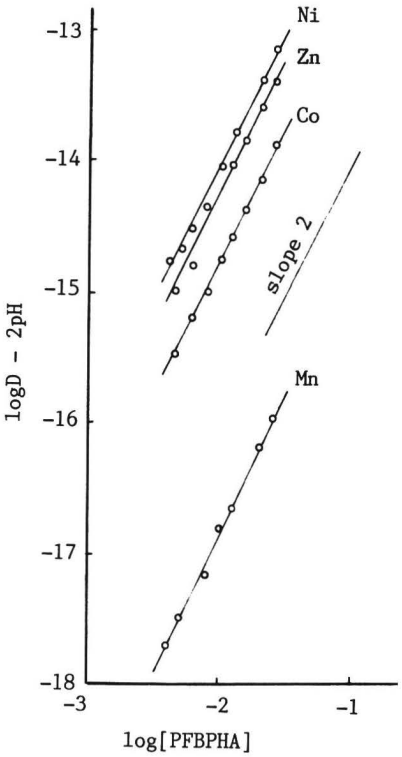


Fig.2. Distribution of metals in the presence of PFBPHA as a function of logD-2pH. $[M^{2+}]=1\times10^{-4}$M, $[PFBPHA]_o$=varied.

was observed that spongy substance floated at interface of two layers after the phase separation, and the quantitative extraction data were not obtained under this experimental condition. Chwastowska et al., reported that metals studied here were extracted quantitatively into chloroform with BPHA from nitrate medium under the definite pH conditions[5]. Therefore, the following experiments were carried out to clarify the discrepancy; 1) The medium of the aqueous phase was changed from structure making ion, SO_4^{2-} to structure breaking ion, ClO_4^-, expecting that hydrolysis would be prevented. 2) Two kinds of BPHA reagent were obtained from different supplier and used for the metal extraction. 3) Metals were extracted by adding BPHA ethanol solution to the aqueous phase, adjusting pH of aqueous phase, and followed by shaking with chloroform. 4)Potassium tartrate was added to the aqueous phase(0.02M) as a masking reagent. However, these attempts to get the quantitaive results with BPHA extraction system were unsuccessful and the reason why BPHA can not extract these metals still remains undissolved.

TABLE 2 Equilibrium extraction parameters

Extracted species		Zn	Ni	Co	Mn	Extraction condition
ML_2	log K_{ex}	-9.94	-10.24	-10.74	-12.70	[HL] = 0.01
	$pH_{1/2}$	6.97	7.12	7.37	8.35	

From these results, it can be said that PFBPHA improves extractability of BPHA since PFBPHA extracts the metals which can not be extracted by BPHA under this experimental condition.

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STUDIES ON THE STRUCTURAL ANALYSIS OF COMPONENTS OF PETROLEUM SULFOXIDES

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ABSTRACT

Petroleum sulfoxides(PSO-II) are mixture. They are a very promising extractant in the industry. We used HPLC to separate PSO-II and obtained a series of purer parts of PSO. And then , used IR and GC-MS to decide their structures. Through analyzing the IR spectra of purer parts, we know that such PSO are alicyclic structural sulfoxides. And through the GC-MS interpretation , We know that they are single alkyl substituted cyclic sulfoxides. We also decide the position of alkyl substituted radical on the ring . It is proved that substituted radical R on the ring is not straight chain , we do not deduce the structure of R, some substituted radical is straight chain and we have decided their structure of R.

1 INTRODUCTION

Petroleum sulfoxides (PSO-II) are a very promising extractant in the industry . Coming from the by-product of pe-troleum and having the excellent selectivity for some metals, it arose a great intrest in the scientific and technological workers whose countries such as U.S.S.R. , China etc, possess of the high S-containing petroleum resources . According to the report from U.S.S.R. references, PSO have extraction and separation abilities for U and Th, Mo and W, Nb and Ta, Zr and Hf, and noble metals. In 1981 from the high S-containing diesel oil (270-330°C) in central china, We have succeeded in the preparation research of PSO-II, possessing non-poisonous character determined by Zhongshan Medical University and carried on a series of its appication research . The results show that our PSO have certain extraction and separation abilities for Zr and Hf , Mo and Re, Nb and Ta, and noble metals, and high extraction efficiency for Ga, In and Tl. Particularly , our PSO have been used to separate Pd and Pt further to obtain pure Pd and Pt in a technical scale from a complex feed solution in a hydro-metallurgical plant. Compared with the traditional precipitation method , the extraction technology process shortens the production period , simplifies the operation , lowers the production cost and increasses the benefit for the plant.

The components of PSO varies with the production place of petroleum and boiling ranges of petroleum sulfoxides. Petroleum sulfoxides are mixed compounds containing many homologues and isomers. As far as we know there is no any public report of the components separation of PSO . The heat stabilities of sulfoxides are conversely proportional to their molecular weight , the heat stabilities of the cyclic sulfoxides are better than chain sulfoxides. Our research employed liquid chromatograph at room temperature for the components separation in case of PSO easy to be decomposed by heat. We obtained a series of PSO components separated by HPLC , and then , used IR and GC-MS to decide their structures.

2 The Components Separation* of PSO

Our PSO-II have been determined: sulfinyl sulfur content 10.3%, average molecular weight 250. According to 10.3/100X=32/250 , We calculated that PSO-II have 80% sulfoxides , and 20% non-sulfoxides .

We used classical atmospheric chromatograph to pretreat PSO and got the following fractions (Table 1).

Table 1. Sulfinyl Sulfur Content of fractions of PSO

Fractions	PSO1	PSO2	PSO3	PSO4
Sulfinyl sulfur %	0	7.99	12.70	0.6

The macro-preparative isolation results are shown in Fig.1 and Table 2. The fractions of PSO3 are named PSO3 a-g.

Chromatographic conditions :
Chromatograph Waters Delta Prep.
---------- 3000 LC. --------
Column: C_{18}ID.57mmX30cm
Mobile phase: 70%CH_3OH - 30% H_2O
Flow rate: 80 ml/min
Sample quantity: 80ml/onebyone
Detector: M 481
Detector wavelength: 254nm
* 57mm and 3.9 are respectively diameter of column (Macroprep and Anal.)

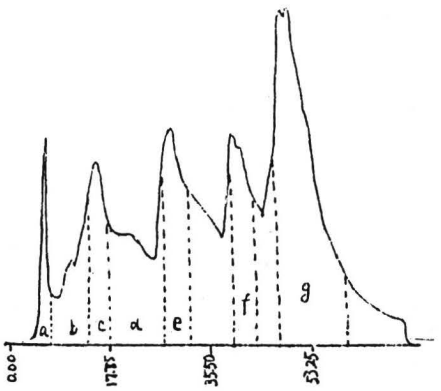


Fig. 1. Prep. LC. map of fractions of PSO3

Table 2. Sulfinyl Sulfur content of fractions of PSO3

Fractions	PSO3A	PSO3B	PSO3C	PSO3D	PSO3E	PSO3F	PSO3G	PSO3
Sulfinyl S%	6.87	7.90	13.6	13.6	12.2	10.8	10.6	12.7

3. Structure analysis of PSO

3.1 IR Spectra analysis of PSO

We can deduce the PSO formulas ($C_nH_{2n}SO$) with their molecular weight for example, $C_{11}H_{22}SO$ from M=202, $C_{10}H_{20}SO$ from M=188. We can calculate the unsaturation degrees (Ω) of CH group in PSO3C is 1 (Fig.2). From IR spectrogram of PSO, ν_{SO} =1025cm^{-1} We know that the C=C does not occur, hence PSO possesses of alicyclic structures.

Comparing its molecular weight with molecular formula, we know that alicyclic ring has been substituted by alkyl group. For both alkyl groups substituted, the ion peaks broken by EI-HS are even, for example 86, 100, 114,... broken ion peaks are odd, such as 87, 101, 115 ..., $C_nH_{2n-1}S$. So we know that PSO are single alkyl substituted cyclic sulfoxides.

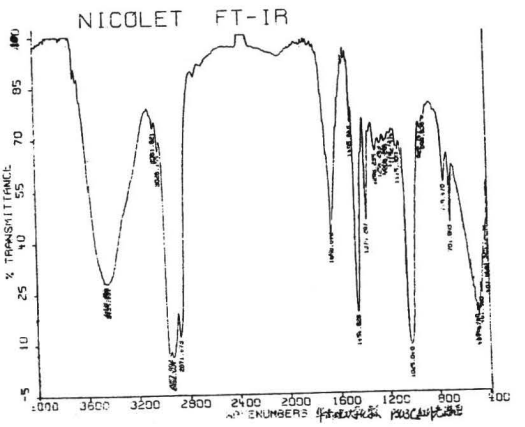


Fig 2. IR spectrogram* of PSO3C

3.2 Interpretation of the mass spectra** of PSO

(i) Basis of Theory

Based on the reference report , there are structures of trimethylene sulfoxide, tetramethylene sulfoxide, pentamethylenen sulfoxide, hexamethylene sulfoxide and poly cyclic stero-structure sulfoxide .

By reference to the data of mass spectra of sulfoxides, generally speaking , the base peak of trimethylene sulfoxide is m/e 41 () , tetramethylene 55 () , pentamethylene 69 (), or 41 ( loss of CH_2 =CH_2) , hexamethylene 83 () or 55 (loss of CH_2 =CH_2) and polycyclic stero-structure M-17 (i.e. loss of OH after γ-H migration to oxygen). We think that above general features of the mass spectra of sulfoxides can be used as basis to decide the ring size of cyclic sulfoxides.

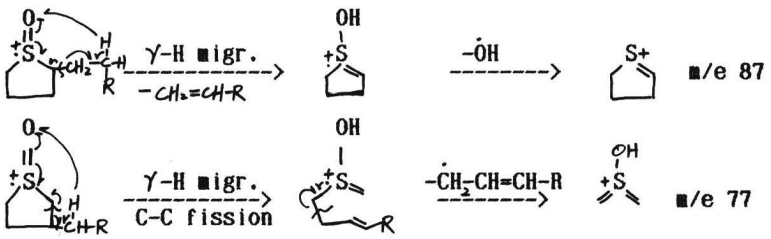
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* IR Spectrograph : 5DXFT-IR Nicolet Company USA product

** The integrated GC-HS : a. Gas Chromatograph HEWLETT PAKARD 5840A Gas Chromatograph hp Company USA OV$_1$ Capillary Column ID0.25mm, length 25 m. b. Mass Spectrometry VGLTD(Eng.) Product, Analytical Organic Spectrometry Carrier He(EI-MS) He(ZAB-MS).

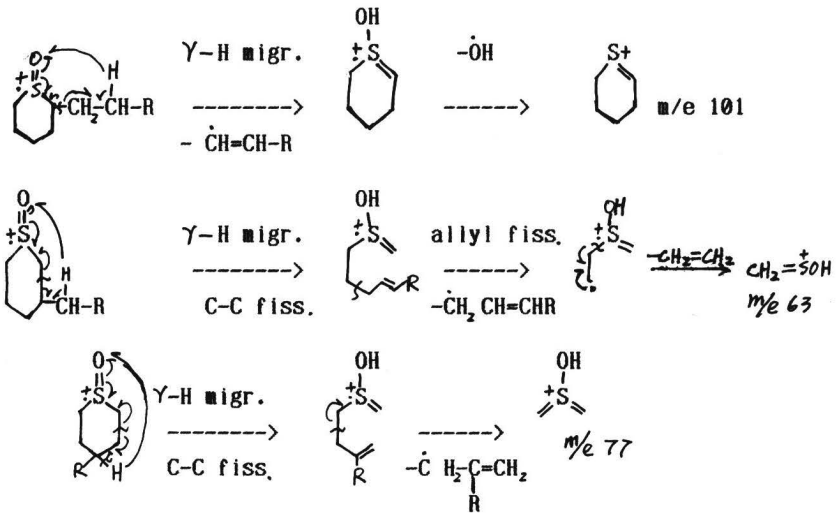
Although the data of the interpretation of mass spectra of single alkyl substituted cyclic sulfoxides have not reported until now , the alkyl substituted position on the ring can be decided. According to the mass spectra of cyclic sulfoxides without alkyl substituted radical in the reference , there are generaly loss of OH , SOH and alkene after hydrogen transfer and it causes all kinds of fragment ion peaks . The migratation hydrogen may be α-H , β-H , γ-H , or δ-H , but the γ—H transfers more easy than the other hydrogen. We can compare the mass spectra fission situation of different alkyl substituted cyclic sulfoxides when their γ-H transfer.

(a) Five-Membered Ring Sulfoxide



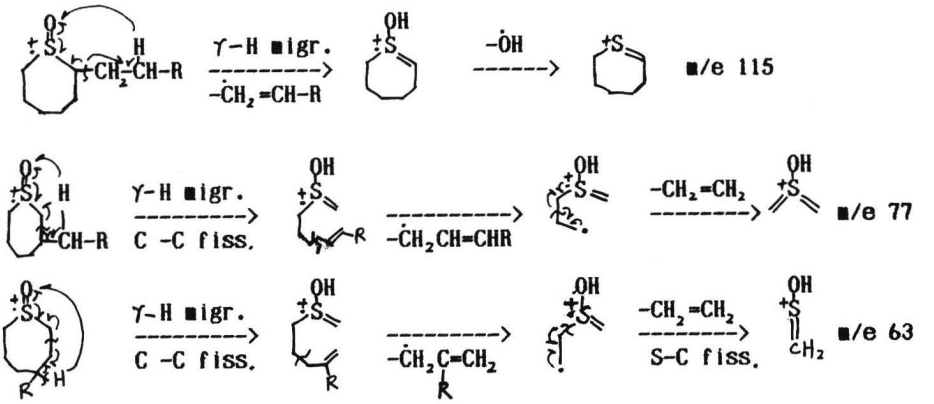
As above it can be seen that it occur higher peak m/e 87 after γ-H transfers for the α-position alkyl substituted five-membered cyclic sulfoxide, but for the β-position, the higher peak m/e 77, i.e. the peak m/e 87 is higher than peak m/e 77 for α-position , and peak m/e 77 is higher than peak m/e 87 for β -position .

(b) Six-Membered Cyclic Sulfoxide



As above it can be seen that it occurs peaks m/e 101 > m/e 63, m/e 77 for the α-position alkyl substituted six -membered cyclic sulfoxide, the peaks m/e 63>m/e 101, m/e 77 for β-position substituted and the peaks m/e 77> m/e 101, m/e 63 for γ-position substituted .

(c) Seven-Membered Cyclic Sulfoxide



As above it can be seen that for the single alkyl substituted seven-membered cyclic sulfoxide the peak m/e 115>m/e 77, m/e 63 when α-position substituted, the peak m/e 77 > m/e 115, m/e 63 when β -position substituted, the peak m/e 63 > m/e 115, m/e 77 when γ-position substituted .

Hence, comparing a series of ion peaks height , we may decide position of substituted radical R.

On the situation of sulfoxides mass spectra fission, there are a series of fragmentation ion peaks $C_nCH_{2n-1}\overset{+}{S}OH$ (i.e. m/e 63,77, 91, 105,119, 133, 147 , ...), $C_nH_{2n-1}\overset{+}{S}$ (i.e. m/e 87, 101, 115, 129, 143, ...), $C_nH_{2n-1}\overset{+}{S}$ (i.e. m/e 55, 69, 83, ...) .

To decide the substituted radical R is straight chain or branched chain. We mainly consider the peaks strength sequence of a series of fragmentation ion peak $C_nH_{2n-1}\overset{+}{S}$.

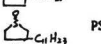
Generally speaking , if the substituted radical R is straight chain , the ion peaks strength of a series of fragmentation $C_nH_{2n-1}\overset{+}{S}$ becomes weaker and weaker with the mass-to-change ratio increses more and more. If the $C_nH_{2n-1}\overset{+}{S}$ ion peaks strength is not according to the above features , it is proved that such substituted radical R is not straight chain, but branch chain. Or if certain ion peak in the the series of fragmentation, $C_nH_{2n-1}\overset{+}{S}$ ion peaks does not occur , it is proved that this position lack of ion peak is substituted by branched chain. As substituted radical carbon chain is longer, and it may contain more branched chains , it is difficult to decide the branched chain position and size . So the sulfoxides structure in this paper is not determined detailly.

(ii) The mass spectra of some components of PSO-II

(This part is not given here. Those who need this may ask a copy to the author (Tiwu Long).)

(iii) The Structure of PSOII

Table 3. The Structures of Main Components of PSO-II

Fraction	GC NO in GC-HS	Mol Wt	Base Peak	Chain Shape	Place	Structral formula
	218	202	83	R Branched Chain	(63>115,77)	
	231	202	83	R Branched Chain	(63>115,77)	
PS03C	222	188	83	R Branched Chain	(115>63,77)	
	247	188	83	R Straight Chain	(115>63,77)	
	227	188	55	R Branched Chain	(77>87)	
	335	230	55	R branched chain	(77>87)	
	347	230	55	R branched chain	(m/e 87>77)	
	357	230	55	R branched chain	(m/e 77>87)	
PS03E	377	230	55	R branched chain	(m/e 87>77)	
	389	230	55	R branched chain	(m/e 87>77)	
	393	230	55	R branched chain	(m/e 77>87)	
	405	230	55	R branched chain	(m/e 87>77)	
	360	258	55	R straight chain	(m/e 77>87)	
	365	258	55	R branched chain	(m/e 77>87)	
PS03g	369	258	55	R branched chain	(m/e 87>77)	
	412	286	55	R Straight chain	(m/e 87>77)	
	416	286	55	R branched chain	(m/e 87>77)	

Fraction	GC NO in GC-HS	Mol Wt	Base Peak	Chain Shape	Place	Structral formula
	427	286	55	R branched chain	(m/e 87>77)	
	432	286	55	R branched chain	(m/e 77>87)	
	386	272	55	R branched chain	(m/e 87>77)	
	392	272	55	R branched chain	(m/e 77>87)	
	396	272	55	R branched chain	(m/e 87>77)	
	448	300	55	R branched chain	(m/e 87>77)	
PS03g	452	300	55	R branched chain	(m/e 77>87)	
	454	300	55	R straight chain	(m/e 77>87)	
	459	300	55	R branched chain	(m/e 87>77)	
	463	300	55	R branched chain	(m/e 77>87)	
	436	328	55	R branched chain	(m/e 87>77)	
	444	328	55	R branched chain	(m/e 77>87)	
	782	216	55	R branched chain	(m/e 87>77)	
	856	230	55	R branched chain	(m/e 87>77)	
PS02g22	1081	272	55	R branched chain	(m/e 87>77)	
	1315	356	55	R branched chain	(m/e 87>77)	
	1394	356	55	R branched chain	(m/e 87>77)	

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PERFORMANCE OF TWO NEW NIL AROMATIC DILUENTS IN THE RECOVERY OF COPPER, URANIUM AND RARE EARTHS.

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ABSTRACT
Shelley, P. and Quan, C., (Shell Chemical (Australia) Pty. Ltd.), 1990. Performance of Two New Nil Aromatic Diluents in the Recovery of Copper, Uranium and Rare Earths. ISEC Proceedings, Kyoto, Japan, 1990.

The increasing requirements for higher metal purity and optimum plant performance make the selection of the correct diluent for a solvent extraction circuit more critical than ever. Shell Chemical have developed two nil aromatic diluents whose performance, together with a low and high aromatic grade, has been evaluated using copper, uranium and rare earth leach solutions. The results show that the performance of each diluent was metal dependant with the low aromatic (Shellsol 2046) and nil aromatic (Shellsol 2037) being equivalent for copper, whilst the Shellsol 2046 was best for uranium and the Shellsol 2037 best for rare earths.

1. INTRODUCTION

Hydrocarbons are used as the diluent in most solvent extraction (SX) processes. For many years these diluents were regarded as being 'inert' in the system, and though it is now known that many properties affect diluent performance, including dipole moment, dielectric constant and interfacial properties (Bailey and Mahi, 1987), it is not possible to predict behaviour based on theoretical considerations. Of the many properties which can be controlled during manufacture, it is the aromatic content that has the greatest effect on circuit performance. Shell Chemical Australia have been supplying diluents to the Australian SX market for 15 years and have now developed two new nil aromatic diluents to complement their range of low and high aromatic products. The following work has been carried out to determine the performance of these new diluents in the recovery of copper, uranium and rare earth elements (REE) from typical pregnant liquors. Shell's low and high aromatic diluents were also included for comparative purposes.

2. EXPERIMENTAL

2.1 Diluents

Table 1 shows the physical characteristics of the diluents used.

TABLE 1

Physical Characteristics of Diluents

Diluent	Density kg/L @ 15°C	Boiling Range, °C	Aromatics % v/v	Viscosity cSt @ 25°C	Flash Point, °C
Shellsol AB	0.895	181-212	100	1.19	63
Shellsol 2046	0.808	200-240	16	1.97	80
Shellsol 2037	0.806	200-240	<1	2.34	80
Shellsol 2358	0.807	235-280	<1	3.33	106

2.2 Extractants

The extractants used were LIX 984 (ex. Henkel) and Acorga M5640 (ex. ICI) for copper, Adogen 364 (ex. Sherex) for uranium, di-2-ethylhexylphosphoric acid (D2EHPA) and Ionquest 801 (ex. Albright & Wilson) for REE. Three modifiers, Isodecanol, Tridecanol and Neodol 1 (ex. Shell), were used in the uranium work.

2.3 Feed Solutions

For copper and uranium, plant pregnant liquors from the sulphuric acid leaching of ores were used, with the copper solution containing 4.0 g/L Cu and 4.8 g/L Fe, whilst the uranium solution contained 0.67 g/L U. The RE chloride solution, containing 140 g/L total REE, was prepared by caustic cracking of monazite and dissolution of the residue in hydrochloric acid.

2.4 Performance Tests

To evaluate all aspects of diluent performance a range of tests were carried out comprising equilibria and kinetics measurements plus phase disengagement tests.

2.5 Analytical Methods

In all cases the feed and raffinate solutions were analysed and the organic concentrations determined by mass balance. Uranium and the REE were analysed by ICP/MS and copper by AAS.

3. RESULTS & DISCUSSION

3.1 Copper

(i) Extraction

Copper extraction isotherms were obtained by mixing in stirred cells for 15 minutes at 22±2°C. A/O ratios were varied from 10:1 to 1:1. In most cases the extraction coefficient was found to increase with decreasing aromatic content (Table 2). Kinetics tests show that Shellsol AB took an unacceptable time to reach optimum recovery, whilst Shellsol 2046, 2358 and 2037 were reasonably close together and within typical design limits for most SX circuits.

TABLE 2

Results of Equilibria, Kinetics and Phase Disengagement Studies

Test Description	Reagent System	A/O Ratio	Shellsol Diluent AB	2046	2037	2358
Copper Extraction						
Coefficient, (E)*	LIX 984	1:1	12.9	20.2	22.9	23.9
Kinetics, secs	Acorga M5640	2:1	900	120	60	90
PDT, secs	LIX 984	2:1	22	23	27	34
Copper Stripping						
Coefficient, (E)	Acorga M5640	1:4	13.7	13.4	15.2	13.4
Kinetics, secs	LIX 984	1:4	480	60	120	120
PDT, secs	LIX 984	1:4	45	110	150	180
Uranium Extraction						
Coefficient, (E)	Adogen/IDA**	1:1	756	515	418	478
Kinetics, secs	Adogen/IDA	2:3	120	120	180	180
PDT, secs	Adogen/Neodol	2:3	115	175	250	320
Uranium Stripping						
Recoveries, %	Adogen/IDA	1:1	98.8	98.0	***	98.5
Rare Earths Extraction						
Y Coefficient, (E)	D2EHPA	1:1	24	64	81	84
Separation, H/L	D2EHPA	1:1	130	65	90	100
Y Kinetics, secs	D2EHPA	1:1	30	60	60	60
PDT, secs	Ionquest 801	1:1	62	46	26	20
Rare Earths Stripping						
LREE Recoveries, %	D2EHPA	1:1	99+	99+	***	99+
HREE+Y Recoveries, %	D2EHPA	1:1	87-99	58-99	***	58-99

* Ratio of equilibrium concentration of the organic phase to that in the aqueous phase.
** Isodecanol
*** Shellsol 2037 was not tested for stripping performance with U and REE.

Phase disengagement times in all diluent systems was excellent, whether aqueous or organic continuous mode, with all primary breaks occurring in less than 35 s.

(ii) Stripping Studies

Stripping tests were carried out using a solution containing 32 g/L Cu and 170 g/L H_2SO_4 and showed that Shellsol 2037 had a slightly better stripping performance than other diluents. Kinetics results (Table 2) show that Shellsol AB took an unacceptably long time to reach optimum recovery compared to Shellsol 2046, 2037 and 2358. Phase disengagement times were significantly higher than in extraction, and showed considerable variation, with Shellsol AB being the best followed by Shellsol 2046, 2037 and 2358.

(iii) Summary

For copper the high aromatic (Shellsol AB) diluent has significantly lower extraction and stripping performance than the low (Shellsol 2046) or nil (Shellsol 2037 and 2358) aromatic diluents. The one exception was phase

disengagement in stripping where the low aromatic diluents was significantly faster than the nil aromatic diluents, though all were acceptable from a design point of view. Technically, there appears little to choose between the low and nil aromatic diluents for the recovery of copper; diluent selection then becomes more a matter of cost effectiveness.

3.2 Uranium

(i) Extraction

Extraction isotherms (Fig.1a) were obtained by mechanically shaking the two phases at 22±1°C for 30 minutes at A/O's between 4:1 and 1:4. In most cases, the extraction coefficient was found to increase with increasing aromatic content (Table 2). Kinetics results show that Shellsol AB and 2046 were slightly faster than Shellsol 2037 and 2358 in achieving optimum recovery. Phase disengagement in the Shellsol AB and 2046 systems were acceptable and significantly better than Shellsol 2037 and 2358. An interfacial crud was observed during the phase disengagement test with the Shellsol AB system, irrespective of the modifier used. All other systems were crud free except for the Shellsol 2037/Neodol 1 system which showed minor secondary phase disengagement problems.

(ii) Stripping Studies

Stripping tests were carried out using 90 g/L Na_2CO_3 at an A/O of 1, and showed no significant differences between diluents in the recovery of uranium, irrespective of the modifier used.

(iii) Summary

The aromatic content of the diluent has a marked effect on the performance of the uranium system. Based on loading alone, the high aromatic diluent (Shellsol AB) was the best. However, because the high aromatic produced a stable interfacial crud, it was ruled out as an option. Next best was the low aromatic diluent (Shellsol 2046) which again was significantly better than the nil aromatic. Shellsol 2037 gave the fastest phase disengagement and had better extraction performance than Shellsol 2358 in Neodol modified systems (Fig.1a); otherwise the two nil aromatic diluents were comparable. Technically therefore, the low aromatic (Shellsol 2046) appears the diluent of choice for uranium recovery.

3.3 Rare Earths

(i) Extraction Studies

In rare earth systems, the determination of extraction isotherms was complicated by the increase in acidity when rare earths displace hydrogen ions from the extractant. Scoping tests showed that equilibrium pH remained fairly constant if the equilibrium curves were obtained by varying the rare

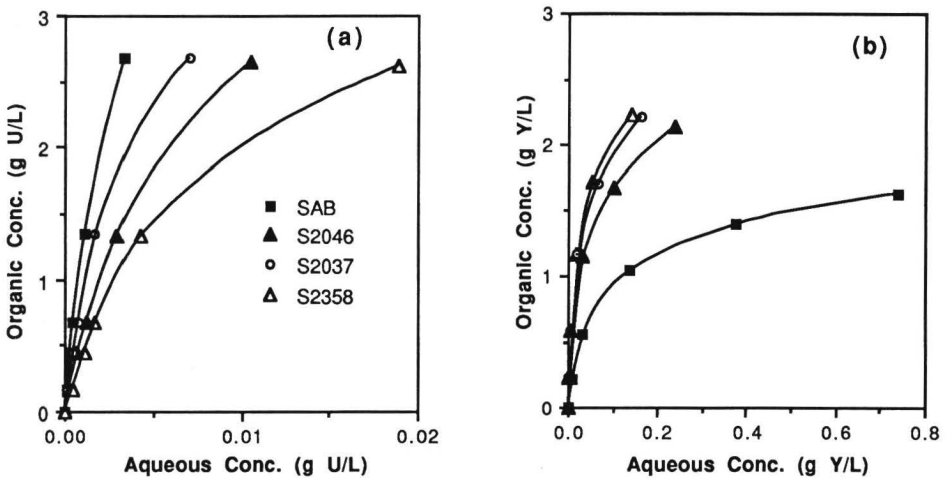


Figure 1. Extraction Isotherms at 22°C for (a) Uranium with 5% Adogen 364 and 3% Neodol 1 and (b) Yittrium with 20% Ionquest 801.

earth concentration from 13-140 g/L at a constant A/O of 1. Figure 1b shows extraction isotherms for Y using 20%v/v Ionquest under these conditions; similar trends are apparent for the other heavy rare earth elements (HREE - Eu to Lu) for both Ionquest and D2EHPA. In contrast to uranium the loading decreased with increasing aromatic content. Typical extraction coefficients are shown in Table 2. As a secondary performance indicator we have chosen the separation factor between the light rare earth elements (LREE - La to Sm) and the HREE+Y ie. HREE+Y/LREE. The results (Table 2) show that Shellsol AB gave the best separation, followed by Shellsol 2037, 2358 and 2046.

Initial kinetics studies were carried out in a stirred cell and showed that overall kinetics were so fast that equilibrium was reached within 30s. To better understand the kinetics, the degree of agitation was reduced, whereupon Shellsol AB proved to be significantly slower in extracting the LREE than did Shellsol 2046, 2037 and 2358. Studies on the HREE+Y did not show clear trends. However, as a general rule Shellsol AB was slightly faster to extract than the other diluents.

Phase disengagement times increased consistently with increasing aromatic content.

(ii) Stripping Studies

The REE were stripped with 6 M HCl at an A/O of 1, with the results indicating that over 99% of the LREE are stripped in a single stage, irrespective of diluent. Minor differences were observed in the recovery of the HREE+Y with Shellsol AB giving the best performance for most elements.

Shellsol 2046 and 2358 were about equal but showed a dramatic decrease in stripping performance with increase in atomic number.

(iii) Summary

For the REE the nil aromatic diluents (Shellsol 2037 and 2358) were superior to the low (Shellsol 2046) and high (Shellsol AB) aromatic diluents in all areas except selectivity between the HREE+Y and LREE, with Shellsol 2037 being the diluent of choice due to better phase disengagement times compared to Shellsol 2358. In some instances the better selectivity of the high aromatic may be seen as an advantage, however, it should not be taken in isolation and should be considered together with the extraction performance, which was inferior to the nil aromatic. Therefore, the nil aromatic diluents, specifically Shellsol 2037, appear the diluents of choice for REE.

4. CONCLUSIONS

Our work has shown that the aromatic content of a diluent does have a marked effect on the performance of an SX circuit. We have also shown that the diluent of choice for one metal may not be appropriate for another. For example, the low (Shellsol 2046) and nil (Shellsol 2037 and 2358) aromatic diluents were similar in performance, but significantly better than the high (Shellsol AB) aromatic, for the recovery of copper. For uranium, the low aromatic was judged to be the best, whilst for the REE the nil aromatic diluents were technically superior, with Shellsol 2037 being the diluent of choice due to better phase disengagement characteristics.

5. ACKNOWLEDGEMENTS

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INFLUENCE OF DILUENTS ON THE EXTRACTION OF FLUORINE FROM WET PHOSPHORIC ACID WITH TRIOCTYLAMINE

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ABSTRACT

It has been found that there exists significant effect of diluent on the extraction of fluorine from wet phosphoric acid with TOA. The experimental data show that the distribution coefficient of fluorine (D_F) is dependent on the properties of diluents. The extractive capacity of fluorine with TOA depends on the interaction between the extracting complex and diluent and the solvophobic properties of the diluent, the stronger the interaction and the weaker the solvophobic properties of the latter are beneficial to the extraction of fluorine. With two-stage extraction scheme, the purified acid contains less than 0.65 g/L F, which conforms to the feed phosphate standard.

1 INTRODUCTION

It is known that wet-process phosphoric acid (W.P.A.) obtained by acidulation of phosphate rock contains substantial amount of fluorine. To produce phosphates for animals feed, the acid must be purified free from fluorine and the fluorine content expressed as F to P weight ratio should not be greater than 1 to 100. Different methods have been suggested. In the extraction process using TOA-diluent as solvent developed by the present authors, it has been found that there exists a significant effect of diluent on the extraction of fluorine from W.P.A. So far the role played by diluent in the extraction of fluorine has not yet been elucidated.

2 EXPERIMENTAL

2.1 Wet phosphoric acid

The compositions of the crude acid supplied by commercial works are as follows: P_2O_5, 173 g/L; F^-, 11.1 g/L; MgO, 24.0 g/L; Fe_2O_3, 4.9 g/L; Al_2O_3, 0.81 g/L.

2.2 Solvent

Trioctylamine (TOA) of A.R. grade and diluents of A.R. or C.P. grade were purchased from Shanghai market. TOA is dissolved in the diluent to form the extracting solvent.

2.3 Analysis

Fluorine was determined by using a model PXS-201 ion-activitymeter with fluorine ion-selective electrode, phosphorus was analyzed using co-

lorimatric method with a model VSU2-P spectrophotometer.

2.4 Procedure

Equal volumes of the solvent and W.P.A. were placed in separatory funnels and shaken mechanically at the speed of 0.3 1/s for 120 sec. (preliminary tests showed that 60 sec. of shaking were sufficient to attain equilibrium). The temperature was controlled at 300 K with thermostat. After shaking, the phases were allowed to disengage. The compositions of both phases were measured before and after equilibration.

3 RESULTS AND DISCUSSION

Experimental data of extracting fluorine are illustrated in Table 1. The data show that there exists significant effect of diluent on the extraction of fluorine from W.P.A. with TOA. It is apparent that both the distribution coefficients of fluorine and phosphoric acid as well as the separation factors vary greatly with different kinds of diluent.

3.1 Extraction equilibrium of acids with amine

The extraction equilibrium of an acid by an amine can be described as follows:

$$\overline{\text{Amine}} + H^+ + A^- \rightleftharpoons \overline{\text{Amine } H^+A^-} \qquad (1)$$

where the superscript "————" represents organic phase and the follows are same. The extraction reaction occured primarily in aqueous phase or at the interface and involves the following three steps:

(a) Amine in organic phase transfers to aeuqous phase or the interface.

(b) Amine reacts with acid forming extracting complex.

(c) Extracting complex dissolves in organic phase.

3.2 Effect of diluents on the extraction of fluorine

The effect of diluents on the extraction equilibrium is mainly in the first and the third step. The interaction between extracting complex and diluent involves both non-specific properties, such as ion - dipole, dipole - dipole, dipole - inductive dipole and dispersion interactions, and the specific properties, such as hydrogen bond, doner and acceptor of electrons. It was found that the effect of diluent depends on the particular part of the amine salt molecule solvated by it and highly on the solvophobic property of the extracting complex. Since TOA is highly aquophobic, when diluent contains much water, the dissolving capacity of extracting complex in the diluent as well as the extracting capacity of fluorine will be strikingly depressed (see Fig. 1).

(i) Effect of aromatic diluents

TABLE 1

Equilibrium data of fluorine extraction from wet phosphoric acid with TOA-diluent mixture

No.	Diluent	Concentration at equilibrium, g/L				D_F	$D_{P_2O_5}$	β_{F/P_2O_5}	μ	ε	δ_d
		$[F]$	$\overline{[F]}$	$[P_2O_5]$	$\overline{[P_2O_5]}$						
1	Benzene	6.59	4.88	167.7	15.1	0.74	0.095	7.8	0	2.28	9.2
2	Toluene	6.90	4.62	167.2	16.7	0.67	0.10	6.7	0.45	2.57	8.9
3	Xylene	6.90	4.75	166.8	18.4	0.69	0.11	6.3	0.37	2.38	8.8
4	Chlorobenzene	5.61	6.03	164.3	19.7	1.10	0.12	9.2	1.69	5.62	9.6
5	Nitrobenzene	4.78	6.79	161.2	21.6	1.42	0.13	10.8	4.22	34.82	10.9
6	Butylalcohol	8.10	3.81	142.2	35.7	0.47	0.25	1.9	1.66	17.5	11.4
7	Octylalcohol	7.92	3.86	165.8	12.6	0.49	0.076	6.4	1.68	10.34	
8	2-ethyl hexyl alcohol	7.72	3.78	168.4	7.98	0.49	0.047	10.4	1.74	8.1-17.1	
9	Decylalcohol	7.64	3.90	170.1	7.16	0.51	0.042	12.1	1.80	8.1	
10	Methyl-isobutyl ketone	6.74	4.66	161.7	16.4	0.69	0.10	6.9	2.8	13.1	8.4
11	Ethyl butyl ketone	6.01	5.29	164.1	11.8	0.88	0.072	12.2		11.9	
12	Di-isobutyl ketone	6.01	5.44	163.4	13.4	0.90	0.082	11.0		13.0	
13	Kerosene	8.23	3.29	148.7	29.8	0.40	0.20	2.0		2.0-2.2	
14	Carbon tetrachloride	8.17	3.35	152.2	27.4	0.41	0.18	2.3	0	2.21	8.6
15	Chloroform	2.42	8.56	173.2	6.93	3.54	0.039	90.8	1.01	4.8	9.3
16	Trichloroethylene	4.70	6.67	161.8	16.3	1.42	0.10	14.2	0.9	3.4	
17	1,1-dichloroethane	3.52	7.50	172.6	9.70	2.13	0.056	38.0	1.95	10.0	9.1
18	1,2-dichloroethane	3.82	7.34	171.2	11.0	1.92	0.064	30.0	2.06	10.4	9.9
19	1,1,1-trichloroethane	2.78	8.09	172.8	7.78	2.91	0.045	64.7	1.79	7.6	
20	1,1,2-trichloroethane	2.18	8.81	173.4	6.93	4.04	0.038	106	1.30	8.8	
21	1,1,2,2-tetrachloroethane	3.32	7.71	171.1	8.21	2.32	0.048	48.3	1.32	8.2	

Wet phosphoric acid, P_2O_5, 173 g/L, F^-, 11.1 g/L, Fe_2O_3, 4.9 g/L, Al_2O_3, 0.81 g/L, MgO, 24.0 g/L; T=300 K; TOA:diluent = 2:8 (v/v).

μ — Dipole moment, ε — Dielectric constant, δ_d — Solubility parameter.

In the system of extracting fluorine with TOA, fluorine amine salt exists in organic phase in the form of ion association. Since the interaction between the cation and the anion in amine salt in organic solvents is mainly electrostatic, the dipole moment and dielectric constant or polarities of the polar diluents will play important role in the extraction equilibrium of fluorine. The D_F using aromatic diluents increases in the order: toluene < xylene < benzene < chlorobenzene < nitrobenzene. It is nearly coincident with the increasing order of dipole moment and dielectric constant (see Table 1 and Fig. 3). Fig. 2 shows that the D_F



Fig. 1 Solvophobic action
□ —— Solvent (Diluent)
○ —— Solute (Extracting complex)
● —— H_2O

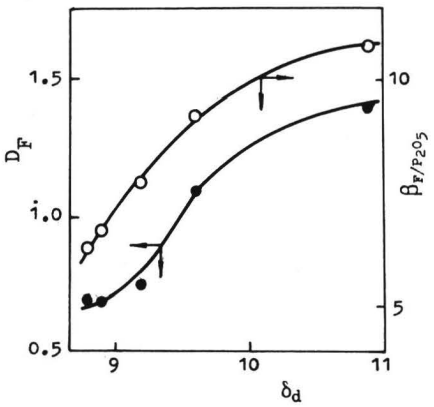


Fig. 2 Effect of solubility parameter of diluents on D_F and β_{F/P_2O_5}
T = 300 K; 20(vol)%TOA-aromatic

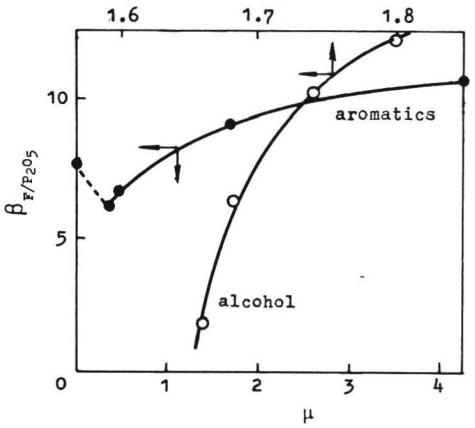


Fig. 3 Effect of μ of diluent on β_{F/P_2O_5}
T=300 K; 20(vol)% TOA-diluent

and the separation factors (β) increase with the increasing of solubility parameter of the aromatic diluents. The relation of separation factor and solubility parameter can be fitted by the following equation.

$$\beta_{F/P_2O_5} = 0.0328\ \delta_d^{2.45} \qquad (2)$$

(ii) Effect of alcohol and ketone diluents

As depicted in Fig. 4, the D_F using alcohol and ketone diluents in-

creases with increasing carbon atoms. This is because the solubility of solvent in water decreases and that in oil increases despite the change of dielectric constant. At the same time, the extraction of phosphoric acid is restrained, which enhances the separation factor correspondingly.

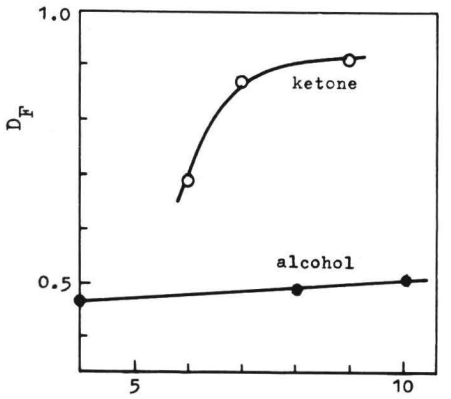


Fig. 4 Effect of carbon atom on D_F
T=300 K; 20(vol)% TOA-diluent

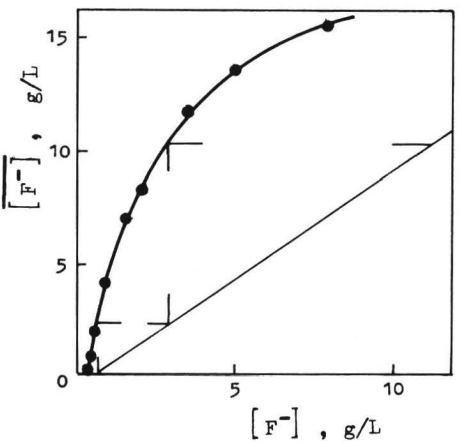


Fig. 5 Extraction isotherm
20(vol)%TOA-1,1,2-trichloroethane;
T=300 K; E/R=1

Fig. 3 shows that the separation factors remarkably increase with the increasing of dipole moment of alcohol diluents. The D_F with alcohol diluents are much smaller than that with incompletely halogenated hydrocarbon diluents. This is because TOA is a hydrogen bond acceptor, it could form a complex with alcohol, the dissolution of TOA in aqueous phase and formation of extracting complex with fluorine are therefore restrained. On the other hand, the solubility of water in alcohols is greater than that in other diluents. The solvophobic action of extracting complex in alcohol diluents is correspondingly stronger. All of these results in small extracting abilities in alcohol diluents.

(iii) Effect of halogenated hydrocarbon diluents

Since the radius of fluoride ion is very small (1.36 Å), its electronegativity is very strong, H-F is a strong polar bond, hydrogen fluoride and fluorosilic acid are strong proton donor and acceptor either. On the other hand, TOA is a proton acceptor having a pair of isolated electrons. The extracting complex of TOA with hydrogen fluoride or fluorosilic acid exhibit strong polarity and is a strong proton acceptor.

The chloroform molecule is a well-known proton donor, in which the electrons of carbon atom as well as those of hydrogen atom are withdrawn to the three chlorine atoms. The hydrogen atom behaves like a proton

combined with a negative counterpart. Stronger interactions between the extracting complex of fluorine with TOA and the chloroform diluent occur which contribute to larger D_F with chloroform diluent. The same situation with other incompletely halogenated hydrocarbons.

For chlorobenzene and nitrobenzene, the electronic density of the C-Cl or C-NO_2 bond increases remarkably because of the conjugate effect, the influence of chlorine atom or nitro on C-H bond is very small, it is hardly a proton donor. The interaction between the extracting complex and chlorobenzene or nitrobenzene is very weak. Thus D_F is small using chloribenzene or nitrobenzene diluent.

Carbon tetrachloride or other completely halogenated hydrocarbons are not proton donor since they have no hydrogen atom. Similar to hydrocarbon's, they can not interact with the extracting complex. The D_F is very small using these diluents.

3.3 Extraction isotherm

The fluorine extraction isotherm with TOA-1,1,2-trichloroethane as solvent at the temperature of 300 K is shown in Fig. 5. For an organic to aqueous phase ratio E/R = 1, a two-stage extraction scheme will be effective for fluorine removal. The purified phosphoric acid contains less than 0.65 g/L F^-. The phosphate produced contains less than 0.2% F^-, which conforms to the feed phosphate standard. When the solvent is pretreated with H_3PO_4, the amount of non-extracted fluorine decreases.

4 CONCLUSION

Significant effect of diluents on the extraction of fluorine from wet phosphoric acid with trioctylamine has been observed. The extraction ability of fluorine with TOA depends on the interaction between the extracting complex and the diluent, as well as the solvophobic property of the diluent. Stronger interaction and weaker solvophobic property of the diluents are beneficial to the extraction of fluorine.

5 ACKNOWLEGEMENT

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EFFECT OF NITRIC ACID ON TRIBUTYLPHOSPHATE HYDROLYSIS

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ABSTRACT

Effect of HNO_3 on hydrolysis of TBP was studied. The accumulation of hydrolysis product – mainly dibutylphosphoric acid (DBPA) in the organic phase has been investigated both for the bulk of organic solution separated from equilibrium aqueous solution of HNO_3 and in the presence of aqueous phase. It is suggested that only TBP represented in the organic phase by complexes with HNO_3: $H_5O_2^+(H_2O)_n(TBP)_mNO_3^-$; $TBP*HNO_3$; $TBP*2HNO_3$; $TBP*H_3O^+(H_2O)_2NO_3^-(HNO_3)$ ungergoes hydrolysis. The rate constant for DBPA formation (by reaction of TBP – water interaction) calculated from the equation $d[DBPA]/dt=K[TBP][H_2O]_{org}$ on condition that [TBP] is the concentration of TBP combined with HNO_3 in the organic phase occurred to be constant and equal to $1.3*10^{-6}$ $h^{-1}*mole^{-1}*l$ for the interval of HNO_3 concentration in the organic phase 0.8–4.1 mole/liter. Hydrolysis of TBP becomes itensified at higher temperatures. The activation energy of this process was estimated as ~8 kJ/mole. The interaction of extractant with water at the interface makes a great contribution to DBPA accumulation in the organic phase. In two phases systems with specific interfacial area equal to $3.7*10^5$ m^{-1} approximately 50% of DBPA is formed at the interface. Decomposition of TBP becomes stronger on increasing of mixing intensity expressed by $n^{1.2}*d^{0.8}$, where n is impeller rotational speed, d is diameter of impeller.

1. INTRODUCTION

Tri-n-butylphosphate (TBP) has become widely used in connection with radiochemical and hydrometallurgical solvent extraction processes. But at the same time with evident advantages TBP has significant shortcoming consisting in its ability to be destructed due to hydrolysis or radiolysis during the extraction process. The products of TBP degradation are di- and monobutylphosphoric acids (DBPA and MBPA) and H_3PO_4 affecting technological parameters of the process. The accumulation of these substances leads to drop in the selectivity of extraction process, makes slower physical separation of phases, promotes the formation of precipitates. Becides that DBPA and MBPA form with some elements so stable compounds that a part of extractable metal is lost at the stripping stage due to the small possibility to extract back this metal from the organic phase. The process of radiolytic decomposition of TBP has been investigated in detail unlike the hydrolysis process. But it is known that great acidity and high temperature effect on TBP leading to its appreciable destruction. The data concerning radiolysis and hydrolysis of TBP are summarized in the reviews of Vladimirova et al. (1984,1989) and Solovkin et al. (1985). In two phases extraction system "extractant-aqueous solution of acid" hydrolysis takes place both in the bulk of phases and at the interface. But in the most of investigations the hydrolysis of TBP dissolved in the aqueous phase was studied and besides that the

data obtained are discrepant especially the rate constant of DBPA accumulation.

2. EXPERIMENTAL AND ANALYTICAL METHODS

In the first section of present work the hydrolysis of TBP exposed to nitric acid and water in the bulk of organic phase has been investigated. Preliminarily TBP was mixing with aqueous nitric acid solution of certain concentration to achieve thermodynamic equilibrium. Then the phases were separated and the concentration of DBPA in the organic phase in the dependence on time was measured. In the second section of work the attempt to estimate the contribution of interface into hydrolysis process for TBP has been undertaken. For this purpose the extractant was mixing with nitric acid solution in the mechanically agitated contactor and after fixed periods of time DBPA concentration in TBP was determined. The area of interfacial contact depended on the mixing intensity.

In the aqueous phase the concentration of nitric acid was varied from 0.5 to 12 mole/liter so in the organic phase it was changed from 0.5 to 4.1 mole/liter correspondingly. The experiments were carried out at 295K exept the study of TBP hydrolysis dependence on temperature. The concentration of DBPA was determined colourimetrically by using reaction of DBPA with Safranin-T.

3. RESULTS AND DISCUSSION

3.1 Hydrolysis of TBP in the bulk of organic phase

Since TBP hydrolysis leads mainly to the presence of DBPA in the organic phase they usually estimate the rate of TBP decomposition only at the first stage of hydrolysis by measurement of DBPA accumulation. In Fig. 1 the kinetic curves for DBPA formation in the organic phase are demonstrated. Fig.2 illustrates the dependence of DBPA concentration on nitric acid concentration in the organic phase for different time of duration.

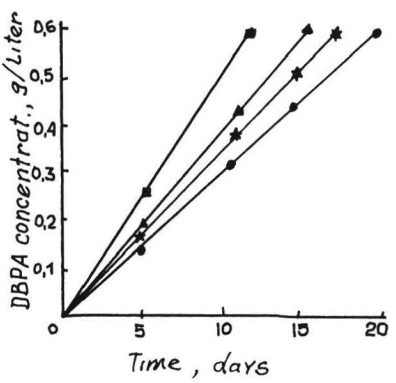


Fig. 1.

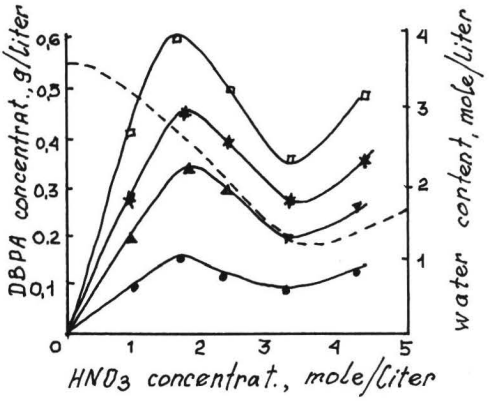


Fig. 2.

Fig. 1. Kinetic curves of DBPA accumulation in the organic phase. $[HNO_3]_{org}$, mole/liter: (✱)–0.8; (▲)–1.18; (■) –1.60; (●)–3.8.

Fig. 2. Effect of nitric acid concentration on DBPA and water content in the organic phase. Duration, days: (●)–3; (▲)–7; (✱)–10; (□)–13.
Dotted line – concentration of water (Nickolotova and Kartashova, 1976, p. 48).

The rate of hydrolysis process is given by equation:

$$-d[TBP]/dt = d[DBPA]/dt \cong \Delta[DBPA]/\Delta t \quad (1)$$

It has been found earlier that the hydrolysis rate at the constant temperature depends not only on TBP concentration but on the concentration of nitric acid as well. So the rate of TBP hydrolysis was represented through the rate constants by the following equations:

$$-d[TBP]/dt = K[TBP][HNO_3] \quad (2)$$

$$-d[TBP]/dt = K'[TBP], \text{ where } K'=K[HNO_3] \quad (3)$$

$$-d[TBP]/dt = K''[HNO_3], \text{ where } K''=K[TBP] \quad (4)$$

Very often they suppose the concentration of TBP in Eq.(2) and Eq.(3) to be constant and the hydrolysis reaction to be a reaction of the pseudofirst order. The values of rate constants for the reactions of the first and the second orders taken from review of Vladimirova et al. (1989) are given in Table 1.

TABLE 1

Rate constants of TBP hydrolysis for reactions of 1 and 2 orders.

Data from review of Vladimirova et al.(1989)				Present experimental data, 295K	
T	$[HNO_3]_{org}$, mole/l	K', h^{-1}	K, $h^{-1}*mole^{-1}*l$	$[HNO_3]_{org}$, mole/l	K, $h^{-1}*mole^{-1}*l$
308K	1.01	$7.0*10^{-6}$	-	0.80	$1.3*10^{-6}$
308K	1.12	$9.0*10^{-6}$	-	1.18	$1.3*10^{-6}$
308K	1.15	$1.0*10^{-5}$	-	1.60	$1.3*10^{-6}$
308K	1.20	$1.0*10^{-4}$	-	2.65	$1.3*10^{-6}$
353K	0.20	$3.4*10^{-5}$	$8.5*10^{-5}$	3.26	$1.3*10^{-6}$
353K	0.52	$9.0*10^{-5}$	$1.9*10^{-4}$	3.80	$1.3*10^{-6}$
353K	0.90	$1.5*10^{-5}$	$4.3*10^{-4}$	4.10	$1.3*10^{-6}$

It can be seen that even small variation of nitric acid content in the organic phase leaded to change the values of rate constant calculated from Eq.(2) or Eq.(3). Consequently these equations for counting of hydrolysis rate constant are not correct.

But it should be noted that nitric acid is only the catalyst for TBP hydrolysis reaction which is the interaction of TBP with water:

$$(C_4H_9O)_3PO + H_2O \xrightarrow{HNO_3} (C_4H_9O)_2\,POOH + C_4H_9OH$$

So for calculation of K concentrations of water and TBP affected by nitric acid must be used. Stoyanov et al. (1990) fixed the presence of 4 kinds of TBP complexes with HNO_3 formed in the organic phase in dependence on nitric acid concentration (Table 2).

TABLE 2.

Composition and concentration of TBP complexes with HNO_3 (Stoyanov et al., 1990)

Complex	Concentration of HNO_3, mole/liter, in org. phase						
	0.71	1.18	1.61	2.65	3.26	3.82	4.17
	Concentration of complexes, mole/liter						
(I) $H_5O_2^+(H_2O)_n(TBP)_mNO_3$	0.467 (1.428)*	0.667 (1.801)*	0.800 (1.92)*	0.706 (1.412)*	0.420 (0.84)*	0.230 (0.46)*	0.170 (0.34)*
(II) $TBP*HNO_3$	0.242	0.518	0.810	1.650	1.750	1.370	1.080
(III) $TBP*2HNO_3$	-	-	-	0.200	0.800	1.550	2.100
(IV) $TBP*H_3O^+(H_2O)_2NO_3(HNO_3)$	-	-	-	0.194	0.260	1.450	1.910

* - concentration of TBP in the form of complex (I).

For the strength of PO...H bond in complexes TBP with HNO_3 the next grade was supposed: (I) < (II) < (III) < (IV). It means that hydrolysis capability grows from (I) to (IV) complex (Sinegribova et al., 1986, p.p. 433-440).

Assuming that only TBP from complexes (I) - (IV) undergoes hydrolysis we have calculated the values of rate constant for TBP hydrolysis from the following equation:

$$d[DBPA]/dt = K[TBP]_{(I)-(IV)} * [H_2O]_{org} \qquad (5)$$

The values of water concentration in TBP were taken from (Nickolotova and Kartashova, 1976, p. 48). The results of this calculation are given in Table 1. The value obtained for K is constant for wide range of HNO_3 concentration.

The complicate shape of curves in Fig. 2 can be explained with regard for changes of water concentration (see dotted line in Fig. 2) and concentrations of different complexes of TBP with HNO_3 in dependence of HNO_3 content in the organic phase.

High temperature intensifies the hydrolytic decomposition of TBP (Fig.3). Activation energy of this process occured to be approximately 8 $kJ*mole^{-1}$.

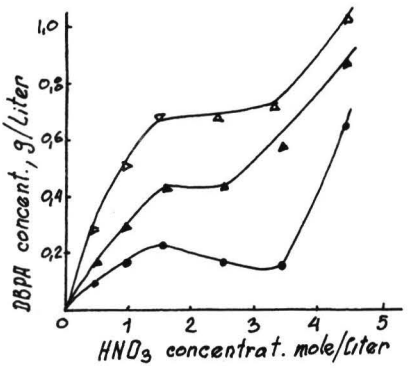


Fig. 3.

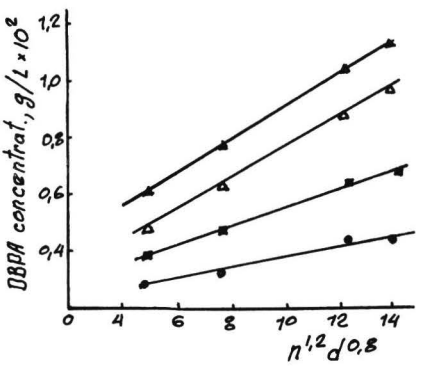


Fig. 4.

Fig. 3. Effect of HNO_3 concentration on DBPA concentration in the organic phase. 6 hours duration, T: (•)-333K; (▲)-338K; (△)-343K.

Fig. 4. Effect of mixing intensity on accumulation of DBPA. $[HNO_3]_{aq}$, mole/l: (•)-1.5; (■)-2.1; (▲)-4.0; (△)-5.1.

3.2 Contribution to hydrolysis of TBP interaction with water at the interface.

If DBPA accumulation was investigated for TBP contacting with aqueous solution of nitric acid in the mechanically agitated contactor the significant increase of DBPA concentration in the organic phase was observed.

The value of specific interfacial area (per unit volume of dispersion) is given by the equation (Laddha and Degaleesan, 1983, p. 126):

$$a = 6x / d_{vs} \qquad (6)$$

where: x – dispersion fraction, d_{vs} – mean volume–surface diameter of drop.

$$d_{vs} / d_R = \text{const} * (We)^{-0.6} \qquad (7)$$

where: d_R – impeller diameter, We – impeller Weber number $= \rho_d * n^2 * d_R^3 * \sigma^{-1}$ (ρ_d dispersion density, n –impeller rotational speed, σ –interfacial tension).

It was found that for the studied extraction system and value of x in the range 0.1–0.5 the value of constant in Eq. (7) is 0.14. Therefore:

$$d_{vs} = 0.14 * n^{-1.2} * d_R^{-0.8} \quad \text{and} \quad a = 42.86 * n^{1.2} * d_R^{0.8} * x \qquad (8,9)$$

The product $n^{1.2} * d_R^{0.8}$ is called as intensity of mixing. Changing rotational speed or a diameter of impeller it is possible to obtain the different values of the specific interfacial area if value of x in the experiment is constant. From the data of Fig. 4. it follows that in the studied range of mixing intensity the dependence of DBPA formation on it is linear. This experiment was carried out in the mechanical agitated contactor (V = 1200 ml) with the ratio of aqueous and organic phases equal to 4, which had ensured to get oil in water type of emulsion and to use Eq. (9) for calculation of specific interfacial area (Table 3).

TABLE 3

Effect of specific interfacial area on the rate of DBPA formation.
$[HNO_3]_{aq}$ = 4.0 mole/liter.

$n^{1.2}*d^{0.8}$. $s^{-1.2}*m^{0.8}$	$d_{vs}*10^{6}$,m	$a*10^{-5}$,m^{-1}	$[DBPA]_{org}*10^{3}$. $g*l^{-1}*h^{-1}$	Contribution of interfacial hydrolysis. %
8.6	3.24	3.7	6.625	50
10.4	2.65	4.5	7.875	55
12.2	2.26	5.3	9.150	61
15.0	1.71	7.0	12.150	68
-	-	-	2.650*	-

* - in separated equilibrium organic phase (due to TBP hydrolysis in the bulk of organic phase.

Comparing the accumulation of DBPA in the separated organic phase and in the similar phase contacting with aqueous nitric acid solution and taking into account that about 10% of DBPA forms in the bulk of aqueous phase (Vladimirova et al., 1989, p. 20) it is possible to evaluate the contribution of TBP hydrolysis at the interface to its total hydrolysis (Table 3).

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EVALUATION OF INDEX ON DEGRADATION DEGREE OF PUREX SOLVENT

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ABSTRACT

It is important to grasp the degree of the solvent degradation. We have studied index products which show the degree of the solvent degradation.

Three materials were found as indicates of the solvent degradation which are irremovable by alkali scrubbing and increase in proportion to the exposure dose.

INTRODUCTION

Solvent (TBP-dodecane) used in the Purex reprocessing forms many degradation, such as DBP and MBP, owing to radiolysis, hydrolysis, and other reactions. These degraded products lower the extraction efficiency of uranium and plutonium, and cause the loss of the decontamination of fission products.[1),2)] From the point of view of process control, it is extremely important to grasp the degree of the solvent degradation.

Normally, most of DBP and MBP are removed from solvent at a solvent regeneration process (alkali scrubbing process) . However, there are many degraded products that cannot be removed by the alkali scrubbing, and the extraction process suffers from these products. The purpose of this study is to find out some materials, except DBP and MBP, that can be used as an index of the solvent degradation.

Following criteria were set in selecting the index-materials.

Criteria :

1. Index materials cannot be removed by the alkali scrubbing and reflect the degree of the degradation.
2. The amount of the degraded materials (index materials) should have a plus correlation to exposure dose.
3. The index-materials should be the degradations of TBP.

EXPERIMENT

1. Preparation of samples
   - Test samples : 30 % TBP-dodecanes were irradiated by γ-rays in a stepwise manner (0 to 2.6×10^4 C/kg) . Fig. 1 shows how the samples were prepared.

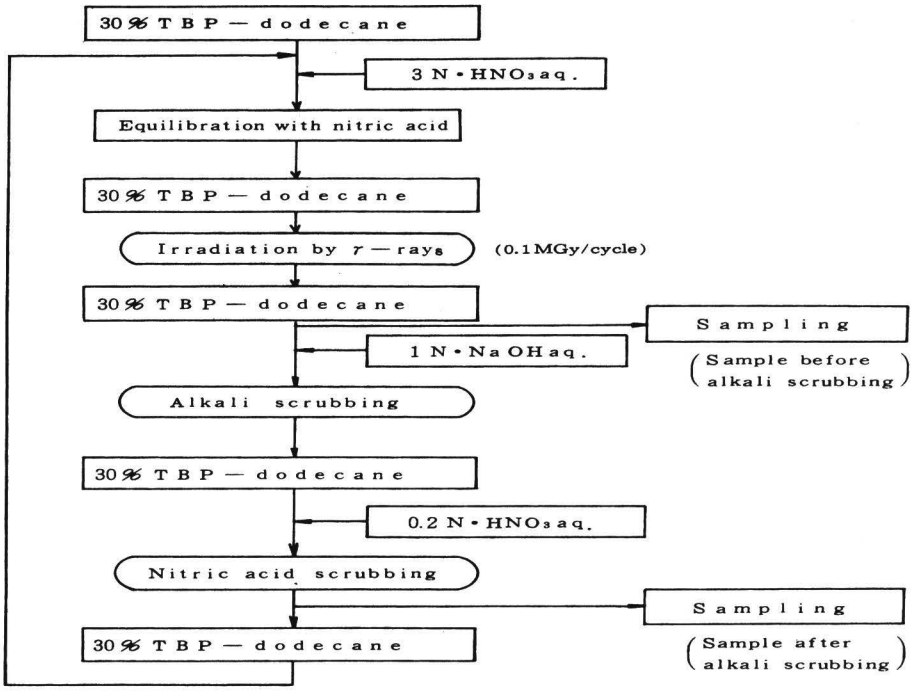


Fig. 1 Flow of preparation of test samples

– Actual samples : 30 % TBP-dodecanes used in the reprocessing of Phenix spent fuels were used.

2. Analytical instruments

– Gas Chromatography (GC) – – – Shimadzu GC15A ; Detector : FID and FPD

– Gas Chromatography/Mass spectrometry (GCMS) – – – Hewlett-Packard 5840A/GC–5985B/MS

– Gas Chromatography/Infrared Spectrometry (GCIR) – – – Hewlett-Packard 5890A/GC–5965A/FTIR

3. Experiments

(1) Alkali scrubbing test

The test samples (irradiated by γ-rays) were scrubbed with alkali (1N of NaOH) and the organic solutions before and after the scrubbing, were measured by Gas-Chromatography.

(2) Confirmation of the correlation between the amount of the degraded products and the exposure dose

The degraded materials in the test samples were measured by Gas-Chromatography (FPD type detector) and the degraded materials were quantitatively determined for every exposure dose.

(3) Analysis and indentification of the degraded materials

The degraded materials were measured by Gas-Chromatography/Infrared-Spectrometry and Gas-Chromatography/Mass-Spectrometry, and the formulae were analyzed. On the basis of these measurements and analyses, standard materials were synthesized to be used as the references.

RESULTS AND DISCUSSIONS

(1) Alkali scrubbing test

Fig. 2 shows the result obtained by FID type detector and Fig. 3 by FPD. FID detects all of the degraded materials while FPD detects only phosphorous compounds. It is obvious from Fig. 2 that there still remains many degraded materials even after the alkali scrubbing. However, Fig. 3 shows that the detectable phosphorous compounds were limited in number, and among these phosphorous compounds, the main residuals after the alkali scrubbing are A, B, and C. These are supposed to be neutral phosphoric esters.

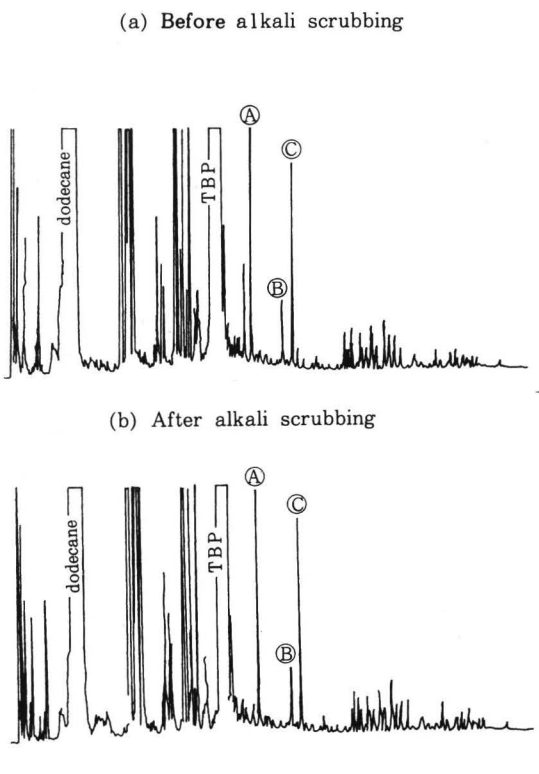


Fig 2 Gas-Chromatogram (FID) of test samples before and after alkali scrubbing

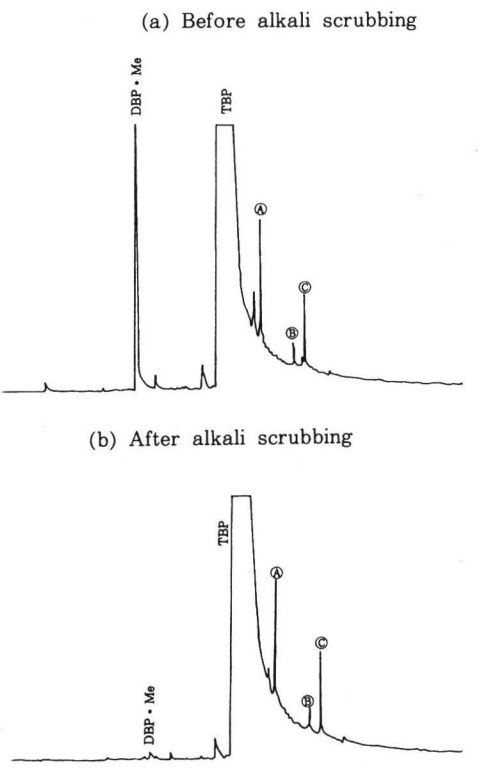


Fig 3 Gas-Chromatogram (FPD) of test samples before and after alkali scrubbing

(2) Confirmation of the correlation between the amount of the degraded products and exposure dose

Fig. 4 shows the degraded materials, A, B, and C increase in proportion to the exosure dose. This indicates that each degraded material, A, B, and C, can be used as an index to check the degree of the solvent degradation.

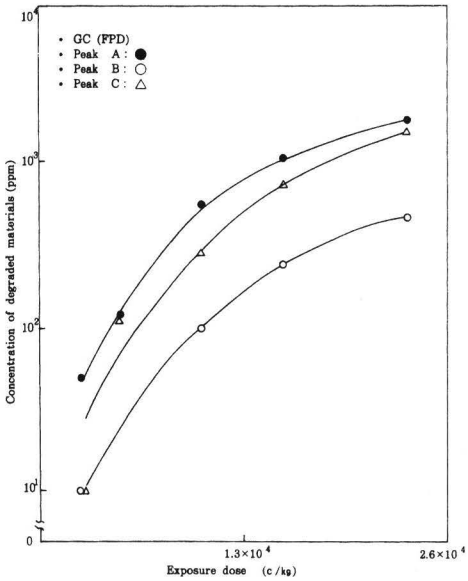


Fig 4 Relation between exposure dose and amounts of solvent degradations

(3) Analysis of the degraded materials

Fig. 5 to 7 show analytical results of the degraded materials, A, B, and C, obtained by Gas Chromatography/ Infrared Spectrometry and Gas Chromatography/ Mass Spectrometry.

The result of mass analysis by Chemical Ionization (CI) method indicated that the molecular weight of the degraded material A was 282. And infrared absorption peaks at 1030 cm^{-1} and 1300 cm^{-1} suggested that this material be phosphoric ester while a peak at 3600 cm^{-1} suggested that it had a hydroxyl radical. And mass analysis by electron impact ionization (EI) method gives the structual fromula as di-n-butyl- 3 -hydroxybutyl-phosphate (Fig. 5) .

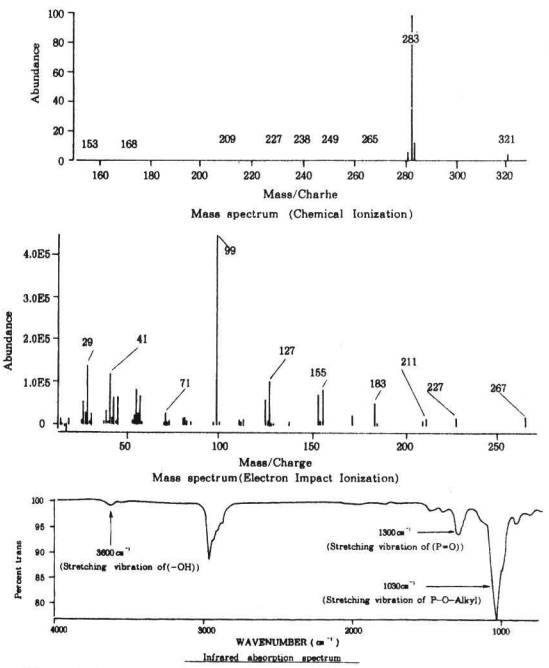


Fig 5 GCMS and GCIR of peak(A) of test sample

The mass analysis (CI method) showed that the degraded material B had a molecular weight of 327. Because it had infrared absorption peaks at 1030 cm^{-1} and 1300 cm^{-1}, which were the samc as the degraded material A, and had a peak at 1570 cm^{-1}, it is supposedly a phosphoric ester with nitro radical. Further study by mass analysis (EI method) indicated that it was di-n-butyl-2-(nitroxy) butyl-phosphate (Fig. 6).

The analitycal results of the degraded material C by mass analysis (CI method) and by infrared Spectrometry were the same as those of the degraded material B, but the mass analysis by EI method suggested that it be di-n-butyl-3 (nitroxy) butyl-phosphate[3),4)] (Fig. 7).

On the basis of the above results, each standard material was synthesized[5),6),7)] and the same analyses were performed on them. As a result, these degraded materials, A, B, and C, were found to be indentical with these synthesized ones (Table 1).

Also, these degraded materials were found in the actual samples.

Table 1 Identification

Peak №	Ⓐ	Ⓑ	Ⓒ
Name	di-n-butyl-3-hydroxybutyl -phosphate	di-n-butyl-2-(nitroxy) butyl -phosphate	di-n-butyl-3-(nitroxy) butyl -phosphate
Molecular Weight	282	327	327
Functional Group	-OH	$-ONO_2$	$-ONO_2$
Structual Formula	$n\text{-}C_4H_9O$ $n\text{-}C_4H_9O$ $OCH_2CH_2CHCH_3$ OH	$n\text{-}C_4H_9O$ $n\text{-}C_4H_9O$ $OCH_2CHCH_2CH_3$ ONO_2	$n\text{-}C_4H_9O$ $n\text{-}C_4H_9O$ $OCH_2CH_2CHCH_3$ ONO_2

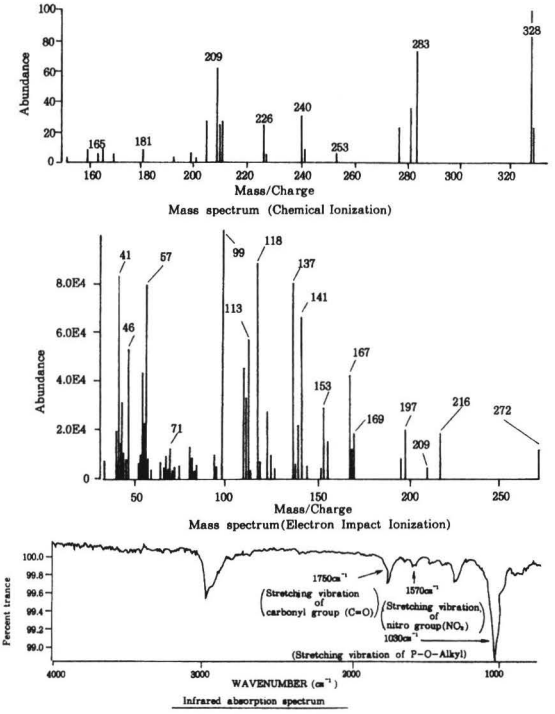


Fig 6 GCMS and GCIR of peak(B) of test sample

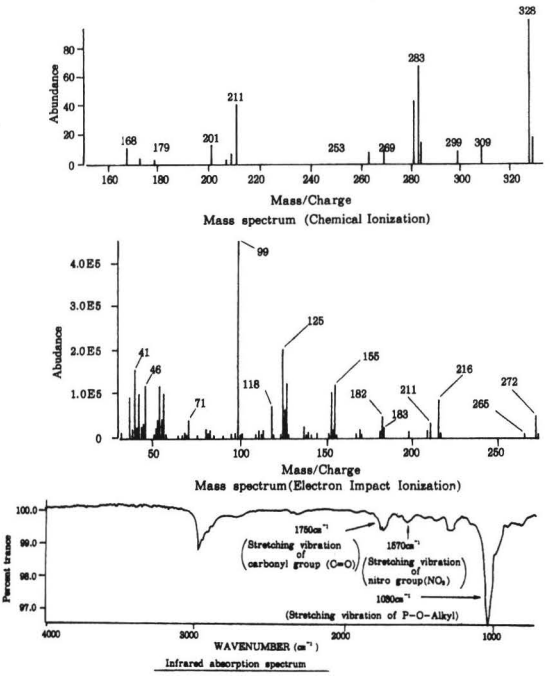


Fig 7 GCMS and GCIR of peak(C) of test sample

CONCLUSION

As the degradations of the solvent, (A) di-n-butyl-3-hydroxybutyl-phosphate, (B) di-n-butyl-2-(nitroxy) butyl-phosphate, and (C) di-n-butyl-3-(nitroxy) butyl-phosphate were found. These degradations are irremovable byalkali scrubbing and increase in proportion to the exposure dose. Thus it may be possible
to use them as the index of the degradation.

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LANTHANOIDE EXTRACTION BY ORGANOPHOSPHORIC ACID IN VARIOUS ORGANIC SOLVENTS

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ABSTRACT

IMAI, M., SAEKI, N., URUSHIYAMA, S. and SHIMIZU, M., 1990. Lanthanoide Extraction by Organophosphoric Acid in Various Organic Solvents. Proc. ISEC'90

The extraction equilibrium of lanthanoide using organophosphoric acid was measured in various organic solvent. The mixing ratio λ of n-heptane and benzene affected on the extraction equilibrium constant of yttrium and neodymium. The change of equilibrium constant with the mixing ratio was presented as following experimental equation:

$$K_{ex} = A \exp(-5.2 \lambda)$$

The extracted species of yttrium and neodymium were same kind of LnR_3 3HR. These were not changed with the mixing ratio λ.

1. INTRODUCTION

Solvent extraction process is a developing field of hydrometallugy of rare metals. The choice of extracting reagent and solvent is important for process design and development of solvent extraction. In industrial extraction processes, some organic phase properties, e.g. viscosity and flash point, were adjusted by preparation of organic solvent.

The organic solvents take a part of an important role with an extracting reagent to extraction equilibrium. Organic solvent affect not only a physical properties of organic phase but an extraction equilibrium have been discussed in previous studies. (Peppard, 1958; Jung, 1976; Komasawa, 1983)

This paper presents the effect of mixing ratio of organic solvent, n-heptane and benzene, on the extraction equilibrium constant and the extracted species of lanthanoide.

2. MATERIALS

The extracting reagents used in this study were di(2-ethylhexlyl)phosphoric acid and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester, abbreviated as D2EHPA and PC-88A, respectively. These were produced by DAIHACHI CHEMICAL INDUSTRY Co.,Ltd. They were purified with 6N-HCl and dried with sodium sulfate,anhydrous. The organic solvents used in this study were n-heptane , benzene and their mixture, purchased from KISHIDA CHEMICAL Co.,Ltd. As the purity levels were more than ca.99%,these solvents were used without further purification.

Distilled water was used for the preparation of aqueous phase. Yttrium chloride and neodymium chloride were dissolved in the aqueous phase. These chemicals were also purchased from KISHIDA CHEMICAL Co.,Ltd. And they had an assay tested purity of more than 99.9%. The ionic strength in the aqueous phase was adjusted by use of sodium chloride, which was maintained 0.3 mol/dm^3 throughout this investigation. The pH in the initial aqueous phase was adjusted by use of 0.1N-HCl and 0.1N-NaOH solutions.

3. METHODS

The extraction of lanthanoide from aqueous phase to organic phase was performed by mixing the two phases for more than 12 hours. It was sufficient time to reach the equilibrium state. The concentration of lanthanoide in the aqueous phase was measured by EDTA titration. Xylenol orange was used as an indicator. The lanthanoide concentration in the organic phase was also determined with the titration. The lanthanoide in organic phase was extracted backward by 6N-HCl beforehand. The mass balance agreed well with the initial amount of lanthanoide. The pH was measured using a pH electrode, type PT-5D purchased from ADVANTEC TOYO Co., Ltd. All experimental runs for different component of solvent were carried out in the described above method. The extraction was performed at a constant temperature 298K.

4. RESULTS AND DISCUSSION

4.1 Extraction with Organophosphoric Acid

Extraction with organophosphoric acid was considered a cation exchange reaction.The overall extraction reaction can be expressed as Eq.(1). In this study, dimerization of the

extracting reagent in the organic phase was assumed.

$$jM^{n+} + 0.5r\overline{(HR)_2} = \overline{(MjRrHh)} + njH^{+} \quad (1)$$

The extraction equilibrium constant K_{ex} was determined by Eq.(2)

$$K_{ex} = \frac{\overline{[MjRrHh]}\ [H^{+}]}{[M^{n+}]^{j}\ \overline{[(HR)_2]}^{0.5r}} \quad (2)$$

The distribution ratio D_M was defined as the ratio of lanthanoide concentration in organic phase to in the aqueous phase.

$$D_M \equiv \frac{j\ \overline{[MjRrHh]}}{[M^{n+}]} \quad (3)$$

The distribution ratio can be represented by the following logarithmic equation.

$$\log D_M = \log jK_{ex} + 0.5r \log[\overline{(HR)_2}] + \log[M^{n+}]^{j-1} + njpH \quad (4)$$

4.2. Extraction with single solvent

The extraction equilibria for yttrium and neodymium using PC-88A and D2EHPA were measured in the case of both n-heptane and benzene as an organic solvent.

Figure 1 shows the effect of pH on the distribution ratio of yttrium in the PC-88A and n-heptane system. The slope in this figure shows nj=3 in Eq.(4). The species of extracted yttrium was therefore found to be a monomer of yttrium. Because the yttrium was an n=+3 cation, the j value equals one. The value of 0.5r equals three that was obtained from the relationship between the equilibrium distribution constant and the concentration of PC-88A. The species of extracted yttrium was found to be YR_3 3HR. This extracted species was same kind in the benzene system.

When D2EHPA was used as an extracting reagent, the extracted species was also YR_3 3HR in the case of both n-heptane and benzene as organic solvent. These results concerning the extracted species were agreed with previous studies.(Imai,1985,Kolarik,1966)

The extraction equilibrium constant, obtained for yttrium extraction by PC-88A in n-heptane system, was found to be K_{ex} = 139.0. The K_{ex} value i benzene system was 0.95. This large difference of equilibrium constant suggests that the choice of solvent component was important for a practical design of lanthanoide extraction. This effect was similar to the finding of previous study. (Komasawa, 1983)

4.3 Extraction with mixture of benzene and n-heptane

The volumetric ratio of sol vent component λ was used as a paramet er in this study. The parameter λ was defined as the following equation.

$$\lambda \equiv \frac{\text{Benzene}}{\text{n-Heptane} + \text{Benzene}} \qquad (5)$$

The change of extraction equilibrium constant of yttrium with various mixing ratio was shown in Figure 2. The slopes of the equilibrium lines were as same as a single solvent system, therefore the extracted species was considered to be YR_3 3HR.

The extraction equilibrium constants in various mixing ratio λ were shown in Figure 3. The relationship between the equilibrium constant K_{ex} and the mixing ratio λ was expressed as following experimental formula:

$$K_{ex} = A \exp(-5.2\,\lambda) \qquad (6)$$

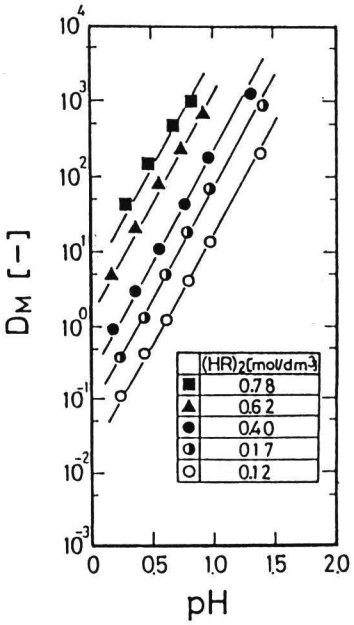


Fig. 1 D_M VS. pH Y, PC-88A, n-heptane

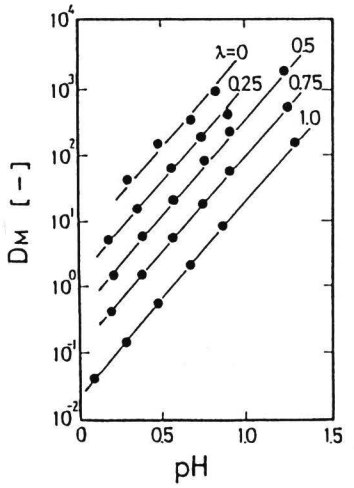


Fig. 2 D_M VS. pH Y, PC-88A=0.6mol/dm³ n-heptane

where $\lambda = 0$ means the system using 100 % n-heptane as the solvent, and $\lambda = 1$ means the system using 100% benzene. The coefficient A changes with the species of extracted reagent and lanthanoide.

The selectivity of extracting reagent was not affected by the mixing ratio λ. Because the difference of equilibrium constant was not changed with λ, as shown in Fig. 3.

In Figure 4, the percent extraction of yttrium in various extraction systems was presented. The percent extraction in the n-heptane system showed high percentage although the pH was low. In these system, backward extraction was seemed to be difficult. It was suggest that the preparation of appropriate solvent is important for practical design of the lanthanoide extraction processes.

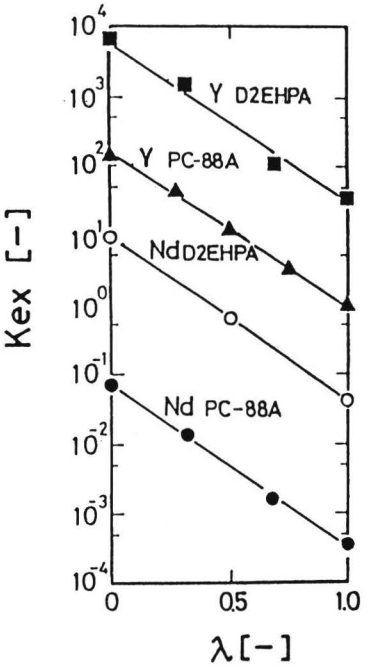


Fig. 3 K_{EX} VS. λ

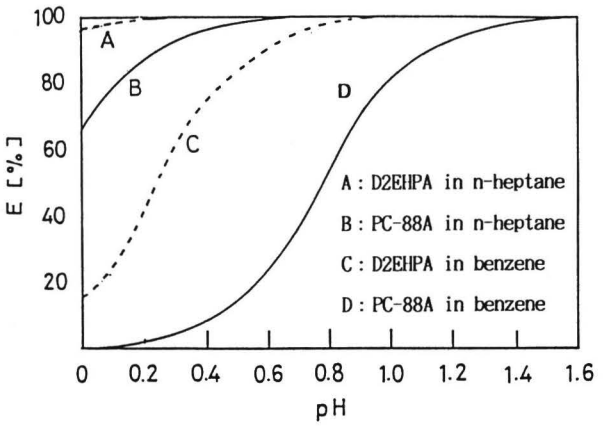


Fig. 4 E VS. pH

5. CONCLUSION

The extraction equilibrium of lanthanoide in various organic solvent was investigated. The mixing ratio of benzene and n-heptane affected on the extraction equilibrium constant.

The change of extraction

equilibrium constant with mixing ratio λ was presented as the experimental formula in Eq. (6).

ACKNOWLEDGMENT

The authors would like to express appreciation for the financial support of IWATANI NAOJI FOUNDATION.

5. NOTATION

D_M	[-]	: distribution ratio of lanthanoide
E	[%]	: percent extraction of metal
H		: hydrogen ion
K_{ex}	[-]	: extraction equilibrium constant
M		: metal ion
n	[-]	: number of electric charge
R		: active component of the anion of the extract reagent
λ	[-]	: solvent mixing ratio defined by Eq.(5)

superscript

——: organic phase

subscript

j : stoichiometric number for the extracted lanthanoide

h,r : stoichiometric number for the extract reagent

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EXTRACTION OF PENTAVALENT VANADIUM FROM ACID SOLUTIONS BY N-DECANOL : DILUTION STUDIES

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ABSTRACT

This study deals with the influence of diluents on the extraction of V(V) by n-decanol. The molecular association of n-decanol molecules and the energy of solvation of the extracted complex, HVO_3, are functions of the nature and the concentration of the diluent. A thermodynamic approach is used to evaluate the two effects by means of activity of the extractant and the free energy of transfer of the complex from undiluted to diluted n-decanol.

INTRODUCTION

The influence of diluent on the extraction of metals is well known /1-5/ although it has been not systematically studied. The diluent acts on both the molecular structure of the extractant and the solvation energy of the extracted complexes. The distribution ratio changes in a way related to the variations of the two effects (when the same aqueous phase is considered and only trace concentrations of the metal are used).

A thermodynamic approach is considered to evaluate these factors in the case of the extraction of pentavalent vanadium from acid solutions by n-decanol in different diluents.

It is assumed that :

- organic materials are insoluble in the aqueous phase,
- extraction of aqueous species introduce only negligible change in the organic phase,
- extraction of only one form, noted ME, of a metal M for which many aqueous forms may exist.

The mechanism of the extraction of M by an alcohol ROH is described by the following equation :

$$ME_{aq} + nROH_{org} \quad <\!\!=\!\!=\!\!=

Thus, the equilibrium constant of (1), K, gives :

$$D = K.f(aqu.).g_{ME}.a^{n}_{ROH} / g_x$$

where g_i and a_i represents the activity coefficient and the activity of species i.

Two factors appear in this equation :

- the first depends only on the aqueous phase (f(aqu.) g_{ME})
- the second depends only on the organic phase if trace concentrations are used.

If two organic phases 1 and 2 corresponding to different dilutions are contacted with the same aqueous phase, and if the state 1 is taken as the standard state for activities ($a_{ROH}=1$ and $g_x=1$, X infinitely diluted in 1) D_1 and D being the respective distribution ratios (subscript 2 omitted); then :

$$D/D_1 = a^{n}_{ROH}/g_x \qquad (2)$$

The ratio D/D_1 is only dependent on the organic solution. This equation is useful to evaluate the activity coefficient, g_x, of the extracted complex if the activity of the extractant is determined :

g_x is the transfer activity coefficient from solvent 1 to solvent 2. It is related to the standard free enthalpy of transfer of the complex by the relation :

$$\Delta G^{\circ}_t = RT \ln g_x$$

ΔG°_t is a measure of the difference in solvation energies of the complex in the two solvents. A negative (resp. positive) value means the solvation is stronger (resp. weaker) in solvent 2 than in solvent 1.

Extraction of Vanadium (V) by alcohols :

In acidic solution (pH < 3) V(V) exists in the monomeric state when its concentration is less than or about 10^{-4} mol/L in perchloric medium /6/. The species present are VO_2^+ and HVO_3. In other aqueous media complexation of the pervanadyl ion may occur /7-10/. In particular, this is the case with sulfate and phosphate anions.

The extraction of traces of V(V) by alcohols was studied by D. Dyrssen and T. Sekine /11/ (pure 2-methyl-pentanol 4 as extractant from perchloric medium) and by A. A. Ivakin /9/ (mixtures of secondary aliphatic alcohols from chlorhydric-perchloric solutions). The extracted form of V(V) is HVO_3. In strongly acid solution another mechanism of extraction involving VO_2^+ is observed /12/.

EXPERIMENTAL PART

n-Decanol, n-hexane, xylene and o-dichlorobenzene used are chemically pure reagents. The equilibria are attained in thermostated reactors (25°C). n-Decanol is always used after being contacted with pure water. Aqueous solutions are obtained by dissolving chemically pure $NaVO_3$ in acid solutions containing $HClO_4$ and $NaClO_4$ or H_2SO_4 and K_2SO_4 or H_3PO_4 and KH_2PO_4.

Vanadium concentration is determined spectrophotometrically after quantitative extraction by n-decanol of the complex formed by V and benzohydroxamic acid /13/ at pH of about 2.2 and reading the absorbance at 450 nm.

It was demonstrated that the method is useful with n-decanol diluted up to 20% in the different diluents used in this study. The organic vanadium concentration is determined directly by contacting the organic phase (if necessary n-decanol is added to reach the minimal dilution) with an aqueous phase containing benzohydroxamic acid in the same conditions as an aqueous phase of V(V).

RESULTS

1- Preliminary results :

With the three aqueous solutions of pH between 1 and 3, the complex in the organic phase is the same as shown by UV spectra. The study of the effect of pH on the extraction from perchloric solution (the ionic stength being constant) shows that the extraction mechanism involves one proton. The absence of polymeric species in perchloric media was checked spectrophotometrically up to 1.5×10^{-4} mol/L and confirmed by the results of the extraction.

The variation of the pH during the extraction suggests the formation of H^+ due to displacement of an hydrolysis reaction. The presence of sulfate or phosphate species decreases the extraction due to the formation of non-extractable pervanadyl sulfate or pervanadyl phosphate.

All these observations confirm the extraction of metavanadic acid under the experimental conditions.

2- Influence of dilution :

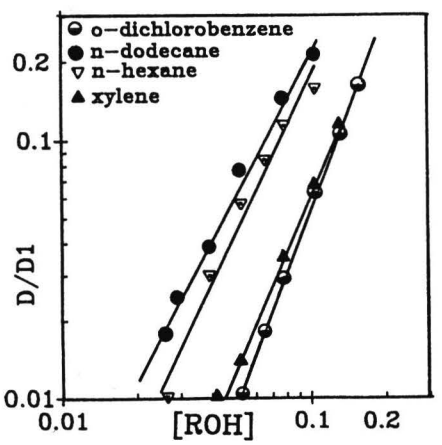


Fig 1: D/D1 vs [ROH] in the range 0.05 < [ROH] < 0.25 mol/L

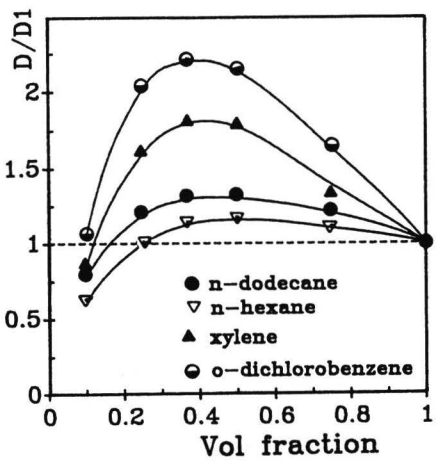


Fig 2: D/D1 vs ROH vol. fraction for [ROH] > 0.5 mol/L

Equilibria involving various concentrations of n-decanol in the range (0.05 - 0.25 mol/L) in the different diluents and the same aqueous solution are achieved. Note that

the free n-decanol concentration is nearly equal to its initial value, bonded molecules to V and acid are negligible (this was checked for perchloric acid extraction, the more extracted acid, and is in accordance with known results /14/). lg D varies linearly versus lg [ROH]. The slopes of the lines obtained are between 2 and 2.5. This is the case whatever the aqueous phase (nature, pH, ionic strength and concentrations of complexing anions). lg D/D_1, is dependent only on the diluent (fig. 1). The effects of the diluents on the extraction are in the following order : D(n-dodecane) > D(n-hexane) > D(xylene) > D(o-dichlorobenzene)

At higher concentrations of n-decanol (above 0.5 mol/L), the variations of the ratio D/D_1 versus the concentration of the n-decanol are given in figure 2. The aqueous parameters have no effect on values of D/D_1. The extraction is enhanced by dilution.It increases in the series : n-hexane, n-dodecane, xylene, o-dichlorobenzene.

Activity of n-decanol

The activity of n-decanol diluted with n-dodecane or xylene is determined by measuring its solubility in water. It has been assumed that the activity of undiluted n-decanol is equal to one and that the activity of n-decanol in water equals its concentration due to its low solubility. The activity of n-decanol in an organic solution is then equal to the ratio C/C_0 where C and C_0 are the concentrations of n-decanol in water contacted respectively with the solution and with undiluted n-decanol. Since the contents of the extracted species (V, acid) in the organic phase are very low, activity values determined with water are valid in other situations. The n-decanol concentration in water is determined, after recovery in n-hexane, by gas chromatography. Tables 1 and 2 give the values obtained.

Table 1 : activity of n-decanol in n-dodecane

% molar	100	78	64	54	41	28
activity	1	0.8	0.72	0.66	0.54	0.46
% molar	12	2.6	1.78	1.19	0.75	0.5
activity	0.38	0.21	0.17	0.156	0.124	0.087

Table 2 : activity of n-decanol in xylene

% molar	100	66	49	39.3	27.5	17.75
activity	1	0.54	0.43	0.38	0.32	0.28
% molar	6.7	2.6	1.63	1.3	0.98	0.65
activity	0.21	0.12	0.08	0.073	0.064	0.04

Solvation number

In the lower range of dilution lg D/D_1 is linear versus lg a_{ROH} (figure 3). The slopes of the lines obtained are close to 3. This suggests the formation of $HVO_3(ROH)_3$ (X) in the organic phase. The difference in the values obtained with the slope analysis using the concentration of the extractant suggests that n-decanol molecular association still occurs at the dilution investigated.

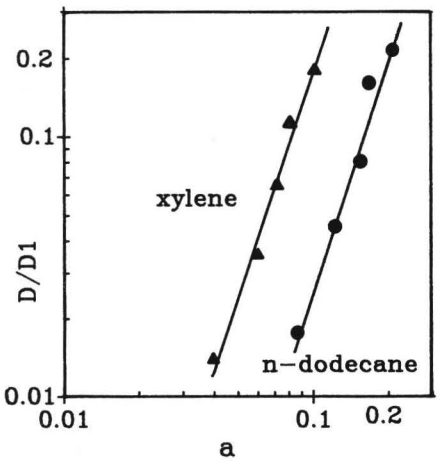


Fig 3: D/D1 vs activity of n-decanol in n-dodecane and xylene

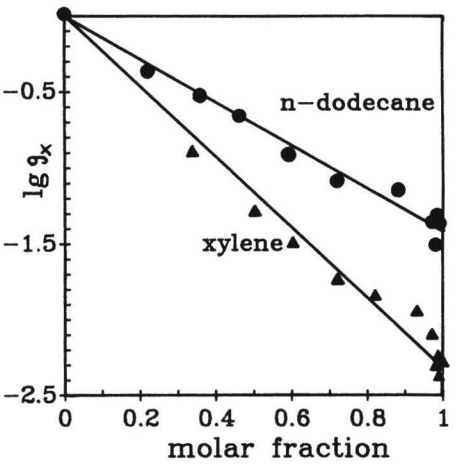


Fig 4: Transfer activity coefficient of the organic complex vs diluent molar fraction

Solvation energy

If the formation of the same complex is assumed at higher concentrations of n-decanol, then equation (2) is valid and one can evaluate the transfer activity coefficient of the complex X in the organic phase. The assumption is made that g_X in undiluted n-decanol is equal to 1. Figure 4 represents the variations of lg g_X versus the molar fraction of the diluent. A linear relation is found. The free energy of transfer of X from undiluted n-decanol to solution in n-dodecane or xylene is thus of the form :

$\Delta G^\circ_t = - \alpha . Y_{dil}$

where Y_{dil} is the molar fraction of the diluent and α is a positive constant dependent on the diluent.

n-dodecane :	lg $g_X \approx -1.4\ Y_{dil}$	$\Delta G^\circ_t \approx - 8.Y_{dil}$ kJ/mol
xylene :	lg $g_X \approx -2.3\ Y_{dil}$	$\Delta G^\circ_t \approx - 13.Y_{dil}$ kJ/mol

The solvation of the organic complex is improved when the n-decanol is diluted. The effect is more pronounced with xylene than with n-dodecane. This is probably due to the breaking of H-bonds in the upper shells of solvation. Components with high dielectric constant and dipole moment are obviously more effective. (xylene used is a mixture of its isomers).

CONCLUSION

In the experimental conditions, the validity of relation (1) confirms the extraction of only one form of the aqueous species of V(V) : HVO_3. In the organic phase this compound is solvated with 3 n-decanol molecules. The organic system shows a synergistic behaviour. This is due to the double action of the diluent :

- on the extractant : dissociation of H-bonds between n-decanol molecules and interactions diluent-extractant.
- on the solvation energy of the complex.

When the concentration of n-decanol is low the interactions n-decanol-diluent predominates. the extraction of HVO_3 increases when the polarity of the diluent decreases : o-dichlorobenzene < xylene < n-hexane < n-dodecane.

(The order hexane < dodecane results from the fact that for the same concentration of n-decanol, the molar fraction is lower in hexane than in dodecane.)

For other dilutions the effect of the diluent on the solvation of the extracted complex predominates. The extraction increases with the dielectric constant of the diluent :

n-hexane < n-dodecane < xylene < o-dichlorobenzene.

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ADVANCE IN ACTINIDES SEPARATIONS BY SOLVENT EXTRACTION. RESEARCH AND APPLICATIONS.

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CEA - DCC/DPR/SCPR - BP n° 6 CEN/FAR FONTENAY-aux-ROSES (FRANCE)

ABSTRACT
The results obtained with three kinds of new solvents for actinides separations are presented.
The use of N,N-dialkylamides (R_2NCOR'), alternative to TBP, can limit the amounts of nuclear wastes produced in the existing reprocessing plants. The N,N-tetraalkyl 2-alkyl propane diamides ($(RR'NCO)_2CHR"$) bidentate extractants are able to remove the actinides ions including the trivalent ones from various type of TRU wastes. The synergistic mixture tripyridyl triazine-dinonylnaphtalene sulfonic acid (TPTZ-HDNNS) proved to be efficient for the selective extraction of the trivalent actinides from nitric aqueous acidic solutions. This paper is focussed on the progress gained for the practical applications of these extractants especially the results of counter-current separations.

INTRODUCTION

New actinides extractants could be advantageous in the existing reprocessing plants or in the future plants built to achieve the back-end nuclear fuels cycles using solvent extraction. The main reasons to replace the organophosphorus extractants have been presented in many instances, for example by Grossi et al. or Musikas in this meeting. Complete incinerability, and non-disturbing degradations products are suitable because of the incentives to limit the amounts of nuclear wastes generated by the separation processes.

In this paper we will focus on the results of counter-current separations of actinides performed in bench-scale mixer-settlers. Three kinds of extractants are presented : the N,N-dialkylamides, alternative to TBP, the N,N'-tetraalkyle propane diamides usable to remove the actinides from various wastes and the synergistic mixture dinonylnaphtalene sulfonic acid-tris 2-pyridyltriazine for the actinides (III)-lanthanides (III) group separation.

N,N-DIALKYLAMIDES

To replace TBP in a PUREX type process, the N,N-dialkylamides RRNCOR' must present as much advantages as possible. The proper choice of R and R' permitts to optimize their properties. The solubility of U(VI) and Pu(IV) nitrato complexes in alkanes is obtained if R = $-CH_2\ CH(C_2H_5)C_4H_9$. There is no third phase formation even for organic phases saturated with U(VI) or Pu(IV)

(~ 120 $g.l^{-1}$ for 1 $mole.l^{-1}$ amide). Branched R' substituents permitt better U(VI)-Pu(IV), U(VI)-Zr(IV) and U(VI)-Ru(II) separations. The presence of short R' allowed easier solvent restorations because of the solubility in aqueous phase of the R'-COOH acid, the main radiolytic product of amides. The distribution ratios of U(VI) and Pu(IV) in traces concentrations between nitric acid solutions and DOBA ($(C_4H_9\ CH(C_2H_5)CH_2)_2\ NCOC_3H_7$) or DO_iBA ($C_4H_9\ CH(C_2H_5)\ CH_2)_2\ NCO\ CH(CH_3)_2$ are shown figure 1.

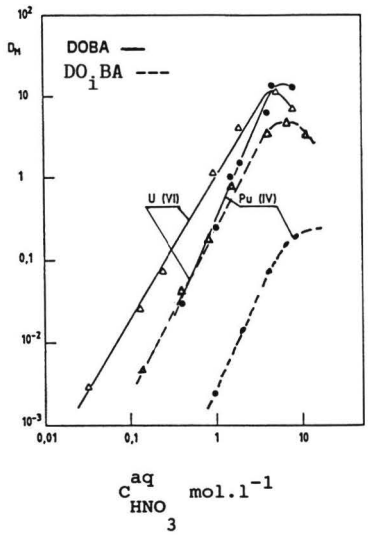


Figure 1 - Distribution ratios of U(VI) and Pu(IV) between 1M DOBA or DOiBA into TPH (branched dodecane) and aqueous HNO_3.

In can be seen that Pu(IV) distribution ratios are strongly depressed by changing $-C_3H_7$ for $-CH-(CH_3)_2$. DOBA alone cannot be used to separate easily Pu(IV) from U(VI). For DOiBA the separations factors are high but Pu(IV) is poorly extracted at high acidities. So mixtures of DOBA and DOiBA have been used for a test of a PUREX process first cycle with a U(VI)-Pu(IV) partition. The flow diagramm used for this bench scale test is shown figure 2. The main results are contained into Table 1.

They were quite satisfaying in spite of some errors in the flow rates adjustment for the partition battery during the experiment. The neptunium follows the plutonium.

The radiolytic stabiliy of amides in the presence of aqueous HNO_3 is not very different from TBP. One have G_{-Amide} 0.6 and 2.2 in the presence of respectively 0.5 and 4N HNO_3 and in these conditions G_{HDBP} values are close to 1 and 1.8.

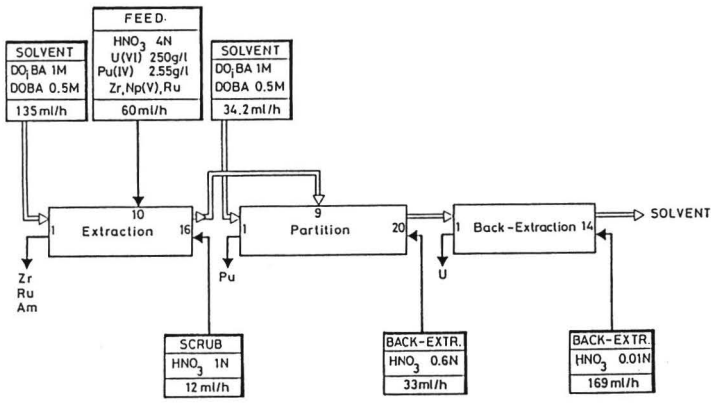


Figure 2 - Flow sheet for a PUREX process first cycle using N,N-dialkylamides as a solvent

THE N,N'-TETRAALKYLE PROPANE DIAMIDES (DIAM)

Within the diamides only malonamides $(RR'NCO)_2$ CHR" extract the trivalent actinides and lanthanides. The selection of R, R' and R" has been made to obtain high distribution ratios of Am(III) R or R' must be CH_3 ; R" is better a long alkyl or oxyalkyl group (C. Musikas, 1987).

TABLE 1
Results of the first cycle PUREX process using N,N-dialkylamides

Flux	U % of feed	Pu	Zr	Ru	Np
Extraction					
(Solvent)	> 99.99	99.999	0.01	0.05	95
(Aqueous)	< 0.0005	0.0008	99.99	99.95	5
Partition					
(Solvent)	99.89	0.006			not detect
(Aqueous)	0.11	99.994			95
U desextraction					
(Solvent)	not detect.	not detected			not detected
(Aqueous)	99.89	0.006			not detected

The higher distribution ratios obtained with substituted tetraalkyle malonamides is correlated with their lower basicity. This can be understood as a competition of Am(III) and HNO_3 for the coordination site of the diamides. Taking into account these results a bench scale separation of the actinides contained into a real waste for which the composition is given Table 2 has been performed with N,N'-dibutyl dimethyl 2(3-oxanonyle)-propane diamide $((C_4H_9\ CH_3\ N\ CO)_2\ CH\ C_2H_4\ O\ C_6H_{13})$ DBM3-ONPDA (Cuillerdier et al.).

TABLE 2
Composition of aqueous phase used in the bench-scale mixer-settler separation

Element	Content	Element	Content
H^+	5M	Fe	500 mg/l
NO_3^-	5.5M	P_{Total}	270 mg/l
Pu	110 mg/l	$Np^{237+239}$	50 mg/l
Am	0.91 mg/l	^{152}Eu	traces
U	5.9 g/l	$\alpha_{activity}$	50 mCi/l
Tc	134 mg/l		

The flow sheet is presented Figure 3 and the results contained into Table 3. It can be seen that the process is efficient for the removal of the α activity from the wastes. During this test we observed that Am(III) was not back-extracted as easily as excepted from the $D_{Am(III)}$ measured with synthetic solutions. After investigations dealing with Am(III)-TcO_4^- coextraction we attributed that to the presence of TcO_4^- which retain Am(III) in the organic phase at low acidity (C_{HNO3} ; 1N).

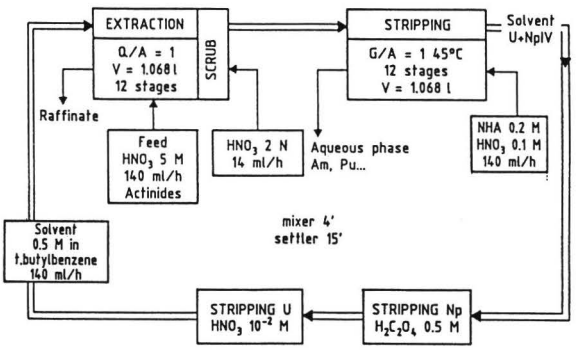


Figure 3 - Flow sheet for the counter current separation of actinide using DBDM 3-ONPDA.

TABLE 3
Decontamination factors obtained in mixer-settler batteries for a waste treatment with DBDM 3-ONPDA compared with TRUEX process one*

Element	DF extraction	DF stripping
Am	$1.26\ 10^4$ - $5\ 10^{4*}$	800
Eu	$6.7\ 10^3$	250
α_{tot}	$1.1\ 10^4$	125
Pu	$> 10^5$ - $> 10^{5*}$	274
Np	144	400
U(VI)	> 1000 - $> 10^{5*}$	
Fe	> 1000	

In Figure 4 we plotted the distribution ratios of Pu(IV) and Am(III) between 5N HNO_3 or 0.5N HNO_3 and 1M diamide into t-butybenzene irradiated in the presence of the aqueous phase as a function of the dose of ^{60}Co γ ray. It can be seen that the distribution ratios vary slightly with the irradiation but no strong retention or antisynergism due to the degradation products is observed. This behavior is quite encourgaging especially when it is compared with the irradiated organophosphates (TBP, CMPO) which forms acidic degradation products which retain the metallic ions in the organic phase at low acidity.

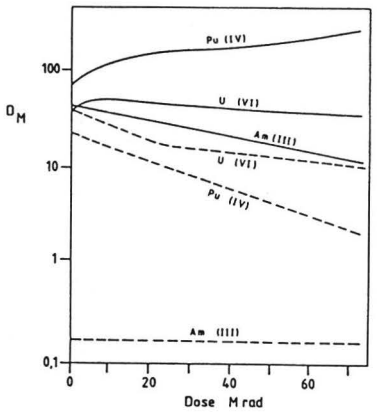


Figure 4. Effect of the ^{60}Co γ dose upon the distribution ratios of U, Pu, Am between 1M DMDB3, 60DPDA into t-butylbenzene irradiated and 5 N —— or 0.5N --- aqueous HNO_3.

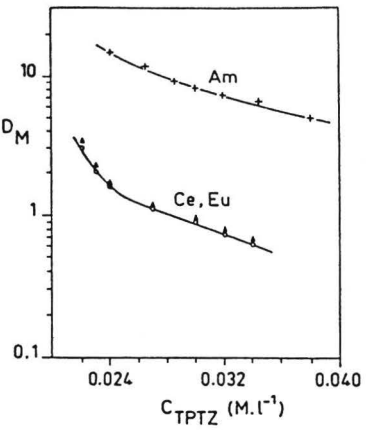


Figure 5. Distribution ratios of Am(III)+, Ce(III)Δ , Eu(III)O, between 0.05M HDNNS, TPTZ into CCl_4 and 0.125N aqueous HNO_3 as a function of the initial TPTZ concentration into the organic phase.

3 ACTINIDES-LANTHANIDES GROUP SEPARATION

The needs for trivalent actinides lanthanides group separations have been given by Musikas in this meeting. The nitrogen or sulfur donor present some interest for actinides-lanthanides (III) group separations (Musikas, 1984). The mixture HDNNS (dinonylnaphtalene acid) plus TPTZ (tris-pyridyl triazine) in solution into carbon tetrachloride has been tested as solvent for the counter current 5f-4f trivalent ions group separation into a laboratory mixer-settler. The distribution ratios with which the flow sheet has been calculated are plotted in figure 5. The flow sheet and the results are given figure 6.

The results are fair, however the HDNNS-TPTZ-CCl_4 solvent has large time phase disengagement and the entrainement of some aqueous phase droplets into the organic phase limited the overall separation factors.

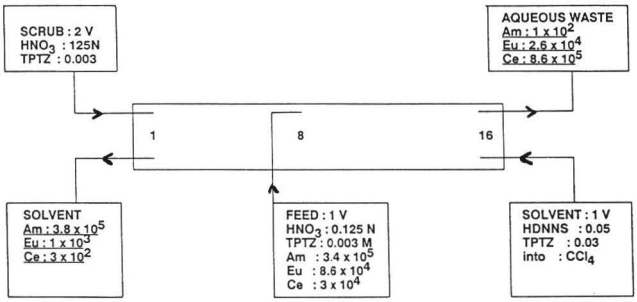


Figure 6 - Flow sheet and result for mixer-settler actinides (III)-lanthanides (III) group separation using a solvent TPTZ + HDNNS into CCl_4.

4 CONCLUSIONS

Completely incinerable extractants such as N,N-dialkylamides giving less distrubing degradation products can be proposed for the present and the future spent nuclear fuels reprocessing plants.

The N,N'-dialkylamides can replace TBP and the N,N'-tetraalkyle 2-alkyle propane diamides can be used to remove the actinides from various wastes within the nowadays stragtegies of major actinides recovery. Trivalent actinides-lanthanides group separations are still in a preliminary stage because no advantageous process for large scale separation is available ; progress in this field are necessary for the future, especially if minor actinides (Np, Am, Cm) partitioning is carried out.

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TWO SYNERGIC PAIRS FOR THE EXTRACTION OF AMMONIACAL Ni

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ABSTRACT

Extraction of Ni from ammoniacal sulfate solution has been studied for two solvent extraction systems that show extraction synergy. The first system uses the extractants 2-hydroxy-5-nonyl benzophenone oxime (LIX 64N) and 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline (Kelex 100). At pH 10, Ni extraction synergy is seen for this chelate-chelate pair in both equilibrium tests and kinetic tests. The second system uses Kelex 100 and dinonylnaphthalene sulfonic acid (DNNSA), a chelate-acid pair. No equilibrium extraction synergy is observed for the second pair at pH 10, but of more practical importance, kinetic synergy is found. In only 10 min of mixing with 0.10 *M* extractant, Ni extraction is 53% for the best LIX 64N/Kelex ratio (3:1) and 87% for the best Kelex/DNNSA ratio (4:1), but none of the three extractants alone extracts more than 43% of the Ni under identical test conditions.

INTRODUCTION

The U.S. Bureau of Mines has developed a hydrometallurgical process for recovery of Ni, Co, and Cu from low-grade laterite ores (Siemens et al., 1975; Nilsen et al., 1982; Rhoads et al., 1977). After reduction-roasted ores are leached with ammoniacal sulfate solution, the metals are extracted from the leachant using solvent extraction processes. Because commercially available extractants perform best at pH values lower than those used for leaching, some ammonia must first be removed from the liquor by air stripping before metal extraction can proceed. A variety of extractant pairs has been tested to find synergic pairs that extract Ni and Cu at high pH well enough to avoid the ammonia removal step.

Most of the published research on synergic extraction of transition metals has focused on extraction from acidic leach liquors. Synergy for Ni extraction has been found for LIX 63 and di-2-ethylhexylphosphoric acid (Joe et al., 1966), LIX 63 and carboxylic acid mixtures (Flett and West, 1971), LIX 63 and DNNSA (Osseo-Asare and Renninger, 1984), and Kelex 100 and carboxylic acid mixtures (Hummelstedt et al., 1974). Other mixtures have been used for Cu extraction (Kordosky et al., 1985). There is a lack of information available, however, on Ni and Cu extraction from ammoniacal media with synergic pairs. The Bureau has found two extractant pairs, each of which synergically extracts Ni at high pH better than available single extractants.

A chelate-chelate pair, LIX 64N and Kelex 100, displays both equilibrium and nonequilibrium Ni extraction synergy. The chelate-acid pair, Kelex 100 and DNNSA, shows an even greater kinetic synergy, but no Ni extraction synergy at equilibrium.

2 EXPERIMENTAL

Three extractants were used: 2-hydroxy-5-nonyl benzophenone oxime (active extractant in LIX 64N--Henkel*), 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline (Kelex 100--Sherex), and DNNSA--Alfa Products. LIX 64N contains two active ingredients. LIX 65N is the major active oxime extractant. LIX 63, the minor constituent, is a kinetic synergist for Cu extraction from acidic leach liquors. Each of these was tested for Ni

*Reference to specific products or manufacturers does not imply endorsement by the Bureau of Mines.

extraction from ammoniacal solutions. LIX 63 additions did not affect Ni extraction, and LIX 65N extracted Ni no differently than LIX 64N. Therefore, LIX 64N was used and studied as a single extractant. Each extractant was diluted with a mixed aliphatic, aromatic kerosene and pretreated by acid washing, Cu loading, repeated acid stripping, and water washing. To prevent third-phase formation, all Kelex 100-containing solutions were prepared to contain 2 mL of isodecanol for each 1 g of contained Kelex 100.

All aqueous solutions contained 2.0 *M* $(NH_4)_2SO_4$, 2.85 *M* NH_4OH (concentrations expected in leach liquors), and Ni as $NiSO_4$. All aqueous solutions were within 0.1 pH units of 10.0, and none changed more than 0.05 pH units after extraction. Reagent recyclability tests used a reduction roast leach liquor that contained Ni, Cu, and traces of other metals.

Extractions were done by contacting aqueous and organic mixtures in either separatory funnels for short contact times or in tightly capped plastic bottles for long (960 min) contact times. Short shakeout tests in separatory funnels were done in an orbital shaker at room temperature using equal 20-mL volumes of each phase (A:O = 1). Equilibrium shakeouts (960 min) in plastic bottles also were done in an orbital shaker at room temperature and at A:O = 1. Extraction was reported either as the distribution coefficient D, where $D = [Ni]_{org}/[Ni]_{aq}$ or as percent extraction.

3 RESULTS AND DISCUSSION

3.1 LIX 64N/Kelex 100 system

Both LIX 64N and Kelex 100 extract Ni from high-ammonia feedstreams. LIX 64N extracts Ni rapidly, but it is a fairly weak extractant in the high pH range. A 10-min shakeout test with 0.10 *M* LIX 64N resulted in Ni extraction of only 42% of a 0.0017 *M* Ni feed solution. Kelex 100 extracts Ni more strongly, but is a slow extractant. An equilibrium test with 0.10 *M* Kelex 100 resulted in 95% Ni extraction, but only 20% Ni extraction was achieved in a 10-min shakeout test. Synergic extraction was observed for this system for both equilibrium and nonequilibrium conditions. A 0.10 *M* mixture of 3:1 (mol:mol) LIX 64N-to-Kelex 100 extracted 97% of the Ni at equilibrium and 53% in 10 min. To study the causes of the observed synergy in this system, equilibrium data were fitted to mechanistic models (defined by a system of simultaneous, nonlinear equations) using an equation-solving program on a personal computer.

The following reaction was found to fit the data for LIX 64N (HL):

$$Ni^{2+} + 2HL \leftrightarrow NiL_2 + 2H^+. \quad (1)$$

In the following expression, a modified equilibrium constant is used because all of the data were generated at the same ammonia concentration and the same pH, so the $[H^+]$ term is dropped:

$$k_1 = [NiL_2]/([Ni^{2+}][HL]^2). \quad (2)$$

Substituting the distribution coefficient D for $[NiL_2]/[Ni^{2+}]$ gives

$$D = k_1[HL]^2. \quad (3)$$

The extraction of Ni with Kelex (HK) was similarly modeled, but three moles of Kelex were required per one mole of Ni, thus

$$Ni^{2+} + 3HK \leftrightarrow NiK_2HK + 2H^+, \quad (4)$$

which gives the following:

$$D = k_2[HK]^3. \quad (5)$$

Figure 1 shows equilibrium Ni extraction data as a function of extractant concentration for each extractant. Curves were fitted to the data by solving equations 3 and 5 for D using assorted values for k_1 and k_2. The values for k_1 and k_2 that best fit figure 1 data were 50 L^2/mol^2 and 26,000 L^3/mol^3, respectively. The modeled curves are not quite linear because of the effect of Ni loading on equilibrium.

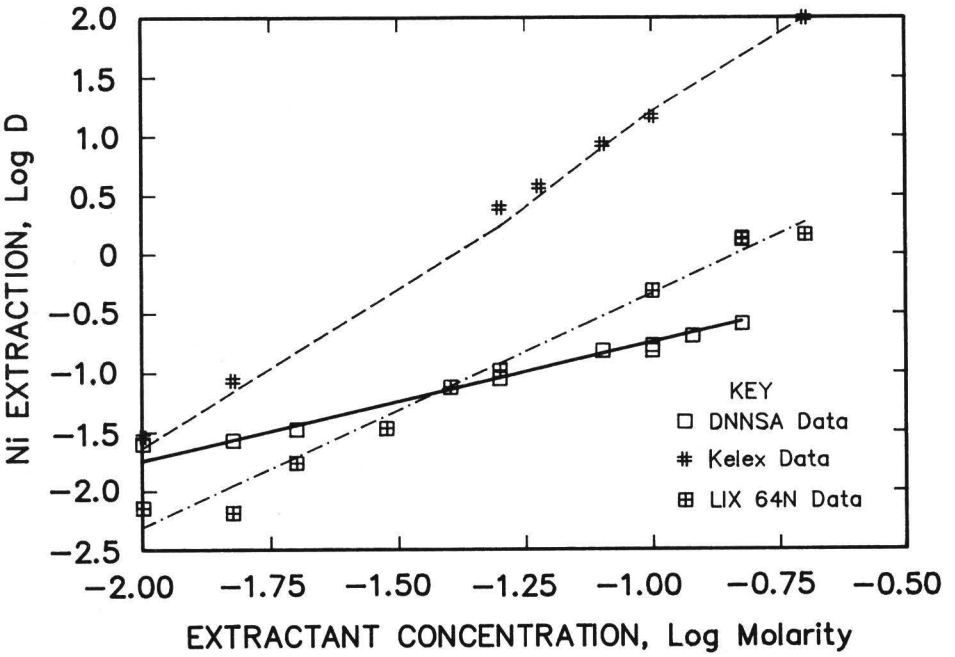


Figure 1. – Slope analysis format for the extraction of Ni. Mechanistically modeled curves are shown with corresponding experimental data for each single extractant. Aqueous feed contains 0.0017 *M* Ni for DNNSA data, and contains 0.0050 *M* Ni for Kelex 100 and LIX 64N data.

A continuous variation plot for this extractant pair is shown in figure 2 for 0.050 *M* total extractant concentration and 0.0017 *M* Ni feed solution. A curve generated by solving equations 3 and 5 simultaneously with a computer equation solving program (shown as a dashed line in figure 2) did not fit the equilibrium (960 min) data. The model, therefore, was expanded to include a reaction producing a mixed species containing both LIX 64N and Kelex 100. No single mixed species was found that could fit equilibrium data. Good fits were obtained, however, when the following reactions were simultaneously considered:

$$Ni^{2+} + HL + HK \leftrightarrow NiKL + 2H^{+}, \quad (6)$$

$$Ni^{2+} + HK + 2HL \leftrightarrow NiKL_2H + 2H^{+}. \quad (7)$$

The distribution coefficients for reactions 6 and 7 are related to the modified equilibrium constants as

$$D = k_3[HL][HK], \quad (8)$$

$$D = k_4[HL]^2[HK]. \quad (9)$$

The following equation represents all four reactions in competitive equilibrium:

$$D = k_1[HL]^2 + k_2[HK]^3 + k_3[HL][HK] + k_4[HL]^2[HK]. \quad (10)$$

Values for k_3 and k_4 were substituted into equation 10 to fit a variety of experimental equilibrium conditions. The best fit values for k_3 and k_4 are 3,000 L^2/mol^2 and 200,000 L^3/mol^3.

The values predicted by the equation 10 model are shown as a solid line in figure 2. Although the close fit between the predicted curve and the experimental equilibrium data is not proof of the formation of the mixed species detailed in equations 6 and 7, it nevertheless provides evidence that the formation of mixed species contributes to the extraction synergy.

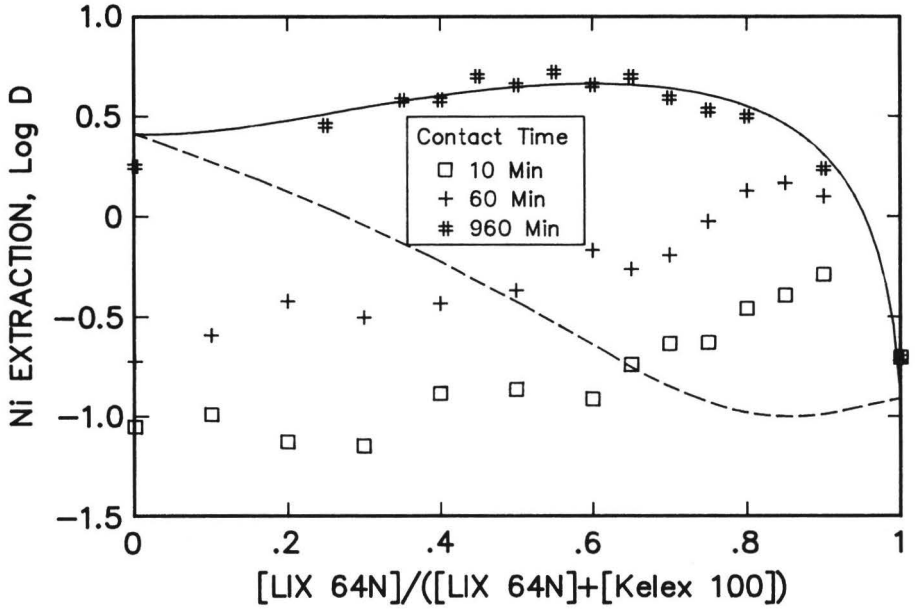


Figure 2. – Continuous variation format for extraction of Ni with the synergic pair LIX 64N and Kelex 100. The modeled equilibrium curves are shown as a dashed line where no mixed species is considered, and as a solid line to represent the mixed species model. Total organic concentration is 0.050 *M*. Aqueous feed contains 0.0017 *M* Ni.

The data shown in figure 2 for 10- and 60-min shakeouts also contribute to an understanding of this mixed chelate system. On the Kelex side of the figure, the rate of extraction is impractically slow and the extractions are far from equilibrium, even after 60 min. The sharpness of the plot maxima for the short extraction times on the right-hand side of the plot provides evidence that a kinetic effect also contributes to Ni extraction synergy. This suggests a kinetic mechanism: the quick-acting weak extractant (LIX 64N) transfers Ni to the slower one (Kelex 100) faster than Kelex 100 can extract Ni unaided.

Evidence for this transfer was obtained by UV/Vis spectrophotometry. When Ni-containing solutions of each extractant were mixed in spectrophotometer cells and monitored at various wavelengths, absorption equilibrium was reached as rapidly as mixing allowed. The equilibration of Ni between LIX 64N and Kelex 100 was virtually instantaneous and independent of the original Ni concentrations in each extractant.

3.2 Kelex 100-DNNSA system

DNNSA extracts Ni faster than Kelex 100, but it is a weak extractant at high pH. A 10-min shakeout test with 0.0017 *M* Ni using 0.10 *M* DNNSA resulted in 12% Ni extraction compared to 20% for Kelex 100. Corresponding equilibrium Ni extractions are 14% for DNNSA and 95% for Kelex 100. A strong synergic effect was observed when a 0.10 *M* mixture of 4:1 Kelex 100-DNNSA extracted 87% of the Ni in only 10 min. To compare the causes of this synergic effect with those affecting the LIX 64N-Kelex 100 pair, equilibrium tests were also done for the Kelex 100-DNNSA pair.

Equilibrium shakeouts were first done for variable DNNSA concentration in the absence of Kelex 100. The aggregated forms of DNNSA have been reported to be the most important species in nonpolar (kerosene) solutions (Osseo-Asare and Renninger, 1984). The extraction data therefore were modeled as a dimerized micelle of the sulfonic acid $(HD)_2$:

$$Ni^{2+} + (HD)_2 \rightleftharpoons NiD_2 + 2H^+ \quad (11)$$

Thus, the distribution coefficient is

$$D = k_5[HD]. \quad (12)$$

The extraction of Ni can be modeled by setting the modified equilibrium constant $k_5 = 1.8$ in equation 12. The data for extraction of 0.0017 *M* Ni feed solution with DNNSA are plotted in figure 1, along with a solid line for the corresponding modeled curve.

Equations 5 and 12 can be combined to describe equilibrium in a combined Kelex 100-DNNSA system that contains no mixed extractant species:

$$D = k_2[HK]^3 + k_5[HD]. \quad (13)$$

The curve generated by solving equation 13 for D at 0.050 *M* total extractant concentration is represented as a solid line in figure 3. The corresponding experimental data are also plotted in figure 3 for 10-, 60-, and 960-min shakeout tests. Although the modeled curve does not fit the 960-min (equilibrium) data perfectly, it confirms that any mixed species that form in this system do not contribute in a major way to the observed synergy for this extractant pair. The equilibrium extraction maximum is on the far right axis (Kelex 100 only), as would be expected if no mixed species forms. Others have proposed mixed Ni-extractant species to account for extraction synergy at low pH for chelate-acid systems (Osseo-Asare and Renninger, 1984), but these data indicate that such species are less important in the extraction of Ni from ammoniacal solutions.

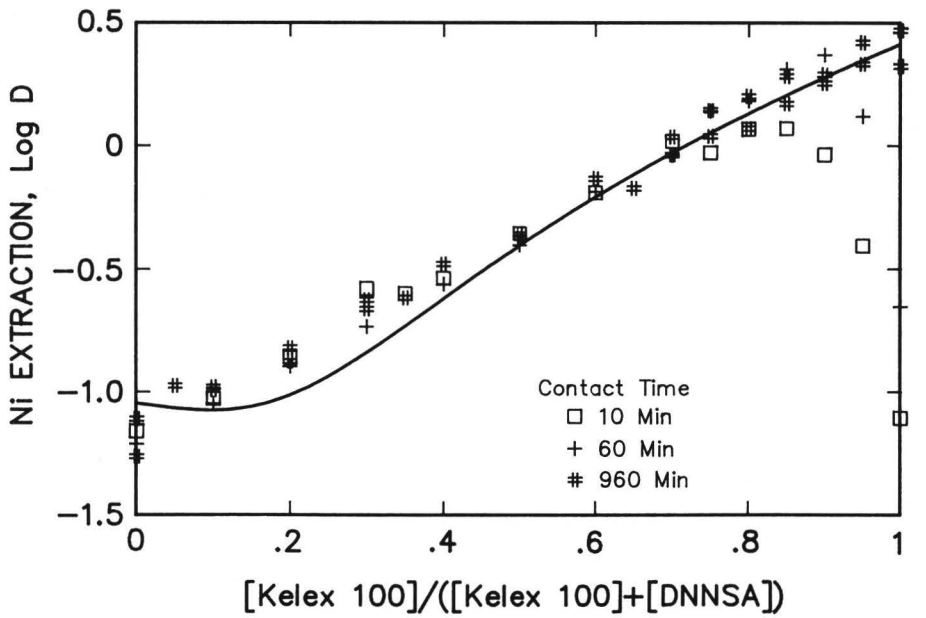


Figure 3. – Continuous variation format for extraction of Ni with the synergic pair Kelex 100 and DNNSA. An equilibrium model curve is shown exclusive of mixed species. Total organic concentration is 0.050 *M*. Aqueous feed contains 0.0017 *M* Ni.

For a 10- and 60-min shakeout to approach equilibrium, figure 3 shows, respectively, that at least 20%-30% and 10% of the extractant must be comprised of DNNSA. No significant synergy is seen at equilibrium, so the role of DNNSA must be as a kinetic synergist, since an increase in its concentration brings the mixture to equilibrium faster. No formal kinetic studies of this extractant pair have been done, but figure 3 shows sharp maxima for nonequilibrium data. As with the LIX 64N-Kelex 100 (L-K) mixture, the Kelex 100-DNNSA (K-D) mixture apparently operates by extracting Ni with DNNSA, then transferring Ni to Kelex 100.

Ni extraction synergy can be compared for the two mixed extractant systems by considering the extractant compositions where each extractant pair achieves highest Ni extraction in a minimum contact time. For 10-min contact time with 0.10 *M* total extractant these ratios are 4:1 K-D and 3:1 L-K. The equilibrium models predict 92% and 97% Ni extraction, respectively, but the 10-min shakeouts result in Ni extraction values of 87% and 53%. The K-D mixture approaches Ni-extraction equilibrium much faster than the L-K mixture. Utility of the L-K mixture is limited because the faster, weaker extractant constitutes the bulk of the extractant, thereby limiting loading capacity. The kinetic synergist in the K-D mixture, DNNSA, initially loads Ni very fast (despite its low affinity for Ni). Since a high extraction rate can be reached with only a small amount of DNNSA, extractant capacity is influenced more by the higher loading Kelex extractant.

3.3 Process considerations

Recycling tests for K-D have not been done, but a series of tests was performed to determine if L-K would lose efficiency with reuse. A series of extraction cycles that included extraction, ammonia scrubbing, Ni stripping, and Cu stripping was done in stirred beakers. After 10 cycles, no loss in extractant efficiency was detected, and no signs of metal buildup or accumulated degradation products were observed. Tests showed that the K-D extractant mixture can be treated to sequential, selective stripping of ammonia, Ni, and then Cu. Soluble extractant losses are less than 5 μg/mL, and no degradation was seen in a single cycle.

4 SUMMARY

The study of mixed extractant synergy for the extraction of Ni and Cu previously was limited mainly to acidic feedstreams. The surprising synergy between LIX 64N and Kelex 100 and between Kelex 100 and DNNSA for Ni extraction from ammoniacal solution shows that extraction synergy may be caused by kinetic effects, by formation of mixed extractant species, or by both of these. Ammonia scrubbing and selective metal stripping for these mixed pairs are as effective as for single extractants, and the pairs are recyclable.

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EXTRACTION OF LOWER CARBOXYLIC ACIDS FROM AQUEOUS SOLUTION BY TRI-N-OCTYLAMINE WITH DILUENTS

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**Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Japan

ABSTRACT

This work is discussing the mechanism depicting the distribution in equilibrium through the following steps. (1)Measurements of the excess volumes in binary systems of amine and acetic acids and in the pseudo-binary systems containing diluents as well and evaluation of the association constants in solutions. (2)Proposal of the model available for predicting the distribution in equilibrium between an aqueous phase including various low molecular carboxylic acids and an organic phase including only tri-n-octylamine and comparison of this model with the experimental data. (3)Extension of the model proposed in (2) to the pseudo-binary systems including diluents as well and elucidation of the relationship between the extracting ability of an organic phase and the physical parameters such as acceptor numbers of diluents.

INTRODUCTION

From the view point of industrial applications in the extraction of low molecular carboxylic acids from aqueous solutions, diluents play significant roles because of their contribution to the improvement of the properties of an organic phase as extracting medium. It would be helpful to designing an extraction process to propose the effective strategy of the selection of diluents. For this reason, this paper investigates the interaction between carboxylic acids and an amine molecule and the effect of diluents on the interaction. In this system, an association is of great importance[5),6),7)]. One of the easiest experiment to discuss the association state quantitatively is the measurement of excess volumes. A model including associating species in an organic phase is proposed to represent the equilibrium in an extraction process. The effect of diluents on the interaction between an acid molecule and an amine molecule is also discussed through 'acceptor numbers'[4)] of diluents.

1 EXPERIMENTS

1.1 Experimental method

(i)Measurement of excess volumes[1)]

In case of three components, by measuring the densities of pure components and a mixture, excess volumes are estimated by the next equation.

$$v^E=(X_BM_B+X_AM_A+X_DM_D)/\rho_{mix}-(X_BM_B/\rho_B+X_AM_A/\rho_A+X_DM_D/\rho_D) \quad (1)$$

Here, subscripts B, A, D and mix denote tri-n-octylamine, acetic acid, diluent and a mixture respectively. Densities are measured by pycnometers.

(ii)Measurement of compositions in equilibrium in aqueous and organic phases[2),3)]

20 ml of TOA, 20 ml of water and carboxylic acid of various concentrations are mixed in a flask and shaken in a water bath at 30° C for three hours. The concentrations of acid and water in each phase are measured by a gas chromatography. The concentration of tri-n-octylamine(TOA) is calculated from the density of the organic phase and the concentrations of organic acid and water in the organic phase.

1.2 Reagents and Apparatus

Organic acids(formic, acetic, propionic and butyric acids), TOA, benzene, o-xylene, di-isobutyl ketone, 2-ethyl hexyl alcohol and ethanol of the extra pure grade are supplied by Wako Chemical Co.,Inc(Japan). Ion exchanged water by Aquarius GS-20N(TOYO Seisakusho Co.,Ltd, Japan) is used. GC-7A(Shimadzu Seisakusho Co.,Ltd) is used as a gas chromatograph. The content of water is measured by a Karl Fisher moisture meter, MKC-3P(Kyoto Electronics Co.,Ltd).

2 MODELING

2.1[1)] Representation of an excess volume in terms of chemical reactions

First, the binary system is discussed. If the volume contraction occurs owing to only a hydrogen bonding, the following equation is derived.

$$v^E_{BA}=\sum_i iC_i\Delta v/(C_A^{\cdot}+C_B^{\cdot}) \quad (2)$$

Where, Δv equals the volume change accompanied by one hydrogen bonding between TOA(B) and acid(A) and is assumed unchanged with the type of bonds. The chemical equilibrium represented by the following equation is assumed[5),6),7)].

$$[BA_i] = K_i[B][A]^i \tag{3}$$

With these two equations, the following is derived.

$$v^E_{AB} = \sum_i iK_i[B][A]^i \Delta v/(C_A^\circ + C_B^\circ) \tag{4}$$

Next, we proceed to the ternary system including a diluent. The following extended equation is led.

$$v^E_{BAD} = (X_B+X_A)v^E_{BA(D)} + (X_A+X_D)v^E_{AD(B)} + (X_B+X_D)v^E_{BD(A)} \tag{5}$$

Where, for example, $v_{BA(D)}$ denotes a pseudo-binary excess volume, a subscript BA(D) meaning that the contraction is induced by the association of B with A under the existence of D. This derives the next equation when $v^E_{AD(B)} = V^E_{AD}$ and $v^E_{BD(A)} = v^E_{BD}$.

$$v^E_{BA(D)} = \frac{v^E_{BAD} - (X_A+X_D)v^E_{AD} - (X_B+X_D)v^E_{BD}}{(X_A+X_B)} \tag{6}$$

2.2 Description of the mechanism of the equilibrium

The dominant associated species and the equilibrium constants are determined from the data of excess volumes. Assuming that an organic phase can be divided into several immiscible parts, each of which consists of a single component of 'j', and the concentration of a free acid in the organic phase could be described as follows[2)]

$$[A]=[B](K_{A,0} + K_{A,N}K_N[A]^N + K_{A,N+1}K_{N+1}[A]^{N+1})C_{A,aq} \tag{7}$$

The values of K_A, $K_{A,N}$ and $K_{A,N+1}$ are estimated by using a SIMPLEX method so as to minimize the objective function, Eq.(8).

$$F = \Sigma \ (1- [A]_{Cal}/[A]_{Exp})^2 \tag{8}$$

where $[A]_{Cal}$ is calculated from Eq.(7). $[A]_{Exp}$ is determined from the experimental data as shown in Fig.1, and the summation is to be carried out over all data points.

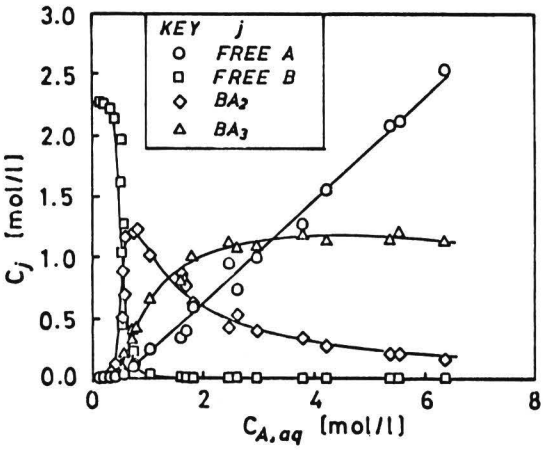


Fig.1 Relation among [A], [B], $[BA_2]$, $[BA_3]$ and $C_{A,aq}$ in the case of acetic acid

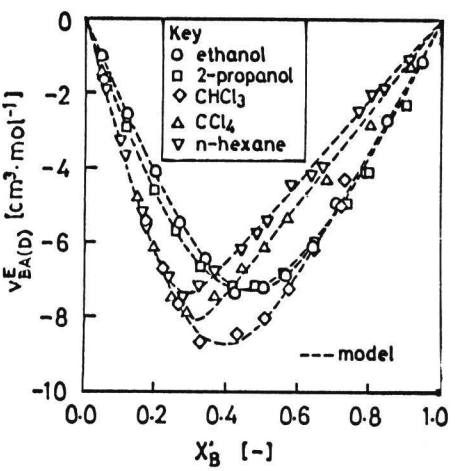


Fig.2 The excess volume vs. the composition of pseudo-binary mixture of TOA and acetic acid at 30°C(R_B=0.5)

2.3 Extension of the model to the system including diluents[3)]

Instead of Eq.(7), the following equation is used.

$$[A]=(K_{A,0}[B]+K_{A,N}K_N[B][A]^N+K_{A,N+1}K_{N+1}[B][A]^{N+1}+K_{A,D}C_D)C_{A,aq} \quad (9)$$

where, $K_{A,D}$ is the distribution constant and v_D is the molar volume of a diluent.

3 Results and discussion

3.1 Excess volumes of the ternary systems

Fig.2 shows excess volumes of TOA/acetic acid/diluent ternary system. The abscissa denotes corrected mole fraction of TOA, $X'_B=X_B/(X_A+X_B)$. Predicted lines calculated with the estimated parameters in Table 1 are also shown in Fig.2. In case of hexane, the behavior is the same with the case in which no diluent is used. In other cases, X'^{min}_Bs shift to the higher values compared with the case without a diluent.

3.2 Dominant complexes and acceptor numbers of diluents

The relationship between X'^{min}_B and an acceptor number of a diluent is shown in Fig.3. There is a good agreement between

them. This tendency may indicate that in using a diluent which has a large value of an acceptor number, the number of the acid associated with TOA becomes smaller.

TABLE 1

The equilibrium constants of the dominant associations, Δv and $X'_B{}^{min}$ for the pseudo-binary mixture of TOA and acetic acid with a diluent at 30° C.

Diluent	(AN)	K_1	K_2	K_3	Δv	$X'_B{}^{min}$
		l/mol	l^2/mol^2	l^3/mol^3	cm^3/mol	-
N-hexane	(0.0)	-	3.01E2	8.61E2	-11.3	0.283
CCl_4	(8.6)	-	2.61E3	2.01E3	-12.55	0.321
$CHCl_3$	(23.1)	3.04E1	3.89E1	-	-18.22	0.396
2-propanol	(33.5)	2.32	1.11E-2	-	-26.63	0.451
ethanol	(37.1)	4.73	7.28E-4	-	-22.56	0.471

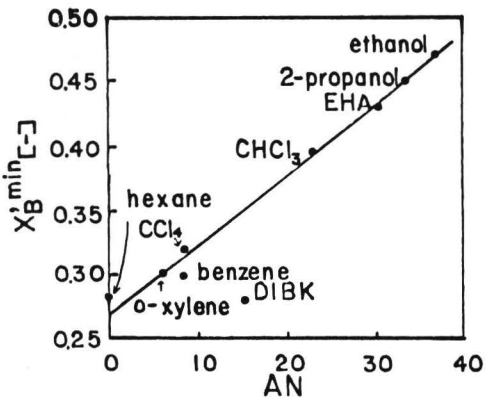


Fig.3 Effect of AN of diluent on $X'_B{}^{min}$(R_B=0.5)

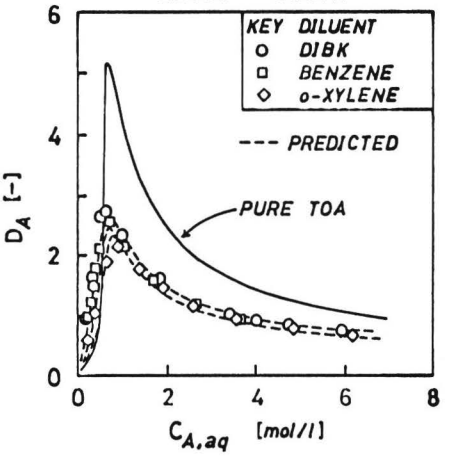


Fig.4 Extraction of acetic acid by mixed solvent of TOA and a diluent(R_B=0.5) at 30° C

3.3 Distribution of acetic acid between the aqueous and the organic phase with diluents.

Fig. 4 shows the effect of $C_{A,aq}$ on the distribution coefficient $D_A(=C_{A,aq})$ of acetic acid when DIBK, Benzene and o-xylene are used as diluents using the estimated data in Table 2. TOA and a diluent are mixed equally in volume.

4. CONCLUSION

The findings in the present paper are as follows.

1) The dominant associating species of TOA with an acid can be estimated from $X_B{}^{min}$. The equilibrium constants of the associations are obtainable from the model proposed in this study by

fitting it to the observed v^E values of the binary and pseudo-binary mixtures.

2) There is the significant relationship between $X'_B{}^{min}$ and the acceptor number of a diluent. The stronger in acceptor character-

TABLE 2

Equilibrium constants of the dominant association, Δv and $X'_B{}^{min}$

Diluent	K_1	K_2	K_3	Δv	$X'_B{}^{min}$
	l/mol	l^2/mol^2	l^3/mol^3	cm^3/mol	-
DIBK	-	3.69E2	1.16E3	-10.23	0.28
o-xylene	-	1.62E3	4.24E3	-11.40	0.30
benzene	-	2.08E3	4.66E3	-13.47	0.30
EHA	1.75E1	9.38	-	-16.32	0.43

istics the diluent is, the smaller the number of the acid associated with TOA becomes.

3) The experimental data of the equilibrium compositions, carboxylic acids and water can be explained by the model involving both the associations and the physical distribution as well as in the case of the system with a diluent. The equilibrium constants estimated from the excess volume of TOA/organic acid binary mixture and TOA/organic acid/diluent pseudo-binary mixture can be applied to the proposed model. It is found that diluents of strong acceptors decrease the associating order of acetic acid with TOA, and make D_A high in the region of low $C_{A,aq}$. This study proposes an approach to the selection of diluents based on these results.

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A NEW LIQUID PHOSPHINE OXIDE FOR THE RECOVERY OF ACETIC ACID FROM SULFITE PULPING LIQUORS

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In the process for the extraction of acetic acid from sulfite pulping liquors, as it ist performed at Chemiefaser Lenzing, Austria, trioctylphosphine oxide is used as the extractant.

The call for a new liquid phosphine oxide which is better to handle and which allows the use of an organic phase higher in extractant concentration led to the development of the sec-butyldioctylphosphine oxide. This new extractant meets not only the above mentioned requirements but has also some unexpected advantageous properties.

The advantages: higher extractability, better stripping by easier thermal decomposition of the acetic acid-phosphine oxide-compound and faster phase separation in relation to the existing extraction process will be described. It will be shown by a cost comparison that substantially cost savings occur.

1 INTRODUCTION

In the acidic sulfite pulping of wood to recover cellulose, a strongly polluting sulfite liquor is obtained as a waste product, which must not enter plant effluents. It is disposed of by evaporation and incineration of the residue. This process yields a condensate containing the volatile constituents acetic acid and furfurol in the concentrations of approximately 1.5 % and 0.8 % respectively.

In the Chemiefaser Lenzing Company in Austria, condensate is obtained at the rate of 100 m^3/hr, and this represents about 12,000 metric tons of acetic acid per year and 6,500 tons of furfurol each year.

Since 1983 they have had a plant in operation that recovers these amounts of furfurol and acetic acid by extraction. This treatment not only recovers valuable chemicals but also removes from the waste water organic compounds that would otherwise have to be degraded in a waste water treatment plant. At the usual average cost of DM 1.50 - 2.00/kg COD, the cost just of disposing of 10,000 tons of acetic acid per year by degradation would amount to DM 16 - 21 million.

2 DESCRIPTION OF THE PROCESS

The condensate, containing about 1 - 2 % acetic acid and 0.5 - 1.5 % furfurol, is brought into contact in countercurrent operation with an organic phase consisting of 40 % by weight tri-n-octylphosphine oxide dissolved in a special high-boiling aliphatic hydrocarbon mixture.
This extraction process removes 85 % of the furfurol and acetic acid, the latter being bound to the weakly basic phosphine oxide. After separation of the phases, the extract-laden organic phase is fed to a column. At temperatures of 140 - 170 °C the acetic acid is split from its bond with phosphine oxide and distilled off together with the furfurol. Then both products are recovered by fractional distillation with such purity that food-quality acetic acid is obtained. The organic phase is recycled to the extraction process.

From time to time the organic phase must be freed of resinification products of furfurol and purified. This is most easily achieved by distillation of the extractant mixture. The extractant used is tri-n-octylphosphine oxide (TOPO), although it is not optimal for the overall process. Its worst drawbacks are its limited solubility in aliphatic hydrocarbons and the fact that it is a solid at room temperature.

Together with Chemische Thermische Processtechnik GmbH (Graz, Austria) we developed a new liquid phosphine oxide with the name Hostarex PX 320, which exhibits considerable advantages for the process of extracting acetic acid.

3 PROPERTIES OF HOSTAREX PX 320

3.1 Physical properties

Table I shows the physical properties of Hostarex PX 320 in comparison with TOPO (Hostarex PX 324).

Table I

Physical properties of Hostarex PX 320 and Hostarex PX 324

	Hostarex PX 320	TOPO (Hostarex PX 324)
Appearance at 20 °C	liquid, clear	solid
Appearance at -10 °C	liquid, clear	solid
Melting point	-26 °C	48 - 51 °C
Density at 20 °C	0.887 g/cm^3	-
Viscosity at 20 °C	47 mPas	-
Solubility	soluble at room temp. in any ratio in aliphatic or aromatic hydrocarbon mixtures	about 20 % by wt. soluble at room temp. and about 40 % by wt. at 40 °C in aliphatic hydrocarbons
Solubility in H_2O	about 2 ppm	about 1 ppm

The advantages of the liquid nature of Hostarex PX 320 are: Easier handling at low outdoor temperatures and no melting required to fill the plant.

3.2 Boiling points

Boiling point of Hostarex PX 320 at 5 mbars about 220 °C
Boiling point of TOPO at 5 mbars about 260 °C

The approximately 40 °C lower boiling point of Hostarex PX 320 is advantageous because of the low thermal stress, especially in the distillative purification of the extractant. In addition, crystallization of the extractant on parts of the destillation plant at low temperatures is avoided.

3.3 Phase separation behaviour

Solutions of 40 % by weight Hostarex PX 320 and TOPO in kerosene at 50 °C were prepared in order to compare the rates of phase separation. The aqueous phase consisted of condensate containing 15 g/l acetic acid and 5 g/l furfurol.

The organic phase was placed in a beaker and the aqueous phase was added with stirring to produce a water-in-oil emulsion. The temperature was maintained at 50 °C and stirring continued for 5 minutes. The phase volume ratio was 1:1.

Phase separation with the organic phase containing Hostarex PX 320 was twice as fast as that with TOPO. This means that the extraction plant can be operated at a higher flow rate.

3.4 Extraction capacity for acetic acid

The extraction trials were conducted with an organic phase consisting of 40 % by weight phosphine oxide and 60 % by weight undecane. The aqueous phase was prepared synthetically by dissolving analytical grade acetic acid in distilled water. The temperature was a constant 60 °C. The equilibrium diagram is shown in Figure I.

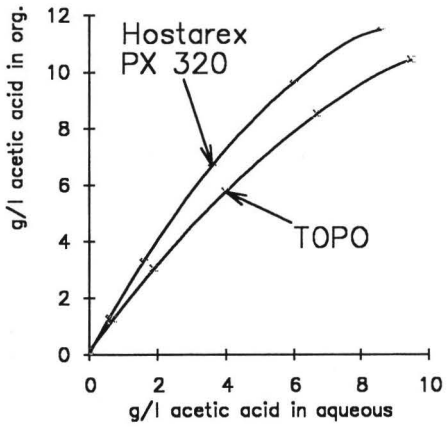


Fig. I Equilibria

The measured distribution coefficients for acetic acid were about 20 % higher in the Hostarex PX 320/undecane mixture than in the TOPO/undecane mixture.

Continuous comparison trials with the above organic phases were conducted in a pilot plant. The aqueous phase consisted of condensate from the Chemiefaser Lenzing Company with an average content of 3 g/l furfurol and 15 g/l acetic acid. The flow rates for the organic and aqueous phases were 100 l/hr each at a temperature of 50 °C.
The organic phase containing Hostarex PX 320 took up 90 % of the acetic acid dissolved in the aqueous condensate, while TOPO extracted only 85 %.
At a production rate of 10,000 tons acetic acid per year this result would mean an additional 500 tons acetic acid each year, equivalent to an added profit of about DM 350,000.

Thus the higher extraction capacity of Hostarex PX 320 was also confirmed in a continuous-run trial.

3.5 Thermal stripping

As previously described, the acetic acid bound to the extractant is distilled off at 140 ° - 170 °C in a vacuum. In order to investigate whether there are any differences in the thermal cleavability of the bond between acetic acid and the two extractants, the organic phases, consisting of 40 % by weight of the phosphine oxides in an aliphatic hydrocarbon mixture, was charged with 10 g/l acetic acid. Then the equilibrium concentrations of acetic acid in the gas and liquid phases were determined at a temperature of 170 °C. The quotient

$$c_{\text{acetic acid}}^{\text{vapour}} / c_{\text{acetic acid}}^{\text{liquid}}$$

yielded a value of 4.0 for Hostarex PX 320 and 3.6 for TOPO. This proves the easier thermal cleavability of the Hostarex PX 320-acetic acid complex.

4 SUMMARY

The newly developed liquid trialkylphosphine oxide, Hostarex PX 320, was tested in comparison with trioctylphosphine oxide (Hostarex PX 324) in an extraction process. The process consisted of extracting acetic acid and furfurol from waste water arising in cellulose production in accordance with the method employed by the Chemiefaser Lenzing Company in Austria. Hostarex PX 320 exhibited distinct advantages in extraction capacity, phase separation behaviour and thermal stripping.

The fact that it is a liquid at room temperature permits Hostarex PX 320 to be used in any desired concentration for extraction.

3. ANALYTICAL CHEMISTRY AND ENVIRONMENTAL SCIENCE

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FACTORS AFFECTING SELECTIVITY OF SYNERGISTIC EXTRACTION

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ABSTRACT

The selectivity of synergistic extraction in the mutual separation of zinc(II) and cadmium(II) was studied using TTA and STTA as chelating agents, and TOPO, Bu_3P and phen as synergists. The best combination of a chelating agent and a synergist for the separation was found to be STTA and phen, and factors controlling the selectivity were discussed in terms of HSAB rule.

1 INTRODUCTION

Synergistic effect caused by adding a neutral ligand to a chelate extraction system is sometimes effective to enhance the extractability of an analyte. This so-called synergistic extraction, however, has an inherent disadvantage, that is, low selectivity for a particular analyte. Various attempts have been made so far to improve the selectivity of the synergistic extraction. After many trials, we have reached the conclusion that factors controlling the selectivity in the synergistic extraction are as follows (Akaiwa and Kawamoto, 1982) :

a. The nature of the diluent.
b. The basicity of the synergist.
c. The structure of the synergist.
d. The nature of the host metal chelate.
e. Kinetic effect.

In the course of our study, the adduct formation has been assumed *a priori*. In other words, synergistic extraction equilibrium is considered to be expressed by the following equation:

$$MR_{n,org} + m\,S_{org} \leftrightarrows MR_nS_{m,org}$$

Accordingly, the nature of MR_n as a Lewis acid as well as that of S as a Lewis base is considered as the most important factor controlling the selectivity.

In the present work, by employing zinc(II) and cadmium(II) as

analytes chemically similar to each other, suitable condition for mutual separation and main factors affecting the selectivity are investigated using synergistic extraction system. Here, two β-diketones, namely, relatively hard thenoyltrifluoroacetone (TTA) and rather soft monothiothenoyltrifluoroacetone(STTA) are employed as chelating agents, and trioctylphosphine oxide(TOPO), tributylphosphine (Bu_3P) and 1,10-phenanthroline (phen) as synergists.

2 EXPERIMENTAL

2.1 Apparatus

A Hitachi Model 170-30 atomic absorption spectrometer was used. It was equipped with zinc and cadmium hollow cathode lamps (Hamamatsu Photonics). A Horiba Model F-80 pH analyzer and an Iwaki KM type shaker were also used.

2.2 Reagents

Chelating agents and synergists obtained from Wako Pure Chemicals were used without further purification. Chloroform and all the other chemicals used were of guaranteed grade. Deionized water was used throughout.

2.3 Experimental procedure

Twenty cubic centimeters of an aqueous solution containing 2.00×10^{-5} M (M = mol dm^{-3}) metal ion and 0.1 M sodium sulfate, whose pH was preliminarily adjusted by adding sulfuric acid and/or sodium hydroxide, was placed in a separatory funnel. An equal volume of chloroform solution containing a chelating agent and a synergist was added; the mixture was then shaken vigorously for 30 min. After the phases were allowed to separate, the amount of metal ion remaining in the aqueous phase was determined with the atomic absorption spectrometer, and the pH was also measured. All experiments were carried out at room temperature (ca. 293 K).

3 RESULTS AND DISCUSSION

3.1 TTA-TOPO system

Extraction curves of zinc(II) and cadmium(II) obtained by using TTA and a mixture of TTA and TOPO are shown in Fig. 1, where zinc (II) is seen to be separated from cadmium(II) at pH 7.25 by employing TTA alone. However, the degree of separation is not quantitative and the optimal pH exists in alkaline region. To improve

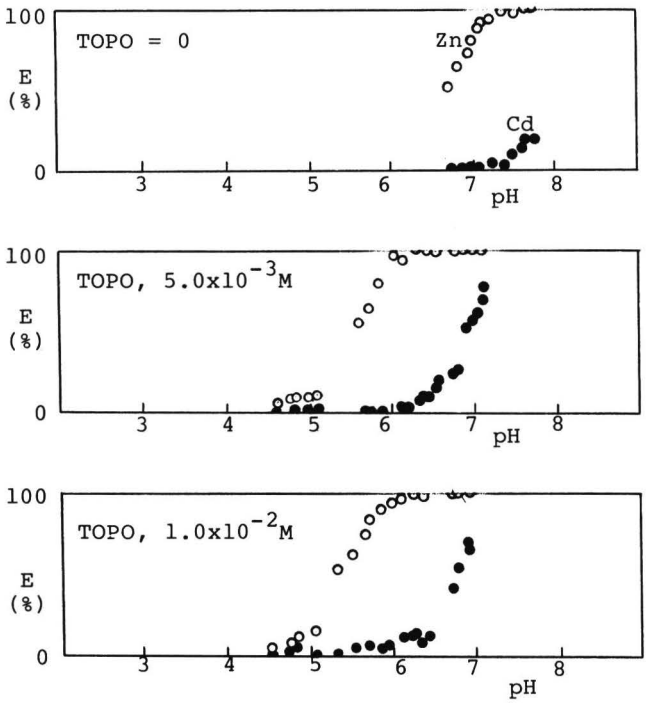


Fig. 1 Extraction curves
TTA, 5.0x10^{-3}M

the degree of separation, TOPO was added. As a result, the optimal pH shifted to the acidic region (pH = 6.25), although the improvement of the degree of separation was not observed. No improvement in selectivity was observed even if higher concentration of the synergist was used. Then, the effect of phen which is bidentate and relatively strong Lewis base on the separation was examined. In this case, though the extraction curves of zinc(II) and cadmium(II) shifted to more acidic region compared with those obtained by TTA alone, the degree of separation remarkably decreased. In order to explain the above results, equilibrium constants involved in the extraction reaction were estimated by conventional method using log-log plots.

The extraction of a metal ion M^{2+} (M = Zn, Cd) with a chelating agent(HR) proceeds according to equations (1) and (2);

$$M^{2+} + 2\,HR_{org} \leftrightarrows MR_{2,org} + 2H^{+} \quad : K_{ex,o} \qquad (1)$$

$$M^{2+} + 2\,HR_{org} + S_{org} \leftrightarrows MR_2S_{org} + 2H^+ \quad : K_{ex,1} \qquad (2)$$

where the subscript org denotes the organic phase and S represents a synergist. The stability constant β° for an adduct MR_2S in the organic phase is defined as;

$$\log \beta^\circ = \log K_{ex,1} - \log K_{ex,o}$$

Various constants thus obtained are summarized in Table 1, where β_1 is the stability constant for $M(phen)^{2+}$ in the aqueous phase.

TABLE 1

Various constants obtained from TTA extraction system

M	log $K_{ex,o}$	log $K_{ex,1}$	log β°	log β_1
S = TOPO				
Zn	-8.58	-4.04	4.54	
Cd	-11.7	-7.39	4.31	
Difference	3.12	3.35		
S = phen				
Zn	-8.58	0.70		6.55
Cd	-11.7	-1.05		5.93
Difference	3.12	1.75		

A difference in extraction constants in the absence of a synergist between zinc(II) and cadmium(II), $\Delta\log K_{ex,o} = 3.12$, is slightly smaller than 4.0 which is the condition for quantitative separation. On the other hand, the value of $\Delta\log K_{ex,1} = 3.35$ obtained from TTA-TOPO system approaches to 4.0, indicating that the degree of separation can be improved slightly by the addition of TOPO. This may be due to higher stability constant for the TOPO adduct of zinc(II) chelate ZnR_2S compared with the similar adduct of cadmium(II) chelate, CdR_2S. In contrast, the use of phen as an additive is inadequate for the separation purpose, namely $\Delta\log K_{ex,1}$ equals to 1.75, which is far smaller than 4.0. This result shows that the addition of phen helps to extract cadmium(II) preferentially and masking effect caused by the formation of complex cation $M(phen)_3^{2+}$ is more remarkable toward zinc(II) judging from the value of $\log \beta_1$.

3.2 STTA-Bu_3P system

Table 2 shows extraction constants for STTA-Bu_3P system and stability constants for adducts $M(STTA)_2Bu_3P$. Here, Bu_3P was employed as an example of soft synergist. As estimated from log $K_{ex,o}$ values, the affinity of STTA toward zinc(II) seems to be slightly higher than to cadmium(II). However, this situation is reversed by the addition of Bu_3P, and preferential extraction of cadmium (II) results by using a mixture of STTA and Bu_3P, as is expected from log $K_{ex,1}$ values. This means that the use of softer chelating agent and synergist gives favorable condition for cadmium(II) extraction. Quantitative separation, however, could not be attained by employing the above system (Fig 2).

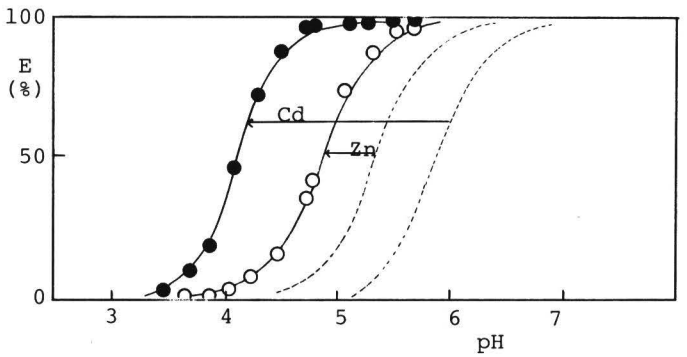


Fig. 2 Extraction curves
STTA, 1.0×10^{-3}M
Bu_3P, ——: 4.0×10^{-3}M; ----: 0.

TABLE 2

Various constants obtained from STTA-Bu_3P extraction system

M	log $K_{ex,o}$	log $K_{ex,1}$	log β°
Zn	-4.90	-1.25	4.31
Cd	-5.93	0.33	6.28

3.3 STTA-phen system (Kawamoto et al., 1989)

Extraction constants for STTA-phen system are summarized in Table 3. It is evident from log $K_{ex,1}$ values that synergistic effect by adding phen is more remarkable in cadmium(II) extraction than in the case of zinc(II). On the other hand, larger log β_1

value for zinc(II) indicates that the masking caused by phen is more effective to zinc(II). That is, phen acts as a synergist on one hand, as a masking agent on the other. This dual facility of phen can be applicable to the separation of cadmium(II) from zinc (II). As is shown in Fig. 3, where the solid curves are obtained by calculation, the quantitative separation of cadmium(II) from zinc(II) is obtained at the pH range from 3.75 to 4.25.

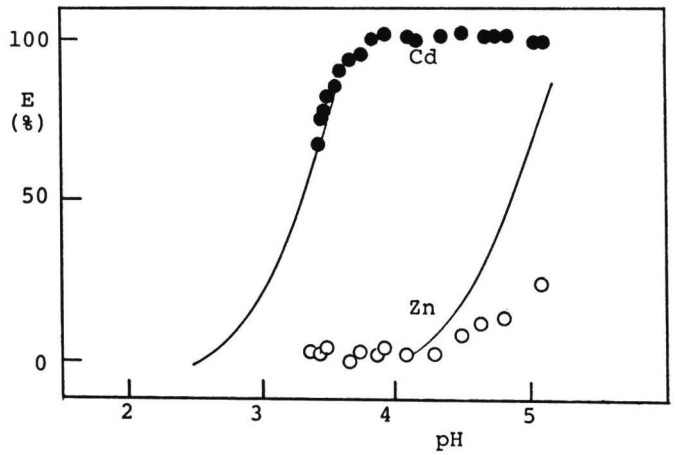


Fig. 3 Extraction curves
STTA, 1.0×10^{-3}M; phen, 2.25×10^{-1}M

Previously, we succeeded in the mutual separation of cadmium (II) and zinc(II) by the aid of the synergistic extraction system, dithizone (H_2dz) and phen (Akaiwa et al. 1978, 1979). The above result together with that of the present work of STTA-phen system leads us to an empirical recognition that the mutual separation of cadmium(II) and zinc(II) is generally feasible by the use of sulfur-containing chelating agent such as STTA or H_2dz and phen as an auxiliary ligand. While, we noticed in the previous study the quantitative extraction of cadmium(II) as a colorless ion-pair, $Cd(phen)_2^{2+} \cdot 2Cl^-$ in the acidic region instead of a synergistic adduct.

This fact combined with the above recognition may support the idea that cadmium(II) becomes softer by the chemical modification with phen forming a stable species with sulfur-containing reagent. This idea also explains the experimental result that cadmium(II) could not be separated from zinc(II) by STTA or H_2dz in the ab-

sence of phen. In other words, the formation of $Cd(phen)^{2+}$ gives us an important key to the mutual separation. To confirm the idea and for the further development of separation scheme, the experimental results are discussed using "Hard and Soft Acids and Bases (HSAB)" concept.

TABLE 3

Various constants obtained from STTA-phen extraction system

M	log $K_{ex,o}$	log $K_{ex,1}$	log $K_{ex,2}$	log β_1
Zn	-4.90	2.00	4.33	6.55
Cd	-5.93	3.65		5.93

3.4 A scheme of mutual separation based on HSAB rule

According to Pearson (1968), an equilibrium constant (K) for the formation of a coordination compound AB is expressed by equation (3);

$$\log K = S_A S_B + \sigma_A \sigma_B \qquad (3)$$

where the subscripts A and B denote Lewis acid and base, respectively. The S represents a strength factor, and the σ represents a soft factor. Several kinds of a dual parameter scale have been proposed for evaluating hard-soft nature of a metal ion as a Lewis acid and a monodentate ligand as a Lewis base. However, as far as polydentate ligands are concerned, little information has been reported so far. In order to rationalize chelate extraction constant, a new dual parameter of S_A and σ_A has been proposed by the authors (Kawamoto and Akaiwa, 1990):

$$S_A = -2\Delta S_h^\circ / 2.30R \qquad (4)$$

and

$$\sigma_A = \Delta H_f^\circ / 2.30RT \qquad (5)$$

where ΔS_h°, R, ΔH_f° and T denote the hydration entropy of a metal ion, gas constant, the heat of formation of an aqueous metal ion, and absolute temperature, respectively. The values of S_B and σ_B

for chelating agents obtained by using the above parameters are given in Table 4.

TABLE 4

Strength and softness parameters for chelating agents

Chelating agent	S_B	σ_B
TTA	0.312	0.101
STTA	0.260	0.287
phen	0.257	0.093

The increasing order of soft factor is phen = TTA $\ll$ STTA, indicating that STTA having $-S^-$ is the softest of three. On the other hand, softness of metal ions is shown in Table 5, where the soft parameter for Cd^{2+} is higher than that for Zn^{2+}. However, strength parameter for Zn^{2+} is greater than for Cd^{2+}, and the fact makes TTA better reagent for Zn^{2+} than Cd^{2+}. Adduct formation has been believed to proceed according to equation (6).

TABLE 5

Parameters for metal ions and chemically modified metal ions

M^{2+} or MS^{2+}	S_A	σ_A	σ_A / S_A	$\Delta\sigma_A / S_A$
Zn^{2+}	32.2	-26.6	-0.826	0.378
Cd^{2+}	28.1	-12.6	-0.448	
$Zn(phen)^{2+}$	23.9	-24.1	-1.01	0.463
$Cd(phen)^{2+}$	20.9	-11.4	-0.547	

$$MR_2 + S \leftrightarrows MR_2S \qquad (6)$$

The relatively hard nature of TOPO gives a favorable condition for zinc(II)-TTA extraction, whereas the addition of Bu_3P as a rather soft additive causes a preferential extraction of cadmium(II)-STTA to zinc(II)-STTA. These facts can be explained reasonably by adduct formation mechanism. However, the addition of phen is little help to zinc(II) extraction in both cases of TTA and STTA though phen is considered as a rather hard ligand (Table 4). This means that synergism caused by adding phen as an additive is difficult

to explain in terms of adduct formation mechanism. The author, therefore, proposes equation (7) instead, where chemically modi-

$$M(phen)^{2+} + 2R^{-} \leftrightarrows MR_2(phen) \qquad (7)$$

fied species $M(phen)^{2+}$ acts as a Lewis acid. Assuming that S_A and σ_A for $M(phen)^{2+}$ could be estimated as residual strength and softness, that is, $S_A\{M(phen)^{2+}\} = S_A\{M^{2+}\} - S_A\{M^{2+}\} \cdot S_B\{phen\}$ and $\sigma_A\{M(phen)^{2+}\} = \sigma_A\{M^{2+}\} - \sigma_A\{M^{2+}\} \cdot \sigma_B\{phen\}$, several parameters for chemically modified metal ions are also summarized in Table 5. Successful separation of cadmium(II) from zinc(II) suggests that a remarkable difference in softness between cadmium(II) and zinc (II), which is caused by chemical modification of metal ions with phen, exists. In fact, as is given in Table 5, a difference in softness parameter($\Delta\sigma_A/S_A$) for $M(phen)^{2+}$ is larger than that for aqueous metal ions.

In conclusion, the selectivity of chelate extraction may be controlled by modifying metal ions in question chemically with an auxiliary ligand like phen. And the present result will be helpful for the design of separation scheme using synergistic extraction.

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MULTISTAGE LIQUID-LIQUID EXTRACTION SEPARATION OF INORGANIC IONS USING A PLANET CENTRIFUGE

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ABSTRACT

Countercurrent chromatography (CCC), a multistage liquid-liquid extraction separation technique, was used for concentration and separation of some inorganic ions using extractants of different classes. Cobalt dicarbollide and dicyclohexo-18-crown-6 in different diluents were used for separation of cesium and strontium. The possibility was shown of separating rare earths from other elements using D2EHPA. Separation of individual rare earths was also achieved. Ortho- and pyrophosphate were concentrated and then separated by elution with HCl solution using dinonyltin dichloride in MIBK. Other elements can be undoubtedly concentrated and separated by CCC.

INTRODUCTION

Multistage extraction separation enables to solve many analytical and preparative problems. Effective separation and enrichment using two-phase liquid systems is achieved by partition countercurrent chromatography (CCC) developed by Ito in USA (1966, pp. 985-987). The method is based on retention of the stationary phase (without a solid support) in a rotating coil column due to a centrifugal force while the mobile phase is passed through the coil. A few devices providing the retention of the stationary phase in the field of mass forces in the absence of solid support have been suggested. The most successful device that has gained acceptance is a planetary centrifuge (Ito, 1986, pp. 65-143) (Fig.1). A column (or a column unit) of a certain configuration rotates around its axis and at the same time revolves around the central axis of the device with the aid of a planetary gear. Whatever the construction of the column unit, its basic element is a tube - a column wound on a rigid or flexible core as a helix.

Solutes are subjected to a continuous partition process and separated according to their partition coefficients. So far, CCC has been used for separation and determination of organic and bioorganic substances (Ito, 1986, pp. 65-143). Some papers were published which described special devices for analytical CCC (Lee,

1988, pp. 75-89), (Ito, 1987, pp. 290-295),(Romanach, 1988, pp. 91-105). We used the technique for concentration and separation of inorganic ions (Zolotov, 1989, pp. 938-944). Amongst partition CCC methods, only centrifugal partition chromatography was used for separation of inorganic ions (Araki, 1988, pp. 2473-2485).

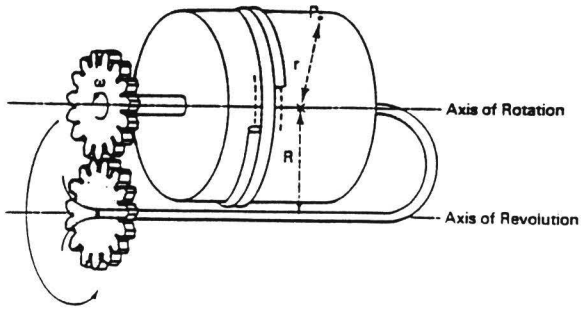


Fig. 1. Design principle of the coil planet centrifuge for CCC, R - radius of revolution; r - radius of rotation (Ito, 1986, pp. 65-143).

2 CONCENTRATION AND SEPARATION OF ELEMENTS

Investigations were made on an installation consisting of a planetary centrifuge with a vertical column drum developed in the Institute of Analytical Instrumentation (Leningrad), a peristaltic pump and a fraction collector. The technique has been recently suggested to be used for separation of inorganic ions in systems of extractant in organic solvent (stationary phase) - aqueous solution (mobile phase). The amount of the stationary phase in the system is characterized by the retention factor (K_r) equal to the ratio of the stationary phase volume to the total capacity of the column. The K_r value depends on the parameters of the planetary centrifuge, its operating conditions and properties of the two-phase system of which the wettability of material of the column with the stationary phase is of importance (Zolotov, 1989, pp. 938-944). The studies of hydrodynamics behaviour of various extractants in different diluents have shown that a number of extraction systems can be used for separation of inorganic cations and anions.

2.1. Cesium and strontium

CCC can be used for solving radioanalytical problems, for example, for the separation of radionuclides of cesium and stron-

tium. Separation of Cs and Sr was carried out in systems: 0.05 mol/l dicyclohexo-18-crown-6 (DCH18C6) + 3% di-2-ethylhexylphosphoric acid (D2EHPA) in chloroform - HNO_3 solution (K_r = 65%) and 0.01 mol/l solution of cobalt dicarbollide in nitrobenzene - HNO_3 solution (K_r = 15%). Fig. 2 illustrates the separation of Cs and Sr using stationary phases based on DCH18C6 + D2EHPA and cobalt dicarbollide respectively. The use of cobalt dicarbollide-based extractant enables to concentrate Cs and Sr from $5 \cdot 10^{-4}$ mol/l HNO_3. CCC makes it possible to separate the elements by one eluent and by using gradient elution. The latter technique is more express and enables to strip the elements by smaller mobile phase volumes.

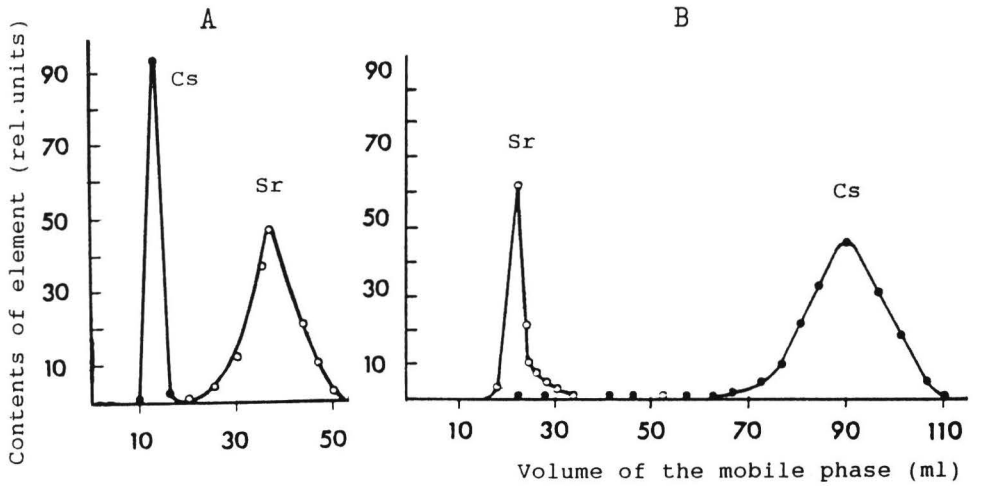


Fig. 2. Separation of Cs and Sr. Element contents in initial solution 100 μg. Mobile phase: 10^{-3} mol/l $Ba(NO_3)_2$ in 0.1 mol/l HNO_3. Pumping rate of the mobile phase - 1.5 ml/min. Stationary phase: A - 0.05 mol/l DCH18C6 + 3% D2EHPA in chloroform; B - 0.01 mol/l cobalt dicarbollide in nitrobenzene.

The elution of Cs and Sr into a mobile phase containing barium nitrate, polyethylene glycol-300 (PEG-300) and nitric acid has been studied (Table). The elution curves obtained with this system have been processed. The Table gives the number of effective theoretical plates (n), observed peak resolution (R) and separation factor (α_s) calculated from equations (1), (2) and (3) respectively:

$$n = 5.55 \, (V_r/w_h)^2 \qquad (1)$$

$$R = 2\,(V_{r,2} - V_{r,1})/(W_2 + W_1) \quad (2)$$

$$\alpha_s = (V_{r,2} - V_o)/(V_{r,1} - V_o) \quad (3)$$

where V_r is retention volume, W_h is half width of peak, W ($=2W_h$) is peak width, V_o is elution volume for an unretained component.

TABLE

The number of effective theoretical plates (n), peak resolution (R) and separation factor (α_s) for the separation of Cs and Sr by CCC

Stationary phase	Mobile phase	n		R	α_s
		Cs	Sr		
10^{-2} M cobalt decarbollide in nitrobenzene	0.1 M HNO_3	246	470	3.9	20
	10^{-3} M $Ba(NO_3)_2$ in 0.1 M HNO_3	159	736	3.6	23.7
	10^{-3} M $Ba(NO_3)_2$ + 0.25% PEG-300 in 0.1 M HNO_3	836	126	1.8	4.3
0.05 M DCH18C6 + 3% D2EHPA in chloroform	0.1 M HNO_3	77	106	2.4	8.0
	10^{-3} M $Ba(NO_3)_2$ in 0.1 M HNO_3	150	105	2.2	5.3

2.2 Rare earth elements

The possibility was shown of separating individual rare earth elements (REE) and their group separation from other elements using 0.05 mol/l D2EHPA in decane as stationary phase (K_r = 50%) and HCl solutions as eluents. Fig. 3 shows examples of the separation of La and Ce, Sm and Eu. The complete separations are achieved with the use of two eluents in both cases.

As other separation techniques, CCC can be used in analytical chemistry for preconcentration of trace elements before their determination by instrumental multielement methods. Quantitative separation of the sum of REE from the constituents of rocks, which interfere with the determination of the elements by simultaneous ICP AES, was achieved. The method developed is based on rock sample fusion and dissolution followed by preconcentration of REE and their separation from other constituents of the sample in its solution. At the stage of REE concentration from 0.1 mol/l HCl,

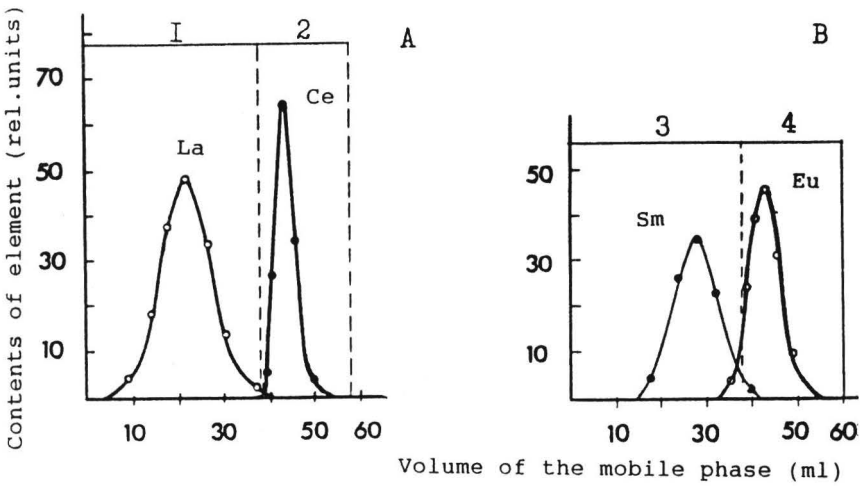


Fig. 3. A - Separation of La and Ce. Mobile phase: 1 - 0.3 mol/l HCl; 2 - 0.5 mol/l HCl. Pumping rate of the mobile phase - 0.5 ml/min. B - Separation of Sm and Eu. Mobile phase: 3 - 0.5 mol/l HCl; 4 - 1 mol/l HCl. Pumping rate of the mobile phase - 0.9 ml/min. Stationary phase: 0.05 mol/l D2EHPA in decane. Element contents in initial solution 10 μg.

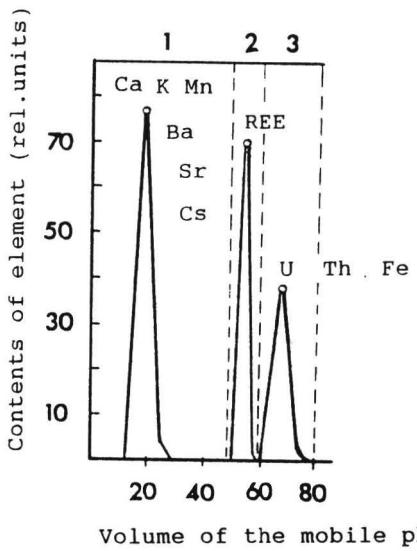


Fig. 4. Separation of REE from some macrocomponents. REE contents in initial sample 10 μg. Mass ratio of sample components: REE:Si:Al:Fe:Ca:K:Ba:Mn:Sr:Cs:U:Th = 1:30000:5000:10000:5000:7000: 5000:7000:1000:1000:10:10. Stationary phase: 0.05 mol/l D2EHPA in decane. Mobile phase: 1 - 0.1 mol/l HCl; 2 - 3 mol/l HCl; 3 - 5 mol/l HCl. Pumping rate of the mobile phase - 0.9 ml/min.

alkali and alkaline earth elements are separated with the mobile

phase. After that, using 3 mol/l HCl the total amount of REE is eluted from the stationary phase and subjected to the analysis. Then the column is washed with 5 mol/l HCl to strip Fe, Th and U from the organic phase (Fig.4). The whole separation procedure takes 30-40 min at a pumping rate of 1.5-2 ml/min.

2.3. Ortho- and pyrophosphate anions

The CCC method can be used for anion separations. Ortho- and pyrophosphate were concentrated by dinonyltin dichloride in methylisobutylketone and then separated by elution with HCl solutions. Phosphate ions were determined in eluates on a flow-injection analyzer using a photometric method based on the formation of molybdophosphoric heteropoly acid in the presence of a reductant. The determination limit for phosphate ions was 10 ng/ml at a water sample volume of 100 ml. Organotin extractants make it possible to separate phosphate ions practically from all metal cations as well as from many anions (Spivakov, 1984, pp. 137-164). For example, it is possible to separate phosphate ions from large amounts of Cu(II), Fe(III), Ni(II), Cr(III), Si(IV), V(V), Cr(VI). Only arsenic (V) is extracted together with the phosphate ions.

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PRECONCENTRATION AND DETERMINATION OF A TRACE AMOUNT OF LITHIUM IN WATER AS ITS THENOYLTRIFLUOROACETONE COMPLEX WITH TRIBUTYLPHOSPHATE BY MEANS OF SOLVENT EXTRACTION AND FLAME PHOTOMETRY

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ABSTRACT

A new method for the preconcentration and determination of a trace amount of lithium in ppb～ppm order in water as its thenoyltrifluoroacetone (TTA) complex with tributylphosphate (TBP) has been established by means of extraction and back extraction combined with flame photometry. The effect of various factors on the extractability of lithium was investigated. On the basis of these results, the recommended procedures are proposed as follows: A sample solution (10～15 ml) containing lithium (0.001～0.01 ppm) adjusted to pH 7.8～8.0 with pH 8 buffer (20 ml) and the same volume of an organic solution of 0.1M TTA-0.2M TBP in benzene were placed in a 30～50 ml glass-stoppered centrifuge tube, and were agitated on a shaking machine for 15 min. After the separation of the two phases by centrifugation at 2000～3000rpm for 5 min, a 5～10 ml of the organic phase was shaken with 0.01M hydrochloric acid solution; the amount of lithium stripped from the organic phase was determined by flame photometry at 670.8 nm. Excellent linearity of the calilbration curve of lithium was obtained in the range of 0.01～0.1 ppm. A 1 ppb of lithium can be determined in the present method, because the volume of the final aqueous solution has no effect on the back extraction recovery of lithium, even at a tenth volume of the organic phase. None of the ions investigated (Na^+, Mg^{2+}, Ca^{2+}, Cl^-, HCO_3^-, and SO_4^{2-}) interfered with the extractability of lithium. Magnesium and calcium can be pre-removed by extraction with 0.1M TTA and 0.2M TBP in benzene at pH 5.0.

INTRODUCTION

The lithium content in natural waters is generally known to be in ppb～ppm order, and it must be separated and/or concentrated prior to its determination by means of an ordinary flame photometry. Moreover, it takes a long time to separate lithium from foreign ions, especially alkali metals, by ion exchange method to avoid their effect on flame photometry (1). It has been reported that lithium is extracted with dipivaloylmethane in diethyl ether at very high pH (2), while in the TTA (thenoyltrifluoroacetone)-TBP (tributyl phosphate)-benzene system, lithium can be extracted as an adduct ($Li(TTA)(TBP)_2$) at an appropriate lower pH region (3, 4). After preliminary experiments on the extraction behavior of lithium at pH about 7 with TTA in various organic solvents such as diethyl ether, isopropyl ether, benzene, o-dichlorobenzene, benzene with TBP, and o-dichlorobenzene with TBP, it was found that the extractability of lithium gave the highest value when using benzene with TBP. On the basis of these

results, the extraction behavior of TTA chelate of lithium in benzene with TBP has been investigated in detail, and a new method for the preconcentration and determination of a trace amount of lithium has been established by means of extraction and back extraction combined with flame photometry.

EXPERIMENTAL

Apparatus. A model AA-646 Shimadzu atomic absorption/flame spectrophotometer; a model Z-6100 Hitachi Polarized Zeeman Atomic Absorption Spectrophotometer; a Taiyo Recipro Shaker, model SR-Ⅱ, and a Tomy Seiko Swing Type Centrifuge, model CD-50R, were used.

Materials. A 1000 mg/l of lithium standard stock solution (f=1.01) in 0.01 mol/l hydrochloric acid (obtained from Wako Pure Chemical Industries, Ltd.) was used by suitable dilution with water purified by ion-exchange treatment. Thenoyltrifluoroacetone (TTA), tributyl phosphate (TBP) purchased from Dojindo Co., Ltd., and Wako Pure Chemical Industries, Ltd., were guaranteed-grade materials. TBP was purified by distillation. Organic solvents used were all reagent-grade materials and were purified if necessary by an ordinary method. All the other chemicals were reagent-grade materials.

Extraction of Lithium. A 10～15 ml of 0.01～0.1 ppm lithium solution was adjusted to the desired pH with buffer solutions of pH 5～10 prepared by mixing an appropriate amount of 0.1M of hydrochloric acid, acetic acid, sodium acetate, boric acid, sodium borate and sodium hydroxide. This aqueous solution and the same volume of an organic solution of 0.1M TTA-0.2M TBP in benzene were placed in a 30～50 ml of glass-stoppered centrifuge tube and were agitated on a shaking machine for 15 min. After the separation of the two phases by centrifugation at 2000～3000 rpm for 5 min, a 5～10 ml of the organic phase was shaken with 0.01M hydrochloric acid solution; the amount of lithium stripped from the organic phase was determined by flame photometry at 670.8 nm. The pH of the aqueous phase was determined again after the extraction. Another alkali(Na) and alkaline earth metals (Mg and Ca) were also extracted with 0.1M TTA-0.2M TBP in benzene, and the concentration of metals was determined by atomic absorption spectrometry at 285.2 nm for magnesium and at 422.7 nm for calcium, and by flame photometry at 589.0 nm for sodium after stripping their metals with 0.01～0.1M hydrochloric acid solution.

RESULTS AND DISCUSSION

Effect of solvent. The effect of organic solvent on the extractability of the lithium TTA chelate with or without TBP was investigated by varying organic solvents such as diethyl ether, isopropyl ether, benzene, and o-dichlorobenzene. The results are summarized in Table 1. The extractability of lithium as the lithium-TTA-TBP chelate adduct (Fig. 1), Li(TTA)·2TBP(3), in benzene gave higher values of all solvent investigated.

TABLE 1.

Effect of organic solvent on the extractability of lithium with 0.1M TTA in various solvents with or without 0.2M TBP

Organic phase	Solubility in water(W/W%)	Aqueous phase (pH)	%E
$C_4H_{10}O$ (Diethyl ether)	6.90	7.40	56.2
$C_6H_{14}O$ (Isopropyl ether)	0.90	6.89	10.0
C_6H_6 (Benzene)	0.18	7.00	5.1
$C_6H_4Cl_2$ (o-Dichlorobenzene)	<0.03	6.02	3.1
C_6H_6 with 0.2M TBP	–	7.16	66.8
$C_6H_4Cl_2$ with 0.2M TBP	–	7.09	51.9

Effect of pH. The effect of pH on the extractability of the lithium-TTA-TBP chelate adduct in benzene was investigated. The result is shown in Fig. 2 along with those of sodium, magnesium, and calcium under the same conditions. The percent extraction (%E) of lithium rose steeply over the pH range 5.5~7.8 and reached a plateau (about 90%) in the pH-range 7.8~9.0.

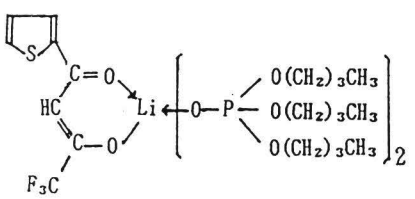


Fig. 1. Li-TTA-TBP adduct

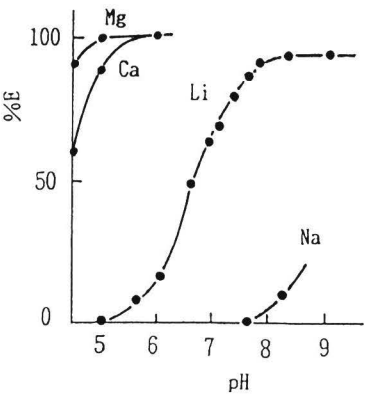


Fig. 2. Effect of pH on the extractability of lithium, sodium, magnesium, and calcium with 0.1M TTA and 0.2M TBP in benzene

Taking this result into account, the pH-value was kept at pH 7.8～8.0 to avoid coextraction of sodium throughout the following experiments.

Effect of extraction volume. When the volume of the organic phase of 0.1M TTA with 0.2M TBP in benzene was kept at 10 ml, and when that of the aqueous phase was varied from 10 to 100 ml, the extractability of lithium decreased in each case from 87.9 to 42.6% owing to its lower distribution ratio (about 9). Therefore, the extraction of lithium was carried out with the same volume ratio of 1:1, after which the back extraction was carried out with 0.01M hydrochloric acid solution with the volume ratio of 1:10; the preconcentration factor being 10. The recovery of lithium was 87.9%.

Calibration curve. A calibration curve of lithium was prepared by measuring the absorption intensity with a flame photometer at 670.7 nm by varying the amounts of lithium in 0.01M hydrochloric acid solution. A good linear relationship was obtained in the range of 0.01～0.1 ppm lithium, indicating that 1 ppb of lithium can be determined by the present method. The recommended systematic experimental procedure is shown in Fig. 3.

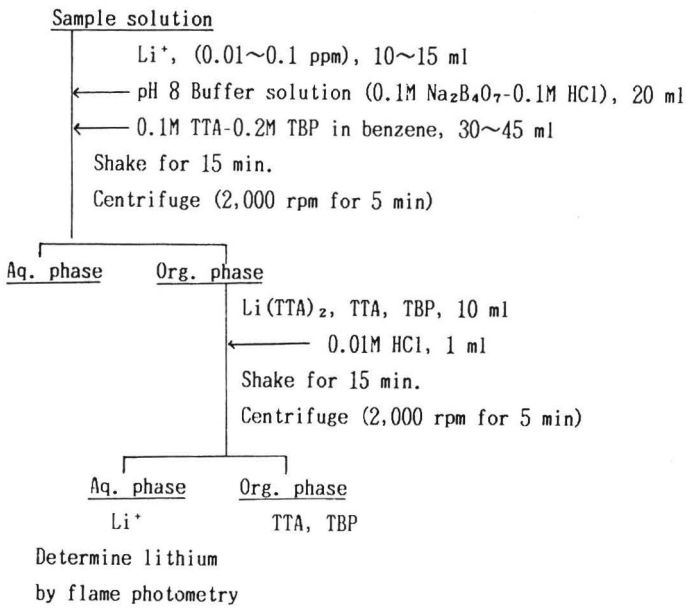


Fig. 3. Analytical scheme for the preconcentration and determination of a trace amount of lithium in fresh water

Effect of foreign ions. The effect of the presence of foreign ions which may exist in fresh water, on the determination of a trace amount of lithium with the recommended method is given in Table 2.

TABLE 2.

Threshhold concentrations of foreign ions at which interference doesn't appear on the determination of a trace amount of lituium (0.1 ppm L)*

Foreign ions	Concentration(times that of Li)
Na^+	<1:100
Mg^{2+}	<1:1,000
Ca^{2+}	<1:500
Cl^-	<1:100
HCO_3^-	<1:5,000
SO_4^{2-}	<1:30,000

*Tolerant limit $< \pm 5\%$, R.S.D <0.8%

These results indicate that none of the ions investigated interferes with the determination of lithium when these ions are within threshold concentrations. Magnesium and calcium can be pre-removed by extraction with 0.1M TTA and 0.2M TBP in benzene at pH 5 (Fig. 2).

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EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF COPPER(II) WITH THIOPHENE ALDEHYDE-4-PHENYL-3-THIOSEMICARBAZONE

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ABSTRACT

A simple method for the extraction-spectrophotometric determination of copper(II) using thiophenealdehyde-4-phenyl-3-thiosemicarbazone(TPS) was developed. The method is based on the formation of the copper(II)-TPS complex, which is extractable into chloroform from aqueous solution in the pH range 4-10 by shaking 15 min. The extracted species has absorption maximal at 380 nm with the molar absorptivity of 37,000 l $mol^{-1}cm^{-1}$ at 360 nm. Beer's law is obeyed over the range 2-20 μg of copper(II) in 10 ml of chloroform at 360 nm. The proposed method is relatively selective for copper(II) and has been satisfactorily applied to the determination of copper(II) in some alloys.

1 INTRODUCTION

Thiosemicarbazones have been widely used as spectrophotometric and extractive reagents.[1] Recently, several phenylthiosemicarbazones with pheny radicals at the end of the thiosemicarbazide molecule heve been studied as spectrophotometric reagents for the determination of metal ions.[2~5] It has been found that these reagents react sensitively with metal ions to form complexes, which are easily extracted; however, phenylthiosemicarbazones of thiophenealdehyde have been little used as analytical reagents.

In this work, a new compound, thiophenealdehyde-4-phenyl-3-thiosemicarbazone (TPS), has been used as a spectrophotometric reagent for the determination of copper(II).

2 EXPERIMENTAL

2.1 Apparatus and reagents

Absorption spectra and absorbance values were measured with a Hitachi automatic recording model U-3200 spectrophotometer using quartz cells of 10-mm path length. A Horiba model F-13 pH meter equipped with a combined glass electrode was used for pH measurements. All chemicals used were of analytical-reagent grade unless stated otherwise.

The TPS was synthesized by refluxing equimolar amounts of 3-thiophenealdehyde and 4-phenyl-3-thiosemicarbazide in 100 ml of ethanol for 1 h. The crude compound obtained on cooling was recrystallized twice from ethanol. The TPS was soluble in virtually all organic solvents. A $5x10^{-4}$ M solution was pre-

pared in chloroform.

2.2 Standard procedure

Transfer the sample solution containing less than 20 μg of copper(II) to a centrifugal precipitation tube, add 4 ml of the acetate buffer solution(pH 5), and dilute to 10 ml with water. Add 10 ml of the $5x10^{-4}$ M TPS chloroform solution and shake vigorously for 15 min. Allow to separate the two phases, and measure the absorbance of the organic phase at 360 nm against a reagent blank.

3 RESULTS AND DISCUSSION

3.1 Absorption spectra

Absorption spectra of the complex formed between copper(II) and TPS in chloroform medium and the reagent blank are shown in Fig.1. The copper complex and reagent have absorption maxima at 360 nm and 316 nm, respectively.

3.2 Effect of experimental variables

The above standard procedure was used to examine the effect of pH. The final pH of each aqueous solution was measured after extraction. The results are shown in Fig.2, from which it can be seen that maximal absorbance can be obtained in the pH range 4-10. In this work, the pH was adjusted to 5 with the acetate buffer solution.

The effect of the concentration of TPS in chloroform on the extraction of the complex was examined. It was found that 10 ml of $2.5x10^{-4}$ M TPS sufficed for less than 20 μg of copper(II) (Fig.3). Hence, 10 ml of $5.0x10^{-4}$ M TPS chloroform solution was adopted in this work.

The shaking time for the extraction was varied from 1 to 30 min. The minimum shaking time for complete extraction of 20 μg of copper(II) with chloroform was found to be 10 min at room temperature. Therefore, a 15 min shaking time was adopted in this work. The absorbance at 360 nm was stable for at least 6 h.

Several kinds of organic solvents were tested in order to achieve extraction of the complex. The complex can be extracted into chloroform (molar absorptivity, $\varepsilon=3.7x10^4$, $\lambda max=360$ nm), toluene ($\varepsilon=3.7x10^4$, $\lambda max=363$ nm), isobutyl methyl ketone ($\varepsilon=1.6x10^4$, $\lambda max=359$ nm), benzene ($\varepsilon=3.7x10^4$, $\lambda max=363$ nm), and ethyl acetate ($\varepsilon=3.9x10^4$, $\lambda max=363$ nm), but not into carbon tetrachloride. Chloroform was selected for its convenience.

A calibration curve for the determination of copper(II) was prepared by the standard procedure. Beer's law is obeyed over the range 2-20 μg of copper(II). The relative standard deviation of the absorbance for 10 μg of copper(II) in 10 ml of chloroform was 0.35 % (determined from five measurements).

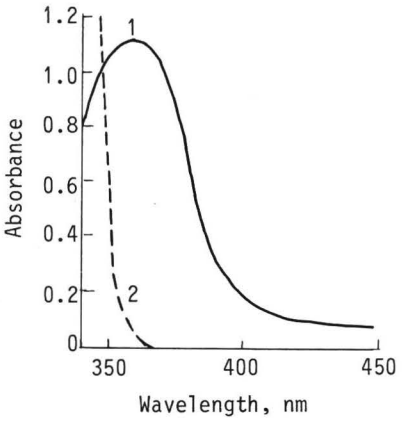


Fig. 1. Absorption spectra of copper(II)-TPS complex in chloroform.
Conditions were as follows; (1) Cu, 20 μg; TPS, 5×10^{-4} M; pH 5.0.
(2) reagent blank.

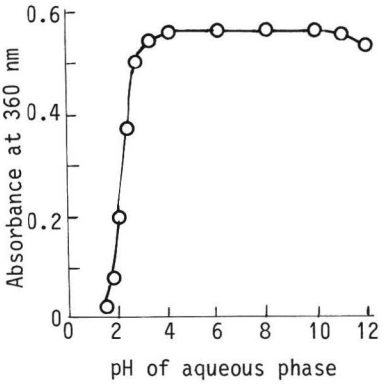


Fig. 2. Effect of pH on extraction of copper complex.
Conditions were as follows; Cu, 10 μg; TPS, 5×10^{-4} M; absorbance measured against a reagent blank.

3.3 Effect of diverse ions

The effect of diverse ions on the determination of copper(II) was examined under the condition of the standard procedure. The most commonly encountered ions were added individually to a solution containing 5 μg of copper(II). The following ions did not interfere: 1000 μg of As(III), Co(II), Cr(III), Mn(II), Mo(VI), Ni(II), Os(IV), Pb(II), Pt(IV), Tl(I), V(V), and Zn(II); 500 μg of Fe(III) and Cd(II); 50 μg of Rh(III); 25 μg of Ru(III); 20 μg of Ti(IV); 10 mg of Cl^-, NO_3^-, F^-, ClO_4^-, SO_4^{2-}, and PO_4^{3-}. Au(III), Hg(II) and Pd(II) interfere seriously, causing positive errors because they also form complexes with TPS and they are extracted into chloroform.

3.4 Composition of the complex

The stoichiometric ratio of the copper complex extracted into the chloroform phase was examined by Job's continuous variation method which gave a ratio 1:2, Cu-to-TPS (Fig.4).

3.5 Application of the method to some alloys

The proposed method has been successfully applied to the determination of copper in Zn, Mg, and Al-alloy samples. Alloy samples were dissolved in hydrochloric acid and small amounts of hydrogen peroxide. On heating on a hot-plate, the mixture was dissolved completely and the excess of hydrogen peroxide was decomposed. The sample was diluted with water in a calibrated flask.

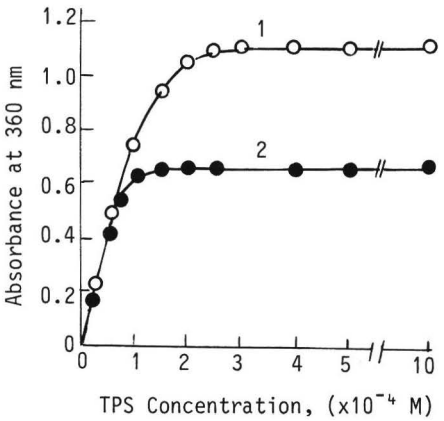


Fig. 3. Effect of TPS concentration. Conditions were as follows; TPS, $5x10^{-4}$ M; pH 5.0; Shaking time, 30 min; (1) Cu, 20 μg; (2) Cu, 12 μg.

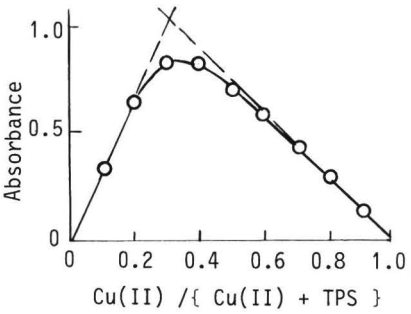


Fig. 4. Continuous variation graph. Conditions were as follows; Cu(II) + TPS = $9.44x10^{-3}$ M; Shaking time, 15 min.

An aliquot of this sample solution was taken and the proposed procedure was followed. The results shown in Table 1 are in good agreement with the certified value or the results by AAS method.

TABLE 1

Determination of copper in alloys

	Cu found* %	Certified value, %	AAS method %
Zn alloy (NBS 629)	1.54 ± 0.04	1.50	
Mg alloy (NBS 171)	0.0117 ± 0.0006	0.0112	
Al alloy (1)	1.04		1.06
(2)	0.407		0.400
(3)	0.591		0.590
(4)	0.207		0.204

*Average value of 5 determinations.

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SOLVENT EXTRACTION SEPARATION OF THORIUM, URANIUM(VI), ZIRCONIUM AND HAFNIUM WITH CROWN ETHERS

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ABSTRACT

A novel method is developed for the sequential solvent extraction separation of thorium, uranium(vi), zirconium and hafnium from each other with macrocyclic polyethers. Thorium was quantitatively extracted with 18-crown-6 (0.065M) in methylene chloride with picric acid (0.04M) as the counter ion while uranium was extracted with DC-18-crown-6 (0.02M) from hydrochloric acid (6.0M). From the aqueous phase unextracted zirconium was extracted with DC-18-crown-6 (0.025M) from hydrochloric acid (8.5M) and finally hafnium was extracted with DC-18-crown-6 (0.070M) from 9.0M hydrochloric acid. The elements after stripping with suitable acids were determined in aqueous phase spectrophotometrically.

INTRODUCTION

Thorium, uranium, zirconium and hafnium were extracted with several crown ethers. 18-crown-6 was used to complex thorium (Costes R.M. et al.,1976). 18-crown-6, DB-18-crown-6 and 4-methylbenzo-15-crown-5 were also used for extraction of thorium from picrate media with 1,2-dichloromethane (Wang W. et al., 1983) An attempt to extract uranium with 18-crown-6 from nitrate, perchlorate and acetate media was unsuccessful (Venkataswaralu K.S.et al.,1982),however, the extraction of uranium from chloride or nitrate solution with DC-18-crown-6 in dichloroethane was successful (Wang W. et al.,1983).

The methods for the solvent extraction separation of zirconium from hafnium are very limited. Tributylphosphate (60%) separated zirconium from hafnium from 6.0M nitric acid (Hure J.,1861). DC-18-crown-6 was ineffective for the separation of zirconium from hydrochloric acid (Caletka R., 1986). The systematic investigations on solvent extraction separations of thorium, uranium zirconium and hafnium with crown ethers are lacking. Such studies are reported in this paper.

EXPERIMENTAL

Apparatus and Reagents :

A model 866C spectrophotometer (ECIL,India) with 10 mm matched corex glass cuvettes, wrist action shaker were used.

The stock solutions of thorium, uranium, zirconium and hafnium were prepared by dissolving 2.0 g thorium nitrate tetrahydrate m 1.083 g uranyl nitrate hexahydrate, 2.5 g zirconium nitrate pentahydrate and 1.5 g hafnium dioxide (B.D.H.,England) in 500 ml deionized water containing 1% mineral acid. They were standardized as per usual procedures. The diluted solution containing 25 µg/ml of each metal was prepared by appropriate dilution. 15-crown-5, 18-crown-6, DB-18-crown-6 and DC-18-crown-6 in 1,2-dichloromethane (Merck, Germany) were used without further purification.

General Procedure :

To an aliquot of solution containing uranium(VI) (50 µg) or zirconium (25 µg) or hafnium (25 µg), hydrochloric acid was added so as to have its concentration 4-10M in total volume of 10ml. The solutions were equilibrated with 10 ml of DC-18-crown-6 (0.02-0.07M) in dichloromethane. From the organic phase concerned element was stripped with suitable stripping agents. Thus, 0.5M hydrochloric (for uranium and zirconium) and 0.1M perchloric acid (hafnium) used for stripping. All elements were determined from the aqueous phase spectrophotometrically with appropriate chromogenic ligands (Sawin S.B., 1964 and Cheng K.L., 1959). However, thorium (25 µg) was extracted at pH 2.0-3.5 with 0.065M 18-crown-6 from picric acid (0.04M). It was stripped with 0.5M nitric acid and determined spectrophotometrically.

RESULTS AND DISCUSSION

Extraction as the function of acidity/pH :

The optimum concentration of hydrochloric acid for the quantitative extraction of these elements was ascertained by extracting them from different concentrations of hydrochloric acid. Uranium(VI) was extracted with 6.0-8.0M hydrochloric acid while zirconium and hafnium were extracted from 8.5-10.0M and 9.0-10.0M hydrochloric acid respectively, with DC-18-crown-6. Thorium was not extracted frokm acid media, but it was extracted from 0.04M picric acid at pH 2.0-3.5 with 18-crown-6 in place of DC-18-crown-6 (Fig.1).

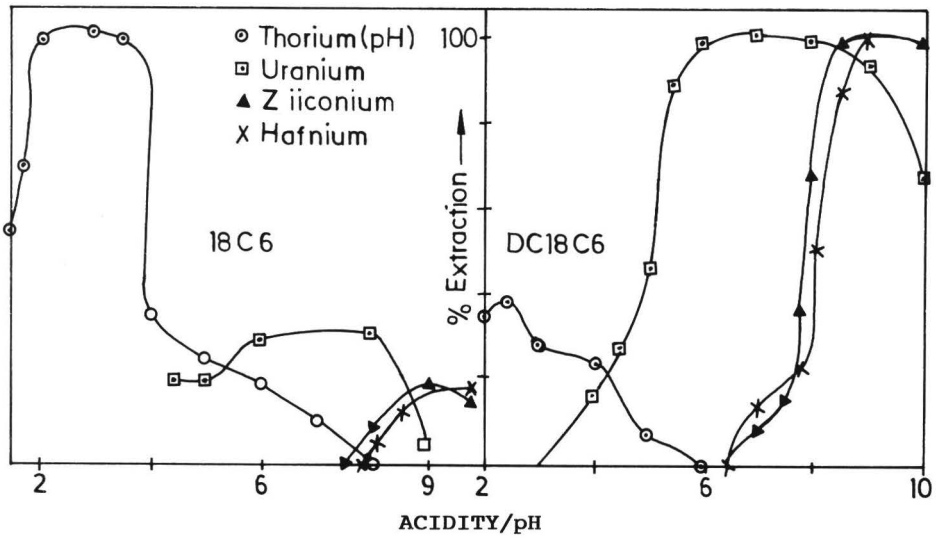


Fig.1. Extraction as the function of acidity/pH

Effect of the crown ether concentration :

The optimal concentration of crown ether for quantitative extraction of thorium, uranium(VI), zirconium and hafnium was ascertained by extracting them with different concentrations of 18-crown-6 and DC-18-crown-6. It was noted that 18-crown-6 in concentration (shown in parenthesis) e.g. thorium (0.065M) and DC-18-crown-6 for uranium (0.02M), zirconium (0.25M) and hafnium (0.7M) in dichloromethane were effective for the quantitative extraction.

Effect of dilutents :

Benzene, toluene, xylene, carbontetrachloride, chloroform, dichloromethane, dichloroethane and nitrobenzene were tested as the diluents with 18-crown-6 (for thorium) and DC-18-crown-6 (for other elements) as extractants. Chloroform, dichloromethane, dichloroethane and nitrobenzene were suitable diluents for crown ether.

Effect of stripping agents :

Thorium, uranium(VI), zirconium and hafnium were stripped with 0.05-7.0M of various mineral acids. Thus, 0.5-3.0M hydrochloric, nitric, sulphuric and perchloric acids were effective for quantitative stripping of all these elements.(Tab.1). 0.5M of nitric (for thorium), 0.5M hydrochloric,

(for zirconium and uranium) and 0.1M perchloric acid (for hafnium) were useful for stripping these elements.

Table 1

Effect of stripping agents (% stripped)

Stripping agent	HCl			HNO_3			H_2SO_4			$HClO_4$		
[M]	0.05	0.1	0.5	0.05	0.1	0.5	0.05	0.1	0.5	0.05	0.1	0.5
Th	31.3	56.6	77	39.0	56.7	100	47.8	89.7	100	25.7	60	100
U(VI)	38.1	50.0	100	10.1	23.0	80	29.0	56.0	100	18.1	40	100
Zr	63.0	79.7	100	47.8	72.3	88	57.1	81.0	100	47.6	76	88
Hf	67.0	89.0	100	67.0	89.0	100	87.8	100	100	79.6	100	100

Nature of extracted species :

The composition of extracted species were ascertained from the plot of log D vs log [crown ether] at fixed acidity/pH and log D vs log [counter ion] at fixed crown ether concentration. The probale species were $[Th(pic)_4.18C6]$ for thorium, $[H_3O^+.DC18C6)_2, UO_2Cl_4{}^{-2}$ for uranium which for both zirconium and hafnium was $[(H_3O^+.DC18C6)_2\ MCl_6{}^{-2}]$ where M = zirconium, hafnium.

Separation from binary mixtures :

These elements were extracted in the presence of various diverse ions. The tolerance limit was set as the amount of diverse ions required to cause $\pm$ 0.5% error in the recovery of these elements. The alkali and alkaline earths were tolerated in the ratio of 1:50 while bismuth, titanium, cobalt, zinc, copper, cadmium, lanthanum, cerium and neodynium were tolerated in the ratios varying from 1:10 to 1:80. The common anions were tolerated in the ratio of 1:100. During the separation from binary mixtures scandium, cerium and barium showed strong interference with thorium extraction while iron, zirconium, hafnium showed interference with uranium(VI) and iron, uranium(VI) were interfered with zirconium and hafnium extraction.

Sequential separation of titanium,zirconium,hafnium and thorium :

The sequential separation of titanium, zirconium, hafnium and thorium was effected by the first extracting thorium with 0.065M 18-crown-6 from 0.04M picric acid at pH 2.5. Then extracting zirconium with 0.025M DC-18-crown-6 from 8.5M hydrochloric acid

and finally from aqueous phase hafnium was extracted with 0.07M DC-18-crown-6 from 9.0M hydrochloric acid. Since titonium was not extracted at all, it was determined directly in the aqueous phase. Some important separations from multicomponent mixtures are described in table 2.

Table 2

Separation from multicomponent mixtures

Sr. No.	Mixture	Amount taken μg	Extractant Crown ether	Counter ion/acidity	Stripping agent	Reagent for determination λmax.nm
1.	Th	50	18C6,0.065M	0.04M Picrate	0.5M HNO_3	A,650
	Zr	25	DC18C6,0.025	8.5M HCl	0.5M HCl	A,660
	Hf	25	DC18C6,0.07	9.0M HCl	0.5M $HClO_4$	B,540
	Ti	50	Unextracted	-	Aq.Phase	C,390
2.	Zr	25	DC18C6,0.025	8.5M HCl	6.0M HCl	A,660
	U(VI)	50	DC18C6,0.025	8.5M HCl	0.5M HCl	A,665
	Hf	25	DC18C6,0.070	9.0M HCl	0.5M $HClO_4$	B,540
	V(IV)	50	Unextracted	-	Aq.Phase	D,560
3.	Sc	50	18C6,0.040	0.04M Picrate	0.05M HNO_3	A,650
	Zr	25	DC18C6,0.025	8.5M,HCl	0.5M HCl	A,660
	Hf	25	DC18C6,0.070	9.0M HCl	0.5M $HClO_4$	B,540
	Y	50	Unextracted	-	Aq.Phase	A,650

A - Arsenazo-III; B - Xylenol orange; C - Tiron; D - PAR.

Separation of zirconium and hafnium :

Zirconium and hafnium are generally associated with each other due to close similarity in their chemical properties arising out of the same atomic size. Their separation was possible by exploiting the difference in concentration of DC-18-crown-6 as well as that of hydrochloric acid for the extraction of zirconium as well as hafnium. Zirconium was first extracted from 8.0M hydrochloric acid with 0.025M DC-18-crown-6, when hafnium was not extracted. Zirconium was stripped with 0.5M hydrochloric acid and determined spectrophotometrically. From the aqueous phase, hafnium was extracted with 0.070M DC-18-crwon-6 from 9.0M hydrochloric

acid and was stripped with 0.5M perchloric acid. The separation of zirconium from hafnium by this procedure was possible in the ratio of 1:4.

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HYDROLYSIS STUDIES OF Tm USING SOLVENT EXTRACTION TECHNIQUES

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ABSTRACT

The Swedish concept for final disposal of spent nuclear fuel is focused on a repository in crystalline rock at a depth of 500m. In order to calculate migration rates from a leakage in such a repository, chemical speciation becomes important.

A method for determining hydrolysis constants for lanthanides using solvent extraction has been developed. The apparatus used is called AKUFVE-LISOL (**LI**quid **S**cintillation **O**n **L**ine) in which D-values between 10^{-5} and 10^{5} can be measured in the pH-range 1-11.

Experiments with Tm and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (HHFAa) as a chelating agent have been performed and from the resulting data, calculations of hydrolysis constants have been made, regarding hydroxide complexes as competing and nonextractable.

The obtained stability constants for the $Tm(OH)_n$ complexes are several orders of magnitude higher than those obtained with potentiometric methods. This has been explained in literature by unknown extraction mechanisms (i.e. mixed complexes $Tm(HFAa)_m(OH)_n$). Calculations of stability constants of the mixed complexes, assuming potentiometric values are correct, have been performed. The results indicate that the stability constants for hydrolysis with extraction methods can not be explained by formation of mixed complexes.

1. INTRODUCTION

The Swedish concept for disposal of high-level nuclear waste has concentrated on a multiple barrier system in crystalline rock at a depth of 500 m (KBS 1983). Burnt-out fuel elements will be put into copper canisters and then placed into granite rock. The copper canisters will be surrounded by bentonite clay which has a very low permeability to water.

In order to predict the mobility of the actinides and fission products through the bentonite backfill and in bedrock fractures, chemical speciation becomes important. The environment around the canisters could be characterized as:

a. low groundwater flow

b. relatively high pH (6-9)

c. low free oxygen content due to corrosion of the copper

d. moderate ionic strength in the ground water (0.008-0.3 M)

Since the sorption/diffusion of an ion mostly depends on its charge, where the tri- and

tetravalent ions show very low diffusion rate in bentonite (Albinsson et al. 1990). Under the above described conditions actinides are expected to be in a tri- or tetravalent state and would accordingly have low mobility. The mobility of the actinides is strongly related to hydrolysis and a better knowledge of speciation is needed in order to predict their mobility.

Much effort has been put into the problem with determining the constants but achieved numerical values are unfortunately scattered, mostly depending on experimental method (Baes and Mesmer 1986).

2. HYDROLYSIS

Hydrolysis of a cation can schematically be described by the following reaction with water:

$$xM^{z+} + yH_2O \rightleftarrows M_x(OH)_y^{xz-y} + yH^+ \quad (1)$$

where it should be noted that polynuclear hydrolysis is common.

In this paper, we prefer to write the reaction as a complexation with hydroxide:

$$mM^{z+} + pOH^- \rightleftarrows M_m(OH)_p^{(mz-p)} \quad (2)$$

with the equilibrium constant β_{mp} defined as

$$\beta_{mp} = \frac{[M_m(OH)_p^{(mz-p)}]}{[M^{z+}]^m[OH^-]^p} \quad (3)$$

3. THEORY

Complexation between a metal M^{z+} and a ligand and/or hydroxide can be described by the stability constant β_{mnp},

$$mM^{z+} + nL^- + pOH^- \rightleftarrows M_mL_n(OH)_p^{(mz-n-p)} \quad (4)$$

$$\beta_{mnp} = \frac{[M_mL_n(OH)_p^{(mz-n-p)}]}{[M^{z+}]^m[L^-]^n[OH^-]^p} \quad (5)$$

The stepwise constant, for example k_{10p}, is defined as $\beta_{10p} = \prod_1^p k_{10p}$.

If the metal concentration is kept at trace level, the polynuclear hydrolysis is negligible (Rydberg and Albinsson 1989) and since the hydroxide complexes are not extractable,

$$D_M = \frac{\lambda_z\beta_{1z0}[L]^z}{1 + \sum_1^n \beta_{1n0}[L]^n + \sum_1^m \beta_{10m}[OH]^m} \quad (6)$$

D_M is the distribution of the metal M between an organic and an aqueous phase and λ_z is the distribution constant for the uncharged species ML_z. In Eq. 6, no mixed complexes ($n \neq 0$ and $p \neq 0$) are included.

The β_{mnp} constants can be obtained by curve fitting. For this we used a downhill simplex

method described by Nelder and Mead (1965).

The calculations of the β_{1mn} constants were done in two steps:

First fitting the β_{1n0} constants in eq. 3 to the distribution curve (Fig. 1) at lower pH up to the points where the extraction becomes constant.

Then fitting the β_{10p} values from the points where the extraction was constant to the end of the curve (Fig. 1). The following function was used:

$$C_1/D_M - C_2 = \sum_1^p \beta_{10p}[OH]^p \quad \text{, where} \tag{7}$$

$$C_1 = \lambda_z \beta_z [L]^z \text{ and } C_2 = 1 + \sum_1^n \beta_{1n0}[L]^n \tag{8}$$

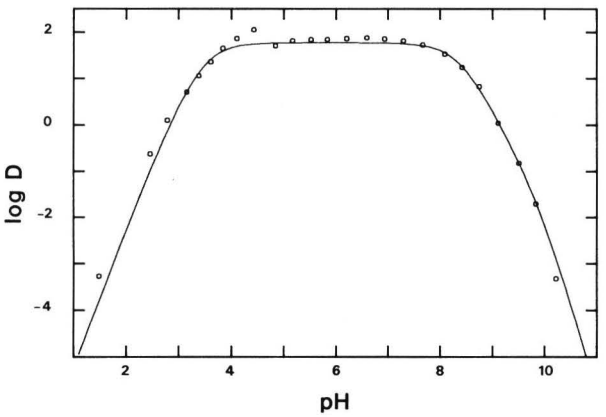


Fig. 1. Distribution ratio D_M of Tm between 1.0 M $Na(H)ClO_4$ and toluene containing 0.10 M HHFAa (circles). The curve is calculated with the experimentally obtained constants β_{1np}.

4. EXPERIMENTAL

The equipment used for the experiments was mainly AKUFVE-LISOL where AKUFVE is a mixing-separating system and the LISOL is a sampling-measuring system (Albinsson et al. 1988), (cf Fig. 2). The advantages of the LISOL system are (i) the system can measure both alpha and beta decays, (ii) the system has overcome the severe problems with sorption in the detector and thus minimized the memory effects. The system is capable of measuring D-values between 10^{-5} and 10^5 (Albinsson et al. 1989).

A schelating agent, hexafluoroacetylacetone (1,1,1,5,5,5-hexafluoro-2,4-pentanedione, Aldrich 96%, in this paper abbreviated HHFAa) diluted in toluene was used. The dilution to 0.1M or 0.05M was done under nitrogen atmosphere since HHFAa is very hygroscopic and easily precipitates as dihydrated crystals (Schultz and Larsen 1949).

^{170}Tm was prepared by reactor irradiation of ^{169}Tm-oxide (>99.999% by Ventron, West Germany) and then dissolved in concentrated perchloric acid. For the experiments ^{169}Tm was added as carrier to get an initial concentration 0.1 mM. In the experiments the aqueous phase

was 1 M $NaClO_4$ (Merck p.a) and pH adjustment was done with fresh 1 M NaOH. pH was measured with a combination electrode with 1 M $NaClO_4$ as supporting electrolyte. To avoid complexation with carbonate, carbon dioxide was driven off with toluene saturated nitrogen, introduced to the system both in the mixing vessel and to the centrifuge. Toluene was continuously added to compensate for evaporation. The temperature was kept at 25°C with a circulating heating/cooling system.

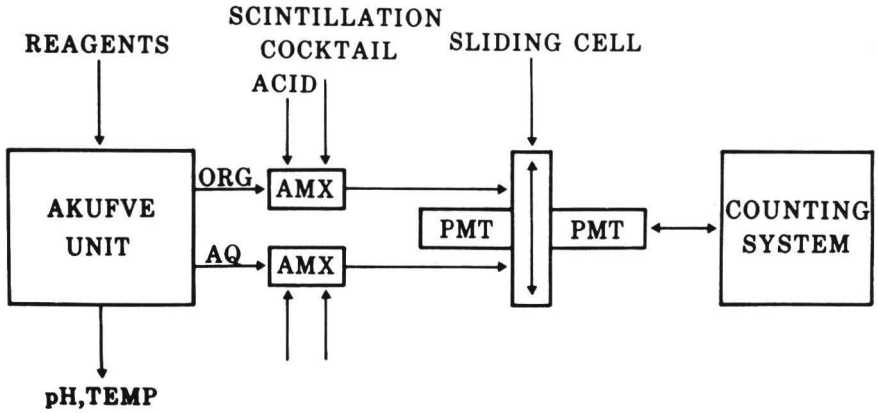


Fig. 2. Schematic of the AKUFVE-LISOL system. The AKUFVE consists of a mixing vessel, a continous flow centrifugal separator and connecting pipings. Samples of the pure aqueous and organic phases are withdrawn from the liquids circulating in the AKUFVE system. These samples are acidified to suppress sorption and mixed with a liquid scintillation cocktail. The radioactivity is measured by photomultiplier counting system which alternatively measures by a sliding cell mechanism on the mixtures coming from the two AMX's.

Quenching is a major problem when using liquid scintillation and experiences with acetylacetone made us check the quenching properties of HHFAa (done in the same manner as Albinsson et al. 1989). HHFAa was found to be a weak quencher compared with acetylacetone and no corrections had to be made in the calculations of the D-values.

5. RESULTS

The obtained β_{mnp} constants are in Table 1 as well as for comparison interpolated literature values (Baes and Mesmer 1986, p.137) recalculated to eq.3 using $pk_w = 13.8$.

As can be seen from Table 1., the hydrolysis is in our experiments much stronger than values obtained with potentiometric methods. However it is unlikely that the stepwise constants are in an increasing order (Mahmood 1988) as in literature values and therefore we conclude that the potentiometric values are very uncertain. On the other hand, our values agree fairly well with those obtained with electrophoresis (Marin and Kinkindai 1969).

In the evaluation of the experiments, formation of mixed complexes $Tm_l(HFAa)_n(OH)_m$ have been neglected. However, the main argument against extraction methods have been that the extraction mechanism has not been fully understood. In order to evaluate the influence of possibly formed mixed complexes $(Tm(HFAa)_n(OH)_p$, we have used literature values obtained with potentiometric methods and fitted the stability constants for all possible mixed complexes. From a rather poor fit (Fig. 3), the obtained stability constants of the mixed complexes seem to be unreasonably high (cf. Table 2.).

Table 1.

Formed species	Cumulative constant	Stepwise constant
$Tm(HFAa)^{2+}$	$\beta_{110}=1.55\cdot10^{2}$	$k_{110}=1.55\cdot10^{2}$
$Tm(HFAa)_2^{+}$	$\beta_{120}=5.47\cdot10^{3}$	$k_{120}=35.2$
$Tm(HFAa)_3$	$\beta_{130}=9.86\cdot10^{4}$	$k_{130}=18\cdot1$
$Tm(OH)^{2+}$	$\beta_{101}=1.70\cdot10^{8}$	$k_{101}=1.70\cdot10^{8}$ $(2.38\cdot10^{5})^{1}$
$Tm(OH)_2^{+}$	$\beta_{102}=9.30\cdot10^{13}$	$k_{102}=5.48\cdot10^{5}$ $(2.51\cdot10^{5})^{1}$
$Tm(OH)_3$	$\beta_{103}=1.11\cdot10^{18}$	$k_{103}=1.19\cdot10^{4}$ $(2.88\cdot10^{4})^{1}$
$Tm(OH)_4^{-}$	$\beta_{104}=5.42\cdot10^{21}$	$k_{104}=4.88\cdot10^{3}$ $(2.40\cdot10^{6})^{1}$

$Tm(HFAa)_{3,org}/Tm(HFAa)_{3,aq}$ $\lambda_3=63$

[1] Values for Yb, Baes and Mesmer, p.137.

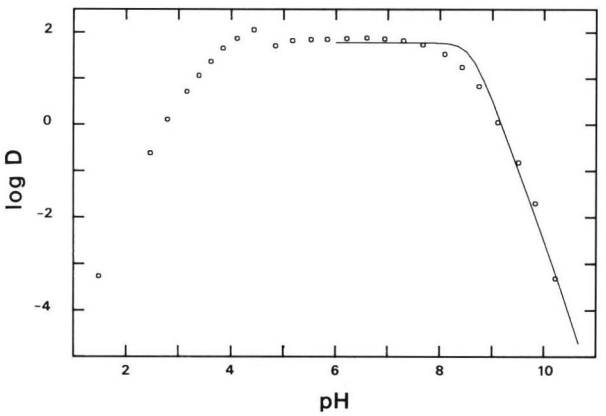


Fig. 3. Distribution ratio D_M of Tm between 1.0 M $Na(H)ClO_4$ and toluene containing 0.10 M HHFAa (circles). The curve is calculated with β_{10p} from Baes and Mesmer and fitted stability constants for the mixed complexes, see Table 2.

From this we conclude that the difference between hydrolysis values obtained with potentiometric methods and extraction methods can not be explained by formation of mixed complexes. It should be noted that the values in Table 2 are of no chemical significance what so ever since they are only a result of mathematical operations.

Table 2.

Formed species	Cumulative constant
$Tm(HFAa)(OH)^+$	$\beta_{111}=5.3\cdot10^6$
$Tm(HFAa)_2(OH)$	$\beta_{121}=4.8\cdot10^7$
$Tm(HFAa)_3(OH)^-$	$\beta_{131}=4.9\cdot10^8$
$Tm(HFAa)(OH)_2$	$\beta_{112}=8.5\cdot10^{11}$
$Tm(HFAa)(OH)_3^-$	$\beta_{113}=4.5\cdot10^{19}$
$Tm(HFAa)_2(OH)_2^-$	$\beta_{122}=7.8\cdot10^1$

6. CONCLUSION

In this paper we have presented a possible way of determining mononuclear hydrolysis constants. Although the obtained values for the stability constants are much higher than literature values, we believe that extraction methods could be of help understanding the mechanisms of hydrolysis.

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EXTRACTIVE RECOVERY OF P-NITROPHENOL FROM ITS MOTHER LIQUOR AND RECIRCULATION TO PRODUCTION

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ABSTRACT

p-Nitrophenol is produced via the sodium salt by reaction of p-nitrochlorobenzene with sodium hydroxide. After the reaction the p-nitrophenol is precipitated with hydrochloric acid. In the following filtration step a mother liquor containing still 0,8 w.-% p-nitrophenol results. The p-nitrophenol can be removed practically completely from the mother liquor by extraction with long chain tertiary amines. Equilibrium data for the system aqueous HCl-tertiary amine - p-nitrophenol, MacCabe Thiele constructions for the countercurrent extraction and a Sankey-diagram of the whole extraction process are given.

INTRODUCTION

p-nitrophenol (PNP) is an important intermediate in the industrial production of pharmaceuticals, dyestuffs and insecticides. On the other hand its a very toxic substance which is practically not degradable in a normal biological waste water purifying plant. According to the German waste water acts it has to be removed from the waste water already at the production unit. In this way not only disturbances in the waste water treatment are avoided but also its overall load of organic pollutants is diminished and a valuable substance (PNP) is recovered.

Generally PNP is produced via the sodium salt by reacting p-nitrochlorobenzene with sodium hydroxide solution (Fig.1). During the reaction, the sodium salt of p-nitrophenol is formed. From the resulting solution the PNP is precipitated by the addition of mineral acid. Afterwards it is separated by filtration. The mother liquor or filtrate contains up to 8000 ppm PNP and 0,8 w.-% of hydrochloric acid. Currently nearly 90 % of the PNP is separated from the mother liquor by extraction with a long chain aliphatic alcohol. The raffinate of the extraction is fed to an activated carbon adsorber where the rest of the PNP is removed from the solution. The purified mother liquor is then directed to the biological waste water purifying plant. The PNP is separated from the alcohol by steam

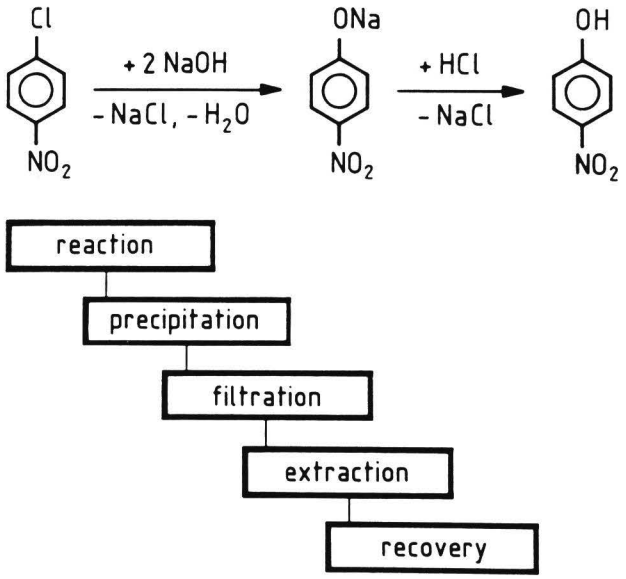


Fig. 1: P-nitrophenol process.

distillation. Afterwards it is recirculated to the precipitation step and the aliphatic alcohol is recirculated to the extraction.

In our investigation of an alternative extraction method we wanted to apply the very high extractive power of tertiary amines for PNP [1], [2]. Using ^{R}Hostarex A 327 from Hoechst AG, a 1 : 1 mixture of trioctyl- and tridecyl amine, we achieved the distribution coefficients (D) shown in Table 1. They range from 300 to 11000 at low concentrations for the extraction of PNP from the mother liquor. The drop of the D-values from 11000 to 7600 in the low concentration range probably shows that the equilibrium was not completely achieved in these experiments.

The high extractive power of the tertiary amine is due to the formation of an amine hydrochloride-water complex which is able to exchange its constitutional water against PNP as shown in fig. 2.

In the case of phenol and sulfuric acid this complex contains 8 molecules of water which are exchanged during extraction against 4 molecules of phenol [3]. The complex may be cleaved again by diluted

TABLE 1

Extractions of p-nitrophenol from its mother liquor using ^{R}Hostarex A 327 at 25 °C.

Concentration Raffinate (ppm)	Extract (mg/g)	D
740	232	310
140	195	1400
47	146	3100
12	73	6100
7.7	76.9	10000
2.7	30.6	11000
1.2	12.0	10000
0.8	6.1	7600

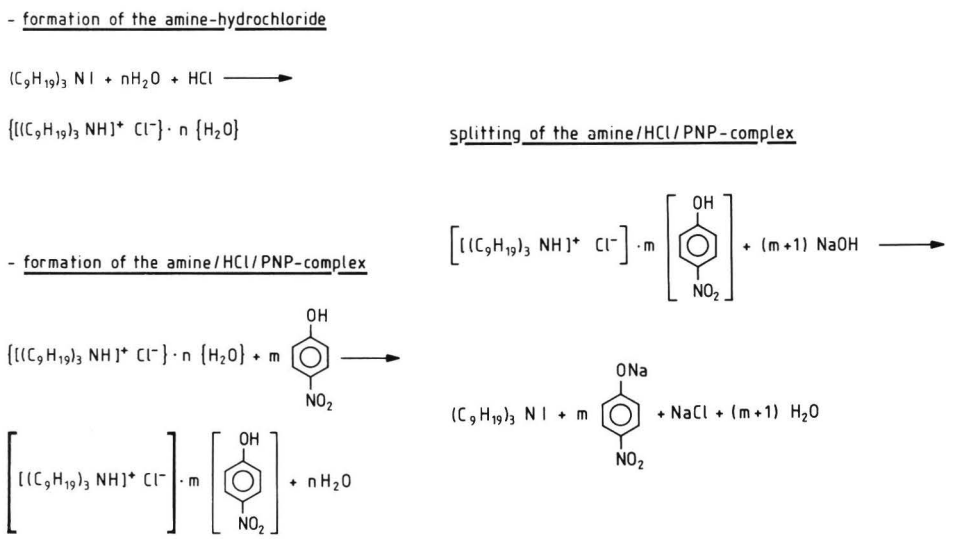


Fig. 2: Possible reaction mechanism of PNP with ^{R}Hostarex A 327.

sodium hydroxide solution in a backextraction step. This is shown in the 3rd reaction equation in fig. 2. The resulting aqueous solution of the sodium salt of PNP is recirculated to the mineral acid-precipitation step in the main PNP process. The gained regenerated ^{R}Hostarex is then directed back to the extraction step.

Fig. 3 shows a comparison of the two systems PNP-mother liquor/n-hexanol and PNP-mother liquor/^{R}Hostarex A 327. On a logarithmic scale the equilibrium lines of both systems are drawn. A MacCabe Thiele construction for a mass phase ratio mother liquor to ^{R}Hostarex A 327 of 22 : 1 is included. Starting from 8100 ppm PNP (not drawn here because of the scale) n-hexanol in two theoretical stages extracts 98.1 % of the PNP. Under the same conditions the extraction with ^{R}Hostarex A 327 results in an extraction efficiency of 98.9 % - however with only one theoretical stage. The construction makes apparent the superior extractive power of the tertiary amine-mixture over the n-hexanol. Under the same conditions as before but with two theoretical stages, the rest-content of PNP in the mother liquor will drop to 0.2 ppm by ^{R}Hostarex extraction. To gain the same result with n-hexanol at least 4 theoretical stages are required.

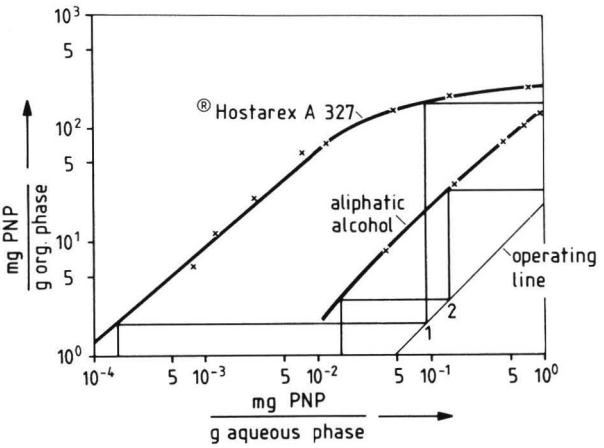


Fig. 3: Determination of the theoretical separation steps.

To check the calculation we performed a 4-stage countercurrent extraction in the laboratory in a Wojtech-mixer-settler unit. Starting from 5900 ppm PNP with 1 part ᴿHostarex A 327 on 32 parts of PNP mother liquor we achieved a residual content of less than 0,1 ppm PNP in the raffinate. After 2 stages the raffinate still contained 7,5 ppm PNP corresponding to an overall stage efficiency [4] of 70 %. The reduced stage efficiency is due to the extreme mass phase ratio and may be improved by applying more ᴿHostarex A 327. However to avoid third phase formation the mass phase ratio may not be less than 1:10.5. Otherwise the HCl content in the mother liquor is not sufficient to transform all the amine into its hydrochloride. Table 2 gives a comparison of the achievable residual content of PNP with 1 and 2 theoretical stages at different mass phase ratios.

TABLE 2

ᴿHostarex-extraction of PNP at different mass phase ratios mother liquor: extracting agent.

stage number (theor.)	residual PNP - content (ppm) at mass phase ratio mother liquor: ᴿHostarex A 327 =		
	10.5:1	21.6:1	32.3:1
1	9.5	32	125
2	< 0.02	< 0.05	0.4

The backextraction of the PNP has to be performed with dilute sodium hydroxide solution. Due to the limited solubility of NaPNP in this solution the sodium hydroxide concentration must not be higher than 0.5 N. To achieve a complete backextraction we found that it is necessary to work with a 2 stage countercurrent extraction. By applying about 103 % of the theoretical NaOH amount only 0,3 % of the PNP will remain in the organic phase. This amount is so low that it does not disturb the recirculation of the extracting agent.

In Fig. 4 the whole mass balance for the extraction/backextraction cycle is shown in the form of a Sankey diagram. About 10 tons of mother liquor per hour are extracted with 298 kg/h of ᴿHostarex A 237. Under these conditions (mass phase ratio) and under the assumption that the extraction is performed in a column with 2

theoretical stages a residual content of 0.4 ppm PNP in the raffinate will result. The extract is then cleaved with diluted sodium hydroxide solution in order to form the NaPNP for the precipitation process with HCl to PNP.

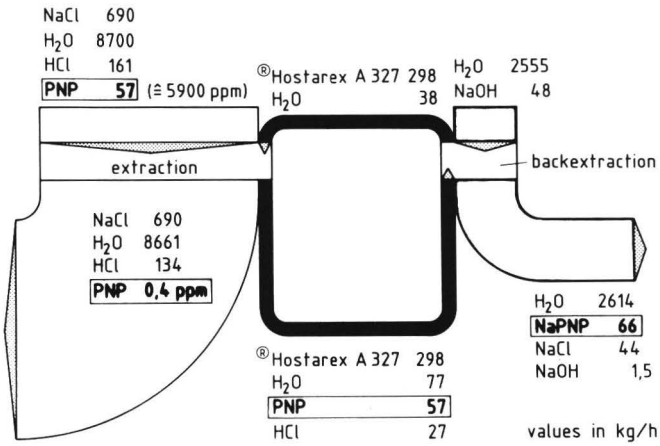


Fig. 4: Sankey-diagram for extraction and backextraction of PNP from its mother liquor at 25 °C. The diagram was computed for a mass phase ratio ®Hostarex: mother liquor = 1:32, 5900 ppm initial PNP-concentration and 2 practical mixer settler stages.

The new extraction-recycling process of PNP has been successfully tested in a pilot plant. For the extraction we used a reciprocating plate column of the Karr-type of a diameter of 25 mm and 2 m length. The mass phase ratio mother liqour to ®Hostarex A 327 was between 10.5 : 1 and 20 : 1.

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SOLVENT EXTRACTION OF MOLYBDENUM (VI) - CATECHOL DERIVATIVE CHELATES WITH AND WITHOUT MALACHITE GREEN

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ABSTRACT

Stoichiometry for the extraction of molybdenum chelates as their acidic forms and their ion associates was studied. The chelates formed between molybdenum (VI) and catechol derivatives were extracted into toluene with and without malachite green. The extraction constants for four catechol derivatives were determined, as well as the acid dissociation constants of molybdic acid in an aqueous medium.

1 INTRODUCTION

Molybdenum (VI) ion is easy to form chelates with such chelating agents as coordinate with oxygen atoms; some of the chelates are well extracted into an organic solvent. As chelating agents, catechol[1,2], catechol violet[3,4], o-nitrophenylfluorone[5], 4-chloromandelic acid[6] have been used. To improve the extractability of the chelates, we synthesized catechol derivatives containing tert-butyl groups, and examined their properties as well as properties of analogous catechols. Of these, 4,6-di-tert-butyl-3-methoxycatechol (DBMC) was recommended for the determination of molybdenum (VI) with malachite green[7]. However, we could not predict the composition of the extracted species on the basis of the coordination number of molybdenum (VI).

In this paper, stoichiometric studies have made to clarify the extracted species by spectrophotometry. The dissociation constant (pKa_3) of molybdic acid has also determined.

2 Experimental

2.1 Apparatus

Spectrophotometric measurements were made on a Shimadzu UV-300

scanning spectrophotometer and a Hitachi 100-10 spectrophotometer. A Hitachi-Horiba F-5 SS pH meter and an Iwaki KM shaker were used.

2.2 Reagents

Standard molybdenum solution (1.00×10^{-3} M). Ammonium heptamolybdate tetrahydrate (Nakarai Kagaku Ltd.) was used. Working solutions were prepared by accurate dilution.

Catechol derivatives: 4,6-di-tert-butyl-3-methoxycatechol (DBMC), 3,5-di-tert-butylcatechol (DBC), 5-tert-butyl-3-isopropylcatechol (BPC) and 5-tert-butyl-3-methylcatechol (BMC). These were synthesized by the same way as in our previous paper[8,9]. These were dissolved in toluene.

Malachite Green (MG) (1×10^{-3} M). Malachite green oxalate (Wako Pure Chemicals Ind. Ltd.) was dissolved in water.

2.3 Procedures

(i) Distribution of molybdenum chelates in the absence of MG

In the further experiments, ionic strength was adjusted to 0.1 M. To a 25 ml of test tube with stopper, transfer 5 ml of 1.00×10^{-5} M molybdenum (VI), a pH-adjusting solution (sulfuric acid or acetate buffer solutions) and ionic strength adjusting solution (sodium sulfate), then make up to 10 ml with water. Shake for 30 min with 5 ml of catechol derivative toluene solution. Determine the concentration of molybdenum (VI) in the organic and/or aqueous phase by the previously reported method[7].

(ii) Distribution of molybdenum chelates in the presence of MG

The procedure was similar to the procedure (i) except in the presence of MG; 0.5 ml of 1.00×10^{-3} M MG solution was added to the aqueous phase.

3 Results and Discussion

3.1 Distribution of molybdenum chelates in an acidic form

The stoichiometry for the extraction of molybdenum chelates was examined. The catechol derivatives are hardly dissolved in water. Hence the distribution equilibrium is presented as follows,

$$H_2MoO_4 + m\ (H_2R)_O \rightarrow (\text{Mo chelate})_O + n\ H^+ + x\ H_2O \qquad (1)$$

where H_2R and $(\ )_O$ denote catechol derivatives and organic phase,

respectively. The extraction constant $K_{E(H)}$ is defined as,

$$K_{E(H)} = [\text{Mo chelate}]_o \cdot [H^+]^n / [H_2MoO_4] \cdot [H_2R]_o^m \quad (2)$$

The distribution ratio of molybdenum (VI) $D_{Mo(H)}$ and a side reaction coefficient of molybdenum α_{Mo} are presented as:

$$D_{Mo(H)} = [\text{Mo chelate}]_o / C_{Mo} \quad (3)$$

$$\alpha_{Mo} = C_{Mo} / [H_2MoO_4] \quad (4)$$

where C_{Mo} is the total concentration of molybdenum in the aqueous phase. From eqns (2), (3) and (4), eqn (5) is derived.

$$\log D_{Mo(H)} = \log K_{E(H)} + m \log [H_2R]_o + n\,pH - \log \alpha_{Mo} \quad (5)$$

Logarithm $D_{Mo(H)}$ is directly proportional to $\log [H_2R]_o$, provided pH and C_{Mo} are kept constant. Figure 1 shows the plots of $\log D_{Mo(H)}$ against $\log [H_2R]_o$ at pH 2.4. The slopes, m, were 3 in all lines for four catechol derivatives.

3.2 Effect of pH and pKa values of molybdic acid

Acid dissociation constants of molybdic acid (pKa) are defined as follows,

$$Ka_3 = [H_2MoO_4][H^+] / [H_3MoO_4^+], \quad Ka_2 = [HMoO_4^-][H^+] / [H_2MoO_4],$$

$$Ka_1 = [MoO_4^{2-}][H^+] / [HMoO_4^-]$$

and, $$\alpha_{Mo} = [H^+]/Ka_3 + 1 + Ka_2/[H^+] + Ka_2 \cdot Ka_1/[H^+]^2 \quad (6)$$

In the region below pKa_3, α_{Mo} can be presented as follows,

$$\alpha_{Mo} = [H^+]/Ka_3 \quad \text{or} \quad \log \alpha_{Mo} = pKa_3 - pH \quad (7)$$

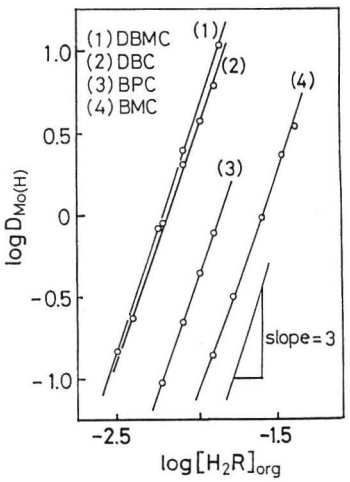


Fig.1 Plots of $\log D_{Mo}$ against $\log [H_2R]_o$ pH, 2.4.

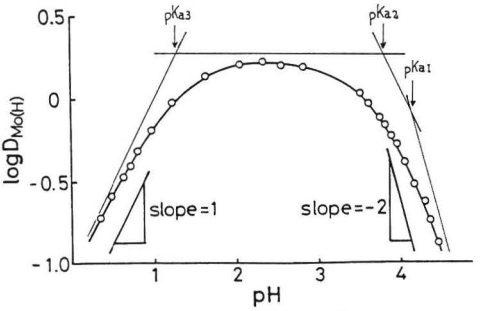


Fig.2 Plots of $\log D_{Mo}$ against pH
$C_{Mo} = 5.00 \times 10^{-8}$ M, $[BPC]_o = 1.60 \times 10^{-2}$ M.

From eqns (5) and (7), under the condition where $\log[H_2R]_o$ is kept constant, the plots of $\log D_{Mo}$ against pH shows straight line with a slope of (n+1). Figure 2 shows the relationship of $\log D_{Mo}$ and pH with 1.6×10^{-2} M BPC toluene solution. In the pH region below pKa_3, the slope can be estimated as 1, which indicates that n is zero. In the pH region above pKa_1, the slope is predicted to be -2 from eqns (5), (6) and the result of n=0. Similarly, in the pH region between pKa_1 and pKa_2, and in that between pKa_2 and pKa_3, the slope is -1 and 0, respectively. Accurate values of pKa and $\log K_{E(H)}$ were determined by using eqns (5) and (6) and by repeating the calculation. The pKa values obtained with DBC and BPC are shown in Table 1.

The acid dissociation constants of molybdic acid in an aqueous solution were also determined by spectrophotometry with UV absorption: the absorbances were measured at 205 or 220 nm 60 min after the preparation of the solution. Figure 3 shows the plots of absorbance against pH. The values obtained by repeated calculation were listed in Table 1. Though the biases of the values of pKa_2 and pKa_1 are larger than that of the value of pKa_3, they are in good agreement with those obtained in the distribution experiment and the reported values. The value of pKa_3 has never been reported. The three kind of pKa_3 values obtained in this work are in good agreement with each other.

TABLE 1 Acid dissociation constants of molybdic acid

	BPC	DBC	Aq.soln. method	Ref.[10]
pKa_3	1.25± 0.03	1.26± 0.03	1.27± 0.03	-
pKa_2	3.80± 0.1	3.81± 0.1	3.71± 0.54	3.61
pKa_1	4.22± 0.1	4.02± 0.1	3.99± 0.89	3.89

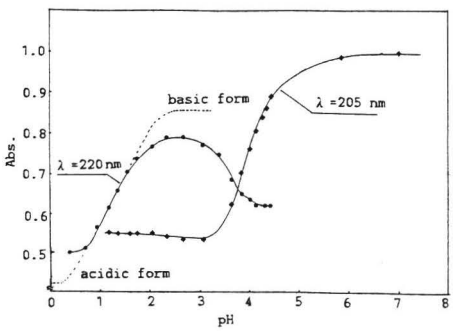


Fig.3 Plots of absorbances against pH for molybdic acid $C_{Mo} = 1.20\times10^{-4}$ M.

The extraction constants, $K_{E(H)}$, were calculated from eq (5). The results were summarized in Table 2.

TABLE 2 Extraction constants of the ion associates

Catechols	log $K_{E(H)}$ *1	log $K_{E(MG)}$ *2	log $K_{E(exCh)}$
DBMC	6.73± 0.04	12.14± 0.19	5.41
DBC	6.64± 0.03	11.49± 0.19	4.85
BPC	5.70± 0.01	11.05± 0.04	5.35
BMC	4.93± 0.03	10.75± 0.08	5.50

*1 Obtained by varying $\log[H_2R]_o$ at pH 2.4.
*2 Obtained by varying $\log[H_2R]_o$ at the constant C_{MG}.

3.3 Extraction constants in the presence of MG

The molar ratio of molybdenum to MG^+ was 1:1 by a molar ratio method, so the distribution equilibrium in the presence of MG is presented as follows:

$$H_2MoO_4 + p\ [H_2R]_o + MG^+ \rightleftharpoons [\text{Ion associate}]_o + q\ H^+ + y\ H_2O \quad (8)$$

$$K_{E(MG)} = [\text{Ion associate}]_o \cdot [H^+]^q / [H_2MoO_4] \cdot [H_2R]_o^p \cdot [MG^+] \quad (9)$$

When distribution ratio, $D_{Mo(MG)}$, α_{Mo}, and side reaction coefficient of MG^+ α_{MG} were taken into consideration, the following equation is derived.

$$K_{E(MG)} = D_{Mo(MG)} \cdot [H^+]^q \cdot \alpha_{Mo} \cdot \alpha_{MG} / [H_2R]_o^p \cdot C_{MG} \quad (10)$$

or

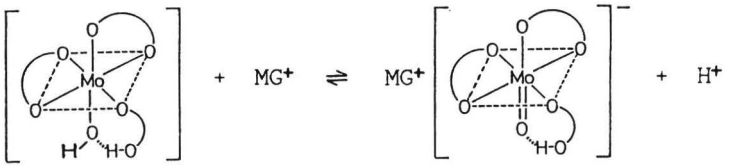
$$\log D_{Mo(MG)} = \log K_{E(MG)} + p\log[H_2R]_o + \log C_{MG} + q\ pH - \log\alpha_{Mo} - \log\alpha_{MG} \quad (11)$$

Logarithm $D_{Mo(MG)}$ is directly proportional to $\log[H_2R]_o$, provided pH are kept constant. The plots of $\log D_{Mo(MG)}$ against $\log[H_2R]_o$ show linear relationship and the slopes of lines for four catechol derivatives were all 3. The effect of pH on the molybdenum distribution was examined at the constant concentration of H_2R by varying the pH from 0.5 to 1. The lines were curved, and these curves were analyzed by the values of α_{Mo} and α_{MG}; the results showed that the value of q was unity. The side reaction coefficient of MG^+ was calculated with the acid dissociation constant of MG which was determined by a common spectrophotometric method, measuring the absorbance at 630 nm in an aqueous solution ($pKa_{(MG)} = 2.62 \pm 0.02$). In Table 2, the extraction constants with MG ($K_{E(MG)}$) are listed.

3.4 The composition of the ion associates

The molar ratios of the molybdenum chelates and MG^+ are 1:1.

Hence, the charge of the chelate must be univalent. Thus the structure of the chelate anion is considered as follows,



Acidic form (HA) anionic form (A^-)

$$K_{E(exCh)} = [MG \cdot A]_o [H^+] / [HA]_o [MG^+] = K_{E(MG)} / K_{E(H)} \quad (12)$$

$K_{E(exCh)}$ is correspond to the cation exchange constant for H^+ to MG^+; the values are also listed in Table 2. As shown in Table 2, the $K_{E(exCh)}$ values are very large. This means that the ion associates are more extractable than the acidic forms and a highly sensitive method of molybdenum determination can be accomplished with MG.

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SISAK - A SOLVENT EXTRACTION TECHNIQUE FOR NUCLEAR AND CHEMICAL STUDIES OF EXOTIC RADIONUCLIDES

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ABSTRACT

The multistage solvent extraction system SISAK is described. The system is used for on-line studies of nuclides with half-lives down to ~1 s. The chemical separation procedures are presented, and the possibility to gain access to nuclides with even shorter half-lives is discussed.

INTRODUCTION

Continuous isolation and measurement of short-lived radioactive nuclides can be achieved by two different methods, on-line mass separation or on-line chemical separation. We chose on-line chemical separation because of an earlier development of liquid flow centrifuges for solvent extraction studies (Rydberg 1969). The method, called SISAK (Short-lived Isotopes Studied by the AKUFVE technique), became operational around 1970. The prototype equipment (Aronsson et al 1974), SISAK 1, was followed by a faster version (Skarnemark et al 1980), SISAK 2. Recently a mini-system (Persson et al 1989), SISAK 3, which is further improved, has been put in operation. This equipment is designed to work with very low liquid flowrates, which will make it possible to feed the effluent from the system directly into an alpha-spectrometric system.

The SISAK method has been used so far for studies of radioactive nuclides of 13 elements. Further measurements on fission products and transactinides are in progress.

2 METHOD

2.1 The SISAK method.

The present experimental set-up comprises four main parts, namely a target/gas-jet system, a degassing unit, a centrifuge battery for rapid solvent extraction processes and a data acquisition system. Fig. 1, taken from Skarnemark et al (1986), shows a typical SISAK set-up.

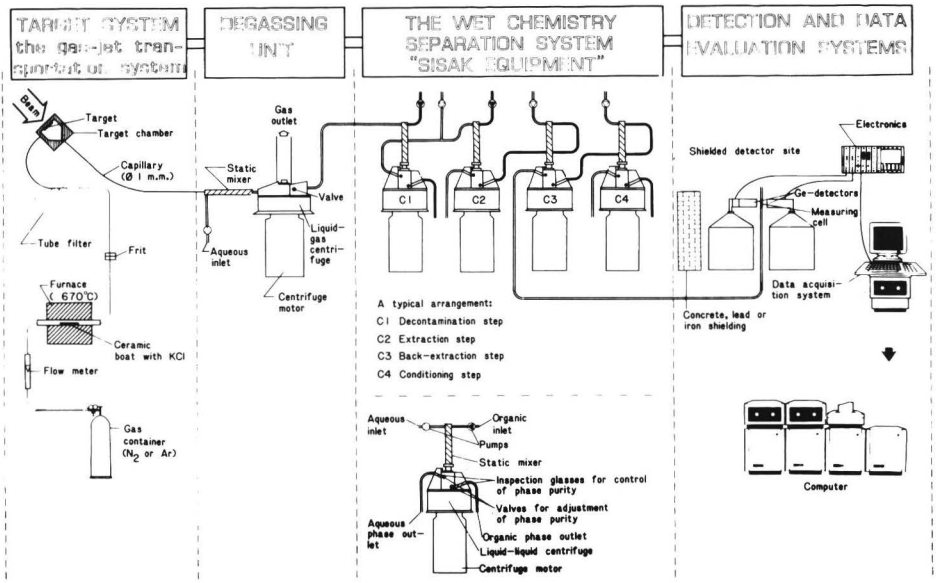


Fig. 1. Schematic drawing of the SISAK system. The different parts of the equipment are not drawn in the correct scale in comparison with each other.

2.2 Target/gas-jet system and degassing unit

For most investigations the SISAK equipment has been used in combination with the gas-jet system (Stender et al 1980) at the Mainz reactor. In this system the fission products recoil out of a thin target. The fission products are thermalized in a pressurized gas in the target chamber, attached to aerosol particles ("clusters") and transported through a capillary out of the irradiation site. The fission products are dissolved in a liquid phase (so far always an aqueous phase) in a static mixer. The mixture of gas and liquid is then fed into a centrifuge designed for gas/liquid separations (Brodén et al 1982). The latest version of this centrifuge (cf. Fig 2) has a hold-up volume of ~0.1 mL, and a maximum liquid flowrate of about 3 mL/s. The degassing efficiency has been measured to be better than 99.5%.

2.3 Chemical separation equipment

The solution leaving the degassing unit is pumped to the centrifuge battery which consists of 1-4 H-centrifuges, depending on the number of extraction steps necessary to obtain a radiochemically pure fraction of the element under investigation. The H-centrifuge is a specially designed

liquid flow centrifuge with the unique ability of absolute phase separation, i.e., under normal running conditions none of the outgoing phases contains more of the other phase than given by their mutual solubilities. The latest version of the equipment, SISAK 3, is based on a centrifuge designated H-0.3 (cf. Fig 2), with only 0.3 mL internal volume and a maximum flowrate of ~3 mL/s per phase, i.e., a minimum hold-up time of only 0.1 s.

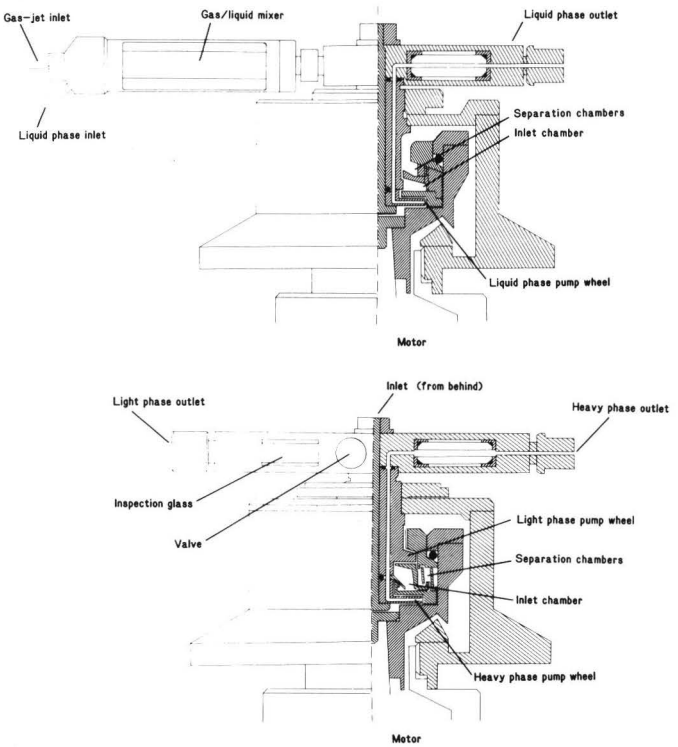


Fig. 2. The HG-0.1 degassing unit (above) and the H-0.3 centrifuge (below)

The aqueous and organic phases are mixed in the Y-formed inlet tube of the centrifuge. A prerequisite is, however, that the extraction is fast enough. If not, the phases have to be mixed in a static mixer before entering the centrifuge. The phase outlets have throttle valves to maintain a proper pressure balance in the centrifuge; this balance is essential to maintain absolute phase separation. The centrifuges are made of palladium passivated titanium, which make them resistant against most acids. The normal speed is 25-35,000 rpm.

All equipment belonging to the wet-chemistry part of the system is made of titanium, PTFE (polytetrafluoroethylene), PVDF (polyvinylidene fluoride), Kel-F (polychlorotrifluoroethylene)

or polyethylene to obtain good chemical resistance.

2.4 The data acquisition system

The data acquisition system comprises standard equipment for γ-ray spectroscopy.

2.5 Chemical separation systems

Chemical separation systems have so far been developed for 13 elements (Skarnemark et al 1986, 1990). These separation procedures are sketched in Fig. 3.

3 RESULTS

The nuclear decay studies performed so far with the SISAK method have been concentrated to two element regions, namely the neutron-rich light lanthanides and the neutron-rich isotopes of Tc, Ru, Rh and Pd. These groups of elements are situated in transition regions between spherical and deformed nuclear shape. Studies of ^{88}Br, ^{243}Np and ^{244}Np have also been carried out (Skarnemark et al 1986, 1990).

4 DISCUSSION

A salient question arising in connection with a fast separation technique like SISAK is the potentiality with respect to the time from production to detection, and whether this transport time can be shortened to give access to nuclides with half-lives considerably below the present limit at ~0.8 s.

One important limiting factor governing the shortest possible hold-up time is the mass transfer in the mixing of the two phases. The rate of this mass transfer depends on parameters such as chemical kinetics, interfacial tension, presence of surface active substances, droplet size, temperature and concentration of extractant. The smaller the droplets, the shorter can the hold-up time in the mixer be. Another factor is the time available for the droplets to coalesce in the separation chamber. The time necessary for coalescence depends on the speed of rotation of the centrifuge, the viscosity of the two solutions, the droplet size distribution, and the centrifuge dimensions. The smaller the droplet size, the longer time must they spend in the centrifuge to coalesce. Thus one should avoid mixing the phases too intensively. Since fast mass transfer requires small droplets and fast coalescence larger ones, there is an optimizing problem with several parameters involved which, in many cases, counteract. The requirements of efficient mass transfer and phase separation makes it difficult to go below 0.1 s in contact and separation time per extraction step. Using 1, 2 and 3 centrifuges, respectively, measurements with the SISAK 3 system, by which the reactor was operated in the pulse mode, showed that the activity appea-

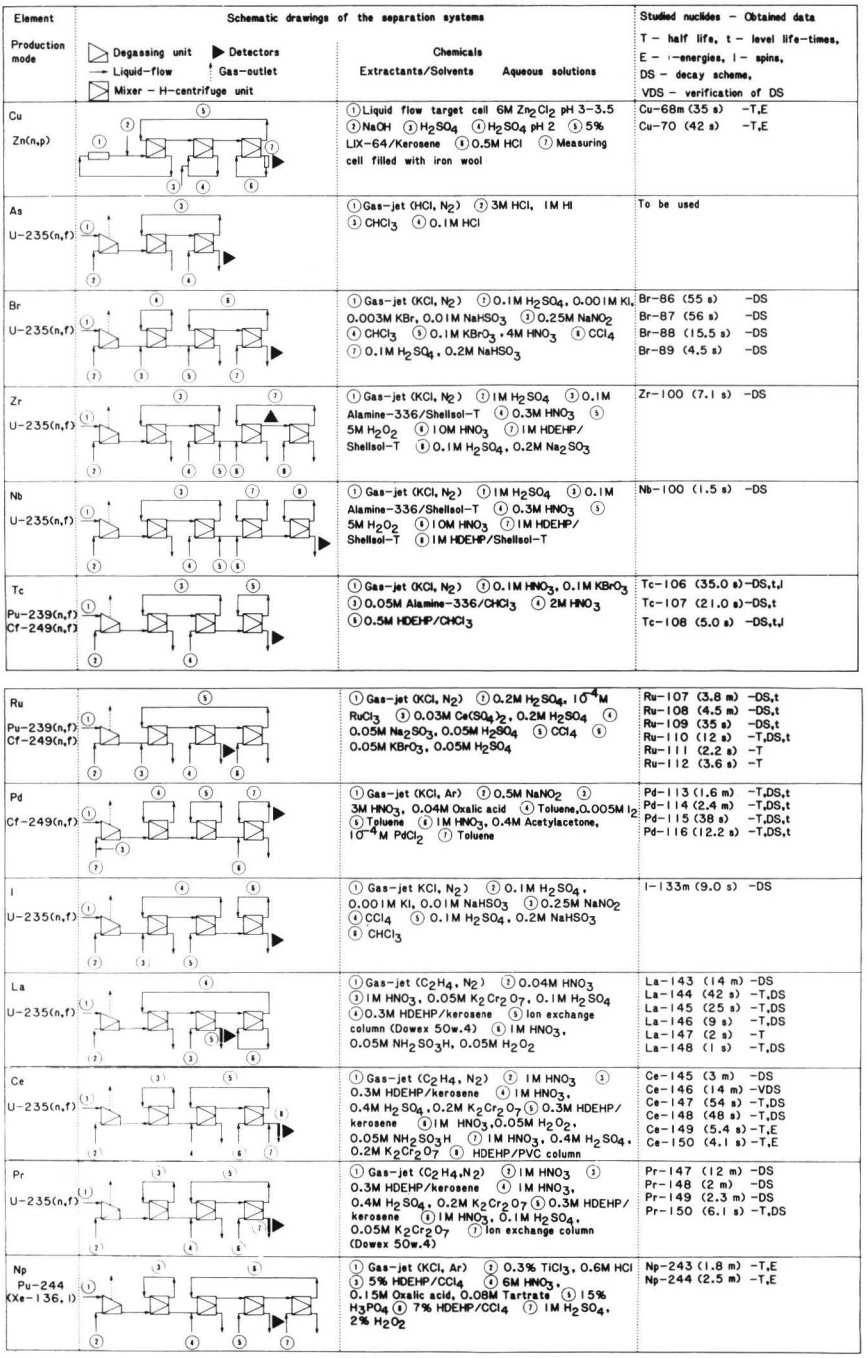


Fig. 3. Chemical separation procedures of the SISAK system as available in 1990.

red at the detector site after 1.6, 1.9 and 2.2 s. This means a minimum hold-up time of 0.3 s per step including the transport time through tubes, valves and connectors, thus resulting in a hold-up time in the H-0.3 centrifuge itself close to the limit of 0.1 s. According to Persson et al (1990) more actual values for the hold-up time with 1, 2 and 3 centrifuges are 1.9, 2.6 and 3.6 s, respectively, which refer to the time when the countrate of the liquid passing the detector reaches half of its maximum value.

A problem when developing chemical separation systems for SISAK experiments is the need for fast solvent extraction kinetics. If running without mixers the phase contact time is only 10-40 ms. Under ideal conditions solvent extraction can be a fast process; a measured value for the transfer of nitric acid from water to tributylphosphate (TBP) is 12 ms (Lunes and Wishow 1958). Nevertheless this time is close to the contact time available in the SISAK 3 system, and it is obvious that it is necessary to choose systems with rapid chemical kinetics (e.g. extraction of species like Br_2, AsI_3 or RuO_4 into the organic solvent) or where the distribution ratio is high enough for extracting a sufficient amount of the activity, even if the extraction is terminated under non-equilibrium conditions. Although many common reagents and standard extraction procedures cannot be used, slow kinetics have not hindered the development of a SISAK separation procedure. The experience shows that chelate, e.g. β-diketonate, extraction usually is too slow for the SISAK technique, while liquid ion exchange, e.g. with amines and complex formation ny organophosphorous acids in most cases show acceptable fast kinetics. The influence of slow kinetics can sometimes be circumvented by preforming a carrier compound which undergoes a fast isotopic exchange. Elevated temperature of the liquids is also important to speed up extraction as well as oxidation/reduction processes.

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APPLICATION OF LASER INDUCED PHOTOACOUSTIC SPECTROSCOPY SYSTEM TO THE DETERMINATION OF TRANSURANIC ELEMENTS

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ABSTRACT

The analytical system of laser induced photoacoustic spectroscopy (LIPAS) has been developed for transuranic elements (TRU) ions in plutonium uranium recovery extraction (PUREX) process. The present LIPAS system is based on a YAG laser driven dye laser and flow type cell with piezoelectric transducer (PZT) for signal detection.

The system was applied to analyze Np(V) in nitric acid. In order to protect PZT from corrosion, the surface of PZT was coated with poly-vinyl chloride. The detection limit absorptivity was found to be $3.59 \times 10^{-5} cm^{-1}$ which is two orders lower than that of spectrophotometry. The detection limit concentration is $1.78 \times 10^{-6} M$.

The intensity of the PA signal is strengthened by increasing uranium concentration. The calibration curve of Np(V) in the presence of uranium agrees well with the curve of Np(V) without uranium by multiplying the specific heat of solution. The detection limit concentration is $2.51 \times 10^{-6} M$, which is about 0.005 times the neptunium concentration of PUREX propcess' the feed solution. This value indicates that the LIPAS system has the potential to detect Np(V) ions in PUREX process.

1 INTRODUCTION

Selective analysis of transuranic elements (TRU) ions of each chemical state at a low concentration is important to understand and predict the behavior of these elements in the process of spent fuel treatment and in the environment. Laser induced photoacoustic spectroscopy (LIPAS) is a newly developed method which has a potential for selective analysis of TRU ions. The analysis of the TRU species has been demonstrated by Stumpe and others.[1] We successfully applied this method to analyze Np(V) ions in 3M HNO_3 aqueous solution with and without uranium. Aiming at the development of a new in-line analytical technique, experiments of Np(V) analysis were conducted using a flow type cell manufactured for the present study.

2 PRINCIPLE OF LIPAS

The photoacoustic process is based on the phenomena of energy conversion from an excitation laser beam via non-radiative relaxation of the excited

species. The excitation beam is irradiated intermittently, then the heat distribution from the excited species fluctuates periodically. This fluctuation causes a periodical thermal expansion of the medium and generates an acoustic or thermoelastic wave which causes the photoacoustic(PA) signal.[2][3]

Kitamori[3] proposed a formula to estimate the magnitude of the PA signal <P> as follows,

$$\langle P\rangle = \frac{\beta}{Cp} \cdot \frac{V}{2\pi\,(r_0\, r)^{1/2}} \cdot \frac{E}{\tau} \cdot \alpha(\lambda), \qquad (1)$$

$$\alpha(\lambda) = \varepsilon(\lambda)\cdot C, \qquad (2)$$

where β is the coefficient of isothermal expansion; Cp is the specific heat at constant pressure; V is sound velocity in the medium; r_0 is the radius of a laser beam; r is the distance between the beam center and detection point; E is the laser pulse energy; τ is the pulse width of laser beam; $\varepsilon(\lambda)$ is the molar absorption coefficient at wavelength λ ; C is concentration of the species.

Because the magnitude of the PA signal <P> is proportional to E, highly sensitive analysis is possible in principle by using an intensive laser beam. However, too intensive laser beams can generate multiphoton reactions, light-induced gas evolution, and chemical reactions which cause undesired photoacoustic signals.

3 EXPERIMENT

3.1 *Preparation of the sample*[4]

Neptunium solution was prepared by dissolving NpO_2 powder of α -purity 97.62% in nitric acid. The valency of Np(V) was adjusted by an electrolytic method and stabilized by adding nitrous acid. The absorption peak at 617nm was applied for the present study. The highest peak of Np(V) at 979.8nm was not used because the absorption of water interferes in the range as shown in Fig.1.

3.2 *Experimental system of LIPAS*

A block diagram of the experimental system is shown in Fig.2. The YAG laser driven dye laser is used as the excitation beam source. The excitation beam is divided into two beams by a beam splitter. One is detected by a photodiode and averaged to measure the laser power and its fluctuation. The signal of the photodiode is used as the trigger for the digital storage oscilloscope to synchronize with the laser emission. The other beam is led to the PA cell, and PA signals detected in the cell are amplified and filtrated. Filtrated signals are averaged by the digital storage oscilloscope and divided by the

above-mentioned average laser power to normalize the PA signal.

A flow type cell manufactured for the present study is shown in Fig.3. A piezoelectric transducer(PZT) is applied to detect the PA signal. In the Np(V) analysis, the surface of PZT is coated with poly-vinyl chloride to protect from corrosion by nitric acid. The whole cell is shielded in a stainless steel container to eliminate the noise which is generated by electromagnetic and mechanical disturbances.

4 RESULTS AND DISCUSSION

4.1 *Analysis of Np(V) in 3N nitric acid*

In order to protect PZT from corrosion by nitric acid, the surface was coated with poly-vinyl chloride. Noise caused by corrosion was eliminated.

The calibration curve of Np(V) shows a clear linearity in the concentration range of 10^{-5} to 10^{-7}M as shown in Fig.4. The detection limit concentration defined by $2\sigma/S$ was estimated from the data and tabulated in the column of no uranium in Table 1, where σ is standard deviation and S is slope of the calibration curve. This definition has been reported by Long and others.[5] and authorized by IUPAC. The product of the detection limit concentration and the molar absorption coefficient is the detection limit absorptivity, which is

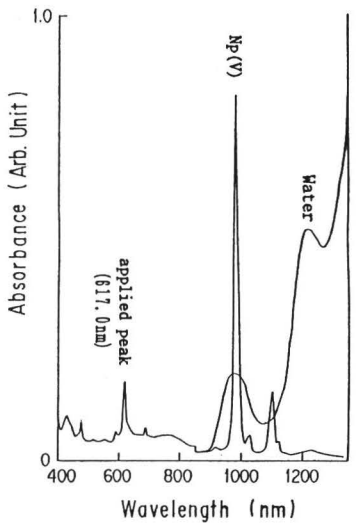


Fig.1 Absorption spectrum of Np(V) and Water

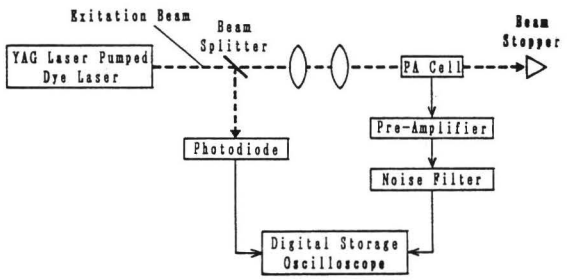


Fig.2 Experimental system of LIPAS

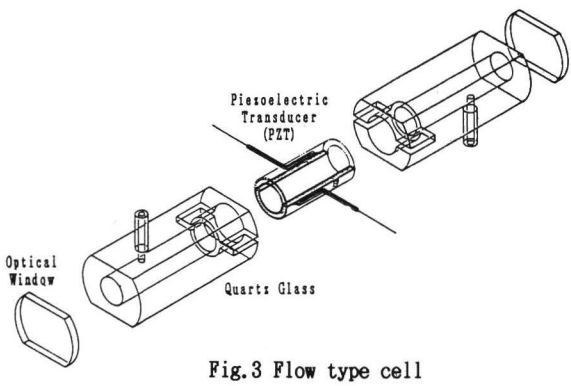


Fig.3 Flow type cell

useful to compare the performance among different analytical systems. The detection limit absorptivity was found to be $3.41 \times 10^{-5} cm^{-1}$, which is two orders lower than that of spectrophotometry, and the detection limit concentration is $1.78 \times 10^{-6} M$. In spite of the smaller value of the molar absorption coefficient by one order at 617nm, the value of the detection limit concentration at the wavelength is one order lower than that of spectrophotometry at 979.8nm. This means LIPAS method is very effective to analyze Np(V) at a low concentration. The calibration curve obtained is expressed by the least squares method as follows,

$$<PA>=3.72 \times 10^{3} \cdot C + 1.71 \times 10^{-1}, \quad (3)$$

where <PA> is intensity of PA signal [Arb. Unit]; C is Np(V) concentration [M].

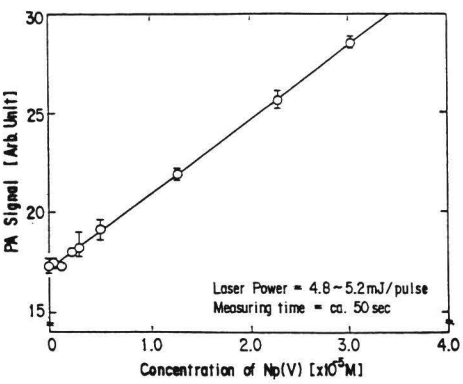


Fig.4 Calibration curve of Np(V)

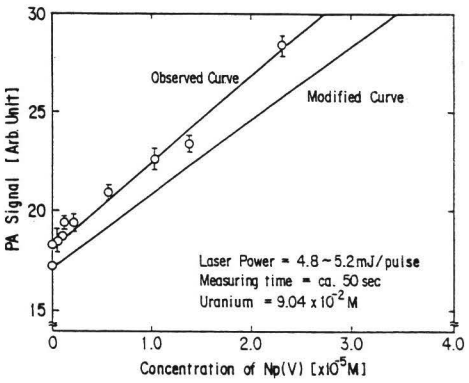


Fig.5 Calibration curve of Np(V) in the presence of uranium

Table 1 Comparison of detection limit of Np(V)

Analytical Method	Spectrophotometry		LIPAS	
Wavelength [nm]	979.8	617.0	617.0	617.0
Sample	no uranium	no uranium	no uranium	with uranium
Molar Absorptivity ε [$M^{-1} \cdot cm^{-1}$]1)	225.15	19.15	19.15	19.15
Slope of Calibration Curve S [M^{-1}]	2.20×10^{2}	1.91×10^{1}	3.72×10^{3}	3.76×10^{3}
Standard Deviation σ	2.54×10^{-3}	1.64×10^{-3}	3.32×10^{-3}	4.72×10^{-3}
Detection Limit Concentration C_L [M]2) (k=2)	2.30×10^{-5}	1.71×10^{-4}	1.78×10^{-6}	2.51×10^{-6}
Detection Limit Absorptivity α_L [cm^{-1}]3)	5.19×10^{-3}	3.28×10^{-3}	3.41×10^{-5}	4.81×10^{-5}

1)Calculated from absorption data, 2) $C_L = k \times \sigma / S$, 3) $\alpha_L = C_L \times \varepsilon$

4.2 *Analysis of Np(V) in the presence of uranium*

The linear calibration curve was obtained as shown in Fig.5. The curve is expressed by

$$<PA>=4.34 \times 10^{-5} \cdot C + 1.81 \times 10^{-1}. \quad (4)$$

No absorption of uranium was observed in the range near 617nm, nevertheless, the intensity of PA signals detected in this case was bigger than that without uranium. Equation (1) expresses that PA signals are inversely proportional to the specific heat Cp. The Cp of uranium solution decreases by increasing uranium concentration.[6] The PA signals of uranium solution without Np(V) ions at 617nm are proportional to the uranium concentration as shown in Fig.6. The modified calibration curve of Np(V) in the presence of uranium, formed by multiplying the Cp of solution, was found to agree well with calibration curve of Np(V) in the absence of uranium. Equation (4) is modified by multiplying the Cp of solution as follows,

$$<PA>=3.72 \times 10^{-5} \cdot C + 1.71 \times 10^{-1}. \quad (5)$$

The detection limit concentration is 2.51×10^{-6}M nearly equal to that in the absence of uranium as shown in Table 1. This value is approximately 0.005 times the neptunium concentration of feed solution in PUREX process. It was indicated that the LIPAS system has the potential to detect Np(V) ions selectively in the process.

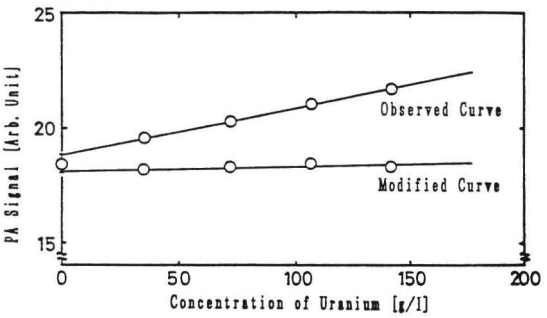


Fig.6 Influence of uranium at 617nm

4.3 *Photoacoustic spectrum of Np(V)*

In principle the PA spectrum is almost the same as the absorption spectrum, however, the PA spectrum measured is broader than the absorption spectrum in the range of 600 to 630nm as shown in Fig.7. The solvent's PA signal is considered to broaden the PA spectrum. The double cell system instead of the present single cell system is needed to exclude the solvent's influence. Despite the solvent's interference, a clear peak of the PA spectrum was observed for the present system.

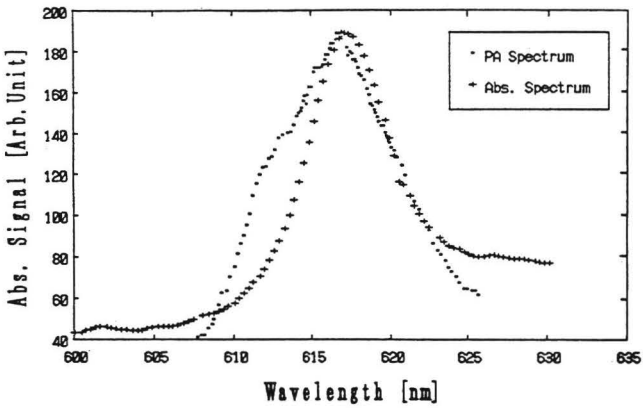


Fig.7 Photoacoustic spectrum and absorption spectrum of Np(V)

5 CONCLUSIONS

The analytical system of laser induced photoacoustic spectroscopy(LIPAS) has been studied in order to develop in-line analysis technology for TRU ions in PUREX process. The conclusions are summarized as follows;

(1)The detection limit absorptivity was $3.41 \times 10^{-5}cm^{-1}$, which is two orders lower than that of spectrophotometry.

(2)By adding uranium, the intensity of PA signals were found to be strengthened following with the decreasing of the specific heat Cp of the solution. By multiplying the specific heat, the calibration curve of Np(V) containing uranium agreed well with that of Np(V) without uranium. The detection limit concentration was $2.51 \times 10^{-6}M$, approximately 0.005 times the neptunium concentration of the feed solution of PUREX process. This value indicates that the LIPAS system has potential to detect Np(V) ions in PUREX process.

(3)The PA spectrum measured was broader than the absorption spectrum because of the influence of the solvent. Even so, a clear peak of the PA spectrum was observed for the present system.

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A STRUCTURAL CONSIDERATION OF IONIC SPECIES AND SOLVENTS FOR ION-PAIR EXTRACTION

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ABSTRACT

Cationic and anionic complexes of cobalt(III) and Pd(II) with pyridylazoaminophenols were studied with special interest for use as counter ions for the extraction of ionic species. These complex ions are inert and intensely colored, and form extractable ion-pairs with oppositely charged large ions such as ionic surfactants. The effects of structure and shape of the ions and solvent molecules on the extractability of the ion-pairs were studied by measuring the extraction constant $K_{ex} = [C^+A^-]_o/[C^+][A^-]$, where C^+ and A^- represent a cation and anion respectively, and C^+A^- represents an ion-pair. Introduction of hydrophobic substituents such as methyl and halogen groups to the ligand increases the extractability. Surfactant ions with longer alkyl chain are more extractable. The value of K_{ex} is larger for extraction systems comprising oppositely charged planar ions and a planar solvent than for the combination of non-planar ions and non-planar solvent, indicating specific intermolecular hydrophobic interactions between the ion-pair and the solvent.

1 INTRODUCTION

The term ion-pair extraction refers to the process by which an ionic species is extracted into organic solvent as the ion-pair with a proper counter ion. Ion-pair extraction is known as one of the simplest methods used for the separation and determination of colorless ionic species such as anionic and cationic surfactants in water. We have proposed a series of inert complexes of cobalt with pyridylazoaminophenols for use as counter ions for the extraction and spectrophotometric determination of anionic or cationic surfactants in water(Taguchi et al,1981, Kasahara et al, 1986,1989). They are quite inert and can be used over a wide range of pH's. Unfortunately, however, the selectivity of ion-pair extraction is usually poor.

Recently we proposed mixed-ligand complex of palladium(II) with a sulfonated pyridylazoaminophenol and a chloride ion as the second ligand for use as counter ions for the extraction of cationic species. In contrast to the spherical geometry of cobalt complexes, the palladium complex has a planar configuration. The present investigation was undertaken to compare the extractabilities of these two different kinds of complex ions in the hope of

gaining information about the geometrical factors governig the extractability of ion-pairs and improving the selectivity of ion-pair extraction.

2 EXPERIMENTAL

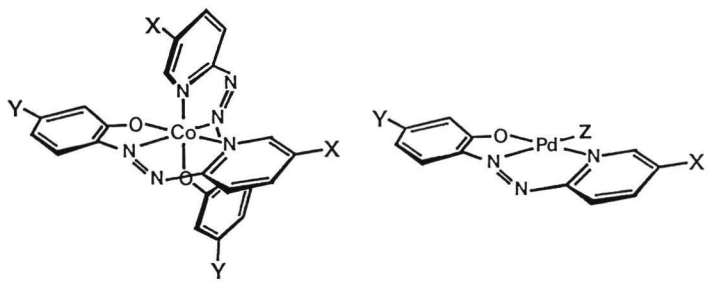
2.1 Apparatus

Hitachi Model U-3200 and 340 double-beam recording spectrophotometers with matched 10 mm quartz cells were used for measurements of absorbance and absorption spectra. The pH was measured with a Toa Electronics Model HM-12H pH meter with a combination glass electrode. A Taiyo-kagaku Type SR-II reciprocal shaker was used for equilibrating the aqueous and organic phases. A Hitachi Model SCT5BB centrifuge was used for phase separation.

2.2. Reagents

Solutions of the derivatives of bis[2-(2-pyridylazo)-5-amino) phenolato]cobalt(III) chloride $[Co(5\text{-}X\text{-}PADAP)_2]^+$ and sodium bis[2-(5-bromo-2-pyridylazo)-5-(N-propyl-N-sulfopropylamino) phenolato]cobaltate(III) $[Co(5\text{-}Br\text{-}PAPS)_2]^-$ were prepared as described earlier. The abbreviations and structure of these complexes are as follows.

Abbreviation	Y	X
$[Co(X\text{-}PADAP)_2]^+$	$N(C_2H_5)_2$	5-H,5-Cl,5-Br,5-CF_3,5-NO_2
		3-CH_3,4-CH_3,5-CH_3,6-CH_3
		3,5-diCl, 3,5-diBr, 4,6-diCH_3
$[Co(X\text{-}DMPAP)_2]^+$	$N(CH_3)_2$	5-H,5-Cl,5-Br
$[Co(X\text{-}PAAP)_2]^+$	NH_2	5-Cl
$[Co(5\text{-}Br\text{-}PAPS)_2]^-$	$N(C_3H_7)(C_3H_6SO_3^-)$	5-Br
$[Pd(5\text{-}Br\text{-}PAPS)Cl]^-$	$N(C_3H_7)(C_3H_6SO_3^-)$,	X = Br, Z = Cl



(a) (b)

Fig.1. Structure of complex ion

The long chain n-alkyltrimethylammonium ions are expressed hereafter as C_n-TMA^+, where n is the number of carbon atoms in the alkyl chain.

Organic solvents were saturated with water before use. All reagents and materials were of analytical-reagent grade and were used as received.

2.3 Measurement of extraction constant

For the equilibrium between organic phase and aqueous phase, extraction constant, K_{ex} , is defined as

$K_{ex} = [C^+A^-]_o / [C^+][A^-]$ (Eq.1)

where C^+ and A^- stands for a cation and an anion respectively, and C^+A^- denotes an ion-pair. Brakets with and without subscript "o" indicate concentrations in the organic and aqueous phases, respectively.

The distribution coefficient of ion-pair, K_D, is given by

$K_D = [C^+A^-]_o / [C^+A^-]$ (Eq.2)

The distribution ratio of a cation or an anion, D, is defined as

$D = [C^+A^-]_o / ([C^+] + [C^+A^-])$ or

$D = [C^+A^-]_o / ([A^-] + [C^+A^-])$ (Eq.3)

Combination of Eqs 1 - 3 leads to

$1/D = 1/K_{ex} \times 1/[A^-] + 1/K_D$ or

$1/D = 1/K_{ex} \times 1/[C^+] + 1/K_D$ (Eq.4)

A plot of 1/D against $1/[A^-]$(or $1/[C^+]$) gives a straight line. Values of K_{ex} are calculated from the slopes of the straight lines.

3 RESULTS AND DISCUSSION

3.1 Structure of complex ions

Two molecules of pyridylazoaminophenols coordinate to a cobalt ion to form a large, univalent complexes of the meridional type. The complexes are either cationic or anionic, depending on the substituents on the pyridylazoaminophenol. These univalent complexes are inert and intensely colored. The shape of the complexes are three demensional(nearly spherical) as shown in Fig.1.

Palladium(II) reacts with one molecule of sulfonated pyridylazoaminophenol and a halogenate ion to form mix-ligand anionic complexes having a planar configuration.

3.2 Effect of substituent on the extractability of complex ion

Extractabilities of cobalt complexes with substituted and

unsubstituted 2-(2-pyridylazo)-5-diethylaminophenols(PADAP's) were studied. Several PADAP's having substituents at position 5 of the pyridine ring (see Fig.1) were synthesized, and complexed with cobalt. The substituents studied are : H, Cl, Br, CH_3, CF_3, NO_2 . Cobalt complexes with 3,5-diCl, 3,5-diBr and 4,6-diCH_3 derivatives were also studied. The sequence of extractability of complex ions was 5-NO_2 $\cong$ 5-H < 5-CH_3 < 5-Cl < 5-Br < 5-CF_3 < 3,5-diCl < 4,6-diCH_3 < 3,5-diBr derivative. A study of the extractability of the cationic cobalt complexes with 5-Cl-pyridylazoaminophenols with different substituent at position 5 of the phenol group gave the sequence of extractabilities: NH_2 < $N(CH_3)_2$ < $N(C_2H_5)_2$. As expected, introduction of hydrophobic groups, such as methyl and halogen groups increases the extractability of the complex ion. Substitution at positions 3 and 5 has more pronounced effects on the extractability of the complex cations. The complex cation having alkylated amino group was more extractable. The effect of the position of substitution on the extractability was studied by comparing the extractabilities of cobalt complexes with PADAP's having a methyl group at positions 3,4,5 and 6 of pyridine ring. A complex cation formed with 3-CH_3-PADAP is more extractable than those with substituents at other positions. This may be an indication for the the steric effect of methyl group on the hydration of the complex cations.

3.3 Alkyl-chain length of ion and the extractability

In ion pair extraction, large ion is more extractable than small one when they have the same charge. The extractability of ion increased with increasing aklyl chain length of alkylsulfonate or alkyltrimethylammonium ions. Plots of log Kex against the number of carbon atoms of counter ions, alkyl sulfonate or alkyltrimethylammonium ions, give a straight line with a slope of 0.5 - 0.7 and 0.4 - 0.6 respectively.

3.4 Effect of the structure of ion and solvent on the extraction of ion pair

Table 1. shows the result of comparison of the extractability of complex anion and organic dye anion when using decyltrimethylammonium ion ($C_{10}TMA^+$) as a counter ion. 7-Iodo-8-hydroxyquinoline-5-sulfonate(Ferron$^-$) and Thymol Blue(TB^-) are plane type monovalent anion. Plane type anions, Ferron$^-$, TB^- and [Pd(5-Br-PAPS)Cl]$^-$, were extracted with $C_{10}TMA^+$ as counter ion by aromatic

solvents. The values of log K_{ex} for $[Co(5\text{-Br-PAPS})_2]^-$ were greater than Ferron$^-$ when extracted with chloroform, dichloromethane and 1,2-dichloroethane but cobalt complex anion was not extracted with aromatic solvents or tetrachloroethane, 1,1,1-trichloroethane, tetrachloroethylene, trichloroethylene under the presence of large alkyltrimetylammonium ion. $[Co(5\text{-Br-PAPS})_2]^-$ was extractable with the solvent which has the structure -C(Cl)H in the molecule. This phenomenon may show the necessity of intermolecular hydrogen bond between cobalt complex anion and solvent for ion-pair extraction when $[Co(5\text{-Br-PAPS})_2]^-$ is used as counter ion. Tetrachloromethane is known as one of the poorest solvent for the extraction of ion-pairs, but tetradecylbenzyldimethylammonium ion(Zephiramine, $Zeph^+$) is easily extracted into this solvent if planar $[Pd(5\text{-Br-PAPS})Cl]^-$ is used as a counter ion.

Table 2. shows the values of extraction constant for the ion-pair extraction systems, cobalt complex cation/dodecylsulfate or dodecylsulfonate/aromatic solvents. As is clear from the values of log K_{ex} shown in Table 2., extracting abilities of solvents decreases in the order: benzene > toluene > o-xylene > mesitylene and benzene > toluene > ethylbenzene > cumene for each anion.

The sequence clearly indicates that the extracting ability of substituted benzenes decreases with increasing number of methyl groups on the benzene ring or with increasing bulkiness of the substituent. Difference between the abilities of substituted benzenes are much smaller for the extraction with Crystal Violet and other planar triphenylmethane type cations. Since there are little differences in dielectric constant between these substituted benzenes, steric factors governing the solvation of the ion-pair and hydrophobic interactions due to π-electrons on the benzene ring may play important roles in determining the extracting ability of substituted benzenes. The values of K_{ex} in Table 2. are usually larger for combination of planar ion and planar solvent than for combination of non-planar ions and non-planar solvent. This indicates specific intermolecular hydrophobic interactions between the ion-pair and the solvent.

4 CONCLUSION

Cobalt and palladium complexes of pyridylazoaminophenol derivatives have excellent characteristics for use as counter ions for the extraction of ionic species. They are inert and intensely colored. Their extractability is controllable over a

wide range by substitution on the ligand.

Extraction constants are greater for the extraction system, planar cation/planar anion than for the system, non-planar cation/non-planar anion,indicating specific intermolecular hydrophobic interactions between the ion-pair and solvent.

TABLE 1
Extraction constants for extraction with $C_{10}TMA^+$ as a counter ion

Solvent	benzene	chloro benezene	1,2-dichloro benezene	$CHCl_3$	CH_2Cl_2	CH_2ClCH_2Cl
$Ferron^-$	<1.0	1.4	1.9	3.2	3.9	3.7
$T\ B^-$	2.9	3.1	3.3	5.4	5.8	5.1
$[Co(5\text{-}Br\text{-}PAPS)_2]^-$	- -	- -	- -	4.6	5.0	4.2
$[Pd(5\text{-}Br\text{-}PAPS)Cl]^-$	3.2	3.6	3.9	+ +	+ +	+ +

- - : not extracted
+ + : extracted with Na^+ as a counter ion

TABLE 2
Extraction constants (log K_{ex}) of different extraction systems

Anion	Dodecylsulfate		Dodecylsulfonate	
Cation	$[Co(5\text{-}Me\text{-}PADAP)_2]^+$	CV^+	$[Co(5\text{-}Me\text{-}PADAP)_2]^+$	CV^+
Solvent				
Benzene	6.1	>6.0	4.6	5.4
Toluene	5.6	6.0	3.9	4.8
Ethylbenzene	5.6	5.9	3.8	4.7
Cumene	4.3	5.3	<2.5	3.9
o-Xylene	5.4	5.7	3.5	4.4
Mesitylene	4.0	4.9	<2.5	3.7

CV^+: Crystal Violet

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DETERMINATION OF GOLD IN ENVIRONMENTAL SAMPLES BY USING EXTRACTION METHODS

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ABSTRACT

The paper presents the results of determining gold in environmental samples by using solid extractant (SE) on the base of tributyl phosphate (TBP). The extractant was used for the recovery of Au from leaching solutions and natural waters. The concentrates were analysed by neutron activation and X-ray fluorescence spectrometry. The study was performed in a wide range of Au content (10^{-8}-10^{-4} M). The determination of the distribution coefficients (D) and the ratio of Au to Cl in the extractable complexes was fulfilled. The influence of extraction conditions and the composition of the solutions to be analysed on D was investigated. The behaviour of some interfering elements (Zn, Pb, As) is discussed. Abnormally high extraction of Pb from HCl solutions under chlorination has been found. Optimal conditions are reported which provide the complete (≥98%) and selective extraction of gold from leaching solutions.

The x.r.f. method of Au determination in geological samples has been developed, which includes the aqua regia decomposition of the sample, recovery of Au by SE(TBP) from the pulp after its leaching, back-extraction of Au with a thiourea solution, evaporation of that solution providing a thin sample layer for secondary x.r.f. For 25 g of the sample material the determination limit is set at 10^{-6}%. The accuracy of the technique has been checked on different reference materials. The results agree within 10 %.

A preconcentration method for Au in natural waters at the sampling site using SE(TBP) is developed as a preliminary step prior to the determination of gold by n.a.a. SE(TBP) was saturated with gaseous chlorine for extracting all species of Au. The detection limit for the overall procedure was 0.2 ng l^{-1} (2×10^{-11}%).

1 INTRODUCTION

Most the methods of Au determination in environmental samples (particularly in natural waters) require preconcentration of Au.

The acidic decomposition stage for complete removal of Au from the sample matrix is rather rough and, therefore, not very selective. Thus not only Au, but also a number of the elements impeding its determination, such as Zn, Pb (x.r.f.) and As (x.r.f. and n.a.a.) were present in the leaching solution. The problem of their separation might be solved by the further concentration of Au from the leaching liquor. In the present work we propose to use a solid extractant on the base of tributyl phosphate (content of TBP in SE was 45%) for the preliminary concentration of Au from leaching solutions and natural waters.

2 DETERMINATION OF GOLD IN GEOLOGICAL SAMPLES

2.1 *Extraction of Au, Zn, Pb, and As from HCl, HNO_3, and aqua regia solutions*

The behaviour of Au, Zn, Pb and As has been studied during the extraction by SE(TBP) in order to obtain optimal conditions for the selective recovery of Au. Literature data are not numerous and sometimes contradictory (Ishimori et al., 1960; Akaza et al.,1970; Yadav and Khopkar, 1970; Shelkovnikova et al., 1973).

The experimental results given in Fig.1 show the distribution coefficient (D) for extraction of Au from HCl and aqua regia solutions into SE (TBP). It is noteworthy that D_{Au} (for HCl solutions) has a maximum value 5×10^5 at [HCl]= 2 - 3 M, and always exceeds 10^4 in the whole concentration range under consideration. In extraction from aqua regia solutions D_{Au} decreased from 10^5 to ca. 10^3 depending on the solution acidity. The concentration of Au in the initial solutions ranged between 10^{-8} and 10^{-4} M. The D_{Au} value was constant (5×10^5) at [Au] ranging from 10^{-8} to 10^{-6} M and decreased to 10^4 as [Au] increased to 10^{-4} M. The ratio of Cl to Au in the SE(TBP) after extraction from 0.1 M HCl solution with the initial gold content 2×10^{-6} - 10^{-4} M was determined by the gamma-activation method. The ratio was equal to ca. 4. The increase of temperature from 20°C to 70°C caused a decrease in D_{Au} from 5×10^5 to 9×10^3(1 M HCl, [Au] = 10^{-8} M). To determine such a high D_{Au} we used gold solutions of high specific activity spiked with ^{195}Au. The ratio of the phases was 1:1000 (SE : solution, g ml^{-1}). The HCl solutions were preliminarily saturated with TBP. The phases were stirred during 2 hours. The relative standard deviation of D determination does not exceed 0.1 and 0.2 for D_{Au} = 10^4 - 10^5 and D_{Au} > 10^5, respectively.

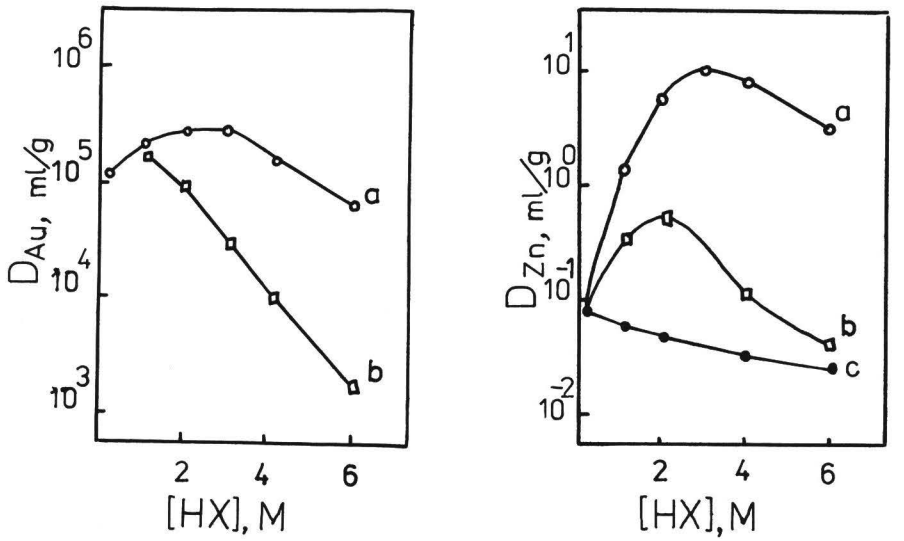


Fig.1. Extraction of Au from HCl (a); aqua regia (b).
Fig.2. Extraction of Zn from HCl (a); aqua regia (b); HNO_3 (c).

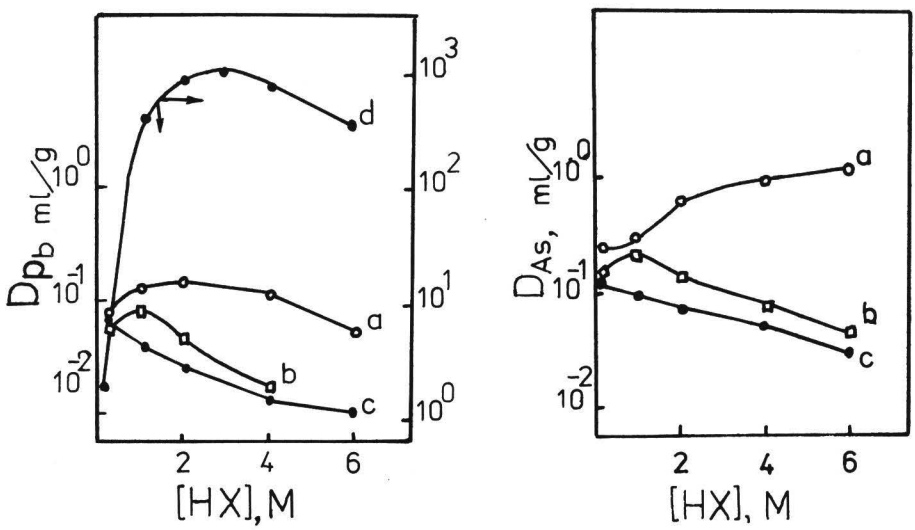


Fig.3. Extraction of Pb from HCl (a); aqua regia (b); HNO_3 (c); $HCl + Cl_2$ (d).
Fig.4. Extraction of As from HCl (a); aqua regia (b); HNO_3 (c).

In Figs.2-4 we have plotted D_{Zn}, D_{Pb}, D_{As} against the concentrations of HCl, HNO_3, and aqua regia solutions. The contents of these elements in SE(TBP) were determined by x.r.f. One can see that in the case of HCl the distribution coefficients are the largest ones. The nitrate complexes were found to be the weakest extractable ones with the D_{Zn}, D_{Pb}, D_{As} values not exceeding 10^{-1} and D decreases with increasing $[HNO_3]$.

The leaching of Au from geological samples in some cases was carried out by HCl under chlorination. Under these conditions we observed a considerable enhancement of Pb extraction, $D_{Pb} \cong 10^3$ (Fig.3d). These values considerably exceed those obtained by us (Fig.3a) in the absence of chlorine, as well as the published data on extraction of chloride complexes of Pb(II) (Zolotov, 1973). Obviously, in chlorine saturated HCl solutions certain conditions for the stabilisation of Pb(IV) are realized. To our knowledge, there are so far no data available on Pb(IV) extraction. Possibly, like Sn(IV), $PbCl_6^{2-}$ is the complex extracted by TBP.

A comparative analysis of Figs.1-4 demonstrates that the optimal systems for the selective recovery of Au were HCl or aqua regia solutions of acidity not exceeding 1 M. The ratio of SE(TBP) to leaching liquor of 1:100 provided the complete (≥99%) and selective recovery of gold.

2.2 *Back-extraction of gold with thiourea solutions*

It is obvious that an increase in the concentration degree of Au in the sample under study should lower its detection limit for x.r.f. We studied the back-extraction of Au from SE(TBP) with thiourea solutions in order to produce thin sample layers. We investigated the effect of diverse factors on the behaviour of ^{195}Au in the TBP - thiourea system and determined optimal conditions for the complete recovery (above 98%) of Au from SE (TBP), i.e. 0.025 M thiourea solution, phase ratio 1:10, equilibrating time 5 min at 80 - 90°C. The gold content of the thin sample layer was determined by x.r.f. in the secondary X-ray excitation mode.

2.3 *Determination of gold content in the reference materials*

The above outlined results enable us to recommend the analysis of geological samples by using the following scheme:

1. Aqua regia decomposition of an original sample (25 g, particle size ≤ 75 μm) after treatment with HNO_3 and sintering at 600°C during 15 minutes (Dmitriev et al., 1990)
2. Extraction of Au from the chloride - nitrate pulp of about 1 M acidity. The ratio of SE(TBP) to leaching liquor of 1:100, equilibrating time 20 min at room temperature. The Au concentration in the SE(TBP) sample is determined by n.a.a. or x.r.f. (for geological samples with the gold content higher than 10^{-5}%).
3. Recovery of Au into the thin sample layer by back-extraction using the thiourea solution with subsequent evaporation.
4. X.r.f. determination of Au in a thin sample layer using the monochromatic radiation of a zirconium secondary target (for geological samples with the Au content higher than 10^{-6}%).

The proposed technique has been tested on the reference materials with certified values (μg/g) of 4.5±0.1 (SZR-1) and 2.0±0.1 (SZH-2). The content of Au in thin sample layers was determined to be 4.3 and 1.9 for SZR-1 and SZH-2, respectively. Six experiments were carried out with each sample. The relative standard deviation did not exceed 0.1. The detection and determination limits were determined according to Currie's (1968) equations and were equal to 0.04 μg and 0.2 μg, respectively. A number of the reference materials having different composition and the gold content from 1.0 to 50.0 μg/g was analysed, and good agreement was obtained.

3 DETERMINATION OF GOLD IN NATURAL WATERS

In natural waters gold is contained as various species. In the present work we propose to use the chlorine-saturated SE(TBP) for simultaneously oxidizing the gold, forming a chloro complex, and for extracting it. 5 g of the chlorine-saturated SE(TBP) was added to a 1-l river water sample containing ^{195}Au tracer (samples with ^{195}Au were stored during 20 days before use to equilibrate with gold). The mixture was shaken for 10 min. It was found that more than 98 ± 2% of ^{195}Au was adsorbed on SE(TBP).

This technique was tested on the samples of original natural waters (Shishkina et al., 1990). We investigated various types of natural waters: surface fresh and mineral waters containing very low levels of gold and waters with a high gold content which were

associated with gold deposits. The preconcentration of Au from natural waters was carried out on the sampling sites which was of great importance for obtaining correct results. The efficiency of the proposed method was confirmed by the simultaneous use of the activated charcoal preconcentration technique (Plyusnin et al., 1979). The samples of SE(TBP) and activated charcoal were analysed by n.a.a. The results allow one to conclude that using the chlorine-saturated solid extractant containing about 45% TBP is very efficient for the concentration of Au from natural waters. The detection limit for gold is equal to 0.2 ng l^{-1}. This method was used in hydrogeochemical prospecting of auriferous deposits and gave good results (Lomonosov et al., 1986).

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LIQUID-LIQUID DISTRIBUTION OF Cu(II), AT TRACE LEVEL, BETWEEN AQUEOUS AND ORGANIC SOLUTIONS CONTAINING MIAMP.

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ABSTRACT

The reaction of Cu(II) with 2-(5'-methyl-3'-isoxazolylazo)-4-methyl-phenol, MIAMP, in aqueous media at I = 0.1 M ($NaClO_4$) was investigated spectrophotometrically. A numerical calculation method was used to establish the equilibria in solution and to evaluate the stability constants of the complexes formed (log β_{101} = 7.65 ± 0.02, log β_{102} = 15.28 ± 0.24).

The liquid-liquid distribution of Cu(II)-MIAMP complexes between 0.1 M perchlorate solutions and a benzene organic phase has been carried out by using measurements of the metal distribution. The experimental data have been analyzed by graphical and numerical methods. The results show the distribution of copper to proceed via the following extraction reactions:

$$Cu^{2+} + 2\ HR_o \rightleftharpoons (CuR_2)_o + 2\ H^+ ;\quad \log K_{102} = -8.60 \pm 0.10$$
$$Cu^{2+} + 3\ HR_o \rightleftharpoons (CuHR_3)_o + 2\ H^+ ;\quad \log K_{113} = -5.26 \pm 0.14$$

Applications of this extraction process to determine copper in drinking waters and medicaments will be presented.

INTRODUCTION

Heteroazo-phenols and -naphthols have been widely used for the spectrophotometric and extraction-spectrophotometric determination of many metal ions, Hovind (1975) and Shibata (1972). However the chemical equilibria involved in the extraction procedure have been seldom studied.

The complex formation equilibria in aqueous solutions between copper (II) and 2-(5'-methyl-3'-isoxazolylazo)-4-methylphenol, MIAMP, have been studied using 0.1 M $NaClO_4$ as backing electrolyte.

When the above Cu(II)-MIAMP solutions at pH = 8.7 are shaken with different inmiscible solvents, the metal distributes between the two phases. Such process gives an intense absorbance with benzene.

A systematic speciation study of the copper distribution between aqueous and benzene solutions has been carried out by determining first the reagent distribution. The extracted species are established and a spectrophotometric method have been developed to determine copper in drinking waters and medicinal drugs. The validity of the mass balance condition in the process

was verified by a proper stripping of the extracted copper.

2 EXPERIMENTAL

2.1 Reagents and solutions

5×10^{-3}M solutions of MIAMP, synthesized and purified as described previously, Pérez Trujillo et al. (1983) were prepared in NaOH 0.01 M and benzene. 10^{-1} M $Cu(ClO_4)_2$ standard solution prepared from copper nitrate by successive digestions with perchloric acid to total removal of nitrate and standardizing complexometrically, Schwarzenbach et al. (1969). A buffer solution of pH = 8.7 (hexamine/$HClO_4$).

Analytical grade reagents and de-ionized water were used throughout with no further purification.

2.2 Apparatus

Spectra were obtained using a Perkin-Elmer 550S recording spectrophotometer with 1-cm matched quartz cell. The pH of aqueous solutions was measured using a Radiometer PHM64 digital pH meter provided with a glass- calomel combinated electrode. Atomic absorption analyses were performed on a Perkin Elmer 3030 A.A. spectrophotometer with deuterium arc background correction. Numerical calculations were performed by using a Digital VAX/VMX 11/780 (V.4.0) computer.

2.3 Experimental techniques

Experimental data for the reagent distribution were collected after shaking during 10 min. equal volumes (10 ml) of both organic (benzene, [MIAMP] = 1.0×10^{-4}M and 1.6×10^{-4}M) and aqueous (0.1M $NaClO_4$, $[H^+]$ = 10^{-12}-10^{-1}M) phases. The concentration of the reagents in both phases were determined by applying a Beer's law at 495 nm (in 0.1M NaOH) and at 405 nm (benzene).

Experimental data for Cu(II) distribution were obtained by shaking during 20 min. equal volumes (10 ml) of both organic (benzene, [MIAMP] = 5×10^{-5}-5×10^{-3}M) and aqueous ($[Cu^{2+}]$ = 2.105×10^{-4}M, 0.1M $NaClO_4$, $[H^+]$ = $10^{-8.7}$M) phases. Copper concentration in both phases were determined by A.A.S. The copper content of the organic phase was measured after stripping with 1M $HClO_4$.

3 RESULTS AND DISCUSSION

As indicated before the study includes a systematic investigation of the reaction involved in the chemical system under consideration.

3.1 Complexation equilibria between copper and MIAMP in aqueous media.

Copper reacts with MIAMP in aqueous solutions at pH higher than 2.0, producing coloured solutions with a maximum of absorption at 560 nm.

Experimental data were generated by measuring the absorbance at 560 nm of solutions at I = 0.1 M $NaClO_4$ in the range of 2 < pH < 7 at various [Cu(II)]/[MIAMP] ratios (1/1, 20/1, 40/1, 60/1 and [MIAMP] = 4×10^{-5}M).

A preliminary treatment of data by applying the continuous variations and mole ratio methods at pH = 6.5 resulted in a stoichiometry Cu(II):MIAMP, 1:1.

A further consideration of the chemical conditions employed including the acidity properties of MIAMP (pK_a = 9.03) let us consider the reaction

$$Cu^{2+} + m\ HR \xrightleftharpoons{K1am} CuH_aR_m + n\ H^+ \quad (a = m - n)$$

as the most logical interaction.

Such hypothesis has been applied to a graphical treatment of the data A = f(pH), Mushram et al. (1969). A value for log β_{101} = 6.91 ± 0.03 was obtained which correspond to the species CuR^+.

Such a results was refined by numerical analysis of data using the computer program LETAGROP-SPEFO, Sillen et al. (1969). By this procedure the "best model" was obtained including the species CuR^+ and CuR_2, and the obtained values for log β and ε (molar absorptivity) are the followings:

CuR^+	log β_{101} = 7.65 ± 0.02	ε_{101} = 6,627 ± 17 l.mol.cm^{-1}
CuR_2	log β_{102} = 15.28 ± 0.24	ε_{102} = 9,000 ± 155 l.mol.cm^{-1}

3.2 Distribution of MIAMP

The distribution of MIAMP between the aqueous perchlorate and benzene can be expressed as follows:

$$HR_w \rightleftharpoons HR_o \qquad K_D = [HR]_o . [HR]_w^{-1}$$

The distribution ratio, D, can be defined as:

$$D = C_{HR_o} . C_{HR_w}^{-1} = K_D(1 + K_a/[H^+])^{-1}$$

where C_{HR_o} and C_{HR_w} are the analytical concentrations of MIAMP in the organic and the aqueous phases respectively and K_a is the ionization constant of the reagent.

Experimental data in the form log D vs pH, were obtained spectrophotometricaly as explained before, figure 1

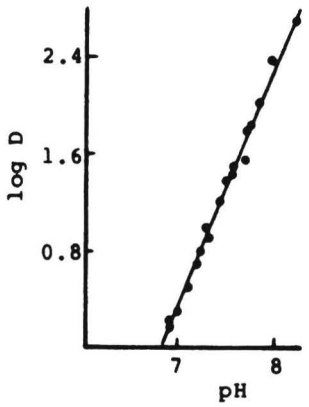


Fig. 1. Effect of pH on MIAMP distribution between 0.1 M $NaClO_4$ and benzene. [MIAMP] = 1.0×10^{-4}M and 1.6×10^{-4}M

When $[H^+] \ll K_a$ it can be written

$$D = K_D[H^+]K_a^{-1} \quad \text{and} \quad \log D = \log K_D + pK_a - pH$$

By plotting log D vs pH, a value for log K_D = 3.37 has been obtained.

This result has been refined by applying a numerical treatment to the experimental data using the LETAGROP-DISTR computer program, Liem (1971). In this case the value obtained was log K_D = 3.46 ± 0.03 which agrees fairly well with that obtained graphically.

3.3 Extraction of Cu(II)-MIAMP aqueous complexes

The distribution of Cu(II)-MIAMP complexes between aqueous and organic benzene phases has been studied by analysis of experimental data as a function of either the aqueous acidity (pH) or the reagent concentration. In both cases MIAMP was always in excess with respect to Cu(II) total concentration. Experimental data are collected in figures 2 and 3.

The solvent extraction process may be expressed by the reaction

$$Cu^{2+} + p\ HR_o \rightleftharpoons (CuH_qR_p)_o + r\ H^+ \qquad (q = p - r)$$

under the experimental conditions polynuclear complexes are neglected. The corresponding equilibrium constant is written as

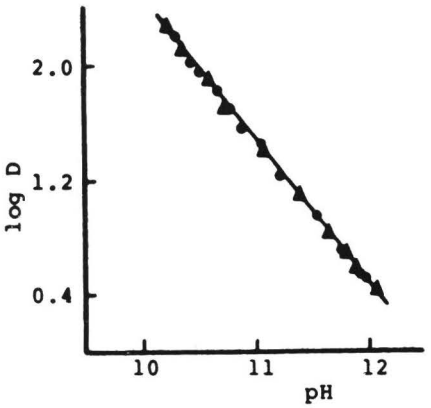


Fig. 2. Effect of pH on Cu(II)-MIAMP distribution between 0.1 M $NaClO_4$ and benzene. $[Cu^{2+}] = 5.20 \times 10^{-5}$M, [MIAMP] = 10^{-3}M

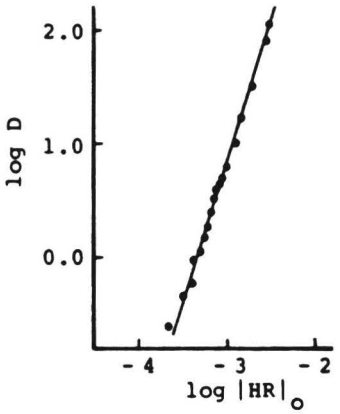


Fig. 3. Effect of log $[HR]_o$ on Cu(II)-MIAMP distribution between 0.1 M $NaClO_4$ and benzene; $[Cu^{2+}] = 2.105 \times 10^{-4}$M pH = 8.7

$$K_{1qp} = [CuH_qR_p]_o \, [H^+]^r / [Cu^{2+}] \, [HR]_o^p$$

The distribution coefficient for Cu(II) will take the form

$$D = \sum_p K'_{1qp} \, [HR]_o^p \, [H^+]^r$$

where $K'_{1qp} = K_{1qp} \, \alpha_{Cu'}$ and α_{Cu} is the side-reaction coefficient due to any side-reaction of Cu(II) in the aqueous phase. From this function the different values for q, p, r and K_{1qp} can be determined.

As shown in figure 2 the plot log D vs pH has a linear dependence of slope = 2, indicating the release of two protons by the complexation reaction, r = 2.

On the other hand, a plot of log D vs log $[HR]_o$ at constant pH (figure 3) shows a linear relationship of slope = 2.44 which may indicate the formation of the complex species CuR_2 and $CuHR_3$ ($CuR_2 \cdot HR$) which may be considered responsible for the Cu(II) extraction.

A numerical treatment of the experimental data carried out by using the LETAGROP-DISTR program, Liem (1971) supports the results obtained graphically.

In this sense, the best model to explain the experimental data was the one which includes the species CuR_2 and $CuHR_3$. The values obtained for the model

considered are the followings:

CuR_2 : $\log K_{102} = -8.60 \pm 0.10$

$CuHR_3$: $\log K_{113} = -5.26 \pm 0.14$

3.4 Analytical applications of the Cu(II)-MIAMP solvent extraction

The solvent extraction of Cu(II)-MIAMP complexes has been applied to analytical purposes. In this sense, the process has been applied to determine copper in samples of various drinking waters (Deionised, Normal municipal and Commercial waters) as well as in some medicinal drugs (Micebrine and Rodrevit). The most important interferences are Ni(II), Co(II), Fe(II and III) and Pb(II) that interfere in Cu(II):ion, 1:1, ratio as ions F^-, Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}, NO_2^-, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Cd^{2+} can be present in ion/Cu(II) ratios > 100.

The determination of copper in the mentioned samples was carried out by applying the following procedure: aqueous buffered solutions of pH = 8.7 (hexamine/$HClO_4$) at I = 0.1M $NaClO_4$, containing different amount of copper (II), ranging from 0.33 - 3.14 ppm were shaken with a MIAMP benzene solution of a constant concentration 5×10^{-4}M. In the mentioned copper concentration range the calibration curve follows the Beer's law with a molar absorptivity of 9.07×10^3 $l.mol^{-1}.cm^{-1}$ at 510 nm. The optimum concentration range for the determination as eveluated by Ringbom's method is found between 0.82 - 3.14 ppm of Cu(II). The relative error in the mean value for ten replicates of 1.34 ppm of Cu(II) is 1.4% and the standard deviation 0.008 (95% confidence level).

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SOLVENT EXTRACTION SEPARATION OF ALKALINE EARTH METAL IONS IN SODIUM PERCHLORATE MEDIA AT VARIOUS TEMPERATURES

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ABSTRACT

The solvent extraction behavior of certain alkaline earth metal ions such as Ba^{2+}, Sr^{2+}, Ca^{2+}, and Mg^{2+}, using a carbon tetrachloride solution containing TTA (thenoyltrifluoroacetone) combined with TOPO (trioctylphosphine oxide) was studied in the temperature range between 298 and 318 K. The distribution ratio and separation factors of the metal ions in these systems were determined. Each alkaline earth metal ion in the aqueous phase was extracted with two TTA(HA) anions. The temperature dependences and the separation factors of alkaline earth metal ions determined by the present method were compared with those given by the ion-exchange reaction on layered dihydrogen tetratitanate hydrate fibers. The separation factor more than 20 was obtained for all combinations of neighboring alkaline earth metal ions by choosing either the solvent extraction or the ion -exchange methods.

INTRODUCTION

The solvent extraction of Mg^{2+} (Poluektov et al. 1970, Akaza et al.1966), Ca^{2+} (Hasegawa et al. 1967,1970), Sr^{2+} (Sekine et al. 1975, Bolomey et al. 1950), and Ba^{2+} (Sekine et al. 1966, Lapitskaya et al. 1967) with extracting reagents, such as TTA (thenoyltrifluoroacetone), TBP (tributyl phosphate), and IPT (isopropyl tropolone), has been studied to separate these metal ions at 298 K. Among these extractants, TTA has been found to be a useful extractant for alkaline earth metal ions in aqueous solutions. The use of neutral ligands such as trioctylphosphine oxide (TOPO) as an adduct forming ligand together with TTA is an interesting approach because of the enhancement of the extraction of alkaline earth metal ions.

The extraction of these metal ions may, however, be dependent not only on the concentrations of TTA and TOPO in the organic phase but also hydrogen-ion concentration in the aqueous solution. In the present study, the distribution of the four alkaline earth metal ions between carbon tetrachloride and an aqueous solution at various temperatures has been measured. The separation factors of these metal ions at various temperatures were calculated by the extraction data and compared with those obtained by an ion-exchange method using crystalline dihydrogen tetratitanate hydrate fibers.

EXPERIMENTAL

The TTA and TOPO were obtained from Dojindo Laboratories. Distilled and deionized water was used throughout. All the other reagents were of a reagent grade. The distribution experiments were done after 20 hours of the dissolution of TTA in carbon tetrachloride in order to establish the keto-enol equilibrium. Stoppered glass tubes were used for the equilibration of an 8 ml portion of aqueous solution (containing each alkaline earth metal ion and acetate buffer) and an 8 ml portion of the organic solution (containing TTA and TOPO) in them. The initial metal chloride concentration was 1.00×10^{-4} M and that of acetate buffer was 5.00×10^{-3} M. The pH was adjusted with a perchloric acid or sodium hydroxide solution. The tubes were shaken by a mechanical shaker which was placed in a thermostated water bath for 2 days. This was found to be sufficient for the equilibration. The ionic strength of the aqueous phase was controlled at 0.1 M with sodium perchlorate. The pH of the aqueous phase was measured after the equilibrium was established. The metal content in the aqueous phase was determined by atomic absorption spectrophotometry (Hitachi 180-80 Polarized Zeeman Spectrophotometer) for Mg^{2+}, Ca^{2+}, and Sr^{2+}, and by an inductively coupled plasma spectrophotometry(Daini Seikosha, SPS 1100) for Ba^{2+}. The distribution equilibria of the alkaline earth metal ions were measured at 298, 308 and 318 K.

RESULTS AND DISCUSSION

The solvent extraction of the alkaline earth metal ions is expressed in terms of the distribution ratio, D:

$$D = C_{M(o)}/C_M \qquad (1)$$

where C represents the total concentration and the subscript "o" denotes the organic phase. The plots of log D as a function of pH agree linearly with a slope of almost +2 at all of these temperatures (Fig. 1). This agreed with the results reported previously(Hasegawa et al. 1967);

$$M^{2+} + 2HA_{(o)} + 2TOPO_{(o)} \rightleftharpoons MA_2(TOPO)_{2(o)} + 2H^+ \qquad (2)$$

where HA denotes TTA and the subscript "o" denotes the chemical species in the organic phase.

Ion-exchange experiments of the alkaline earth metal ions which were done previously (Komatsu et al. 1983) by using crystalline dihydrogen tetratitanate hydrate fibers, $H_2Ti_4O_9 \cdot nH_2O$, were referred in order to compare the results with those of the present solvent extraction study. The potassium tetratitanate fibers, $K_2Ti_4O_9$,were synthesized by the method reported

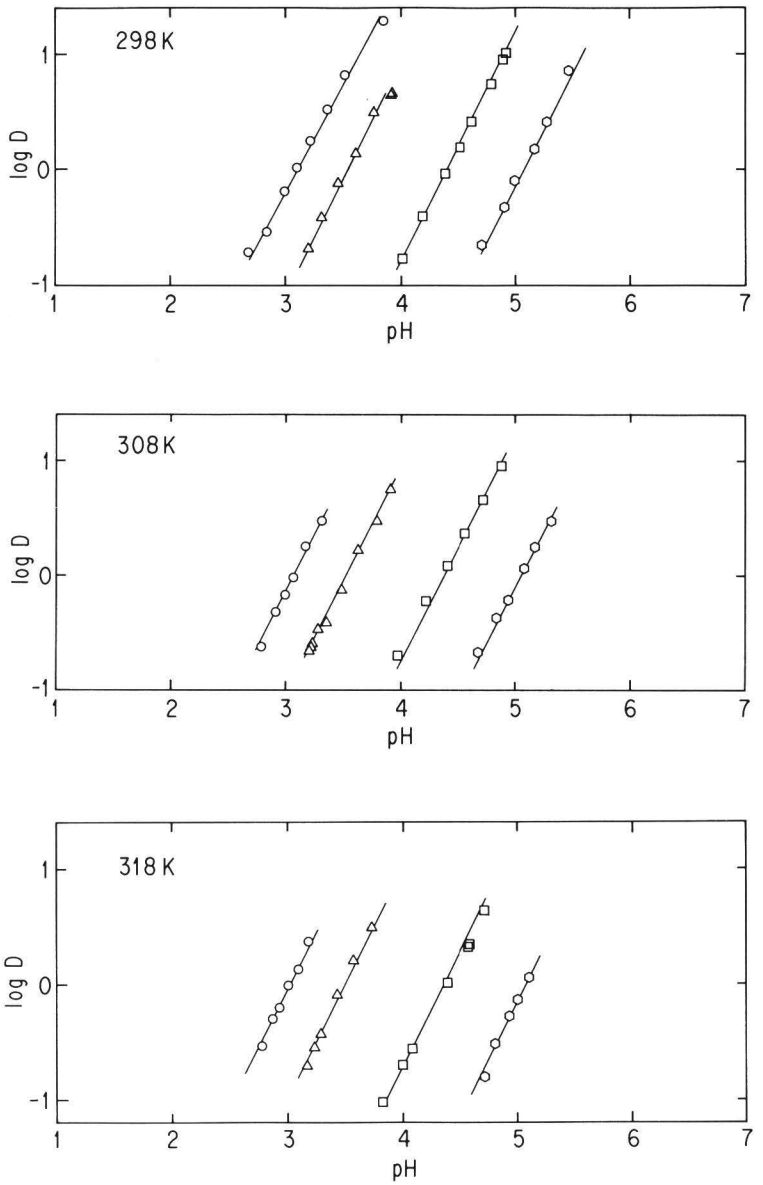


Fig. 1. Distribution ratio of alkaline earth metal ions as a function of pH in aqueous solutions at various temperatures.
Aqueous solution: 0.1 M (Na,H)ClO_4 containing 1 x 10^{-4} M alkaline earth metal ions and 1 x 10^{-3} M of acetate buffer.
Organic solution: Carbon tetrachloride containing 0.1 M TTA and 0.1 M TOPO.
Ba^{2+}(⬡), Sr^{2+}(□), Ca^{2+}(△), and Mg^{2+}(○).

previously(Fijiki et al. 1980). The measurements of the ion-exchange equilibria were made in a similar way. The distribution coefficient, K_d, was calculated as:

$$K_d = \frac{\text{mole of } M^{2+} \text{ per 1 g of solid}}{\text{mole of } M^{2+} \text{ per 1 cm}^3 \text{ of solution}} \quad (3)$$

where M denotes alkaline earth metal ions.

The ion-exchange experiments were continued for fifteen days or more at 298 K in order to establish the equilibrium, ten days at 313 K, seven days at 333 K, and three days at 353 K. On the other hand, the solvent extraction equilibrium was reached within two days.

The $pH_{1/2(ion\text{-}exchange)}$ in the present paper was defined as the pH value at which 5×10^{-5} M of the alkaline earth metal ions in a 10 cm^3 portion of aqueous solution was exchanged with hydrogen ions on a 0.1g portion of crystalline dihydrogen tetratitanate hydrate fibers in order to make a reasonable comparison of the ion-exchange data with the solvent extraction

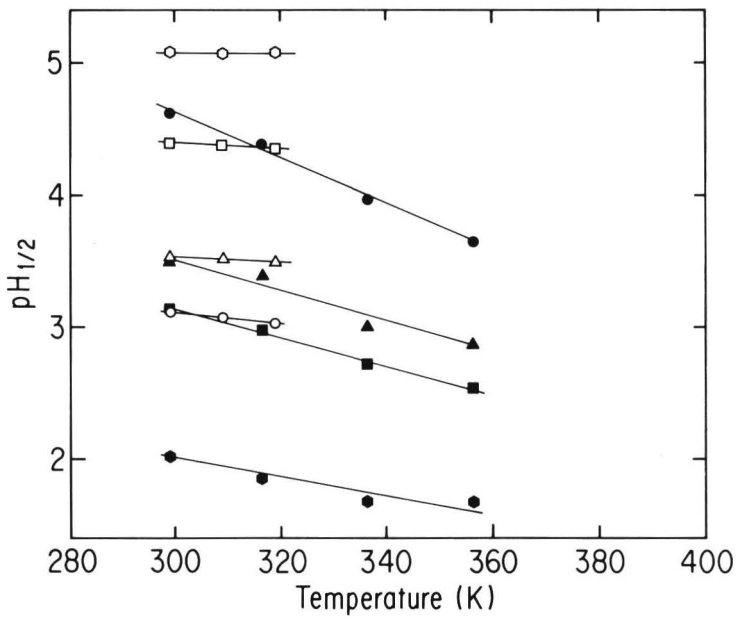


Fig. 2. Temperature dependence of $pH_{1/2}$ values given by solvent extraction and ion-exchange method.
Open symbols: $pH_{1/2}$ values by the solvent extraction system.
Ba^{2+}(⬡), Sr^{2+}(□), Ca^{2+}(△), and Mg^{2+}(○).
Closed symbols: $pH_{1/2}$ values by the ion-exchange system.
Ba^{2+}(⬢), Sr^{2+}(■), Ca^{2+}(▲), and Mg^{2+}(●).

data. The $pH_{1/2(\text{solvent extraction})}$ is defined as the pH value where the half of metal ions in the aqueous phase is extracted when the organic phase contains 0.1 M of TTA and 0.1 M of TOPO. Figure 2 shows the values of $pH_{1/2(\text{solvent extraction})}$ and $pH_{1/2(\text{ion-exchange})}$ for the alkaline earth metal ions as a function of the temperature. The results in Fig. 2 can be summarized as follows: i) The $pH_{1/2}$ vs. temperature plots of both the ion-exchange and solvent extraction experiments are linear, but the slope is much larger with the former. ii) The solvent extraction at a certain pH is better in the order of $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$, but the ion-exchange is better in the order of $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$. This should be explained in terms that the degree of solvent extraction is mainly dependent on the ability of the metal ion to form .LH8

TABLE 1

Summary of separation factors by the solvent extraction with TTA-TOPO and by ion- exchange on crystalline dihydrogen tetratitanate hydrate fibers system.

A By solvent extraction with TTA-TOPO into CCl_4

	Mg-Ca	Ca-Sr	Sr-Ba
298 K	6.61	52.5	22.9
308 K	7.94	52.5	22.9
318 K	8.71	52.5	27.5

B By ion-exchange on $H_2Ti_4O_9 \cdot nH_2O$.

	Mg-Ca	Ca-Sr	Sr-Ba
298 K	174	5.25	174
313 K	100	6.92	174
333 K	87.1	3.63	120
353 K	36.3	4.17	60.3

[Note] Separation factor for the solvent extraction is antilogarithm of 2 x $(pH_{1/2(\text{solvent extraction})}(M_1) - pH_{1/2(\text{solvent extraction})}(M_2))$ while that for the ion-exchange is antilogarithm of 2 x $(pH_{1/2(\text{ion-exchange})}(M_2) - pH_{1/2(\text{ion-exchange})}(M_1))$.

the extractable coordination complex, which is more stable as the ionic radius is smaller. However, the degree of ion exchange is mainly dependent on the strength of hydration of the metal ions which are weaker and consequently adsorbed better when the ionic radius is larger. The log K_d value in Eq. 3 is linear for the pH of the aqueous phase with slopes of almost +2 under the substantially constant concentration of the hydrogen ion in the solid. From the results of ion-exchange experiments, the following equilibrium can be written:

$$mM^{2+}_{(aq)} + H_2Ti_4O_9 \cdot nH_2O_{(s)} \quad 2mH^+_{(aq)} + M_mH_{2(1-m)}Ti_4O_9 \cdot nH_2O_{(s)} \qquad (4)$$

where the subscripts "aq" and "s" denote the aqueous and solid phase and $0 < m < 1$.

From the values of $pH_{1/2(\text{solvent extraction})}$ and $pH_{1/2(\text{ion-exchange})}$ in Fig. 2, the separation factors were obtained as listed in Table 1. These indicate: (1) The separation factors determined by the ion-exchange decrease with an increase in the temperature. On the other hand, the separation factors in these solvent extraction systems are nearly constant in the temperature range between 298 K and 318 K. (2) The separation factors of Ca-Sr and Sr-Ba by solvent extraction and those of Mg-Ca and Sr-Ba by ion-exchange are larger than a value of 20 in entire temperature range studied. Table 1 indicates that the solvent extraction is more favorable for the separation of Ca^{2+} and Sr^{2+} while the ion-exchange is more favorable for that of Mg^{2+} and Ca^{2+}, and Sr^{2+} and Ba^{2+}. Thus, by combining these two methods, these four metal ions could be separated effectively.

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CORRELATION AND PROGNOSING THE DISTRIBUTION COEFFICIENTS OF PHENOL COMPOUNDS IN DIFFERENT EXTRACTIVE SYSTEMS

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Procedure of correlation is widely used to define the rules of extraction of organic compounds with similar phisical-chemical properties including homogologues and isomers from water solution. Such approach is useful for description of organic compounds extraction, and prognosing the quantitative process characteristic (Korenman, 1989). The main idea of the procedure is to determine the dependance of distribution coefficients of initial (standard) substance (D_0) and its substituent (D_y), which is, in general, described by equation:

$$\lg D_y = \sigma \cdot \lg D_0 + \pi \qquad (1)$$

where σ is constant depending on character of distributed compound and extragent nature;
π is parameter Hansch (Hansch, 1976):

$$\pi = \frac{K_s' \cdot K_h}{K_s \cdot K_h'} \qquad (2)$$

K_s and K_h, K_s' and K_h' are constants of solvate and hydrate formation of initial compound and its substituent. For investigation of extraction of aromatic hydroxide compounds it is reasonable to use standard data for phenol.

Investigation of extraction by different solvents, including homologues permits to describe isomers and homologues extraction rather full. The value of Hansch parameter depending on extractant nature and property of extracted compound characterizes relative stability of extracted hydrates and solvates. For example, such value π as 0.1-1 shows practically the same stability of phenol solvates and hydrates and their derivatives which is usual for higher alcohols extraction. Alkylacetate extraction shows larger stability of phenol solvate substitutes

(Korenman, 1989) than phenols. As an example basic bilog distribution coefficient dependances of dihydroxybensols and phenol are shown on fig. 1. The values of σ and π are calculated on their basement.

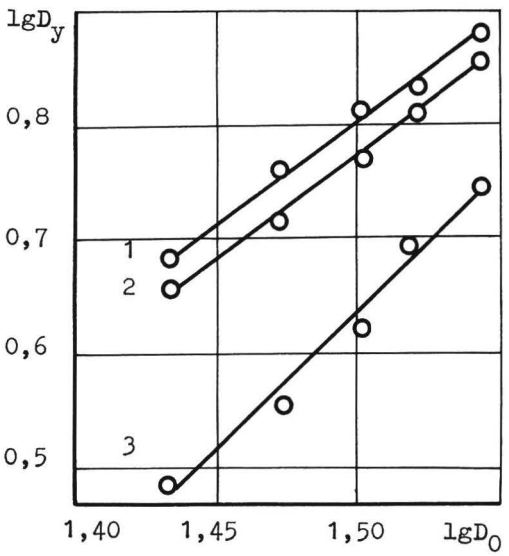


Fig.1. Bilog dependance between distribution coefficients of pyrocatechol (1), resorcinol (2), hydroquinone (3) and phenol in higher alcohols - water systems.

Physical-chemical properties of extractants substantially influences the interfase phenol distribution and permits to base the extractant selection. The standard way to search and analyse the connection of "structure-property" type is to give off compounds with substitute properties and to establish correlative dependance between structure and property parameters. For property describtion of substituent constants the equation of Gammet, Gammet-Taft (Palm, 1977) or derivative equations are used.

To charachterise the structure of extracted compound the Taft constants may be used but at phenol consentration with neutral phosphorus organic compounds (NPOC) it is more reasonable to use σ^p - constants which are additive according Kabachnic equation. The shown constants summarize the substitute effect and do not describe the homogeneous formal interaction. Kabachnic equation:

$$lgk = lgk_0 + \rho \Sigma \sigma^p \qquad (3)$$

is applied to compounds with varied substituents directly connected with phosphorus atoms in reactive centre composition.

The established limits of phenol distribution coefficients practically equil to concentration extractive constants, that

is why equation (3) may be used for correlative analysis as:

$$\lg D_{xx'x''} = \rho \sum_{xx'x''} \sigma^p + \lg D_0 \qquad (4)$$

where $D_{xx'x''}$ - is distribution coefficient in organic solvent with its substitutes xx'x''-water; ρ is proportional coefficient.

Here are summarized constants for $\sum \sigma^p$ investigated phosphorus organic solvents: tripropylphosphate (TPP), tributylphosphate (TBP), tricresylphosphate (TCP), dibutylphenylphosphate (DBPP), triisobutylphosphate (TiBP), di (2-ethylhexyl)phenylphosphate (D (2EH) PP):

Solvents	TPP	TBP	TiBP	DBPP	D(2EH)PP	TCP
$\sum_{xx'x''} \sigma^p$	-0.96	-1.23	-0.90	-0.88	-0.82	-0.42

Between phenol distribution coefficients in NPOC - water system and $\sum \sigma^p$ extractants linear interconnection is established (Fig.2). Correlation coefficients are 0.919-0.956; the best correlation have halogenphenols (Fig.3) that is explained by uniformity of halogenphenol interaction with NPOC and the absence of steric influence.

In general insufficient high correlative coefficients are defined by systematic "lack" of value $\lg(D_{xx'x''})$, corresponding resulting constant for substituent. Probably it may be explained by necessity of calculation the specific factors of the system, for example, the steric influences and interaction of phase solubility. Coefficients of correlation dependances $\lg D_{xx'x''} = f\left(\sum_{xx'x''} \sigma^p\right)$ for investigated series of extractants are possible to increase by conforming $\sum_{TiBP} \sigma^p$ with the scale of used constants. We have realized such correction on the base of 23 reactive series by means of points displacement for $\lg D_{TiBP}$ parallel to axis of abscissa on straight line $\lg D_{xx'x''} = f\left(\sum_{xx'x''}, \sigma^p\right)$ drawn up without calculation of TiBP - water system. Resulted value of $\sum_{TiBP} \sigma^p = 1.10 \pm 0.0067$ was used in subsequent correlation analysis (Table 1).

The necessity of previous calculation of D in equation (4) is avoided by selecting as a standard one practically any solvent of investigated series, for example TCP. Then:

$$\lg D_{xx'x''} = \rho \sum \sigma^p + \lg D_{TCP}. \qquad (5)$$

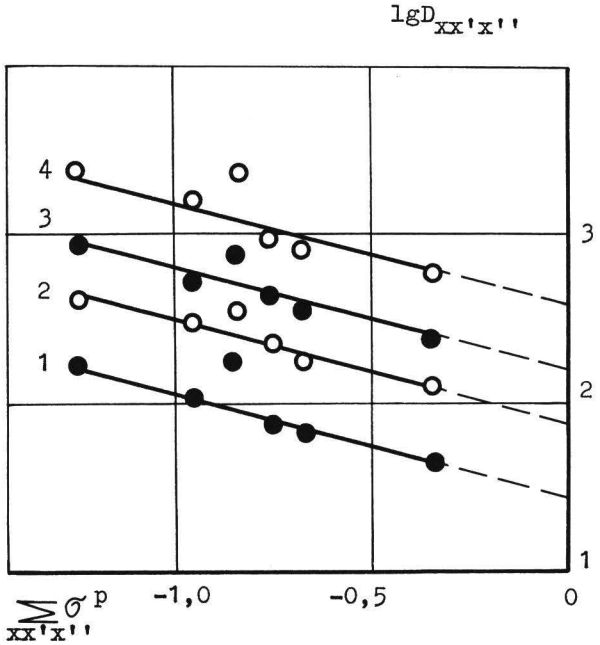


Fig.2 The distribution coefficient dependance of phenol (I), 4-cresol (2), 2-cresol (3) and 4-ethylphenol (4) on summarized constants of σ^{p} extractants.

Fig.3 The distribution coefficient dependance of 2-fluorophenol (I), 3-chlorophenol (2), 4-bromophenol (3) and iodophenol (4) on summarized constants of σ^{p} extractants.

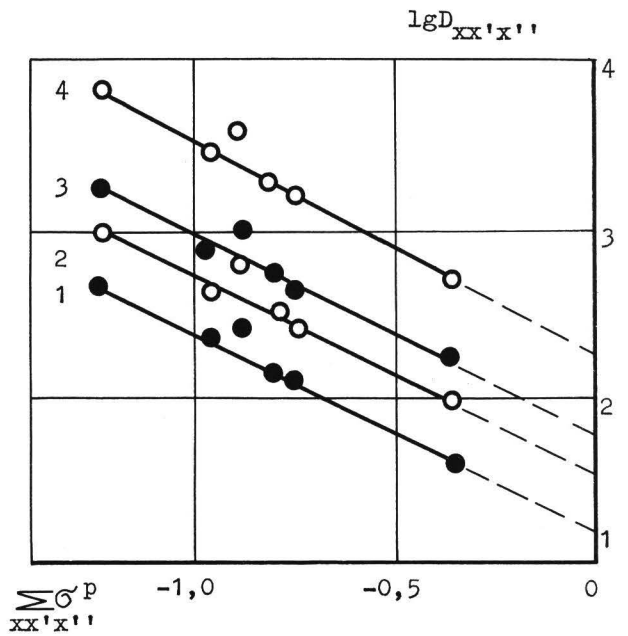


TABLE 1

Linear correlative parameters for separate reactive series

Phenols	ρ	S_ρ	lgD	S_{lgD}	Correlative coefficients
Phenol	-1.313	0.144	1.140	0.135	0.9768
o-Cresol	-1.274	0.106	1.585	0.099	0.9864
m-Cresol	-1.331	0.110	1.468	0.103	0.9867
p-Cresol	-1.425	0.122	1.343	0.115	0.9856
2-Chlorophenol	-1.592	0.027	1.374	0.026	0.9994
3-Chlorophenol	-1.613	0.022	1.788	0.021	0.9996
4-Chlorophenol	-1.606	0.022	1.623	0.020	0.9996

In similar approach it is taken into account the influence of substituent in phenol molecula to its reactiveness. But attemps to establish interconnection of phenol distribution coefficient with known substituent coefficients for phenol substituents (Taft, Gammet constants) do not lead to positive results. Correlation coefficients do not exceed 0.721. In such cases it is used particular scales of substituent constants in equation(1) Equation (1) and (5) describe one and the same process (phenol extraction by phosphate); both correlations are linear, that is why they are compatible on the base of polylinear principle. For such a case a standard extractive system is selected.

For example, for halogenophenols we have taken 2-fluorophenol distribution coefficient in TCP-water system (lgD_{TCPF}). Then (for halogenophenols):

$$lgD_{xx'x''y} = lgD_{TCPF} + \rho\cdot(\sum_{xx'x''} \sigma^p - \sum_{TCP} \sigma^p) + \pi. \qquad (6)$$

Parameter ρ practically constant for all halogenophenols have been calculated by resulted data of 12 reactive series (ρ = -1.606 $\pm$ 0.031). The angle dependance coefficient $lgD_y = f\ (lgD_F)$ equals to 1.039 $\pm$ 0.022. So:

$$D_{xx'x''y} = 1.74 - 1.606\ (\sum_{xx'x''} \sigma^p + 0.42) + \pi. \qquad (7)$$

Equation (7) may be used for interpretation of natural phenomenon of halogenophenol extraction by all investigated ethers, in spite of pecularities of interphase fluorophenol distribution. That is why it has been selected as standard one.

Table 2 shows halogenophenol distribution coefficients in systems with some phosphorus organic solvents calculated by equation (7) and experimentally confirmed. More or less such

approach may be used for analysis of experimental data of extraction of phenols with different substituents of phosphate. For example, we determine the phenol of planned concentration coefficient and degree of extraction that are equal to 20 and 0.95 correspondingly. So phenol distribution coefficient must exeed 400.

By equation (7) it is possible to calculate D of phenol in NPOC series and to establish particular planned extractant. In investigated series of extractants, the phenol distribution coefficients above 400 are typical for TBP and TiBP systems. Moreover having solved the equation (7) about ($\Sigma\sigma^p$) with given D_y, it is possible to determine what number of substituents at phosphorus atom in NPOC molecule can provide the necessary effective extractive system.

TABLE 2

Halogenophenol distribution coefficients ($lgD_{xx'x''y}$) calculated (1) and experimentally recieved (II)

Phenols	Extractants					
	TPP		TBP		DBPP	
	I	II	I	II	I	II
2-Fluorophenol	2.60	2.61	2.98	3.04	2.45	2.48
3-Fluorophenol	2.76	2.58	3.23	3.19	2.60	2.45
4-Fluorophenol	2.63	2.61	3.08	3.03	2.47	2.47
2-Chlorophenol	2.93	2.87	3.32	3.30	2.76	2.74
3-Chlorophenol	3.36	3.27	3.76	3.70	3.20	3.14
4-Chlorophenol	3.18	3.03	3.59	3.46	3.02	2.90
2-Bromophenol	3.15	3.11	3.54	3.54	2.98	2.98
3-Bromophenol	3.18	3.18	3.62	3.61	3.04	3.05
4-Bromophenol	3.39	3.25	3.84	3.68	3.20	3.12
2-Iodophenol	3.46	3.41	3.86	3.84	3.29	3.28
3-Iodophenol	3.85	3.79	4.25	4.22	3.68	3.66
4-Iodophenol	3.78	3.73	4.19	4.16	3.62	3.60

Practical value of established dependances is the possibility to prognose phenol distribution coefficients in organic solvent-water systems that simplifies the extractant selection in solving particular analytical problem.

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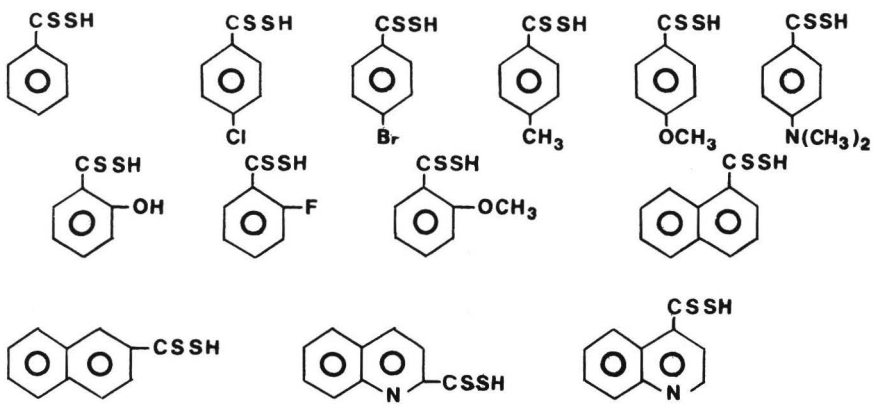
EXTRACTION OF DITHIOCARBOXYLATES OF PLATINUM METALS

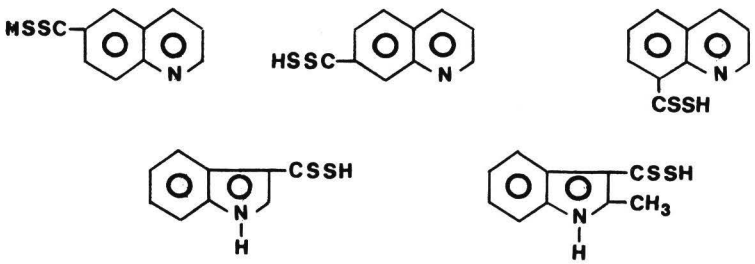
Mežaraups G., Jansons E., Garnaka Z.
University of Latvia, Riga, Latvia.

The extraction of benzene-, naphthalene-, quinoline- and indole dithiocarboxylates by means of various organic solvents has been studied. It has been found that palladium dithiocarboxylates can be extracted from strong acidic solutions, but benzenedithiocarboxylate even from the medium containing concentrated hydrochloric acid. This fact made it possible to work out selective spectrophotometric extraction methods for the determination of palladium having comparatively high sensitivity. It has been found that 4-quinolinedithiocarboxylic acid cannot be extracted with chloroform as distinct from 2-, 6-, 7- and 8-quinolinedithiocarboxylic acids. Similarly, the extraction of 4-quinolinedithiocarboxylates of platinum metals with chloroform and other organic solvents does not take place as readily as that of other quinolinedithiocarboxylates of platinum metals. However, the extraction of 4-quinolinedithiocarboxylates increases in the presence of aliphatic amines, and this phenomenon found its practical application in the development of methods for the determination of osmium traces in various objects.

The composition of all the investigated dithiocarboxylates of platinum metals has been determined by use of various spectrophotometric extraction methods.

We have studied the extraction of benzene-, naphtalene-, quinoline- and indoledithiocarboxylates of palladium(II), platinum (II,IV), rhodium(III), iridium(III,IV7, osmium(III,IV) and ruthenium(III). We used the following dithiocarboxylic acids:





Interaction of dithiocarboxylic acids with platinum metal ions has been studied using spectrophotometry. Platinum metal complexes (except palladium complexes) are completely formed only at the heating of corresponding components during 50-60 min. in a boiling water bath. The most inert ions occur to be rhodium(III) and iridium(III,IV) ions.

It has been found that palladium dithiocarboxylates can be extracted from acidic solutions, but benzene-dithiocarboxylate even from the medium containing concentrated hydrohloric acid.

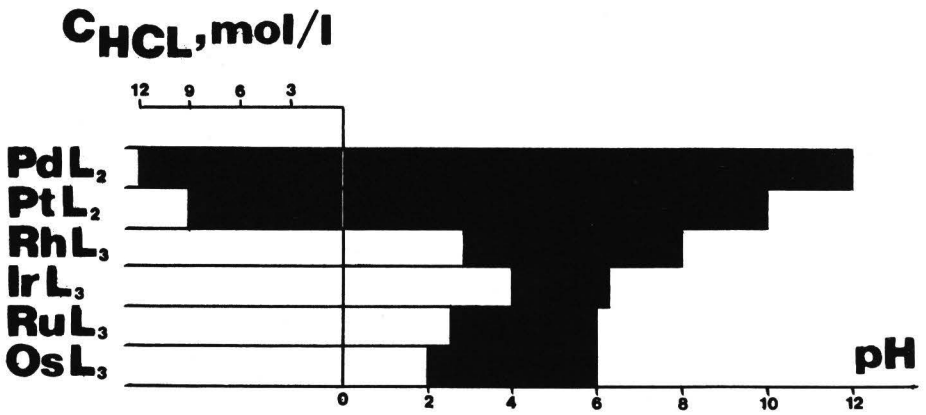


Fig. 1. Extraction properties of benzene-dithiocarboxylates of platinum metals

Composition of the formed complex compounds in $CHCl_3$ is determined by mole-ratio, continuons variation methods, shift of equilibrium and by means of the Bjerrum function and Asmus method and is found to be: PdL_2, PtL_2, PtL_4, RhL_3, IrL_3, OsL_3, OsL_4, RuL_3 (L - dithiocarboxylate- ion).

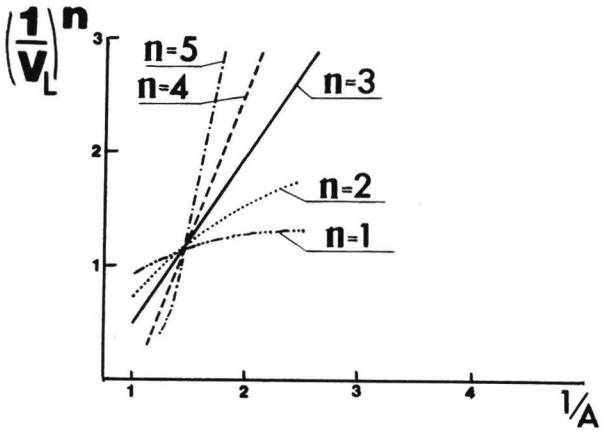
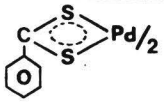
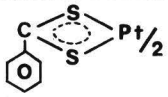
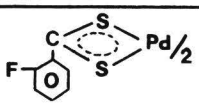
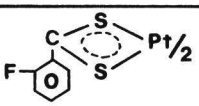
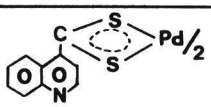
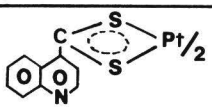


Fig. 2. Composition of ruthenium 4-methoxybenzenedithiocarboxylate in chloroform extract by Asmus method

It has been found that 4-quinolinedithiocarboxylic acid cannot be extracted with $CHCl_3$ as distinct from 2-,6-,7- and 8-quinolinedithiocarboxylic acids. Similary, the extraction of 4-quinolinedithiocarboxylates of platinum metals with $CHCl_3$ and other organic solvents does not take place as readily as that of other quinolinedithiocarboxylates of platinum metals. The extraction of 4-quinolinedithiocarboxylates increases in the presence of aliphatic amines and this phenomen found its practical application in the development ofmethods for the determination osmium traces in various objects.

Extraction constants for dithiocarboxylates of platinum metals in the system water-chloroform(1:1) have been determined by means of the computer.

Table 1. Extraction constants of some platinum metals dithiocarboxylates

Complex	K_{ex}
	$1,9 \cdot 10^{19}$
	$1,2 \cdot 10^{22}$
	$4,3 \cdot 10^{25}$
	$1,5 \cdot 10^{28}$
	$2,3 \cdot 10^{9}$
	$1,0 \cdot 10^{10}$

It has been found that reagents containing $\geq C=S$ and -SH groups (Yoshino Y., Uehiro T., Saito M. -Chem.Lett. 1978,p.487) in aqueous solutions react with aquahydrogenethylenediaminetetraacetato ruthenium(III), We have studied the extraction of $[RuYL]^{2-}$ in the presence of hydrophobous cations: diphenylguanidinium(DPG), triphenilguanidinium(TPG) in isopentanol:chloroform (3:7), isopentanol, butanol and chloroform.

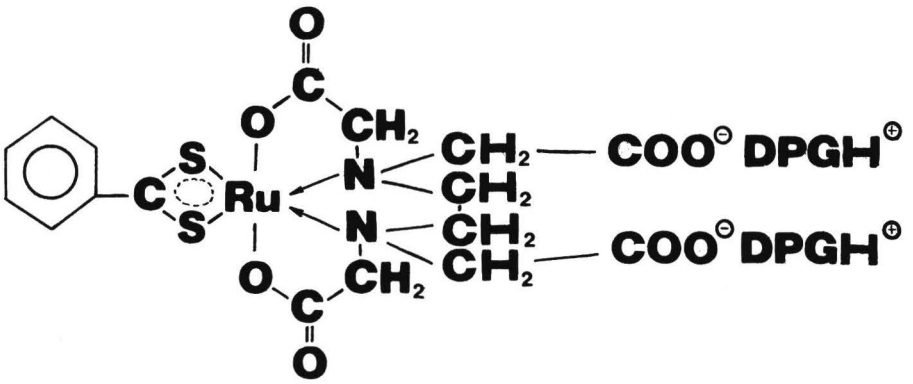
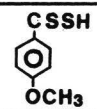
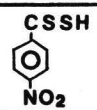
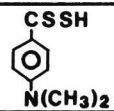
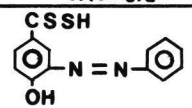


Table 2. Extraction degree(%) of the ruthenium(III) ionic associates containing benzenedithiocarboxylate-ions

Organic solvents	Hydrophobous cations	
	$DPGH^+$	$TPGH^+$
Isopentanol : chloroform (3:7)	99,9	99,9
Isopentanol	85	81
Butanol	80	79
Chloroform	31	22

Table 3 represents the data of spectrophotometric determination of platinum metals using several dithiocarboxylic acids. We have also developed a spectrophotometric extraction method for the determination of platinum in the anti-tumour preparation (cis-diaminodichloroplatinum) by use of tetraethylammonium benzenedithiocarboxylate.

Table 3. Spectrophotometric determination of platinum metals

Reagents	Me	μg/ml	$\varepsilon \cdot 10^{-4}$	λ, nm	Acidity
	Pd(II)	1 - 6	2,4	380	12M HCl - pH 10,0
	Pd(II)	0,2 - 1,2	2,3	305	4M HCl - pH 7,1
	Ir(III)	0,05- 25	2,8	420	pH 6,0- 7,9
	Rh(III)	0,01 - 3,5	10	455	pH 3 - 6
	Pt(II)	0,008 - 3,00	23	500	1M - 3M HCl
	Ir(III)	0,01 - 3,5	18	495	pH 8,0 - 12,5

Reference: Mežaraups G. - Platinum metal dithiocarboxylates. Izv. AN Latv.Ser.Chem. 1987. № 2, pp. 192-198

4. NUCLEAR FUEL CYCLES

Solvent Extraction 1990, T. Sekine (Editor)

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THE USE OF SOLVENT EXTRACTION IN THE NUCLEAR FUEL CYCLE, FORTY YEARS OF PROGRESS

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ABSTRACT

The high degree of purity required for the fissile and fertile elements used as fuels in nuclear reactors has made solvent extraction the choice as the purification method in the different steps of the fuel cycle. This technique, owing to its specificity, and its adaptability both to continuous multi-stage processes and to remote control, has served to achieve the requisite purities with safe, reliable operation. A review of the different steps of the cycle, including uranium and thorium production, uranium enrichment, reprocessing, and the recovery of transuranics, highlights the diversity of the solvents used and the improvements made to the processes and the equipment. According to the different authors, this technique is capable of meeting future needs, aimed to reduce the harmful effects associated with the nuclear fuel cycle to the lowest possible levels.

FOREWORD

Solvent extraction in the nuclear fuel cycle! Not a new subject. Spence [14] at the 1971 ISEC and, more recently, Naylor [27] at the 1986 ISEC have discussed it brilliantly.

Today, I should like to review the general features of the method, its application in the different steps of the cycle, including the elements of nuclear importance such as thorium and transuranic by-products of reprocessing.

INTRODUCTION

The first question that comes to mind is: why solvent extraction? A historical review of the first nuclear applications of this technique has been compiled by Spence. He showed that the purity required for the uranium feeding the first atomic reactors was far above the usual standards for industrial metals. The need accordingly arose for a separation method involving the specific properties of uranium, particularly the property of uranyl nitrate of being soluble in ethyl ether. A first industrial installation was built in the United States, in which countercurrent extraction in a cascade succession of stages achieved good recovery of the uranium, and thorough purification by means of effective washing. A few years later, the reprocessing of fuels from natural uranium reactors drew on the same technique to recover and purify the unconsumed uranium and the plutonium formed, with comparable properties at the same degree of oxidation. For reprocessing, the objective of recovering fissile species was compounded by extremely high decontamination standards concerning the ß/γ emitter fission products. To minimize personnel irradiation, the process was implemented in remote-controlled and maintained installations. The extraction technique proved to be ideal for these constraints.

As to the process, the refining of uranium and the reprocessing of natural uranium fuels underwent similar developments in the first few years, with respect to the choice of solvents and their application in a continuous, high-performance process.

Ethyl ether being highly flammable, it was supplanted by less flammable ethers and ketones, which were applied in industrial installations. Very soon tributylphosphate replaced the ethers and ketones which demanded a high concentration of nitrate ions in the aqueous phase, playing the rôle of salting out agents.

The first extraction processes already set the structure of the now classic flow charts: extraction/scrubbing/stripping cycle, applied to the purification of an element, extraction/ washing/partition/stripping cycle for the combined purification of two elements and their separation.

Extraction units are divided into three classes: mixers/settlers, columns, and centrifugal extractors. The selection criteria are based on transfer kinetics in two-phase systems, speed of resolution of emulsions, capacity, and extractor size, factors influencing the investment costs, and, in some cases, criticality constraints. Over the years, constant improvements were made in each class of equipment, tending to boost efficiency, capacity and reliability in a hostile environment.

URANIUM PRODUCTION

Uranium is produced in two steps: (1) extraction from ores with a usual assay of 10^{-3} or sometimes less, yielding a solid compound containing more than 70% uranium (normally uranates), and (2) refining of this compound to obtain uranium of nuclear purity.

In the hydrometallurgy of uranium, solvent extraction emerged as an effective means of concentrating and purifying the element conveniently. From 1956, researchers at the ORNL [9] investigated amino compounds for the extraction of uranium and thorium from the aqueous solutions produced by the sulphuric leaching of uranium ores. This oxidized aqueous solution contains hexavalent uranium in the form of anionic uranyl sulphate complexes, which can be fixed on anion exchange resins or be extracted by amino solvents. The solvent extraction process developed (Amex process), over fixation on a fixed resin bed, offers the advantage of continuous operation with higher capacity. Tertiary amines are generally employed, diluted in aliphatic diluents containing a small amount of heavy alcohol (preventing the appearance of insolubles) or in aromatic diluents. This process is in widespread use today (United States, Canada, South Africa, France etc). Note that in South Africa [8,15] and France, some installations have used a mixed process (Eluex process) in which extraction by amines was performed on eluates of ion exchange resins. Due to the slow kinetics of the transfer reaction, the industrial installations use mixers/settlers of various types, and the current trend favours models in which circulation of the phases and agitation are performed by the same turbine.

Another important source of uranium is the recovery of this element as a by-product of the manufacture of phosphoric acid from phosphates. In the early 1970s, the following three processes were developed [29], given here by order of importance.

(1) The TOPO/D2EHPA process (trioctyl phosphine oxide/di-2 ethyl hexyl phosphoric acid) which uses two purification cycles, and in which the extracted species is hexavalent uranium.

Uranium is stripped in the first cycle by reduction to U (IV) by the Fe (II) ion in phosphoric medium. Oxidation is then necessary to extract the hexavalent uranium in the second cycle, and stripping is carried out with ammonium carbonate. Improvements to this process have been proposed [1], aimed to reduce it to one cycle (URPHOS process) or to replace the two solvents by more efficient compounds of the same class, di-n-hexyl methoxy phosphine oxide for TOPO, and bis-dibutoxy 1-3 propyl phosphoric acid for D2EHPA, but these modifications did not lead to industrial applications.

(2) The OPPA process, which was used in the production of super phosphates. The solvent, octylpyrophosphoric acid, is employed diluted to 3% in kerosene. It extracts the tetravalent uranium, which is stripped by hydrofluoric acid in the form of the tetrafluoride UF_4. This process was used by Gardinier Inc.

(3) The MOPPA/DOPPA process, in which the solvent consists of an equimolecular mixture of mono- and di-octylphenyl phosphoric acids, extracting tetravalent uranium. Stripping takes place in 10 M phosphoric acid medium in the first cycle. In the second cycle, stripping is carried out with ammonium carbonate. The process has been used in Canada.

Many solvents were considered, but developments in the uranium market in the 1980s led to the closure of many production units, and the TOPO D2EHPA process is the only one used today in the area of phosphoric acid. R and D projects were simultaneously curtailed.

Mixers/settlers are generally used today. Pilot experiments in pulsed columns have been described on the TOPO/D2EHPA process [7] and in centrifugal extractors [18] (ISEC 1986) on the process using mono- and di-alkyl phosphoric acids.

After dissolution in nitric acid and, if required, clarification, the concentrates are refined by extracting the uranyl nitrate with tributylphosphate. The uranium solution (about 400 $g \cdot t^{-1}$) is sent to the extractor against a countercurrent stream of organic solution, consisting of TBP diluted to 20 to 40% in a paraffinic hydrocarbon. The desired purity is obtained by washing the solvent with nitric acid or purified uranyl nitrate. The nitrate is then stripped in deionized water. These liquid/liquid extractions take place in mixers/settlers or, more generally, in pulsed or mechanically-agitated columns.

THORIUM PRODUCTION

Unlike uranium, thorium does not have a fissile isotope, but like ^{238}U, ^{232}Th can lead to a fissile isotope by the capture of a neutron. The uranium 233 formed can hence allow a chain reaction. The thorium thus represents a potential reserve that is interesting for the supply of nuclear power. The possibility of regeneration has been inventoried, leading to programs for the purification of thorium and the production of uranium 233. While this alternative has not to any degree enjoyed the development comparable to that of uranium, work has been carried out on it in many countries.

Monazite is one of the most important of natural thorium resources. Concentrates are obtained after sulphuric or sodium leaching by precipitation methods. However, several solvent extraction processes have been employed on solutions from sulphuric leaching [17]. They are based on the

ORNL work already mentioned, thorium being extracted preferentially by primary or secondary amines. The uranium present is removed by extraction in a tertiary amine. The thorium is then extracted in a primary amine.

Also noteworthy is the use of di-alkyl phosphoric acids to perform extraction, with the thorium then recovered in sulphate form after stripping with 10 M sulphuric acid.

For uranothorianite ores, the presence of thorium and uranium leads to the simultaneous purification of both elements by the extraction of their nitrates with tributylphosphate. Since thorium is less extractable, the aqueous phase must contain large amounts of nitrates. For example, the Bouchet plant (France) used 33% TBP in kerosene to extract an aqueous solution of U and Th nitrates containing 1 M HNO_3 and 4 M $NaNO_3$. The U and Th nitrates were recovered by stripping with water from TBP, and the thorium was precipitated from this solution by oxalic acid [12].

Thorium is refined from impure concentrates in a tributylphosphate extraction cycle [6]. The concentration used varies from one country to another. The diluent may be paraffinic (kerosene) or aromatic (Solvesso-150, xylene). Weldon Spring (USA) extracted thorium from a nitric solution in a concentration of 0·5 M in acid, 1·25 M in magnesium nitrate. The 45% solvent in hexane was treated with water, thus achieving incomplete partition of the thorium and small amounts of uranium present. The aqueous solution obtained was purified by extracting the uranium entrained with the thorium, by 10% TBP.

These nitrate extractions with TBP were performed in mixers/settlers or in columns.

ENRICHMENT

Enrichment is the step of the fuel cycle that involves the physical separation of the two uranium isotopes 235 and 238, by gaseous diffusion and by centrifugation in present industrial processes, and possibly by laser extraction in the future. It is interesting to note that the separation technique by chemical exchange, investigated since the 1960s, has led in France to a process which, although lacking industrial implementation, reached the pilot stage before closing process development in 1988. This is the Chemex process, a term which incorporates the two components, chemistry and extraction. The main features of this process were reported recently [20].

The exchange reaction occurs between the species U^{3+} and U^{4+}, with the isotope 238 being concentrated in the trivalent species. Separation is based on liquid/liquid extraction exploiting the different behaviours of the two species in hydrochloric medium. Tetravalent uranium is extracted in tributylphosphate, whereas U^{3+} remains in the aqueous phase. The TBP is used at about 40% in a commercial mixture of alkyl benzenes (Solvesso 150). The U concentration is 0·5 to 0·6 $mol \cdot l^{-1}$. The aqueous phase contains 4·6 to 5·2 $mol \cdot l^{-1}$ of hydrochloric acid, and 1·5 to 1·8 $mol \cdot l^{-1}$ of uranium consisting of 94% trivalent uranium.

Pulsed columns are used for this exchange reaction, operating in a continuous organic phase. Given the large number of stages necessary to achieve significant enrichment, the columns are mounted in series. The cascade has a reflux recycling the uranium at its two ends: in the aqueous phase after reduction, and in the organic phase after oxidation and extraction.

In the pilot plant experiment conducted in Grenoble, 16 columns were used in series, each of them 150 mm in diameter and 50 m high.

REPROCESSING

The goal of this operation is to recover the non-transmuted uranium and the plutonium formed for subsequent uses: recycling after enrichment for U, fabrication of weapons or mixed fuels for Pu. These elements are purified in a liquid/liquid extraction step after dissolution of the fuels in nitric medium.

Due to the high radioactivity of the irradiated fuels, considerable R and D work and constant improvements in industrial operation have been carried out to guarantee (1) quantitative recovery of perfectly decontaminated species (decontamination factor 10^6 to 10^8), (2) safe conditions for operating personnel, (3) maximum reduction of wastes, and (4) packaging of the wastes.

Historically, after the implementation of the Redox process using methylisobutylketone as solvent in the United States [11], and the Butex process using dibutoxy di-ethyl ether in the United Kingdom [16], tributylphosphate became the sole choice in the 1950s. Today, as observed by Naylor [22] at ISEC 1988, it still represents the universal solvent for the nuclear fuel cycle, because of its many favourable properties: satisfactory extraction power eliminating the need for salting out agents, good chemical stability, good physical properties although its density and viscosity require its dilution in heavier solvents than water, carbon tetrachloride CCl4, for example, or lighter solvents such as paraffinic hydrocarbons. Some installations have operated with CCl4, while most of the others use either n-dodecane, mixtures of isomers of hydrogenated tetrapropylene, or saturated hydrocarbons containing naphthenes.

No single extraction flow sheet with TBP exists, but many flow sheets adapted to the problem at hand [28]. For natural uranium or slightly enriched fuels, the TBP concentration normally used is 30%. The uranium and plutonium are co-extracted and then separated by reducing partition, in which the plutonium reduced to the trivalent species is returned to the aqueous phase. The uranium is then stripped with very dilute acid. This partition can be carried out either in the first cycle or in the second. In every case, it is followed by one or more purification cycles for each of the elements.

In the processing of highly-enriched fuels (often based on U/Al alloy), the plutonium in very small quantities is not recovered. In reduced form (Pu III), it follows the fission products. The uranium purification cycles use dilute TBP (less than 10% as a rule).

The reprocessing of mixed fuels from fast breeder reactors (UO_2/PuO_2 mixture), already carried out in pilot installations, is characterized by an increase in the Pu/U mass ratio.

Irrespective of the type of fuel reprocessed, the U/Pu separation operation is essential, and the decontamination factor of U in Pu is close to 10^6. The reducing agents used to perform this separation are ferrous sulphamate, a rapid reducing agent but presenting the drawback of introducing foreign salts into the system, uranous nitrate stabilized with hydrazine, also rapid, whose ions increase the uranium inventory, and hydroxylamine nitrate stabilized with hydrazine, whose action is slower than the other two, but without increasing the salt content. The use of electrolysis in

stabilized medium help to avoid the introduction of a reducing chemical reagent [25]. It has not yet been applied to large industrial units.

Among the specific features of nuclear fuel reprocessing, the effect of α/ß/γ radiation on the solvent causes a change in its properties. The appearance of di- and mono-butyl phosphoric acids has many consequences. On the one hand, these compounds are strong chelatants to the ions and species in solution such as uranyl ions, tetravalent plutonium and zirconium, and their extraction is increased, while their stripping becomes more difficult.

Losses of fissile material in the effluents, and a concomitant increase in their activity are observed. As to zirconium, this chelating action is reflected by an increase in the γ activity of the solvent and possibly the appearance of precipitates at the interface of the two aqueous and organic liquids. These solids accumulate, causing increasing solvent degradation and decreasing performance.

Some of these compounds also display surfactant properties. If their content is too high, the operation of the extractors is disturbed, particularly by the physicochemical change in the materials, such as wettability.

Prevention of the formation of these acidic compounds relies in particular on the maximum possible reduction of contact time between the aqueous phase containing the fission products and the organic phase. Short contact time extractors have been employed, including columns and centrifugal extractors. The latter have been used since 1966 at the American Savannah River plant in the first extraction cycle, with highly satisfactory results [23]. At the Marcoule plant where mixers/settlers are employed, the process has been altered, since prevention by reducing contact time was unfeasible. The introduction of hydrofluoric acid into the aqueous solution in strictly calculated quantities has led, through selective chelating of zirconium, to a significant improvement in performance [5]. This process has been in operation for 20 years.

Very close attention has been paid to these processes and to their consequences in the design and construction of the large facilities in service and being built in France. Bernard and Chenevier [3] have described the improvements made to the process and to the equipment of the UP3 plant. They include the following.

(1) Special treatment of the solvent discharged from the plutonium purification cycles before its regeneration and recycle. This consists of stripping the tetravalent uranium in mixers/settlers, traces of plutonium subsisting in the TBP after stripping with hydroxylamine nitrate.

(2) Vacuum distillation of the solvent, regenerated in the standard manner by carbonate and caustic washing. This operation, performed on a part of the stream, achieves additional decontamination and serves to remove the heavy products resulting from the degradation of TBP.

(3) Diluent washing of all the aqueous streams leaving the extractors to remove the soluble or entrained TBP. The subsequent degradation of the TBP tends to disturb the operation of the evaporators. This organic washing stream has a low throughput and is added to the rest of the solvent at the regenerator inlet.

(4) New extraction units are planned in the first cycle. These are annular columns designed to solve criticality problems. They are fitted with baffle plates. It has been shown that this type of

plate is far less sensitive to a variation in wettability of the material than sieve trays. If the acidic alkyl phosphorus compounds are deposited on the surfaces, they become hydrophobic and considerable disturbances are observed in the hydrodynamic conditions and hence in performance. These consequences are absent with baffle plates.

It is interesting to note that, in addition to TBP, tertiary amines have been used in some installations [30]: La Hague, Eurochemic in the plutonium purification cycle, Eurex in the reprocessing of irradiated U/Al fuel. At the La Hague plant, extraction by trilaurylamine was performed in nitric medium of moderate acidity, the extracted species being $Pu(NO_3)_6(R_3HN)_2$. The plutonium was stripped without changing the oxidation state, by placing the solvent in contact with a sulphuric aqueous solution. The low capacity of the solvent, and the presence of sulphate ions, led to the replacement of this purification cycle by a tributylphosphate cycle after seven years of operation.

After nitric dissolution of metallic thorium, or of the oxide ThO_2 or the mixed oxide ThO_2/UO_2, irradiated thorium was reprocessed from the 1950s in the United States, and also, on a smaller scale, in the United Kingdom and France. The process used is similar to the Purex process (Thorex process). It employs TBP [4]: the main differences are as follows: (1) the low extraction coefficient of thorium compared with uranium, hence the need to salt out by aluminium nitrate in weak acid medium, or by strong nitric acid, (2) thorium/uranium partition is performed without a valency change, exploiting the difference in extractibility of the two elements, and (3) the limited solubility of thorium nitrate in the TBP/paraffinic diluent mixture leading to low saturation and to decontamination of fission products lower than that obtained in the Purex process.

One of the planned uses was the reprocessing of ThO_2/UO_2 fuels from high-temperature reactors. The limited development of these reactors and of the uranium 233/Th reactor led to the abandonment of these projects.

RECOVERY OF TRANSURANIUM ELEMENTS

Among the by-products of the reprocessing of irradiated fuels, the transuranium elements Np, Am and Cm have given rise to recovery for subsequent use in various applications, chiefly to supply the programme of isotopic power generators. The irradiation of these elements in high-flux reactors has led to the production of plutonium 238 and curium 244, as well as transcurium elements. Although these activities appear as auxiliary to the fuel cycle, they are associated with it by their general characteristics: very high radioactivity of the isotopes, high purity required. Thus the methods of approach to the treatment of targets benefited from the experience gained in reprocessing and, in exchange, provided information about the extraction of trivalent actinide species, and the degradation of solvents containing short-lived emitters, two problems that reprocessing may have to contend with in the future.

In the extraction processes, neptunium 237 has properties similar to those of uranium and plutonium in the same valency state. The species NpO_2^+ is relatively unextractible and stable. By slight changes in the conditions of the Purex process [13], neptunium can, in the first cycle, either accompany the fission products, or accompany the U and Pu, most of it following one or the other in

partition. It is then separated from them in their respective purification cycles. Since it is in very dilute solution, it can be recycled to the process for concentration. Final purification is carried out on anion exchange resin or by liquid/liquid extraction using a tertiary amine, the extracted species being the hexanitrate $Np(NO_3)_6(R_3NH)_2$. In the treatment of irradiated targets for the production of plutonium 238, the same separation methods are found, namely ion exchange or liquid/liquid extraction, as indicated above for the purification of neptunium. In the latter case, the first cycle is designed to extract the tetravalent species of neptunium and plutonium, with the separation of plutonium being performed by reduction to the trivalent state, followed by a purification cycle for each element [2].

The elements americium and curium have properties very similar to those of rare earths, particularly in oxidation state +3 of the ions in solution. Their extraction from high-level waste solutions was described by Orth [24] at the 1971 ISEC. Batch processing by 50% TBP of these extremely radioactive solutions, whose acidity has been reduced and the nitrate concentration raised to 6 M, leads to the recovery of the mixture of trivalent actinides and lanthanides. The separation of these two families of compounds represents the delicate part of the purification step. It has been the subject of many liquid/liquid extraction investigations: (1) extraction cycles in concentrated chloride medium, the solvent being a tertiary amine: the species $M\,Cl_5(R_3NH)_2$ are more stable in the case of actinides, which allows their separation (Tramex process), (2) extraction by TBP in nitric medium followed by separation by chromatographic development with diethylene triamine pentacetic acid (DTPA) on ion exchange resin, and (3) the Talspeak process using extraction in nitric medium by di-2-ethylhexyl phosphoric acid (D2EHPA) in the presence of DTPA: a similar process was developed with trilaurylamine and then TBP as solvents, and implemented in the extraction chromatography technique [21].

In recent years, research has been directed towards the extraction of the actinide elements from aqueous reprocessing effluents. The goal is to minimize the presence of long-lived emitters in the wastes to be stored, to limit their long-term detriment. The search for solvents capable of extracting the trivalent elements in highly acidic medium, without the addition of nitrates, has been guided towards bidentate compounds. Carbamoyl methylene phosphonates and phosphine oxides have been suggested by American researchers, and were reviewed by Schulz [26] at ISEC 88. They allow extraction in up to 7 M nitric or hydrochloric acid medium. The Truex process has thus been tried out in American production sites to treat high- and medium-level liquid residues [19]. The solvent is octyl phenyl N-N-di-isobutyl carbamoyl methyl phosphine oxide (CMPC), which can be used in a mixture with TBP. The trivalent elements are stripped by dilute acid, and the tetravalent elements by the HNO_3/HF mixture.

Another class of solvents, currently under development in France in particular [10], is represented by the diamides of carboxylic acid, which offer the advantage over organophosphorous compounds of being completely incinerable. Here also, extraction can be achieved in highly acidic medium, with stripping by dilute acid.

CONCLUSIONS

As we have seen, the solvent extraction process has been applied for over 40 years to a wide variety of purification problems in the different steps of the fuel cycle, and often in extremely severe irradiation conditions. The experience gained concerns many organic compounds involving the main mechanisms of extraction: solvation, cation exchange and anion exchange.

This experience has furnished an invaluable body of data to pursue the essential objectives: enhanced recovery performance of valuable elements, and reduction of the activity of wastes to be packaged.

Intensive fuel reprocessing may prove advisable in the long term. One could then consider not only the separation of uranium and plutonium, but also that of all the elements with long-lived isotopes, whose detriment would be unacceptable for future generations. Should such a programme become necessary, solvent extraction will occupy an important place in the processes, given the qualities hitherto exploited in the fuel cycle.

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THE DEVELOPMENT OF A THREE-CYCLE CHEMICAL FLOWSHEET TO REPROCESS OXIDE NUCLEAR FUEL

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ABSTRACT

The Thermal Oxide Reprocessing Plant (THORP) is currently being built and commissioned at Sellafield. Theoretical studies and early laboratory work suggested that five solvent extraction cycles would be required. Uranium and plutonium would be separated in the first cycle and each of these products would then be passed to two further purification cycles.

Subsequent laboratory basic chemistry studies and development work using alpha and fully active miniature pilot plants showed that careful control of technetium, neptunium and plutonium redox chemistry allowed product specifications to be met by the first of each of these pairs of purification cycles alone. It was therefore possible to delete two solvent extraction cycles from the plant and achieve a significant reduction in its size, cost and complexity.

1. INTRODUCTION

Magnox uranium metal fuel has been reprocessed at the Sellafield site of British Nuclear Fuels for over twenty-five years using the Purex solvent extraction process with tri-n-butyl phosphate (TBP) diluted with odourless kerosene (OK). The Thermal Oxide Reprocessing Plant (THORP), which is currently being built and commissioned at Sellafield, will reprocess uranium oxide fuel from United Kingdom, Japanese and European light water and advanced gas-cooled reactors. The Purex process was also selected for THORP but account had to be taken of the differences between Magnox and Oxide fuel.

The flowsheet design and chemical development work was governed by the need to meet product purity specifications against the increased input and different proportions of the fission products and by the need to reduce the environmental impact and operator radiation dose of the new plant. A flowsheet was therefore developed which, whilst giving a high degree of product purity, minimised the number of waste streams and the overall size and complexity of the plant and which avoided adding indestructible reagents to the process which would emerge in waste streams and restrict their further treatment.

This flowsheet is shown in simplified form in Figure 1. Separation of uranium and plutonium from fission products and from each other is carried out in the first (HA) cycle using pulsed columns and this is followed by separate single cycles for uranium purification (UP) using mixer settlers and plutonium purification (PP) using pulsed columns.

2. FLOWSHEET DEVELOPMENT

The first step in the development of the flowsheet was to define a specification for the uranium product (Table 1); this allowed the decontamination factors (DFs) required for the various species across the process to be calculated.

TABLE 1
THORP product specification and required decontamination factors

Species	Specification	Decontamination factor required (1)
Total alpha (Bq g^{-1} U)	250	
Plutonium (Bq g^{-1} U)	208	7.65×10^5
Neptunium (Bq g^{-1} U)	42	3.14^5
Ruthenium (KBq g^{-1} U)	10	6.7×10^5 (2) 4.2×10^4 (3)
Other gamma (KBq g^{-1} U)	1.1	
Technetium (ppm)	4	274

(1) Decontamination factor (DF) = Contaminant/U in feed / Contaminent/U in product

(2) One year-cooled fuel

(3) Five year-cooled fuel

Difficulties were expected in the achievement of the specification for technetium, because it is produced in high yield in oxide fuel and is relatively extractable and neptunium, because of its complex chemical and solvent extraction behaviour. It was necessary to ensure good DF's for these species whilst maintaining satisfactory U-Pu separation.

Process chemistry development work on the behaviour and control of technetium, neptunium and plutonium was therefore carried out using basic laboratory chemical studies and a range of pilot plant facilities. These included a 1/6000 scale full active replica of all the THORP solvent extraction cycles using irradiated oxide fuel as feed stock (the Miniature Pilot Plant), a 1/5000 scale alpha active glovebox facility using uranium, plutonium, neptunium and technetium as feed stock and a 1/250 scale alpha active pulsed column facility using uranium, plutonium and technetium.

3. TECHNETIUM AND NEPTUNIUM BEHAVIOUR IN THE HA SOLVENT EXTRACTION CYCLE

The HA solvent extraction cycle of THORP separates uranium and plutonium from the fission products in an extract and scrub system and then separates uranium from plutonium in the 1B system using uranous nitrate (U (IV)) to reduce Pu (IV) to Pu (III). The reduced forms of uranium and plutonium are stabilised against nitrite re-oxidation by the addition of hydrazine.

3.1 Technetium

It was expected that some technetuim would co-extract with uranium and enter the 1B system. Fully active trials in the Miniature Pilot Plant showed, however, that zirconium present in irradiated fuel enhanced technetium extractability causing 100% of it to enter 1B. This technetium was shown to backwash with the plutonium and then follow the waste stream in

the PP cycle so that product qualities were not affected. A large amount of development work (Denniss and Phillips, 1990) was however necessary to minimise the effects of the technetium-hydrazine reaction in 1B whilst ensuring a satisfactory plutonium DF for the uranium stream and avoiding the complexity of a technetium removal system in the HA cycle.

3.2 Neptunium

Neptunium is present in the irradiated fuel feed largely as extractable Np(VI). It therefore follows the uranium-plutonium stream from the first extract and scrub contactor into the 1B system. Here the uranium (IV) reducing conditions are sufficient to reduce neptunium to the extractable (IV) state and it therefore follows the uranium-in-solvent stream to the UP cycle. The DF for neptunium on the uranium stream in the HA cycle is thus poor and it was therefore necessary to design the UP cycle to remove the bulk of the neptunium as well as removing residual plutonium and fission products.

4. NEPTUNIUM AND PLUTONIUM BEHAVIOUR IN THE UP CYCLE

Plutonium has three common valency states (III, IV and VI) and two of these are important in the solvent extraction process; Pu (IV) which is extractable and Pu (III) which is inextractable and can be produced by reduction of Pu (IV). Neptunium exists also in three common valency states (IV, V and VI) which can be readily inter-converted by redox or disproportionation reactions (Guillaume, 1984). Neptunium (IV) and (VI) are extractable but neptunium (V) is not (Guillaume, 1984).

4.1 Neptunium in the UP cycle first contactor

The most efficient way of separating neptunium from uranium was considered to be the formation of inextractable Np(V) followed by forward extraction of the uranium in the first UP cycle contactor, UP1 (Figure 2). The feed to the UP cycle contains 100% Np(IV) and so the requirements for an oxidising pre-treatment were examined by laboratory experiments. Heating Np(IV) at low acidity had been reported to form Np(V) (Srinivasen, 1974) and a series of trials allowed the optimum conditions to be determined. A low acid feed is not suitable for uranium extraction and further laboratory trials were carried out to establish the temperature conditions which allowed subsequent acidification without destroying the Np(V).

4.2 Plutonium in the UP cycle first contactor

During the neptunium conditioning process, plutonium will remain as extractable Pu (IV). A simple UP1 uranium extraction contactor, whilst providing a good neptunium DF, would therefore not provide any decontamination from plutonium. Use of uranium (IV) to reduce the plutonium as in the 1B system would reduce the Np(V) to extractable (IV) and was thus ruled out.

Hydroxylamine nitrate (HAN) however was known to reduce Pu (IV) to Pu

(III) but not Np(V) to Np(IV) (Guillaume, 1984) and so the effect of a low temperature, low acid hydroxylamine scrub feed to UP1 was examined in alpha active experimental trials. It was necessary to optimise by experiment the temperature and acidity, these being required to be low to minimise disproportionation of Np(V), whilst higher acidities are ideally required for efficient uranium extraction.

4.3 Neptunium and plutonium in the UP cycle second contactor

Instead of following UP1 with the usual uranium backwash contactor, it was considered that further useful decontamination of the uranium from neptunium and plutonium could be achieved in a compound plutonium backwash and uranium re-extraction contactor. Plutonium backwash is achieved by using HAN again, with a higher temperature and a low acidity optimised experimentally to give the best balance of plutonium and neptunium removal from the uranium. The first UP cycle is completed by a third contactor, UP3, providing a simple low acid backwash of the uranium.

5. EXPERIMENTAL VERIFICATION OF THE UP CYCLE FLOWSHEET

Initial testing of the flowsheet was carried out in the alpha-active 1/5000 scale facility at Sellafield using the expected quantities of plutonium, neptunium and technetium in the UP1 feed and a small amount of ruthenium derived from the Magnox plant. Very good DFs were demonstrated as shown in Table 2, which compares achieved DFs with those required to meet the specification. It can be seen that for plutonium, neptunium and technetium a single UP cycle is more than capable of meeting the product specification and with five-year cooling of fuel before reprocessing, the ruthenium specification is also comfortably met.

TABLE 2

Decontamination factors measured in alpha active trials

	Plutonium	Neptunium	Ruthenium	Technetium
DF required across UP Cycle (1)	232	190	37 (2) 2.3 (3)	1
DF achieved in UP cycle	>560	$>3.7 \times 10^3$	18	10

(1) DF required to achieve specification
DF achieved in HA Cycle.
(2) One year-cooled fuel.
(3) Five year-cooled fuel.

Confirmation of these findings was provided by full testing of all cycles of the flowsheet using the Miniature Pilot Plant and actual irradiated oxide fuel. A total of 50 days active operation was carried out in five separate trials using different samples of AGR and LWR fuel. The results confirmed the findings from the alpha-active trials and demonstrated that the uranium product specification could be met comfortably by a single purification cycle (Table 3). It was thus possible to delete from the THORP

design the entire second UP cycle complete with the evaporator feeding it, thus reducing very significantly the size and complexity of the plant and the volume of effluent generated.

TABLE 3

Compositions of uranium product from miniature pilot plant
(corrected to basis of reference fuel, 40 Gwd/tU burn-up, five year-cooled)

Uranium product (UP3AP)	Pu alpha Bq/g U	Np 237 Bq/g U	Tc 99 ug/g U	Ru 106 Bq/g U
Pilot plant	<2	<1	<1	<200
Specification	208	42	4	10000

Parallel flowsheet development work on the plutonium purification cycles showed that the original provision of two cycles in this flowsheet was also unnecessary since the product specification was met by the first of these. This allowed the second plutonium purification cycle to be deleted to leave a THORP chemical flowsheet consisting of three solvent extraction cycles only.

6. CONCLUSIONS

The chemical development work carried out for THORP has allowed a flowsheet to be adopted using three solvent extraction cycles only. This has considerably reduced the size, complexity and cost of the plant and has reduced the number of waste streams requiring treatment.

Major contributors to these simplifications of the THORP process have been the development of an efficient uranium purification cycle using novel principles to obtain decontamination from neptunium and the ability to test the whole flowsheet under fully realistic highly active conditions, thus providing the essential confidence in the results.

The work has demonstrated the value of integrating the research and development closely with the design process so that each can influence the other, leading to an efficient process and a high degree of confidence in its performance.

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Fig 1. **Thorp Chemical Separation Plant**

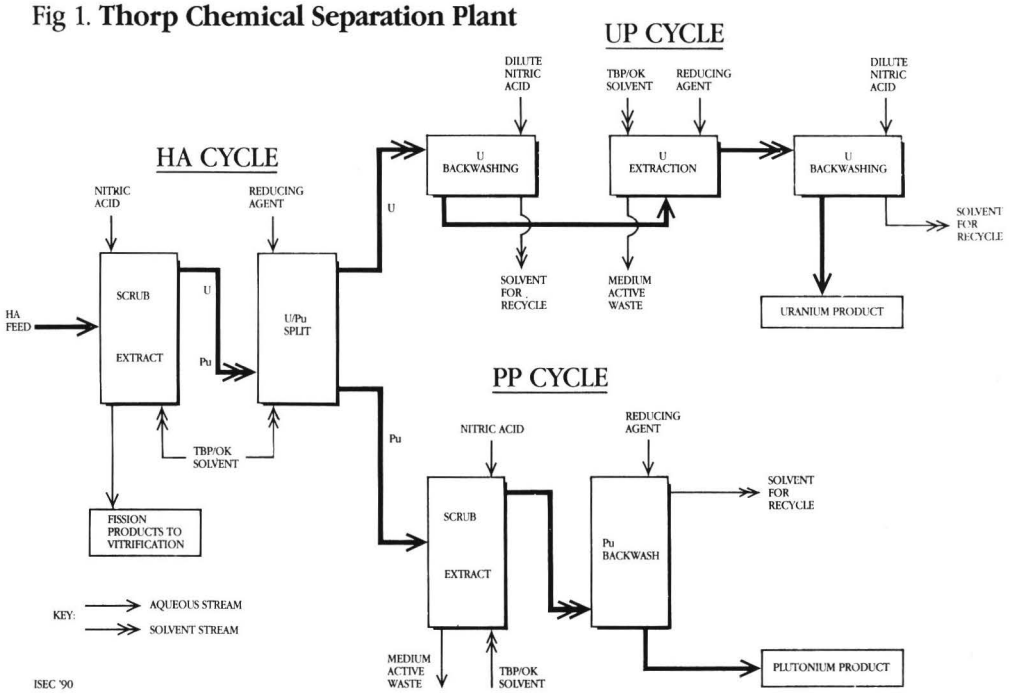
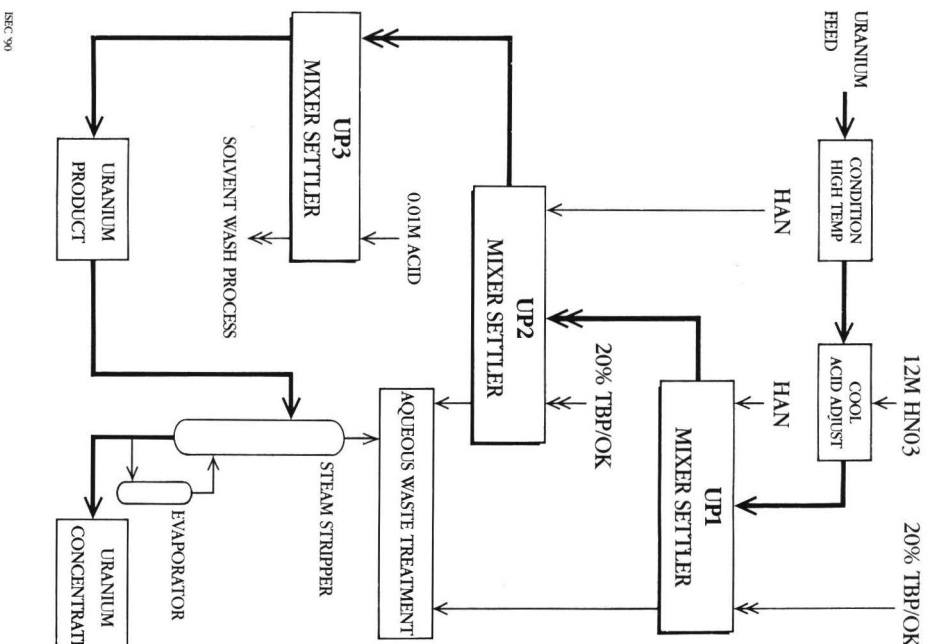


Fig 2. **Thorp UP Cycle**



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PROGRESS IN THE DEVELOPMENT OF A ONE-CYCLE PUREX PROCESS (IMPUREX)

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ABSTRACT

This paper presents our latest experimental results for the development of an IMproved PUREX process (IMPUREX) for the reprocessing of spent nuclear fuel. The new process allows to reach the product spefications required for the commercial process in one single extraction cycle instead of the traditionally employed five cycles. Waste and equipment minimization increase availabilty and reduce costs.

In two series of experiments in the highly-shielded laboratory-scale MILLI reprocessing facility true (i.e. not partially simulated) fuel of 31.5 GWd/t and 170 GWd/t respectively was reprocessed. The feed solution was first filtered and then clarified in an adsorption bed. The ultra-high loading of the solvent over almost all of the first extractor HA has to be considered as an inherent fission product scrubber and explains the observed excellent decontamination values. For additional Np decontamination an electroreductive first scrubber HS1 is proposed.

The IMPUREX process requires an efficient process control to keep the position uf the U-extraction front at a constant location close to the raffinate discharge of HA. As a controlling condition the temperature profile was employed. This works even in the very small mixer-settlers of MILLI with the associated noisy temperature signals.

A twofold feed clarification by a sintered metal filter and a diathomaceous earth adsorption bed resulted in processes without any hydraulic maloperations or interfacial deposits. The IMPUREX flowsheet reliably avoids Pu(IV) accumulations and associated criticality problems. Pu(VI) has to be reduced to Pu(IV) in the feed solution. The influence of the position of the U-extraction front in the first extractor on the decontamination factors of Cs, Ce, Ru, Zr, Tc and Np is discussed.

The MILLI results show that product requirements for reprocessing can be met in one extraction cycle as predicted theoretically. For occasionally occuring maloperations in industrial operation further product refinement by crystallization is proposed.

1. INTRODUCTION

A particularity of the Purex process is the extreme product purity required today. Decontamination factors have to be of the order of 10^5-10^6. In addition the product yield has to be better than 99% and the cost of radioactive waste is extremely high. R&D activities are therefore primarily directed to cost reduction by simplification of the traditional

5-extraction-cycles process. This paper discusses recent progress in the development of an IMproved 1-cycle-PUREX process IMPUREX.

2. THEORETICAL BACKGROUND

Simulations with the computer model VISCO (Petrich et al., 1986) predicted the possibility to avoid Pu-accumulations in the high-active first extractor (HA) of the Purex process by increasing temperature and/or acidity. Later experiments (Petrich and Schmieder 1988) fully confirmed the predictions. A detailed description of the theory was published by Schmieder and Petrich 1989.

3. EXPERIMENTAL RESULTS

After the 1986 discovery of the potential (Schmieder et al. 1987) of the new process conditions the following experiments were performed:

1986 First validation of the possibility to avoid Pu-accumulations in a highly saturated flowsheet in the lab-scale alpha-tight LABEX mixer-settler equipment (Petrich and Schmieder 1988)

1986 First test in the miniature pulsed columns of MINKA: no Pu-accumulations even at room temperature (Schön 1990).

1987 Numerous tests in LABEX concerning solvent degradation, Np and Tc extraction (Schmieder et al. 1987).

1988 First experiment in the highly shielded lab-scale mixer-settler facility MILLI with high burnup (170 GWd/t and 16 months cooling time) fast breeder reactor fuel (Bleyl et al. 1990).

1990 Second MILLI experiment with LWR fuel (31.5 GWd/t, 31 months cooling time).

3.1 Feed clarification and solvent degradation

In none of the hot experiments crud or hydraulic maloperations were ever observed. This is mainly attributed to a greatly improved feed clarification: after a preceding solid/liquid separation through a 1um sintered metal filter, the feed solution was further clarified in a diathomaceous earth adsorption bed first proposed by Benker et al. 1984. It was not yet possible to investigate the deposits in the filters. None of the samples taken later in the process showed any sediments.

The increased acidity and temperature of the IMPUREX process is increasing solvent degradation by hydrolysis. It came as a surprise to find smaller degradation in the MILLI runs under IMPUREX conditions than previously under conventional conditions. The reason obviously is the reduced exposition of the solvent to radiation:

* lack of interfacial deposits
* fission product accumulation is limited to the narrow low-U-saturation area.

3.2 Pu accumulations and Pu(VI) reduction

The original aim in the development of the new flowsheet was to reliably avoid Pu accumulations that can lead to criticality problems. This turned out to be easily achievable if there is no or only little Pu(VI) present in the feed solution. Pu(VI) is less extractable than

U(VI) and tends to accumulate close to the raffinate in the same way as all other extractable species that are successfully separated by the new process conditions. Special care has therefore to be taken to reduce Pu(VI) in the feed solution to the highly extractable Pu(IV) if Pu-losses to the raffinate are to be avoided.

The reduction of Pu(VI) to Pu(IV) was done electrochemically in the MILLI experiments. But while the 1988 experiment resulted in Pu-losses of about 0.2% (25 mg/l) the 1990 values were still higher and identified spectroscopically as Pu(VI). This increase is due to the not yet optimized electrochemical process.

3.3 Process control

The position of the U front in an IMPUREX-flowsheet is not a stable one. It is very sensitive to variations of most process parameters and should be kept constant by a closed loop controller for constant separation efficiency. In the MILLI and MINKA experiments the variation in the temperature profile generated by the extraction enthalpy of U-transfer was used as the controlling condition for automatic adjustment of the solvent flow. In the case of the small MILLI-mixer-settlers (50 ml/stage) the maximum extraction-induced temperature difference between two stages was 0.3°C at 56°C with a very poor signal/noise ratio of less than 1. Nevertheless, this was sufficient to keep U_{org} constant to within ±1 g/l at the position of the steepest gradient (Bleyl et al. 1990). In pulsed columns much larger temperature peaks facilitate this kind of automatic control.

3.4 The position of the U-extraction front

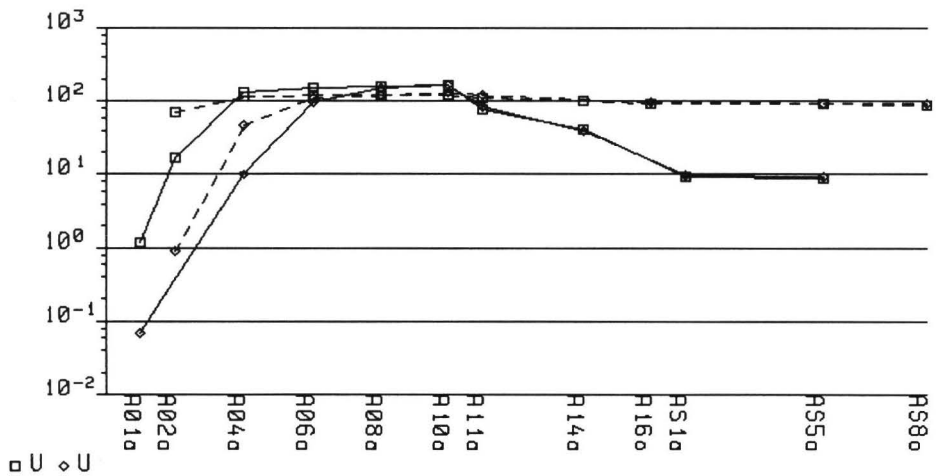


Fig.1. MILLI 1990: Organic (dashed lines) and aqueous (solid lines) U [g/l] profiles in the HA-extractor (stages A01-A10), HS1-scrubber (stages A11-A16) and HS2-scrubber (stages AS1-AS8) extractors. Organic product leaves at AS8o, Feed enters at A10a, raffinate leaves at A01a.

The diamond-marked profile of Fig.1 shows an U-loss of 70 mg/l and is referred to as "narrow-saturation" because the highly U-loaded zone extends over comparatively few stages and the U-extraction front is fully within the extractor. The square-marked profile, however, shows an U-loss of 1 g/l and is referred to as "wide-saturation": the extraction

front is cut off at the raffinate outlet and almost all of the HA-extractor is highly saturated. In this case the accumulation zone for fission products will be very narrow and extremely high decontamination can be expected.

3.5 Neptunium

Np(VI) is almost as well extractable as U(VI) and therefore is expected to leave the HA/HS extractors largely with the organic phase. This is illustrated in Fig.2 by the two organic Np239-profiles. In the "narrow-saturation" case the maximum of the Np peak is well within the HA-extractor. In the "wide-saturation" case the Np peak is "pushed into the raffinate", more Np leaves with the raffinate and the Np product concentration is lowered by a factor of 3. The gradients of the Np profiles in the scrub sections (A11-AS8) are not changed, however, since U, HNO_3 and flow ratio are the same in both cases.

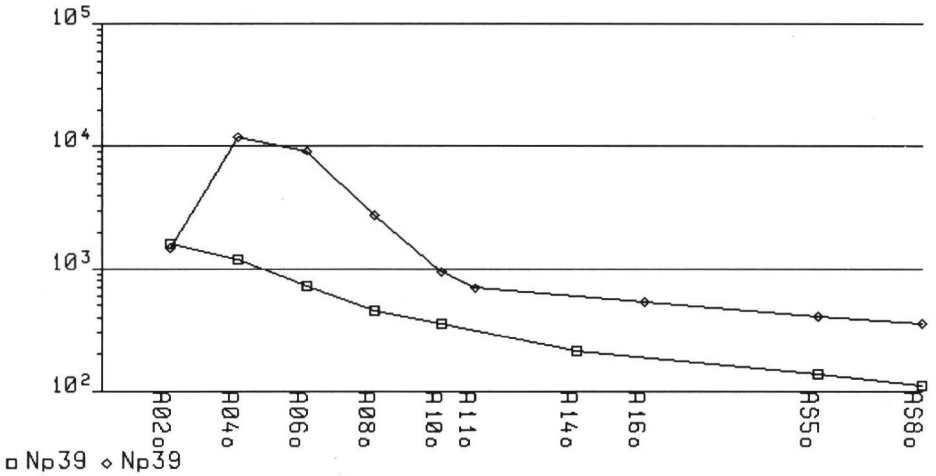


Fig.2. MILLI 1990: Organic Np profiles for the "narrow-" and "wide-saturation" cases (c.f. caption of Fig.1).

Np decontamination can be greatly improved by the use of an electroreductive scrubber as described by Schmieder et al. 1987. Under these conditions U(VI) and Pu(IV) are also partly reduced but in contrast to the less well extractable lower Np valencies they are rapidly reoxidized in the extraction section.

3.6 Zirconium

The separation of Zr is reduced by increased acidity and temperature. It is closely related to Tc-separation which is described by Kolarik et al. 1990. The 1988-MILLI run was carried out to prove reproducibility and stability: the U-front was kept extremely stable and a low-acidity second scrub was used. Then the result was an almost constant gross-gamma contamination of the Pu-product of 1 to 30 uCi/l/gPu (Ru-106 = <4..20, Cs-137 = 13..90, Ce-144 = 2..50, Zr-95 = 15..30 uCi/l).

In the 1990-MILLI run, however, a high-acidity flowsheet for the second scrubber was employed to study Tc-optimization. This led to the result of Fig.3.

In Fig.3 the solvent loading of stage 2 (which is a measure of the position of the U-front

close to the raffinate in stage 1) correlates well with the gamma contamination of the electrochemically separated (for recent progress see Galla et al. 1990) Pu-product. This contamination is almost exclusively due to Zr-95. More than 99% of Zr are found in the Pu-product. The closer the U-front is to the raffinate, the higher is the loading in stage 2, the more extends the Zr-peak "into" the raffinate and the better is the decontamination.

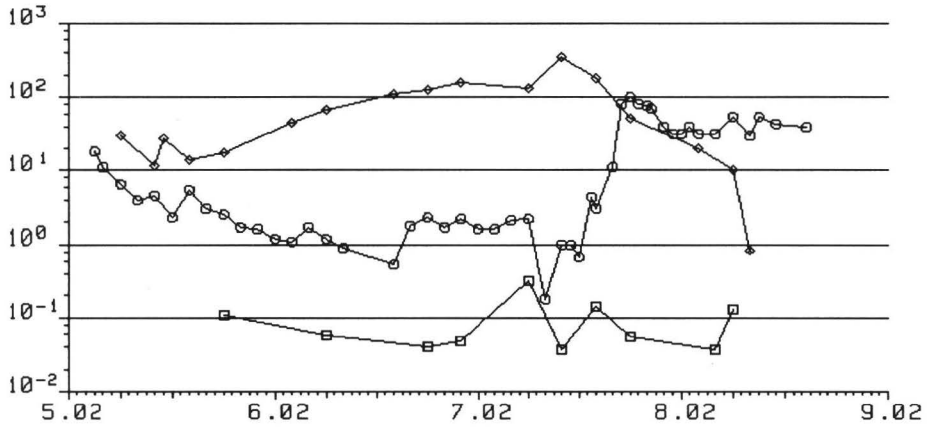


Fig.3. Correlation between the position of the U-extraction front (circles = organic U-concentrations in g/l in stage 2 of the first extractor) and decontamination (diamonds = gross-gamma contamination of the 1BSP-Pu-product after U/Pu-split in uCi/l/gPu, squares = gross-gamma contamination of the 1CU-U-product after U-backwash in uCi/l/gU) as a function of date.

3.7 Other fission products and product quality

The U-product quality in Fig.3 is independent of the position of the U-front. This is also observed for Ru, Cs and Ce in the Pu-product. The remaining contaminations are well below the permissible limit and are probably colloidal impurities. In some cases analytical problems with contaminated samples allow only to give the low limit of the decontamination factors.

Table 1: U-product decontamination factors

	FBR MILLI ([1]) conventional	FBR MILLI 88 ([1]) IMPUREX	required([2]) for LWR	LWR MILLI 90 IMPUREX
Cs-137	1.7E4	5.0E5-1.3E6	ca. 1E6	7.4E5-9.6E7
Ce-144	6E4	1.5E6-4.5E6	ca. 1E6	1.7E6- >5E8
Ru-106	1.7E2	1E5-3E5	ca. 1E4	3E5-2E6
Zr-95	6E2	1E4-1.5E4	ca. 1E4	5E4-8E5
Tc-99	n.a.	5E2		>2E4

([1]) HS2P ([2]) 33 GWd/t, 7a

3.8 IMPUREX in pulsed columns

Feasibility of the IMPUREX flowsheet in the MINKA miniature pulsed columns was demonstrated already in 1986. In 1989 further experiments were conducted to study the separation of Np and Tc. There were no principal differences observed in comparison to the mixer-settler results (Schön et al. 1990). The experiments were hampered somewhat by

an insufficient heating and temperature control equipment for the first extraction column and by difficulties in feed adjustment.

3.9 Medium active waste minimization

Solvent wash with CO_2-loaded hydrazine instead of sodium carbonate demonstrated in both MILLI-runs how the major portion of medium active waste is avoided (Schmieder and Stieglitz 1974).

3.10 Product crystallization

Traditionally further extraction cycles are added to the Purex process to obtain the necessary product quality. Under IMPUREX, additional product refining may occasionally be needed for the technical process in the case of moderate maloperations. Henrich et al. 1987 proposed a simple crystallization procedure as a refining step. Experiments showed high additional DFs: in the 1990 MILLI experiment they were greater than 100 for most impurities in the uranylnitrate extraction product (Bauder 1990).

4. CONCLUSIONS

There is very little doubt that the IMPUREX process described above is feasible also for industrial scale reprocessing. Its one-cycle operation will improve process availability and will cut costs. Criticality problems are reliably avoided. Necessary prerequisites are sufficiently good feed clarification and a reliable control of the U extraction front. Process optimization depends largely on the specific requirements. Additional product refining by crystallization seems very promising. A technical scale demonstration facility would be the logical next step.

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BEHAVIOUR OF TECHNETIUM IN THE EXTRACTION WITH TRIBUTYL PHOSPHATE IN THE PUREX PROCESS

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ABSTRACT

Tc(VII) is coextracted with Pu(IV) in the form of the species $Pu(NO_3)_3(TcO_4).2TBP$. The coextraction is strongly suppressed at increased concentration of nitric acid. In the simultaneous extraction of U(VI) and Pu(IV) in the Purex process the behaviour of Tc(VII) is governed by its coextraction with U(VI) and the fission product Zr(IV). A flowsheet for improved separation of Tc(VII) from U(VI) and Pu(IV) was found by mathematical modelling of the behaviour of Tc(VII) in a counter-current extractor. The loaded solvent must be scrubbed at a sufficiently high scrub flow and the separation of Tc(VII) is improved by enhancement of the HNO_3 concentration in the scrub solution. The flowsheet was tested in hot counter-current experiments. Decontamination factors of 30 - 50 were attained with feed solutions obtained from irradiated LWR and fast breeder fuels.

INTRODUCTION

It has been shown that, in the extraction of nitrates with tributyl phosphate (TBP), pertechnetate ions are coextracted very strongly with Zr(IV) and less pronouncedly with U(VI) (Vialard, 1986; Kolarik, 1989, and references therein). Tc(VII) is also coextracted with Pu(IV) (Vialard, 1986). The coextraction can be troublesome in the first extraction cycle of the Purex process. A substantial part of the Tc fission product accompanies U(VI) and Pu(IV) in the solvent stream and follows them to the subsequent operation, namely the reductive separation of Pu from U. The efficiency of the separation can then be deteriorated, because Tc(VII) reacts with hydrazine and facilitates reoxidation of U(IV) and Pu(III). The performance of the Purex process is improved, if the fraction of Tc(VII) coextracted with U(VI) and Pu(IV) is kept as low as possible. To reach this aim, it has been suggested to introduce an additional contactor into the first extraction cycle of the Purex process (Boullis et al., 1988). Elsewhere it has been suggested to add oxalic acid to the feed solution (Vialard, 1986). This lowers the concentration of Zr(IV) in the organic phase and, consequently, suppresses the coextraction of Tc(VII). Our effort was to improve the separation of Tc from U and Pu without application of additional extractors or chemicals. We concentrated on the behaviour of Tc in a recent modification (Impurex) of the conventional Purex process. U and Pu are in the Impurex process extracted at elevated temperature, a high concentration of nitric acid and a

high loading of the solvent (Schmieder, 1989; Petrich et al., 1990). We gained more extensive data on the coextraction of Tc(VII) with Pu(IV), modelled the distribution behaviour of Tc(VII) in the simultaneous extraction of U and Pu(IV), and investigated the behaviour in counter-current experiments.

EXPERIMENTAL PART

Distribution experiments and determinations of Tc(VII), U(VI) and HNO_3 have been described elsewhere (Kolarik, 1989). Pu was determined by an x-ray flurescence method or α-spectroscopy. Counter-current experiments with a simulated feed solution were performed in a glove-box, laboratory scale mixer-settler device (total throughput <500 ml/h). The simulated feed contained 260 g U/l, 2.6 g Pu/l, 1 g Zr/l, 0.2 g Tc/l, 5.1 M HNO_3 and radioactive tracers (^{96}Tc and ^{95}Zr). Hot experiments with a real feed solution were made in the heavily shielded mixer-settler device MILLI (total throughput <1500 ml/h). The real FBR fuel feeds contained 190 - 220 g U/l, 27 - 29 g Pu/l and 4.9 M HNO_3, and the real LWR fuel feed contained 280 g U/l, 3.0 g Pu/l and 5.25 M HNO_3. The burn-up of the fuels was ~170 MWd/t (FBR) and ~30 MWd/t (LWR). Diluent denoted below as "alkanes" consisted of mixed n-alkanes, mainly decane to dodecane.

RESULTS AND DISCUSSION

The coextraction of Tc(VII) with Pu(IV) is illustrated in Fig. 1. At 25°C and under otherwise identical conditions the D_{Tc} values are higher by a factor of 1.5 - 2.5. Noticeable is the strong suppression of the coextraction efficiency at increased HNO_3 concentration. It corresponds to the replacement of 2 nitrate ions by TcO_4 ions from the extracted $Pu(NO_3)_4.2TBP$ species. This phenomenon has not been observed in the coextraction of Tc(VII) with U(VI) and Zr(IV). There the distribution ratio of Tc(VII) (henceforth D_{Tc}) is approximately a reversed first power function of the total nitrate concentration in the equilibrium aqueous phase. To determine the number of the TcO_4^- ions reacting with a $Pu(NO_3)_4.2TBP$ species, we measured the D_{Tc} value in varying the initial Tc(VII) concentration in the aqueous phase from 0.0001 to 0.05 M. At constant equilibrium concentrations of Pu(IV) in the organic phase (~0.1 M) and of HNO_3 in the aqueous phase (4.6 M and 5.6 M), the D_{Tc} value did not vary with the Tc(VII) concentration. This shows that the Tc(VII) is coextracted with Pu(IV) in the reaction

$$\overline{Pu(NO_3)_4.2TBP} + TcO_4^- = \overline{Pu(NO_3)_3(TcO_4).2TBP} + NO_3^-,$$

i.e. analogously as with U(VI) and Zr(IV) (Kolarik, 1989). The D_{Tc} value is described as $^0D_{Tc} + 34[\overline{Pu(NO_3)_4.2TBP}][NO_3]^{1.72}$ at 50°C and as $^0D_{Tc} + 220[\overline{Pu(NO_3)_4.2TBP}][NO_3]^{2.43}$ at 25°C. $^0D_{Tc}$ is the distribution ratio of Tc(VII) in the absence of coextracting elements

and equations for its calculculation are given elsewhere (Kolarik, 1989). The noninteger and excessively high exponents express inconstancy of activity coefficients.

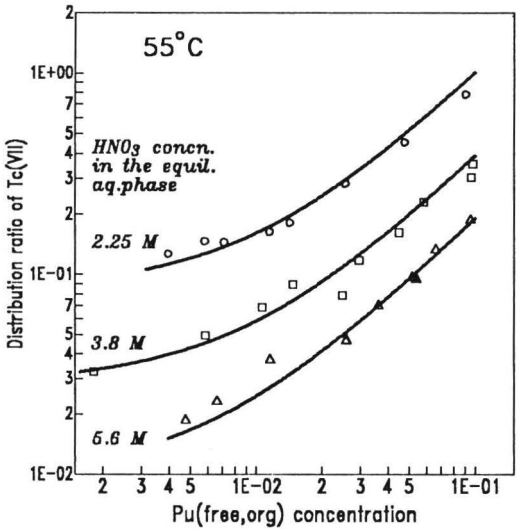


Fig. 1. Coextraction of Tc(VII) in the extraction of Pu(IV) with 30 vol.% TBP/dodecane from HNO_3 solutions. Initially 0.002 M Tc(VII) in the aqueous phase, $Pu_{free, org}$ is Pu(IV) not bound to Tc(VII). Solid lines are calculated.

An important practical conclusion can be drawn: At >4 M HNO_3, Tc(VII) is coextracted mainly with Zr(IV) and U(VI) and the coextraction with Pu(IV) plays a minor role. The coextraction with Zr(IV) can be suppressed, if the solvent is highly loaded with U(VI) and Zr(IV) is so displaced into the aqueous phase. Then U(VI) remains the only element coextracting Tc(VII) and, at e.g. ~5 M HNO_3 , D_{Tc} = 0.3 - 0.4. (Kolarik, 1989). Thus, Tc(VII) can be scrubbed out from the loaded solvent in a wash section of a countercurrent extractor at an appropriatelly high scrub flow. The displacement of Zr(IV) from the loaded solvent by U(VI) in the wash section must necessarily cause accumulation of Zr(IV) between the feed point and the aqueous raffinate outlet. This in turn evokes accumulation of Tc(VII). In spite of the accumulation, U(VI) and Pu(IV) can satisfactorily be decontaminated from Tc(VII), if the HNO_3 concentration and flows are appropriately adjusted for all aqueous flows. We sought a favourable adjustment for 24 mixer-settler stages, divided to an extraction and two scrub sections. The flowsheet was first optimized with the aid of mathematical modelling, and then tested experimentally.

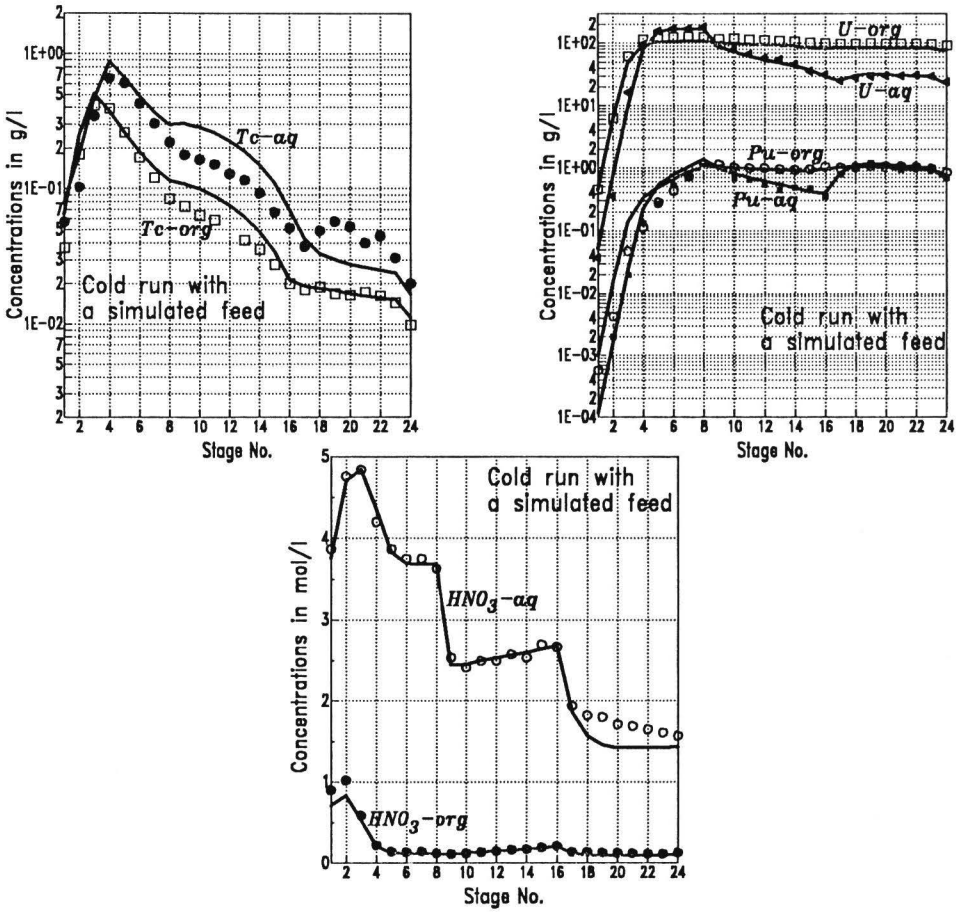


Fig. 2. Behaviour of Tc(VII) in the extraction of U(VI) and Pu(IV) from a simulated feed solution. Solvent (stage 1): 30 vol.% TBP/alkanes, 355 ml/h. Feed (stage 8): 118 ml/h. 1st scrub (stage 16): 5 M HNO_3, 38 ml/h. 2nd scrub (stage 24): 1.5 M HNO_3, 95 ml/h. 51 - 53°C in stages 1 - 16 and ambient temperature in stages 17 - 24. Points are measurments, lines are calculated profiles.

Empirical equations for the calculation of distribution ratios of Tc(VII) and Zr(IV) were introduced into the simulation programme developed by one of us (Petrich et al., 1986). The ratios were described as functions of the equilibrium concentrations of HNO_3, Zr(IV) and U(VI) in the aqueous phase. The extended programme simulated the counter-cur-

rent extraction behaviout of Tc(VII) fairly well (see a demonstration with results of foregoing investigations in Fig. 2). Deviations of the calculation from the experiment are not serious. Concentration profiles of pronouncedly accumulating components are rather instable and desire a long operational time for approaching a steady state.

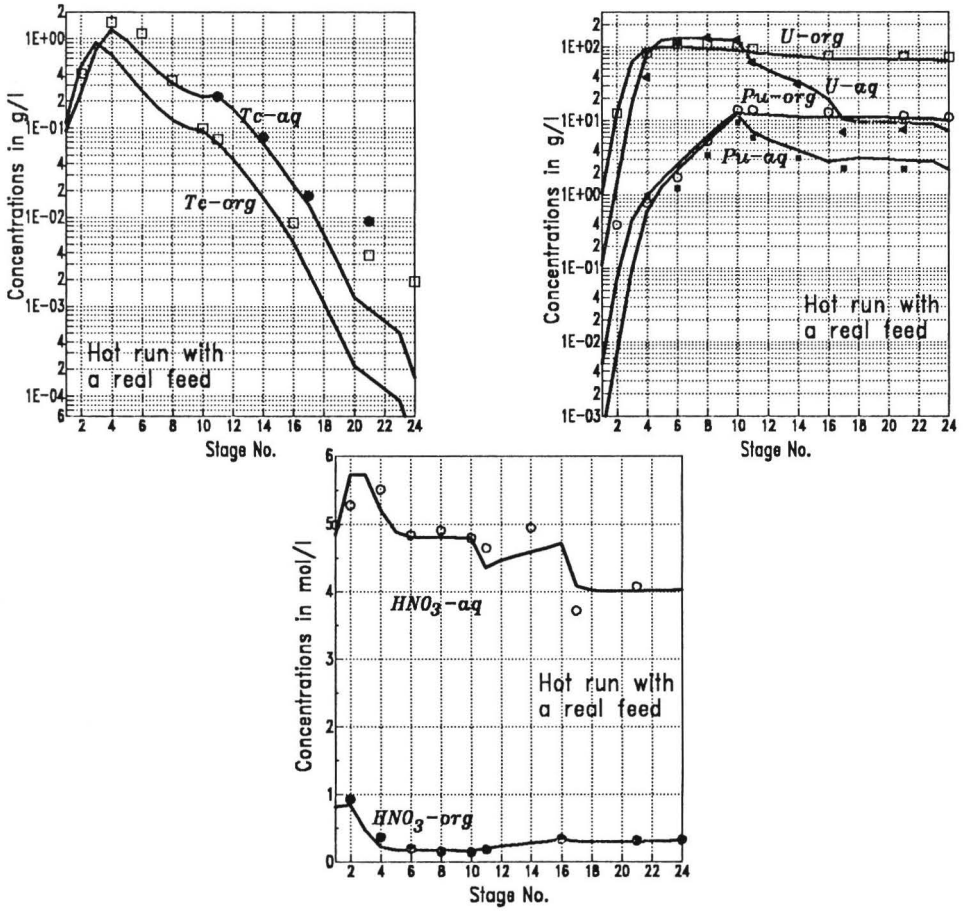


Fig. 3. Behaviour of Tc(VII) in the extraction of U(VI) and Pu(IV) from a real feed solution (FBR). Solvent (stage 1): 30 vol.% TBP/alkanes, 780 ml/h. Feed (stage 10): 280 ml/h. 1st scrub (stage 16): 8.7 M HNO_3, 40 ml/h. 2nd scrub (stage 24): 3.5 M HNO_3, 300 ml/h. 51 - 53°C in stages 1 - 16 and ambient temperature in stages 17 - 24. Points are measurements, lines are calculated profiles.

The run with the simulated LWR fuel feed solution confirmed that Tc would be separated inefficiently (decontamination factor 5.4) at a low flow and a low acidity of the second scrub solution. A still lower decontamination factor for Tc (2.6) was achieved with the same flowsheet in a hot experiment, performed with the FBR fuel feed solution. No Tc(VII) was washed out from the loaded solvent in the stages 17 - 24, where coextraction with Pu(IV) was not insignificant due to a low HNO_3 concentration (1.5 - 1.8 M).

The mathematical modelling revealed that for a good separation of Tc(VII) from U(VI) and Pu(IV) it was very important to increase the flow and the HNO_3 concentration of the scrub introduced into the end extractor stage. The other scrub was to have a low flow and a high concentration of HNO_3. In this way the volume of the raffinate was not necessarily enlarged, but the aqueous to organic flow ratio and the HNO_3 concentration were kept sufficiently high in the whole extractor. The flowsheet was tested in a hot experiment with a fast breeder fuel feed. It is seen in Fig. 3 that the decontamination factor for Tc was not so good as predicted, but still satisfactory (34). Using practically the same flowsheet, a decontamination factor of 30 - 50 was then reached in another hot run with the LWR fuel feed. The importance of the solvent loading could clearly be demonstrated in the run with the LWR fuel. The good separation of Tc from U and Pu was reached only at the solvent loading as high as it is illustrated in Figs. 2 and 3. When e.g. the U concentration in the solvent in the second stage was reduced to ~1 g/l, the decontamination factor for Tc decreased to ~5.

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Development of a Centrifugal Contactor

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Abstract

The purex process has been applied in the reprocessing of light water reactor (LWR) fuel. Application of the purex process to Fast Breader Reactor (FBR) fuel reprocessing will likely encounter a severe environment owing to high burn up and high plutonium-content of the fuel. A centrifugal contactor with short residence time and low holdup volume has particular applicability to the reprocessing of FBR fuel by the purex process. Power Reactor and Nuclear Fuel Development Corporation (PNC) has been developing a centrifugal contactor and carring out uranium tests to study steady-state and transient behavior.

A high extraction efficiency was obtained for uranium. The results of the tests were evaluated with the calculation code named "MIXSET" which was developed at the Tokai reprocessing plant in PNC. The results of the calculations corresponded well with the concentration profiles obtained from uranium tests for steady-state and transient behavior. A correlation between the transient rate of the uranium concentration profile and the magnitude of the upset condition was obtained from a transient behavior study. The drive unit of the contactor was also improved for maintenance and compactness.

1. Introduction

The recovery of plutonium and uranium from irradiated fuels by solvent extraction is often limited by the solvent degradation products. Several solvent extraction cycles are usually necessary to achieve the required degree of purification of the plutonium and uranium. Adaptation of the purex process to the recovery of plutonium and uranium from FBR fuels requires the development of advanced technology. The centrifugal contactor has excellent phase separation characteristics and a smaller holdup volume than that of conventional contactors such as mixer-settlers and pulse columns. These characteristics lead to the following advantages over conventional contactors:

- Reduced exposure of solvent to radiation
- Reduced inventory of aqueous and organic phases
- Reduced space requirements
- Improved criticality safety

PNC has been developing a centrifugal contactor to apply in the purex process of FBR fuels since 1986. This paper gives a brief explanation of the contactor which was developed in this R&D activity and also describes results obtained from uranium extraction tests.

2. Centrifugal Contactor

Fig.1 shows the basic structure of the most recent type of contactor being developed. The housing was designed based on that of an annular type centrifugal contactor which was developed at Argonne National Laboratory (ANL) [1, 2]. Feed solutions are fed to the annular region between the spinning rotor and its housing through the feed room. The liquid-liquid dispersion formed in the annular zone enters the rotor where it is separated. The separated phases are discharged from the rotor into the organic and aqueous collector rooms. A sepecific design feature of this contactor is the application of a magnetic coupling to drive the rotor so that the motor can be replaced independently of the rotor. This feature provides an easier mode of remote maintenance and decreases the space requirement on the upper side when replacing the motor.

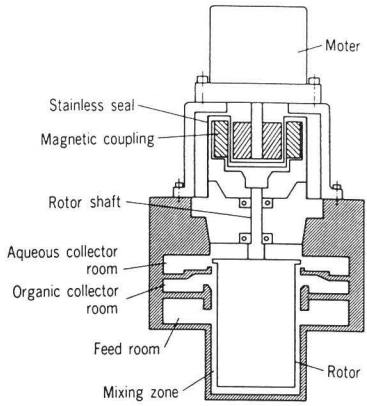


Fig.1. View of the centrifugal contactor

3. Engineering Test Equipment

Fig.2 shows an overview of the engineering test equipment used in uranium tests. This equipment was fabricated and assembled in 1987 and consists of uranium extraction, scrubbing, stripping, and solvent washing sections. The contactors are installed in a multi-tiered rack having three tiers as shown in Fig.2 and can be operated as a continuous system. PNC has been carrying out not only solvent extraction tests with uranium but also diluent washing and solvent washing tests using this equipment.

4. Extraction Efficiency

In the early stages of development, the extraction efficiency for uranium was confirmed

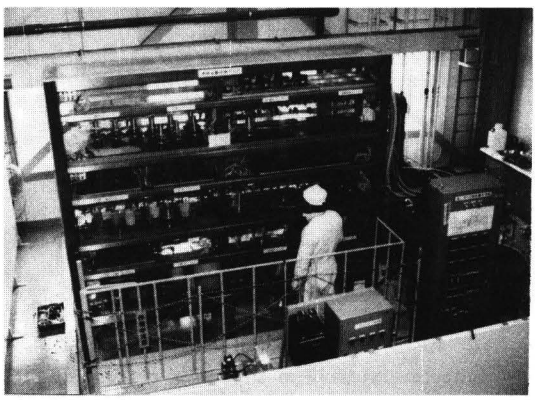


Fig.2. Engineering Test Equipment

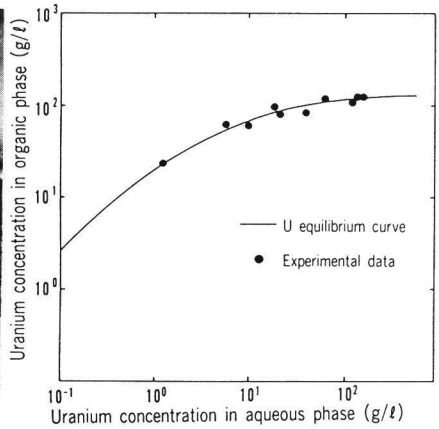


Fig.3. Comparison of uranium equilibrium curve and uranium extraction efficiency

through uranium extraction tests in the contactor. An equilibrium curve for uranium in a 30%-TBP/n-dodecane and 3 mol/h nitric acid system calculated by MIXSET is shown in Fig.3. For comparison, the results obtained from the extraction tests are also shown in this figure. This figure indicates that the extraction efficiencies are nearly 100% as reported in previous papers [2, 3, 4, 5, 6, 7].

5. Uranium Concentration Profile

Many uranium-concentration profiles obtained by uranium extraction tests were evaluated by the calculation code "MIXSET." Fig.4 shows one of the experimentally obtaied profiles and the MIXSET profile prediction. In this case, the code prediction corresponds well with the experimentally obtained concentration profile by assuming a 99% stage efficiency. Based on these and other past results, MIXSET can predict steady-state behavior in centrifugal contactors over a uranium concentration range of 10^{-3} to 10^{2} g/l if a stage efficiency greater than 95% is assumed.

6. Transient Behavior Study

When considering process operation and control of a centrifugal contactor system, it is very important to understand the transient behavior of the uranium concentration profile. This is because the low holdup volume of the centrifugal contactor results in a more rapid movement of transients through the system than in other types of contactors. A series of tests was

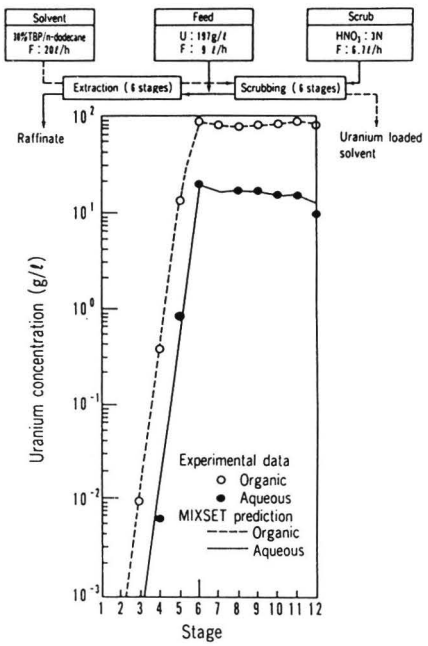


Fig.4. Uranium concentration profile at steady-state

Table 1. Test conditions for transient behavior study

Run No.	Solvent flowrate (ℓ/h)	Feed flowrate (ℓ/h)
1	20.3	9.0 ⟶ 15.0
2	19.9	8.7 ⟶ 12.5
3	20.1 ⟶ 13.6	8.1
4	20.0 ⟶ 14.3	8.4
5	18.4 ⟶ 14.8	9.0

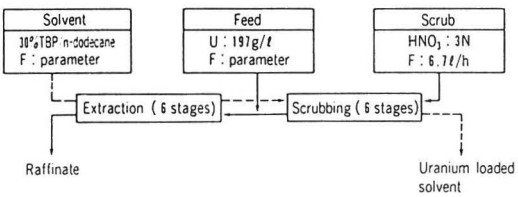


Fig.5. Test Flowsheet

conducted to study the transient behavior in the extraction section as a function of uranium loading in the organic phase.

Fig.5 and Table 1 show the flowsheet conditions chosen for this study. The test procedure can be divided into two parts as follows:

(1) Establish steady-state and measure the uranium concentration profile.

(2) Change the flowrate of feed or solvent and measure the transient rate of the uranium concentration profile by taking samples at periodic intervals from each stage.

In Runs 1 and 2, the feed flowrate was increased, and in Runs 3, 4 and 5, the solvent flowrate was decreased to introduce an upset condition to the system.

Fig.6 shows the transient behavior of the uranium concentration profile in the aqueous phase in Run 3 as a representative example of the experimental data obtained in these tests. Uranium profiles as predicted by the MIXSET code are also shown in this figure. The transient rate of the uranium concentration profile, R, which is defined in equation (1), is almost constant except in the region very close to steady-state, and nearly equal for every stage. Predicted behavior by MIXSET correspond well with the experimental data.

$$R = \frac{d\log C}{dt} \tag{1}$$

C : uranium concentration
T : time

In Fig.7, transient behavior at the 4th stage in Runs 1, 2, and 4 is compared to examine

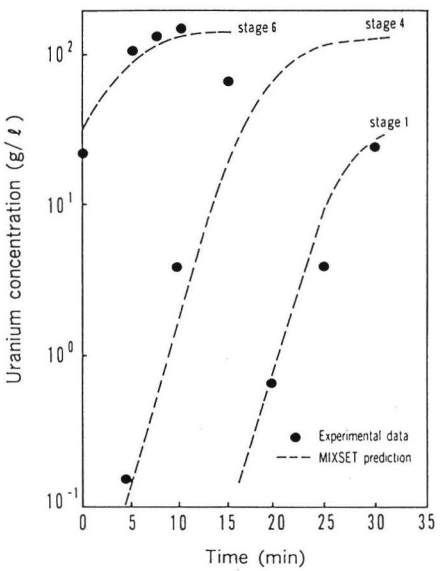


Fig.6. Transient behavior of the uranium concentration profile in aqueous phase (Run 3)

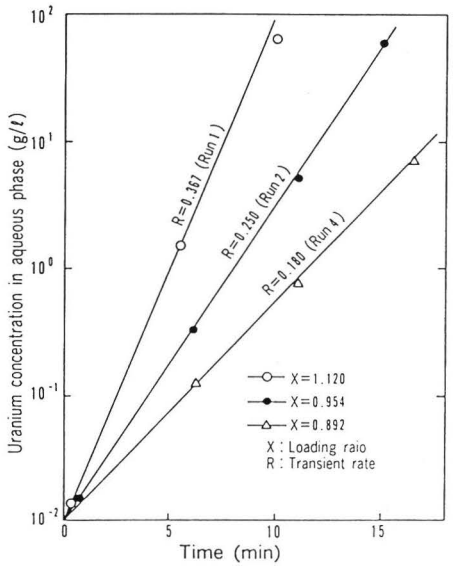


Fig.7. Effect of the loading ratio on transient rate

the effect of uranium loading. In this figure, the loading ratio, X, is defined in equation (2) as:

$$X = \frac{Cf \cdot Ff}{Fo} \Big/ Co,max \qquad (2)$$

Cf : Uranium concentration in feed
Ff : Flowrate of feed after change (Run 1 and 2) or
Unchanged feed flowrate (Run 3, 4 and 5)
Fo : Flowrate of solvent after change (Run 3, 4 and 5) or
Unchanged solvent flowrate (Run 1 and 2)
Co,max : Theoretical maximum loading of uranium in 30%TBP/n-dodecane (129.7g/l)

Note that X does not mean the real uranium loading in the organic phase but it expresses the magnitude of the upset on the system. Fig.7 indicates that the transient rate depeneds on the loading rate X.

The results of this study are shown in Fig.8 which describes the correlation between loading ratio, X, and transient rate, R, for all Runs. Fig.8 indicates that the transient rate R is proportional to the loading ratio, X, over a given set of experimental conditions. This figure also shows that the effect of two different upset conditions, i.e. change in the feed flowrate or solvent flowrate, on the transient rate, R, can be expressed in the same manner by equation (2) for these types of upsets.

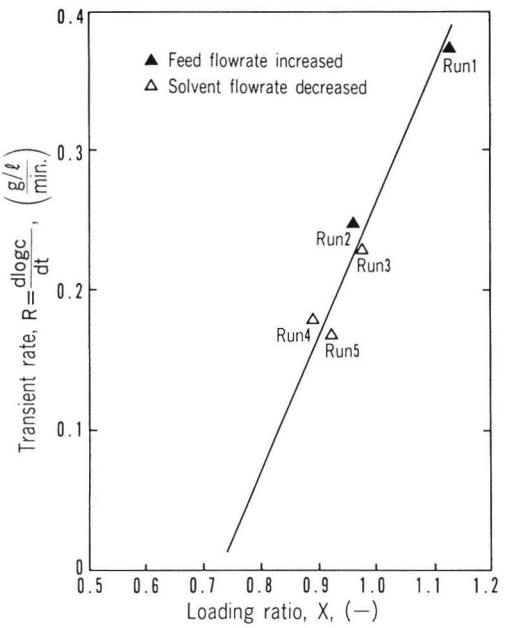


Fig.8. Correlation between Loading ratio and Transient rate

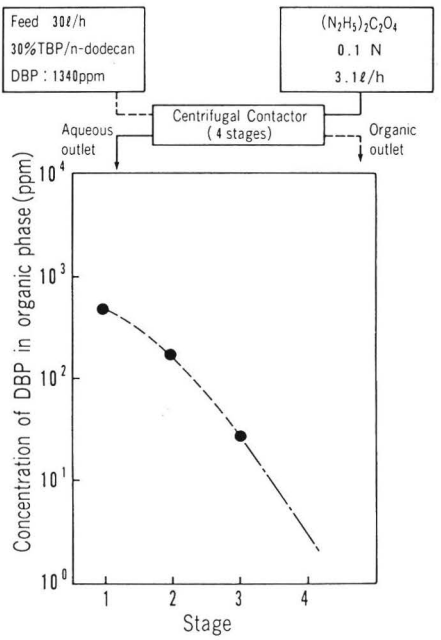


Fig.9. Result of solvent washing test

7. Solvent Washing Test

Application of a salt-free reagent in the solvent washing process is favorable to reduce the volume of radioactive waste. Hydrazine oxalate is one of the candidate washing reagents which can be decomposed to gases. In this test, washing of simulated degraded solvent, 30%TBP/n-dodecane containing DBP, by hydrazine oxalate using a 4-stage centrifugal contactor was performed under various conditions. Fig.9 shows one result of this test. As shown in this figure, the concentration of DBP dropped from 1340ppm to less than 10ppm within 4 contactor stages. In this case, the feed molar ratio of hydrazine oxalate to DBP was 1.6. Detailed studies revealed that the scrubbing efficiency in the centrifugal contactor was almost the same as that in breaker scale tests which were also performed as part of this program.

8. Conclusion

A compact and easily maintained centrifugal contactor was developed and uranium tests were conducted to study the steady-state and transient behavior of uranium. A high extraction efficiency was obtained for uranium. The tests results were evaluated using the calculation code "MIXSET", and predictions corresponded well with the test data for steady-state and transient behavior. The transient rate of the uranium concentration profile is proportional to the loading ratio defined in equation (2). Solvent washing test using hydrazine oxalate in contactors were conducted and good scrubbing efficiency was obtained. Further development of centrifugal contactor system is being pursued as a joint effort with the Oak Ridge National Laboratory under the USDOE/PNC collaboration. PNC plans to demonstrate centrifugal contactor technology as applied to FBR fuel reprocessing in a hot facility.

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ELECTROCHEMICAL OPERATIONS IN EXTRACTIVE SEPARATION OF URANIUM AND PLUTONIUM IN CENTRIFUGAL CONTACTORS

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ABSTRACT

The paper presents the results of "hot" experiments at the Physical Energy Institute (Obninsk) where countercurrent quantitative uranium/plutonium separation was studies using solutions of fresh and spent mixed FBR-fuels in a cascade of centrifugal contactors with diaphragm-free cells installed on aqueous phase tubes during U-Pu-separation and extract polishing from plutonium traces during weak acid co-extraction of both the actinides.

The paper presents the main parameters of the pilot devices employed and data on the actinide separation with use 30% TBP.

INTRODUCTION

Major purpose: Probability and feasibility compatibility of centrifugal extractors and electrochemical cells (selective Pu-stripping operation). Efficiency comparison of quantitative U-Pu-separation extractive processes - using both "in situ" electrochemically generated U(IV) and outside U(IV) flow introduced. Search for conditions of commeasurability of extractive (centrifugal contactor) and electrochemical (cell) stage work volume.

Due to apparent design difficulties in placing electrodes inside a centrifugal extractor and the requirement to have a particular type of emulsion in a mixing chamber ("oil in water") it seemed promising to resolve the problem by the interstage placement of small flow electrolytic cells on the clarified aqueous phase line. This can additionally afford such advantages as simplification of maintenance of a removable electrode block, a reduced destruction of an extractant in an electrolyzer, high linear rates of an aqueous flow to intensify the electrolysis process etc.

It is known that one of the first versions of spent fast reactor fuel reprocessing was multicycle co-reprocessing of uranium and plutonium from the core without their separation by alternate co-extraction and weak-acid co-stripping of uranium and plutonium.

The feasibility of this process was shown by us previously using mixer-settlers and centrifugal extractors. However, in

this case we found out the incomplete stripping of plutonium from TBP into weak nitric acid due to the formation of strong Pu (IV) complexes with acid alkyl phosphates and first of all with DBP; as a result unextracted plutonium is discharged with wastes from the operation of the soda regeneration of an extractant. (To date there is a mathematical model of plutonium stripping from TBP that adequately describes the effect of DBP (Solovkin, 1987)). We have previously found that in the course of "ageing" of a plutonium-bearing extractant (30% TBP in n.-dodecane) there takes place a linear accumulation with time of plutonium "nonstrippable" into a dilute acid; it reaches several gr per litre, e.g., when plutonium (IV) organic solution (21 g/dm^3) is held for 4 days (61°C) (Renard, 1985).

It is found that plutonium in the complex with DBP is quantitatively stripped with aqueous solutions of oxalic or hydrofluoric acids or with an aqueous solution of uranium (IV) stabilized with hydrazine.

Therefore, one can expect that low concentrations of uranium (IV) in the co-stripping flow stripping of U and Pu made it possible in the U stripping zone to deeply reextract quantitatively microconcentrations of plutonium retained by extractant (trialkyl phosphate) destruction products.

The processes of electrochemical U-reduction and Pu-stripping in pulse columns and mixer-settlers has been investigated in USA, FRG.

1 EXPERIMENTS

Small size centrifugal contactor (throughput to 25 dm^3/h) with a rotor 33 mm dia was used as a extractor (Renard, 1988).

2.1 Experiment with uranium polishing in co-stripping of uranium and plutonium (electrochemical stripping of plutonium from unirradiated fuel organic solvent on multistage cascade of centrifugal extractors, 20°C)

During weak acid (0,05 mol/dm^3 HNO_3) uranium and plutonium (U:Pu=4:1) co-stripping operation the electrochemical generation of ~ 1 g/l U(IV) in the aqueous stripping flow results in the

3-4 times reduction of plutonium losses with the organic raffinate.

A multi-electrode electrochemical diaphragm-free cell was used having electrodes of platinated titanium sheets (coating thickness 60 μm); the use was made of commercial frequency (50 s^{-1}) a.c.

2.2 The cold experiment with the full separation of uranium and plutonium

On electrochemical stripping of Pu macroconcentrations in the operation of the full quantitative U and Pu separation using unirradiated FBR-fuel (U:Pu=9 : 1) solution, two a.c. electrochemical diaphragm-free cells and 15 centrifugal extractor stages the factor of decontamination of U from Pu equal to 550000 were reached at 99.998% extraction of Pu in its product.

The optimal conditions of electrolytic, diaphragm-free interstage cell operation: the platinated titanium electrodes; the a.c. voltage of 2 V; the current density of no more than 7 A/dm^2; the S/V ratio of about 7 dm^{-1}; the temperature not higher than 45°C; the time less than 15 min; the acidity of the re-extractant-electrolyte 0.15-0.50 $mole/dm^3$ HNO_3; hydrazine content not more than 0.25 mol/dm^3.

A two-point reductant introduction was simulated, viz. into the region of stripping major amounts of plutonium and into the region of plutonium microconcentration removal from a uranium extract (Renard, 1988). It is at those two points of the stripping block that two electrolyzers were placed.

The major technological characteristics of the separation are practically independent on the kind of Pu reductive stripping - electrochemical or with U(IV) introduced from the outside (0,9 g. U(IV) per 1 g. Pu(IV)), although electrochemical stripping is carried out at lower steady-state concentrations of uranium (IV).

2.3 "Hot" experiments on electrochemical selective plutonium stripping in multistage cascade of centrifugal extractors. Flowsheet with full separation of uranium and plutonium.

The above results attained for unirradiated fast reactor mixed U-Pu fuel were confirmed in "hot cell" experiments with high burn-up fast reactor mixed fuel.

Three "hot" cells accomodate a 43-stage extraction unit

mounted according to the flowsheet (fig.) having mixing chambers of variable volumes. It is equipped with pilot metering and pumping apparatures and a system of continuous remote analytical control. The described centrifugal extractors were also used by 6 interstage diaphragm-free a.c. electrolyzers having platinated titanium electrodes. The cells are mounted in series on the aqueous phase at two points of the second (separation) block where macroconcentrations of uranium and plutonium are separated and uranium is polished.

The object of the development of the tube type electrolyzers was to generate about 3 g/dm^3 uranium (IV) by each one in the stripping flow (0.6-0.8 dm^3/h, that is U(IV) ($\sim$1g. per g. Pu(IV)) production has been proposed. The working volume of cell I (40 cm^3) approaches that of a single stage of the centrifugal extractor (8-20 cm^3).

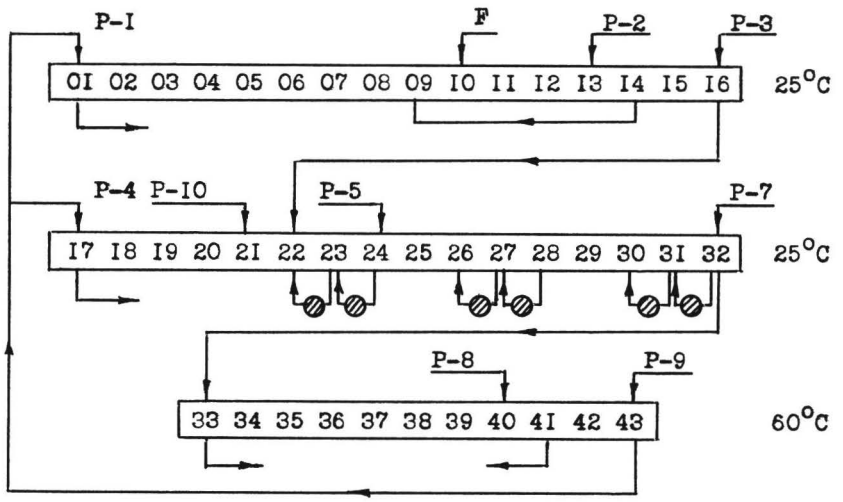


Fig. First cycle spent FBR-fuel reprocessing flowsheet with quantitative U-Pu-separation (centrifugal extractors).
⊘ - electrochemical cells

Two experiments were performed in succession using electrolyzers in the uranium and plutonium separation block I (experiment IAZ-1) and using externally introduced tetravalent uranium (as a comparison experiment, experiment IAZ-2). The composition of the feeding flows is given in table 1.

TABLE 1

Feeding flows, I cycle flowsheet (centrifugal extractors; FBR spent fuel, the average burn-up of 60 GW·day/t, exposure of 2 years)

Flow index	Flow rate, cm^3/h	Composition				Notes
		HNO_3 mol/dm^3	U g/dm^3	Pu g/dm^3	Hydrazine mol/dm^3	
F	970	4.3	165	23	-	xxxxx)
P-1	2000	-	$1.5 \cdot 10^{-3}$	$1.0 \cdot 10^{-4}$	-	30% TBP
P-2	115	10	-	-	-	10 g/dm^3
P-3	270	0.5	-	-	-	
P-4	800	-	$1.5 \cdot 10^{-3}$	$1.0 \cdot 10^{-4}$		30% TBP
P-5	263	0.6	75 x)	trace	0.20	IAZ-2
P-6	460	0.15	11 xx)	trace	0.16	IAZ-2
P-7	800	0.8 xxx)	-	-	0.30 xxxx)	IAZ-1
P-8	3200	0.01	-	-	-	
P-9	400	-	-	-	-	soda, 5% mass
P-10	64	10	-	-	0.05	

x) includ. 70 g/dm^3 U(IV); xx) includ. 10 g/dm^3 U(IV); xxx) 0.15 mol/dm^3 in exp. IAZ-2; xxxx) 0.18 $mol./dm^3$ in exp. IAZ-2; xxxxx) β,γ-activity $\sim 6 \cdot 10^{12}$ Bq/dm^3 ($\sim 4 \cdot 10^3$ $\mu R/s.dm^3$)

TABLE 2

Major characteristics of electrochemistry use for liquid-liquid extractive U-Pu-partition from FBR (fresh and spent) fuel solution (15-16-stage blocks of centrifugal extractors)

DF	U-Pu-partition with use of			
	U(IV)		electrochemistry	
	spent fuel	fresh fuel	spent fuel	fresh fuel
U from Pu	$3.6 \cdot 10^3$	$(2+10) \cdot 10^5$	$1.1 \cdot 10^5$	$5.5 \cdot 10^5$
Pu from U	40	240-760	660	900
U from FP	$7.1 \cdot 10^4$	-	$1.1 \cdot 10^5$	-

Centrifugal extractors with low phase residence time (2-10 s) were shown to be suitable for quantitative (above 99.9%) extraction of actinides from high-activity fuel ($\sim$ 900 Ci/dm^3) and for decontamination of actinides from fission products by up to

150000 times at the first cycle with U-Pu separation by the method of Pu reductive stripping (factor of decontamination of U from Pu is up to 110000) (table 2).

Although the limited amount of the high radioactive solution (initial aqueous) did not allow us to reveal all the features (the reserves included) of the plutonium electrochemical stripping process, nonetheless the presented results can be used as an actually realized operation of electrochemical (salt-less) separation of uranium and plutonium macroamounts as applied to the process of extractive reprocessing of macroplutonium containing fuel using present-day quickly operating centrifugal extractors and just as compact interstage electrolyzers.

3 CONCLUSIONS

The serviceability is confirmed of the combined unit consisting of individual stages of centrifugal extractors and interstage sited on the aqueous phase pipes of the diaphragm-free electrolytic cells having platinated titanium electrodes. The application of electrochemical a.c. low voltage cells with platinated titanium electrodes helps to resolve the problems associated with the introduction of electrochemical operations in the aqueous extraction process of NPP (FBR) fuel reprocessing using quickly operating centrifugal extractors.

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CHARACTERISTICS AND BEHAVIOUR OF INTERFACE SLUDGES FORMED IN THE FIRST EXTRACTION CYCLES OF THE PUREX PROCESS

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ABSTRACT
The importance of clarification for the volume of sludges has been demonstrated. However, even very good clarification does not totally eliminate the extraction sludges. If their volume is considerably increased by the presence of dissolution fines that have excaped clarification, this only slightly alters the hydrodynamic behaviour of the pulsed column in the first cycles. The sludges obtained with and without feed clarification have been characterized and their origin recalled. The management of these bulky remains problematic for reprocessing.

1 INTRODUCTION

The importance of clarification quality in the performance of the Purex process is considered today a vital matter, especially because of its repercussions on the formation of interfacial sludges. In fact, this clarification operation, generally performed by filtration or centrifugation, is not always totally effective, because the dissolution fines mainly consist of colloidal substances [2] whose properties could justify more specific clarification methods, such as ultra-filtration, treatment by flocculents etc.

Tests of the first cycle were performed in hot cells on clarified and unclarified dissolution liquors, issuing from PWR UOX and MOX fuels. These tests were conducted in mixers/settlers and in a small pulsed column in order to :

- monitor the formation and behaviour of the sludges accumulating at the extraction interfaces,
- define the origin and the characteristics of the sludges,
- determine the influence of the degree of clarification of the dissolution liquors on the hydrodynamics of the pulsed columns,
- identify the problems associated with the industrial management of these products.

The results discussed below are still partial, because they are part of a broader study, associated in particular with that of dissolution fines.

2 FORMATION AND BEHAVIOUR OF SLUDGES IN THE FIRST EXTRACTION CYCLES

The fuel, dissolved for these mixers/settlers tests, was MOX fuel containing 5% Pu, irradiated to 30,000 MWD.t^{-1} and cooled for four years. The feed solutions were clarified 24 hours after dissolution by micro-filtration on Millipore 1.2 and 0.3 μm membranes. These

feeds were stored for an average of three months, and then again clarified one week before being sent to extraction (see. extraction flow sheet, (a) in Figure 1).

Despite very good clarification, it is found that large quantities of blackish sludges (example (b) in Figure 1) are formed at the interfaces of the settlers. These sludges appear from the very onset of extraction in the feed introduction stage, and then advance progressively, throughout the extraction section and in diluent washing, in the flow direction of the aqueous phase. On the scale of a few hundred hours of operation, no sludges are entrained with the raffinates beyond the extractor. The total volume of the sludges is an average of 7·3 $l.t^{-1}$ (HM), 60% in extraction and 40% in diluent washing. This total volume varies slightly with the initial quality of the solvent used ('new' solvent, plant solvent, plant solvent regenerated by vacuum distillation), but naturally, provided it has been treated first to remove the TBP degradation products.

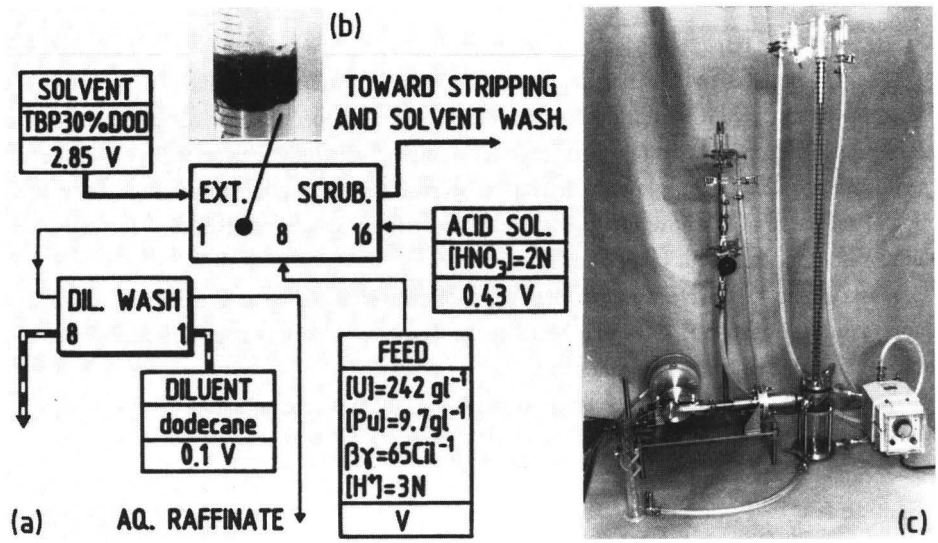


Figure 1 (a) Extraction cycle in mixers/settlers. (b) Example of interfacial sludges recovered after extraction of clarified MOX feeds. (c) Section of pulsed column used for the tests.

The same applies to a small pulsed column (see (c) in Figure 1, and flow sheet in Figure 2), operating with a continuous organic phase, with feeds from the dissolution of UOX fuels, irradiated to 55,000 MWD•t^{-1}, cooled for four years and clarified by micro-filtration 24 hours after dissolution, using the procedures indicated above. In these conditions, the volume of sludges collected was equivalent to about 14 $l.t^{-1}$ U, and no significant decrease in this volume was observed for feeds clarified 24 or 72 hours before extraction.

Finally, these volumes of sludges are not at all negligible and certainly represent minimum volumes formed in the first cycles operating in standard conditions, with perfectly clarified dissolution liquors.

Influence of dissolution fines on the sludges and on the operation of pulsed columns

If the dissolution liquors are not clarified at all, the apparent volume of the sludges, accumulating in the bottom settler of the pulsed column, reaches 125 $l.t^{-1}$ U. A large part of the fines, about 30%, is not held in the emulsion, and is deposited on the blanket of sludges at the interface, and finally falls to the bottom of the settler. A small fraction of fines or sludges is entrained with the solvent and proceeds to the FP washing section. This could limit the decontamination performance of the cycle. The volume of sludges rapidly becomes disturbing for the operation of the column, and may require their withdrawal.

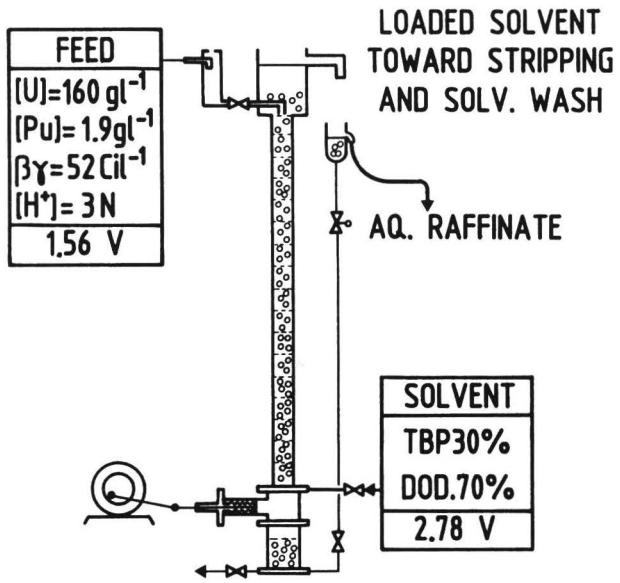


Figure 2 Extraction flow sheet employed in pulsed column tests.

To determine whether the presence of fines in the extraction feeds has any effect on the hydrodynamic behaviour of pulsed columns and particularly on their capacity (possible flooding due to the influence of solid particles on the size of the emulsion), we measured the variation in the average DPHU rates (dispersed phase hold-up), as a function of the total specific throughput (ranging from 1 to 2.5 $l.h^{-1}.cm^{-2}$) and the pulsation conditions : constant amplitude of 2·5 cm, pulser frequency 35 to 85 pulses/min.

The DPHU curves obtained by operating in a continuous organic phase, with a uranyl nitrate solution used as a reference (non-irradiated U) and with clarified and unclarified

dissolution liquors (UOX fuel described above), are compared in Figure 3, for the same operating conditions. There is finally little difference and consequently, the presence of dissolution fines in the extraction feeds has no significant effect in principle on the hydrodynamic behaviour of the column. However, it is possible that, in a continuous aqueous phase or at the flooding limits of the column, this influence could be more pronounced. For the optimal operating zone, between 1·5 and 2.5 $l.h^{-1}.cm^{-2}$, there should be not loss of capacity in industrial installations, if the clarification efficiency is not total. Note, however, that the accumulation of large volumes of sludges, which only occurs if clarification is insufficient, could force the operator into frequent shutdowns, especially if he does not have a system for the continuous removal of the sludges in the settler.

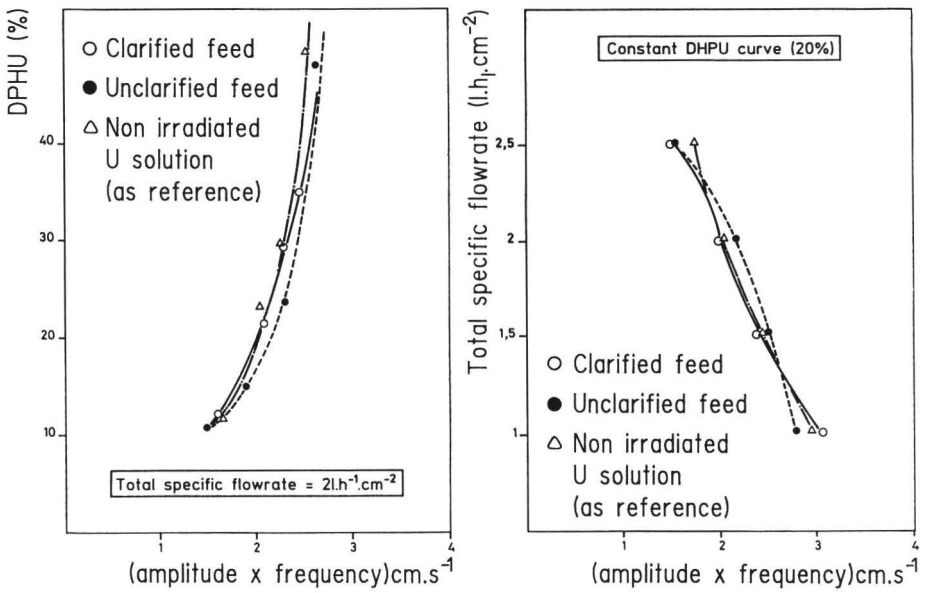


Figure 3 Comparison of DPHU (a) and constant 20% DPHU (b) obtained in a pulsed column as a function of the operating parameters and the state of clarification of the feed.

3 CHARACTERISTICS OF INTERFACIAL SLUDGES AND ORIGINS

The sludges formed with perfectly clarified MOX dissolution liquors were characterized after rinsing and separation by centrifugation. The mass of dry extract recovered and dried at 60°C is equivalent to $\approx$ 24 $g.t^{-1}$ of heavy metals, which, related to their initial volume, corresponds to an apparent specific volume of about 200 to 300 $cm^3.g^{-1}$. This very high value is characteristic of the stable emulsions which make up the sludges and have already been pointed out by various authors [1].

These sludges are stable, because, after one and a half months, they still occupy 70% of their initial volume, and then only 10% after centrifugation. They are unaffected by acide treatment, cold or hot, but their volume increases by a factor of 2 to 3 in basic medium. This property does not facilitate their removal in plants where caustic soda is often used to rinse extraction units.

Their average composition determined by ICP analysis after mineralization and total dissolution is as follows :

- main elements — P = 30 to 50% (relative %)
  Pd = 7 to 30%, Zr = 6 to 17%, Fe = 8.8 to 16%,
- Secondary elements — Mo, Ru, Rh, Tc from 0.3 to less than 5%,
- minor elements — U = 0.3 to 1%, Pu = 0.1 to 0.25%.

The mass of palladium held in the sludges is not negligible, and corresponds to about 0.15% of the quantity formed during irradiation of the fuel.

Since they contain Mo, Ru, Rh and the main elements making up the dissolution fines, their total mass corresponds to less than O.1% of the mass of fines separated after clarification, which is 4.7 $kg.t^{-1}$ of U + Pu. This demonstrates that the clarification of dissolution liquors by micro-filtration is extremely effective for fines whose colloidal dimensions make this operation very difficult.

The activity of these sludges is low (1.5 to 2 $Ci.l^{-1}$ ^{106}Ru, ^{137}Cs, ^{144}Ce) compared with the activities of the aqueous solutions from which they were extracted ($\simeq$ 50 $Ci.l^{-1}$), probably indicating that these emulsions are rather of the W/O type.

For sludges formed without clarification, their composition (UOX tests in pulsed column), is slightly different from the average composition of the dissolution fines, apart from phosphorus.

The composition of the sludges that we determined conform to the data generally found in the literature, concerning the origin of these products, which can be classed as follows :

- precipitated organo-phosphorus compounds such as DBP-Zr complexes [4], to which DBP-Fe complex, also very insoluble, is certainly added,
- palladium metal, resulting from the reduction of Pd^{++} by the radiolysis of dissolution liquors [3],
- dissolution fines that have escaped clarification.

Each of these products, by its surfactant or stabilizing properties [5], favours the formation of stable emulsions, in other words sludges.

These experiments have demonstrated that, if the dissolution liquors are suitably clarified, the first two categories predominate. However, their volume is related to the irradiation characteristics of the fuel, and the residence time of the solvent in the extractors. These parameters condition the degradation of the solvent and *ipso facto* the precipitation of the organo-phosphorus compounds. If the solutions have been insufficiently clarified, the third category becomes preponderant, and the accumulation of large quantities of very radioactive

fines at the interfaces tends to accelerate the degradation of the solvent and accentuates the precipitation of organo-phosphorus compounds.

4 CONCLUSIONS

In this preliminary investigation, we have demonstrated that intensive clarification of extraction feeds does not totally eliminate the problem of extraction sludges. However, the presence of significant amounts of dissolution fines increases their volume considerably, but without disturbing the operation of the first cycles in pulsed columns. The management and transfer of these very bulky products remains problematic for reprocessing, and the more sludges are formed in the extractors, the higher the solvent losses are likely to be. It is therefore important to improve the clarification efficiency and to devise methods to treat these sludges so as to restrict their volume and to recycle the solvent held in these stable emulsions.

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SEPARATION OF NEPTUNIUM FROM HIGH-LEVEL WASTE BY EXTRACTION WITH DIISODECYL PHOSPHORIC ACID

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ABSTRACT

Continuous extraction of Np initially in the pentavalent state with diisodecyl phosphoric acid (DIDPA) was studied using a miniature mixer-settler in the aspect of developing a partitioning process for high-level waste (HLW).

The ratio of Np extracted from HNO_3 solution was only 45.4 % by 7-stages extraction because of the slow rate of the extraction. The ratio was considerably increased to 92.7 % by the addition of H_2O_2 to scrub solution. The extraction from a simulated HLW solution further proceeded because of the catalytic effect of some elements in HLW, but it was accompanied by fast decomposition of H_2O_2. When the number of extraction stages was doubled and H_2O_2 was added to two of the stages, over 99.96 % of Np was extracted, which confirms that this extraction is a promising method for Np separation from HLW.

The results of the continuous extraction agreed with the results of batchwise extraction using 1-stage mixer without the liquid flow. This gave a good prospect of designing a large scale extractor.

1 INTRODUCTION

Partitioning of high-level waste (HLW) has been studied for the purpose of establishing an advanced waste management system for HLW and for the purpose of utilizing some of the elements in HLW (Kubota et al. 1984, 1989). Separation of ^{237}Np is particularly important to reduce the long-term potential hazard of HLW.

In previous studies (Morita et al. 1987), Np initially in the pentavalent state was found to be extracted with diisodecyl phosphoric acid (DIDPA), which was used as an extractant for americium, curium and rare earths in the partitioning process previously developed. This extraction proceeds through disproportionation of Np(V), which is considered to be initiated and accelerated by interaction of Np(V) with DIDPA. The rate of the extraction was not fast enough, but H_2O_2 was found to accelerate the extraction (Morita et al. 1988). In this case, the extraction proceeds through the reduction of Np(V) to Np(IV), still maintaining the importance of the interaction of Np(V) with DIDPA.

The present paper describes the results of the studies on the counter-current continuous extraction of Np(V) with DIDPA from simulated HLW using a miniature mixer-settler. These studies are particularly important because the extraction is determined by the rate not by the distribution ratio at equilibrium.

2 EXPERIMENTAL

2.1 Reagents

A stored ^{237}Np solution was used without further oxidation state adjustment. In this solution, over 98% of Np was pentavalent, which was verified by spectrophotometry.

Table 1 shows the composition of simulated HLW used. Concentrations of the elements except Np were calculated and estimated on condition that 1 m^3 of HLW was produced per 1 t of spent fuel by reprocessing. Three other major elements in HLW, Zr, Mo and Te, were not added. They are to be separated as precipitates at the denitration step preceding the extraction step. Nevertheless, the simulated HLW prepared as 2 M HNO_3 solution was denitrated with formic acid. After denitration, the concentration of HNO_3 in the simulated HLW was adjusted to 0.5 M. Finally, Np(V) was added to it.

TABLE 1

Composition of simulated HLW.

Element	Conc.(M)	Reagent used
Na	0.038	$NaNO_3$
Cr	0.0046	$Cr(NO_3)_3$
Fe	0.019	$Fe(NO_3)_3$
Ni	0.0030	$Ni(NO_3)_2$
Rb	0.0037	$RbNO_3$
Sr	0.0083	$Sr(NO_3)_2$
Cs	0.019	$CsNO_3$
Ba	0.010	$Ba(NO_3)_2$
Ru	0.017	$RuNO(NO_3)_3$
Rh	0.0040	$Rh(NO_3)_3$
Pd	0.0090	$Pd(NO_3)_2$
Np	$6.8\times10\text{-}6$	NpO_2^+

The extractant, DIDPA, obtained from Daihachi Chemical Industry Co., Ltd. was used without further purification. n-Dodecane was used as a diluent. Tributyl phosphate (TBP) was also added to the solvent.

2.2 Procedure

A 16-stages miniature mixer-settler was set in a thermostatted air bath. The settler volume was 49 ml and the mixer volume was practically 7 ml. The operating conditions are shown in Fig. 1 (a) and (b). The condition shown in Fig. 1 (a) is the same as that in the partitioning process studied for the separation of Am and Cm (Kubota et al. 1984), except for the addition of H_2O_2.

Experiments on batchwise extraction were also carried out using a 1-stage mixer which was modified to prevent the liquid flow.

3 RESULTS AND DISCUSSION

Table 2 shows the experimental conditions of the continuous extraction. The ratio of Np extracted was also shown as one of the results.

Figure 2 shows concentration profiles of Np in the No. 4 run as a typical case. The Np concentrations in aqueous phases at the extraction section (stage No.7 to 1) decreased with the stage numbers. This decrease depends on the extraction rate of Np. The plots of the aqueous concentrations gave a straight line since the extraction of Np in the presence of H_2O_2 is the first-order reaction with respect to the Np concentration. The first-order rate constant (k) can be

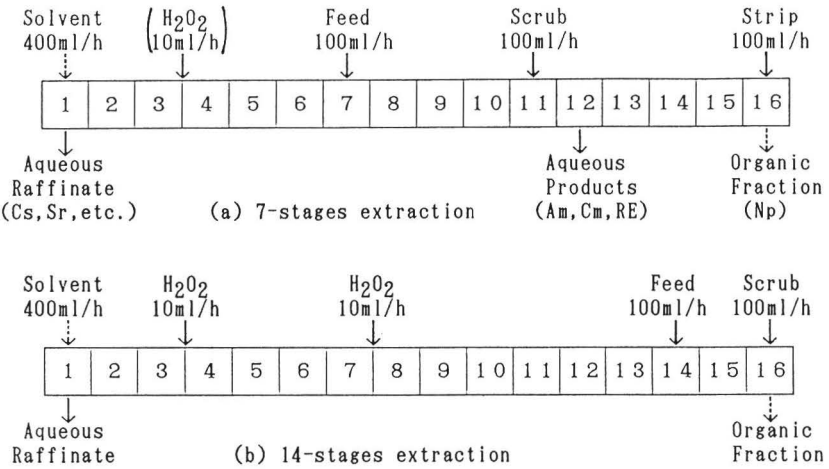


Fig. 1. Operating condition of the mixer-settler
Solvent: 0.5 M DIDPA, 0.1 M TBP in n-dodecane
Feed : 0.5 M HNO_3, Np alone or simulated HLW
Scrub : 0.5 M HNO_3, $[H_2O_2]$=0, 0.5, 1.0 M
Strip : 4.0 M HNO_3
H_2O_2 solution: 0.5 M HNO_3, $[H_2O_2]$=0, 5.0, 8.0 M

TABLE 2

Experimental condition of the continuous counter-current extraction and the ratio of Np extracted.

Run No.	Temp. (℃)	Feed solution	Extracting stages	$[H_2O_2]$ in scrub (M)	Addition of H_2O_2 Stage No.	Addition of H_2O_2 Conc. (M)	Extracted (%)
1	25	Np alone	7	0	-	-	24.6
2	45	Np alone	7	0	-	-	45.4
3	25	Np alone	7	0.5	-	-	78.8
4	45	Np alone	7	0.5	-	-	92.7
9	25	Simulated HLW	7	0.5	-	-	92.1
10	45	Simulated HLW	7	0.5	-	-	95.6
12	25	Simulated HLW	7	0.5	3	5.0	95.5
13	45	Simulated HLW	7	0.5	3	5.0	98.2
14	45	Simulated HLW	7	1.0	3	8.0	99.0
15	45	Simulated HLW	14	1.0	3 & 7	8.0	>99.96

calculated from the slope of the line and residence time of aqueous phase in the mixer. The value of k in the No.4 run was found to be 9.0×10^{-3} s^{-1}. At 25 ℃ (the No.3 run), k was 5.4×10^{-3} s^{-1}, 1.7 times as large as at 45 ℃.

In the present study, it is thus important to investigate the concentration profile of Np in aqueous phase at the extraction section. Figure 3 shows the profiles in the runs at 45 ℃.

When the simulated HLW used as a feed solution (the No.10 run), the extraction of Np became faster in particular at the stages closer to the feed point, and

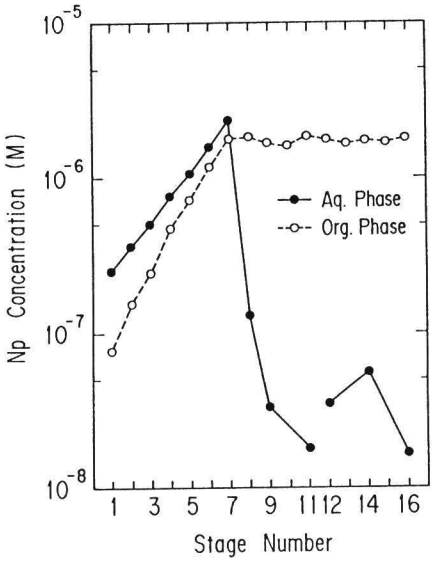


Fig. 2. Concentration profile of Np in the mixer-settler. -No.4 run-

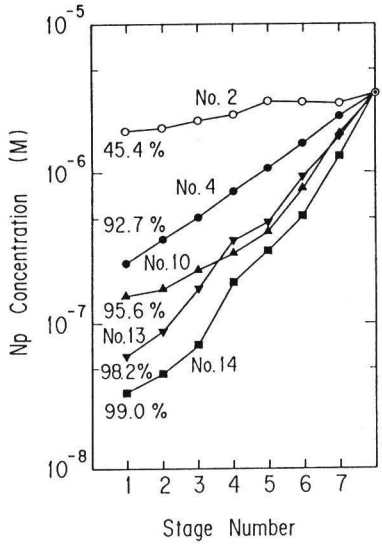


Fig. 3. Concentration profile of Np in aqueous phase at the extraction section. -runs at 45 ℃-

95.6 % of Np was extracted. This acceleration was caused by the catalytic effect of some elements in the HLW. Previous experiments on batchwise extraction showed that Fe and Pd were the main contributors to the acceleration (Morita et al. 1989). The rate constant, k, at the first stage was found to be 1.75×10^{-2} s^{-1}, which was 1.9 times as large as in the No.4 run without catalyst.

On the contrary, the extraction of Np became slow at the latter stages (stage No.3 to 1). This deceleration was due to the decomposition of H_2O_2. The presence of elements in the HLW accelerated not only the extraction of Np but also the decomposition of H_2O_2. The additional feed of H_2O_2 to compensate its decomposition increased the extraction ratio of Np. As shown by the plot for the No.13 run, the rate of Np extraction increased again at the No.3 stage where H_2O_2 solution was poured into. When the concentration of H_2O_2 increased (the No.14 run), Np extraction was further accelerated and 99.0 % of Np was extracted.

In the No.15 run, number of extracting stages was doubled and H_2O_2 solutions were poured into two of the stages, and over 99.96 % of Np was extracted from the simulated HLW, as shown in table 2. This result confirms that this extraction is a promising method for Np separation from HLW. The reason why such a high recovery of Np was achieved is that the reduction and extraction of Np occurs simultaneously in the presence of DIDPA and H_2O_2.

It seems that more quantitative discussion is necessary for the application of this method to a large scale plant. As the first step, a experiment on batchwise

extraction of Np was carried out using a 1-stage mixer, keeping the initial condition the same as at the first extracting stage in the No.14 and No.15 runs. Figure 4 shows the comparison of the results between the batchwise and the continuous extractions. Plots for the batchwise extraction (●) lay well on the curve representing the results of the continuous extraction (○ and □, which were plotted against the total residence time in the mixer). This agreement indicates that the progress of the Np extraction was determined by the contacting time of the aqueous and the organic phases regardless of contacting manner, with or without the liquid flow, and with or without settling of the two phases. In the continuous extraction, the aqueous phase stays in the settler for a longer time (around 500 s) than in the mixer (42-43 s). However, the settling does not affect the Np extraction. The result of another batchwise extractions which had the settling time showed that the Np extraction was independent of the length of the settling time (Table 3). It can be considered that both the change of Np oxidation state (reduction) and the decomposition of H_2O_2 in the settler is negligible for the Np extraction. These findings show that it is possible to make a quantitative estimate for Np extraction in a counter-current extractor from the experiment on batchwise extraction.

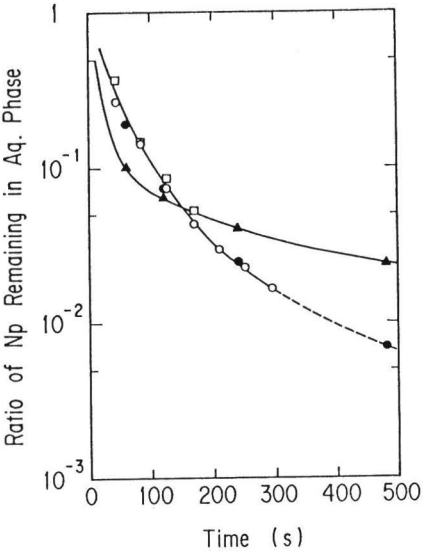


Fig. 4. Comparison of the batchwise extraction with the continuous one. 45 ℃. Initially $[H_2O_2]$=0.5 M.
Continuous extraction.
□ : No.14 run, stage No.7 to 4.
○ : No.15 run, stage No.14 to 8.
Batchwise extraction.
● : Denitrated simulated HLW.
▲ : Not denitrated simulated HLW.

TABLE 3

Dependence of the Np extraction on the length of settling time in the batchwise extraction. Initial condition was the same as in Fig. 3.
Mixing : 40 s × 3 times = 2 min.
Settling : variable length, twice.

Settling time (min)	Ratio of Np remaining in aqueous phase
2×2= 4	0.0794
5×2= 10	0.0757
10×2= 20	0.0767

As mentioned above, some elements catalyze the Np extraction and the H_2O_2 decomposition. These catalytic effects may depend on the chemical form of the elements. To examine such phenomena, aqueous solution was changed to the simulated HLW which was directly prepared as 0.5 M HNO_3 solution without denitration,

where the chemical form of the elements may be different. The results was also plotted by ▲ in Fig. 4. The Np extraction was very fast in the beginning but soon became slow, which means that H_2O_2 decomposed faster. As was expected, the chemical form of the elements influenced the Np extraction behavior. However, even when H_2O_2 decomposes faster, further addition of H_2O_2 must keep the high recovery of Np because the Np extraction is very fast at the beginning and at the point where a new H_2O_2 solution is poured into. In other words, the influence by the difference in chemical forms of the catalyzing elements can be reduced by designing the best way to add H_2O_2.

The denitration of HLW might make each element in a particular chemical form. If that is the case, only the chemical form after denitration should be examined for the Np extraction and the H_2O_2 decomposition.

4 CONCLUSION

In counter-current continuous extraction with DIDPA using a mixer-settler, 95.6 % of Np was separated from simulated HLW by 7-stages extraction at 45 ℃ with the addition of H_2O_2 to scrub solution. Some elements in the simulated HLW accelerated not only the Np extraction but also the H_2O_2 decomposition. Therefore, further addition of H_2O_2 to the extraction section was required to increase the ratio of Np extracted. The 14-stages extraction and twice addition of H_2O_2 increased the Np recovery to over 99.96 %. This result showed that the Np extraction with DIDPA in the presence of H_2O_2 was a promising method for the separation of Np from HLW with very high recovery.

The results of the continuous extraction agreed with the results of batchwise extraction using 1-stage mixer without the liquid flow. This gave a good prospect of designing a large scale extractor.

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Separation of Actinides and Lanthanides from Nuclear Power Reactor Fuel Reprocessing Waste Solution by DHDECMP

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Abstract

A multistage countercurrent extraction process was developed for the removal and recovery of actinides and lanthanides by 30 % bidentate organophosphorous extractant DHDECMP in diethyl benzene from 3mol/l nitric acid solution of simulated nuclear power reactor fuel reprocessing waste solution.

Introduction

Since the synthesis of several bidentate organophosphorous compounds was published by Siddal in the early 1960's[1,2], many scientists have been using these compounds as new liquid-liquid ertractants to extract actinides and lanthanides from acidic nuclear waste solution. Some of them can selectively extract actinides and lanthanides from acidic nuclear waste solution. Up to now some conceptual flowsheets have been performed.[3-8]

In order to put forward a conceptual flowsheet for removal and recovery of actinides and lanthanides from nuclear power reactor fuel reprocessing waste solution.The extraction behavior of actinides, lanthanides and fission products with bidentate dihexyl-N,N-diethyl carbamyl methylene phosphonate(DHDECMP) in diethyl benzene(DEB) has been studied[9,10] .The experiments of single-stage(batch) extraction and multistage countercurrent extraction have been performed and a conceptual flowsheet for removing and recovering actinides and lanthanides from the simulateted solution of nuclear power reactor fuel reprocessing waste has been suggested.

2.Experimental

2.1.Materials and Instrument

(a).DHDECMP(~95% pure): Institute of Uranium Mineral Processing,Beijing;(b).^{233}U,^{238}Pu,

Table 1.The Effect of HNO_3 Concentration on Distribution Ratios of Actinides,Lanthanides and Fission Products
Conditions:Phase ratio:O/A=1,Contact time:5 min.
Organic phase:30(vol.)% DHDECMP-DEB

Concentration of HNO_3,mol/l	Distribution Ratios						
	U(VI)	Np(IV)	Pu(IV)	Am(III)	Gd(III)	Zr-Nb	Ru
0.1	2.20	0.01	1.9	0.08	0.03	0.28	0.08
0.3		1.8	4.2	0.06	0.08	0.30	0.20
0.5	12.5	14.0	7.7	0.20	0.15	0.30	0.26
1.0	29.6	65.0	40.7	0.50	0.37	0.42	0.36
2.0	53.3	140.0	64.4	1.2	0.90	0.48	0.42
3.0	72.2	220.0	102.0 2.9[a]	2.2	1.6	0.49	0.41
4.0	90.1	350.0	136.0	2.9	2.2	0.52	0.28
5.0	123.0	550.0	114.0	3.3	2.3	0.57	0.18
3.0mol/l HNO_3,0.05 mol/l $H_2C_2O_4$	30.3[b]	60.0	4.2				

a.Pu(III) b.3mol/lHNO_3-0.05mol/l $H_2C_2O_4$ of simulated feed solution

^{237}Np, ^{239}Np, ^{241}Am, ^{151}Gd, $^{85+89}Sr$, ^{137}Cs, ^{103}Ru and $^{95}Zr-^{95}Nb$ tracer: radiochemically pure, Our institute; (c).Other reagent:C.P.or A.R..(d).Well-type NaI(Tl) Scintillation gamma counter,gamma spectrometer and ZrS(Ag) α-detector were used.

2.2.The composition of simulated nuclear reactor fuel reprocessing waste:U,5g/l;$^{237}Np+^{239}Np$, ^{239}Pu,^{241}Am, trace amount; Gd, 6g/l, the concentration of other lanthanites, fission products, chemical addictive and corrosive products is based on the concentration of them in real 1AW waste solution,evaporated to 3mol/l nitric acid.

Adjustment of the valence:The valence of Np and Pu was adjusted with $Fe(NO_3)_3$ to tetravalence state and trivalence state in simulated feed solution (R-AF) respectively.

2.3.Experimental and Analitical Procedures

6 extraction stages and 2 scrub stages were used to recover U,Np,Pu,Am and Gd in the R-A coextraction cycle.In the R-B cycle 6 stripping stages were used for stripping Pu,Am and Gd from organic phase.Finally,6 stripping stages were used in the R-C cycle for stripping Np and U.All experiments were performed at room temerature. When a chemical steady-state was reached, aqueous and organic phase were sampled and analyzed. All distribution ratios have an uncertainty of about $\pm 10\%$.

Table 2.Back-Extraction of Actinides,Lanthanides in Batch Experiments

Stripping Solution	Back extraction percentage				
	U(VI)	Np(IV)	Pu(IV),(III)	Am(III)	Gd(III)
0.05mol/l HNO_3, 0.05mol/lHNO_3,-0.05 mol/l $Fe(NO_3)_3$	6.60	1.2	1.0 71.8	74.2	82.7
0.05mol/lHNO_3,-0.05 mol/l Oxalic acid	26.5	91.7	89.0	82.5	Oxalate precipitate

Organic phase:30%DHDECMP-DEB charged with actinides,lathanides and 0.56mol/l HNO_3

3.Results and Discussion

3. 1.The batch extraction experiments for actinides,lanthanides and fission products were performed.The results were shown in table 1 and 2.

Table 3.Conditions of the multistage counter-current experiment

Name of cycle	R-A cycle	R-B cycle	R-C cycle
stage number	six extraction stages and two scrub stages	six stripping stages for Pu, Am,Gd	six strinpping stages for U and Np
composition	R-AF:simulated 1AW feed solution containing 3 mol/lHNO_3, and 0.05mol/l $Fe(NO_3)_3$ R-AX:30% DHDECMP-DEB R-AS:3mol/lHNO_3, with diluted oxalic acid	R-BF:from R-AP R-BX:0.05mol/l HNO_3, +0.005 mol/l$Fe(NO_3)_3$	R-CF:from R-BW R-CX:0.01mol/l HNO_3, +0.05 mol/l oxalic acid
flow rate	F:X:S=1.5:2.0:0.5	F:X=1:1	F:X=1:1

F:feed solution,X:stripping solution in R-B and R-C, S:scrub solution.

Table 1 and 2 showed that the actinides and lanthanides can be quantitively extracted at higher acidic solution(~3mol/l HNO_3) with multistage countercurrent extraction process, and the most part of trivalent actinides and lanthanides in organic phase can be stripped by lower acidic solution ($\leqslant$0.1mol/l HNO_3).Then the remaining actinides in organic phase after first stripping can be further stripped by the stripping solution containing dilute oxalic acid.

Table 1 also showed that a part of the Zr—Nb can be extracted into organic phase and can be removed from organic phase by the scrubbing solution containing 3mol/l HNO_3 and 0.05 mol/l oxalic acid.

3.2.Results of cascade experiment

(1) .On the basis of data of batch experiment and calculation,the conditions of the cascade experiment were shown in table 3.The flowsheet of three cycle was shown in figure 1.

The results of three cascade cycle were shown in table 4,5,6.The concentration profile

Table 4.The result of cascade experiment in the R—A

Run No.		1	2	3	4	material balance (%)
Recovery efficiency(%)	U	99.95				100.5
	Np	~100	99.40			98.1
	Pu	99.95				100.8
	Am	~100	>99.59		>99.30	97.0
	Gd		>99.82	>99.70	>99.30	97.8
Decontamination factor	Zr	>3600			5.6	
	Nb	>3700				
	Ru	6.6				
	Sr	>2800				
	Cs	7800				

*.Run No.1—3 scrubing solution:3mol/l HNO_3+0.05mol/l $H_2C_2O_4$
Run No.4 scrubing solution:3mol/l HNO_3

of different stage were shown in figure 2,3,4.

The results show that U,Pu,Am,Np and Gd can be effectively removed from the nuclear

Table 5.The results of cascade experiment in the R—B cycle

Run No.			1	2	3	material balance (%)
Recovery efficiency(%)		Am	>99.65			102.6
		Gd	>99.70	>99.75		108.8
		Pu	96.58			112.0
		U	93.84			98.1
		Np	93.20		97.33	100.6
Decontamination factor	R—B	Zr			>4.2	
		Nb			>2.9	
		Ru	3.0		4.1	
	R-A+R-B	Zr			>23.5	
		Nb			>80.0	
		Ru			21.3	

waste solution in R—A cycle.

The results from table 5 show that the stripping efficiency of Am, Pu and Gd was

Table 6.The results of cascade experiment in the R—C cycle

stripping solution	recovery efficiency (%)	
	U	Np
0.05mol/l HNO_3 — 0.05mol/l $H_2C_2O_4$	57.47 56.96	97.94 97.03
0.01mol/l HNO_3 — 0.05mol/l $H_2C_2O_4$	98.02	99.95
material balance (%)	103	105

>99.65%,96.58% and 99.70%,respectively.

The results of cascade experiment in R—C back extraction cycle show that the recovery efficiency of U and Np is 98.02% and 99.95%,respectively.

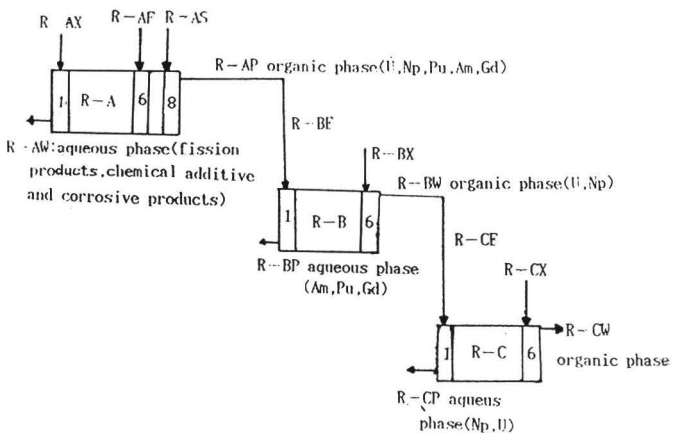


Figure 1.The flowsheet for separation of actinides and lanthanides

4.Conclusion

(1).According to the batch extraction experiment of actinides,lanthanides and fission products, multistage counter—current extraction experiments have been performed for the removal and recovery of actinides and lanthanides from the simulated nuclear power reactor fuel reprocessing waste solution by 30% DHDECMP—DEB.

(2) . The experimental results in the R—A extraction cycle show that the recovery efficiency of U, Np, Pu, Am and Gd is 99. 95% , ~100% , 99. 95% , 100. 00% and >99.82%,respectively,and the decontamination factor for fission products is DF_γ>3.6×10' ,DF_γ>3.7×10',DF_γ=6.8,DF_γ>2.8×10',and DF_β>3.9×10' respectively.

(3) . Stripping of Pu,Am,and Gd from organic phase was carried out in the R—B cycle.Stripping efficiency for Pu,Am and Gd is 99.65%,96.58% and 99.70%,respectively.

(4) . Np and U were further stripped from the organic phase in the R—C cycle, the stripping efficiency is 99.95% for Np and 98.02% for U.

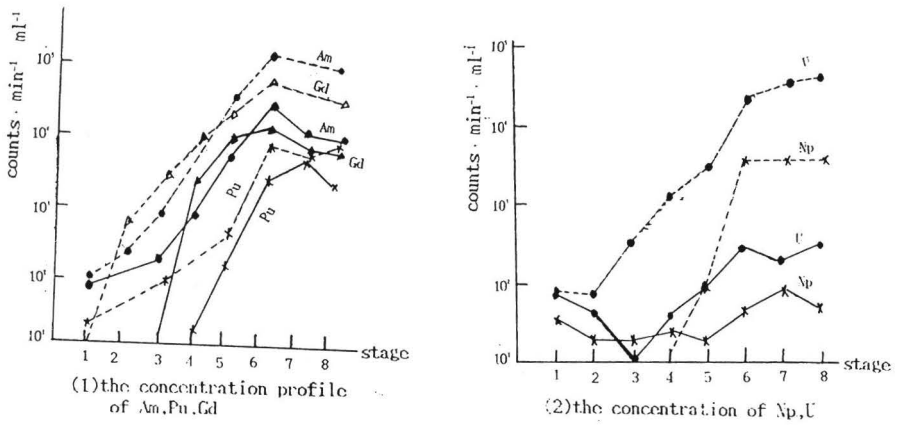


Figure 2.The concentration of Am,Pu,Gd,Np,U in different stage of the counter current experiment at steady-state condition in the R-A cycle
——aqreous phase .....organic phase

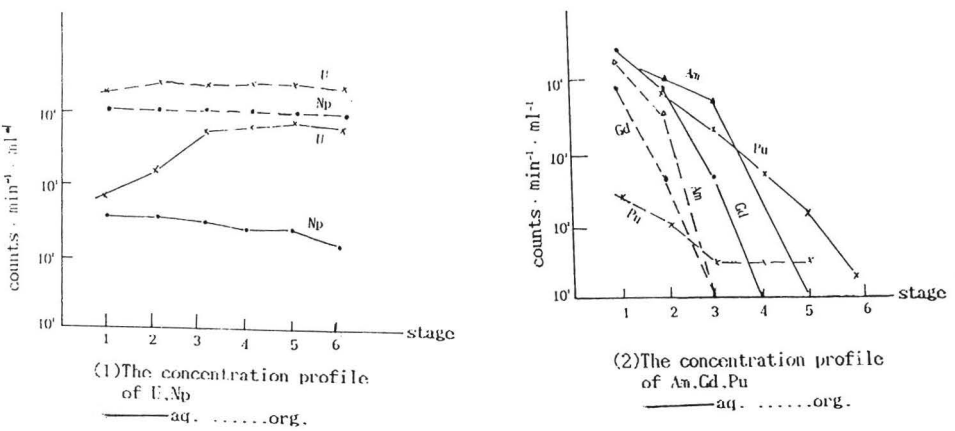


Figure 3.The concentration of U,Np,Am,Gd,Pu in different stage of the counter current experiment at steady-state condition in the R-B cycle

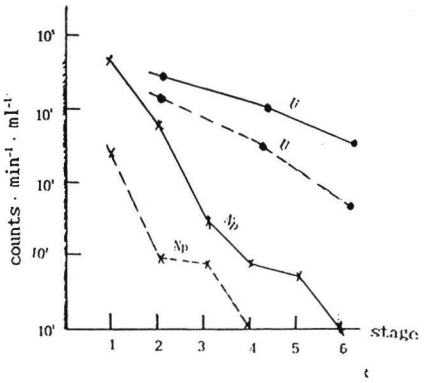


Figure 4.The concentration of U,Np in different stage of the counter current experiment at steady --state condition in the R—C cycle

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A NEW REAGENT FOR URANIUM - PLUTONIUM PARTITIONING

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ABSTRACT
We have investigated the feasibility of achieving uranium-plutonium partition of the Purex Process by using a new reagent : Uranous nitrate - hydroxylamine nitrate.
Laboratory test tube studies and uranium-plutonium partitioning runs have shown that plutonium stripping efficiency is good and comparable to the efficiency obtained with U(IV)-hydrazine system.

INTRODUCTION

Uranium-plutonium separation is one of the major step in fuel reprocessing. Although this partitioning has been proved in laboratory studies to be achievable without the use of reducing agents, most of industrial processes involve Pu(IV) reduction to Pu(III) by uranous nitrate.

However trivalent plutonium is rapidly oxidized by HNO_3-HNO_2 couple in usual conditions of the partitioning. Stabilizers are then necessary to avoid Pu(III) reoxidation in the aqueous phase, sulfamate ions and hydrazine nitrate which react very rapidly with nitrous acid are the most commonly used.

Advantages and drawbacks of these two products are listed above :

	Advantages	Drawbacks
Sulfamic Acid	Very efficient nitrite scavenger	no volatile by-product
Hydrazine nitrate	Very efficient nitrite scavenger	- Safety (N_3H, NH_4^+). - Reaction with Technetium (stabilisation efficiency limited with time). - formation of gas (N_2) involves hydraulic perturbation.

We have studied the use of hydroxylamine nitrate (HAN) as stabilizing agent for U(IV) and Pu(III). HAN destroys HNO_2 according to the reaction :

$$NH_3OHNO_3 + HNO_2 \rightarrow N_2O + HNO_3 + 2H_2O$$

HAN presents three main advantages over hydrazine and sulfamic acid :

1) Product of reaction with HNO_2 is chemically inert.

2) N_2O is aqueous and organic soluble. (no hydraulic perturbation in pulsed column).

3) Excess of HAN is easily destroyed by nitric acid.

The new reagent studied is : $U(NO_3)_4$-HAN.

2 TEST TUBE STUDIES

2.1 Reagent stability

Before checking the efficiency of such a reagent, we had to verify its stability with time. Instable reagent would not be very convenient in a plant, indeed.

U(IV) solutions were prepared by catalytic reduction of uranyl nitrate. Composition of solutions were :

$[U(IV)] = 100\ g.l^{-1}$

$[HNO_3] = 1\ M$

$[HAN] = 0.1$ to $0.6\ M$

and light-sheltered at 22 ± 1°C. [U(IV)] was measured spectrophotometrically (648 nm) every week.

10 % of U(IV) is reoxidized within 9 weeks and 20 % within 7 months. [HAN] has no effect on the stability.

In the same conditions, the reoxidation rate of U(IV)-Hydrazine reagent is 3.5 to 5 % per week (1) (2).

U(IV)-HAN reagent may be considered as stable.

2.2 Effect of nitrous acid on U(IV)-HAN stability

In order to check HAN efficiency as stabilizing agent, we followed evolution of HAN and U(IV) concentrations in aqueous phase with time of bubbling of NO gas (Figure 1).

HNO_2 formed in solution is destroyed by HAN. U(IV) is not reoxidized as far as HAN concentration is higher to 0.01 M.

HAN stabilizing effect is strong enough to avoid U(IV) oxidation.

2.3 U(IV) stability in organic phase

Figure 2 shows that there is no significant difference between HAN and HN on U(IV) stability in organic phase. U(IV) was extracted from aqueous solution ($U(IV) = 20\ g.l^{-1}$; $HNO_3 = 1\ M$; HAN or HN = 0.2 M) by 30 % TBP preequilibrated with nitric acid).

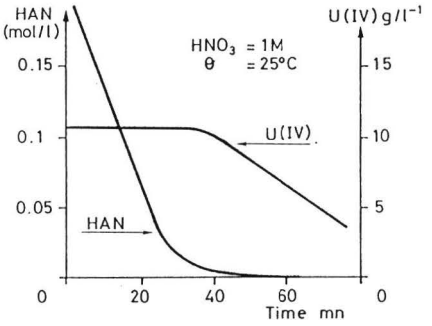


Figure 1 . Evolution of HAN and U(IV) concentrations in aqueous phase with time of bubbling of NO gas.

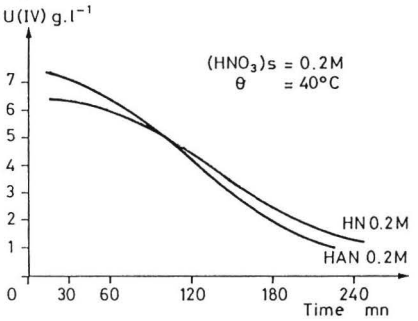


Figure 2. Stability of U(IV) in organic solution as function of aqueous phase composition

2.4 Plutonium stripping

Pu decontamination factors obtained with U(IV)-HAN or U(IV)-HN are the same. In the following conditions (4 contacts V/V, 3 mn, 25°C, U(IV)/Pu = 2, [HAN], [HN] = 0.2 M), we obtained DF of 1.1 10^3 (first cycle conditions) and 1.5 10^4 (plutonium cycle conditions).

2.5 Effect of Technetium on U(IV) and Pu(III) stability

2.5.1 Effect of Tc on U(IV)-HAN solutions

Tetravalent uranium is quite stable in a nitric acid solution containing hydroxylamine nitrate.

However, in the presence of technetium ions, U(IV) is oxidized by nitric acid. This oxidation is catalyzed by Tc ions. We investigated the kinetics of this reoxidation reaction and determined the orders with the respect of [U(IV)] ; [Tc] and [HNO_3].

We observe (Figure 3) that : initially U(IV) is quickly oxidized then the reaction slows down, after which the U(IV) concentration decreases linearly with time.

At the end the reaction accelerates until the U(IV) disparition.

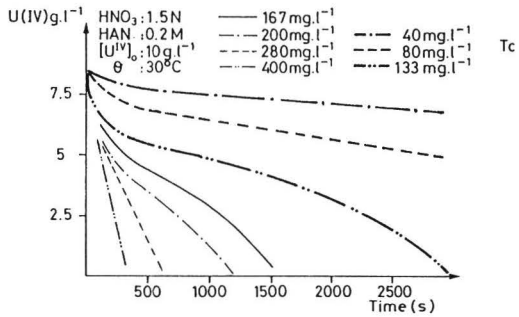


Figure 3. Influence of technetium concentration on U(IV) stability in aqueous phase.

The first part of the reaction agrees with the oxidation of U(IV) by Tc(VII), the linear part corresponds to the oxidation of U(IV) by HNO_3, catalyzed by technetium ions (back oxidation of lower valence forms of Tc by HNO_3).

The rate of U(IV) oxidation is higher than with hydrazine stabiliser (3) (4).

2.5.2 Effect of Tc on Pu(III)-HAN solutions

Trivalent plutonium is stable in nitric acid solution containing HAN, even in presence of technetium ions. We notice no reoxidation of Pu(III) at 40°C during 2.5 hours in the medium :

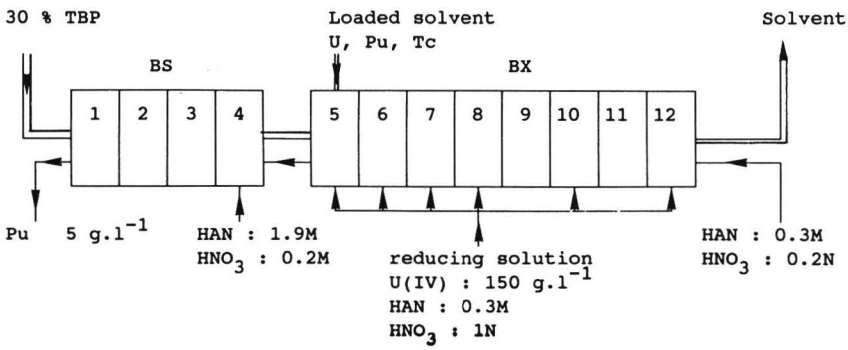
HNO_3 : 2.6 M ; HAN = 0.2 M ; Tc(VII) = 0.4 $g.l^{-1}$

In the same conditions with hydrazine, the reoxidation of Pu(III) would be complete.

3 URANIUM-PLUTONIUM PARTITIONING

3.1 Mixers-settlers experiment

The tested Flow-sheet was :



The chemical conditions were :

Fuel : LWR 33.000 MWJ.t^{-1} (simulated)

BX : 8 stages ; O/A = 7.1 ; U(IV)/Pu = 5.5 ; U(IV)/NHA = 0.33

BS : 4 stages ; O/A = 1

Temperature : 27.5°C.

Result

The plutonium profiles (Figure 4) are satisfactory : rather flat in BS section and the slope in BX section indicates that the plutonium stripping is very efficient (DF >> 4.10^3) - HAN consumption is very weak (Figure 5) and equal to U(IV) excess.

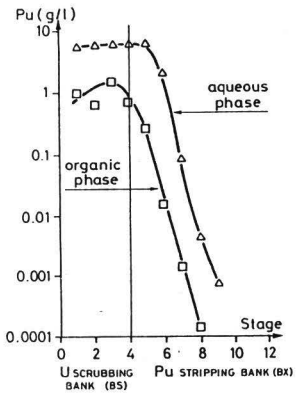


Figure 4. Plutonium Profiles

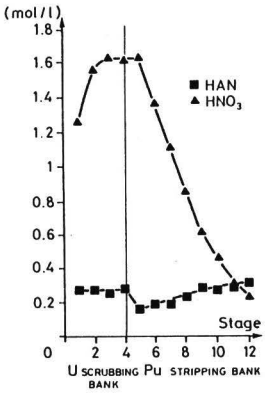


Figure 5. HNO_3 and HAN profiles in aqueous phase

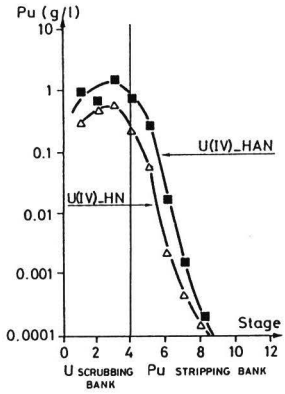


Figure 6. Comparison of Pu profiles in organic phase

Comparison of U(IV)-HAN and U(IV)-HN systems : in BS section, Pu reflux (Pu reoxidation) is higher with HAN system. Nevertheless Pu profiles in BX section and decontamination factors are comparable.

3.2 Pulsed column experiment

Plutonium-uranium partitioning of the Purex process was tested in pulsed columns. Pu stripping and U scrubbing columns were operated in aqueous continuous mode.

Results have shown, that U(IV)-HAN reagent is as efficient as U(IV)-NH reagent, as was observed in mixers-settlers.

4. CONCLUSIONS

Laboratory studies and preliminary runs in mixers-settlers and pulsed columns show that hydroxylamine nitrate could be substituted to hydrazine nitrate as U(IV) stabiliser. Their efficiencies for plutonium stripping are comparable.

Partitioning Process feasibility using uranous nitrate stabilized by hydroxylamine nitrate was demonstrated. Nevertheless studies have to be pursued to get a better knowledge of reaction mechanisms to permit process optimisation and industrial application.

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APPLICATION OF SALT-FREE TECHNOLOGY TO THE PUREX PROCESS FOR FBR FUEL REPROCESSING.

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ABSTRACT

For the purpose of reducing radioactive waste from LMFBR spent fuel reprocessing, a series of basic experimental studies on the application of salt-free technologies to U/Pu partition, successive Pu re-oxidation, and solvent regeneration has been carried out. In the U/Pu partition process, U and Pu were separated from each other in tests using hydroxylamine-nitrate (HAN) with and without hydrazine, and in each case nearly the same DF (decontamination factor) of Pu in U product was achieved. HAN as well as hydrazine were decomposed rapidly in an electro-oxidation cell in separate tests using Ce(Ⅲ) and Fe(Ⅱ) to simulate Pu(Ⅲ). The oxidation rate depended on the electro-chemical characteristics of each metal ion. In solvent regeneration tests, it has been confirmed that the total decontamination factor with salt-free reagents such as hydrazine carbonate and hydrazine oxalate was almost the same as that of conventional alkali scrubbing, and the pH dependency on the scrubbing efficiency of Ru, one of the contaminants in the simulated degraded solvent, was well determined. Both hydrazine carbonate and hydrazine oxalate were decomposed with high efficiency in an electro-oxidation cell. Through this series of studies, a PUREX flowsheet incorporating salt-free processes was established.

INTRODUCTION

The purex process, based on solvent extraction, has been carried out in spent fuel reprocessing for over three decades world-wide. In spite of such successes even in industrial scale reprocessing, the need to reduce overall reprocessing costs still exists. As for the purex solvent extraction process, the generation of salt-containing waste is one major cause of the rising costs associated with reprocessing today. To settle this matter, direct application of electrochemistry as an alternative to conventional chemical reagent processes was considered. One direction of such application was to develop in-situ electro-reductive U/Pu partitioning equipment including a mixer-settler, pulsed column[1], and if possible, centrifugal contactor[2]. Electro-oxidation, as adapted mainly to the Pu reoxidation process in KfK, was another possible direction to achieve a salt-free purex process if it could be extended to the entire solvent extraction process. While electro-oxidation is said to have a potential corrosion risk, on the other hand it is capable of decomposing organic materials as well as changing the ionic state of some elements in a controlled and moderated manner. A salt-free purex process based principally on adaptation of electro-oxidation technology extensively to the solvent extraction process will be described herein.

SALT-FREE TECHNOLOGY IN U/Pu PARTITION AND REOXIDATION

(1) U/Pu Partition using HAN with or without hydrazine

HAN has been employed as a reducing reagent for the U/Pu partition process with irradiated fuel from the fast experimental reactor "JOYO" in the CPF (Chemical Processing

Facility). In earlier studies, hydrazine has been added to HAN to stabilize it in a typical flowsheet. In recent studies, however, a partition flowsheet using HAN without hydrazine has been devised to obtain a simpler flowsheet while keeping high efficiency in U/Pu partition.

Table-1 Test conditions and results of partition

Case	HAN (mol/ℓ)	Hydrazine (mol/ℓ)	HAN/Pu ratio	A/O ratio (Pu strip)	Pu in org. phase (mg/ℓ)	DF Pu Pu/U(p) Pu/U(f)
1	0.22	0.2	5.8	0.52	0.2	3.2E4
2	0.27	0.2	3.1	0.65	—	3.6E4
3	0.19	0	2.7	0.53	1.2	9.6E4
4	0.28	0	3.2	0.73	—	6.9E4

Profile of case 1 and case 3 are shown in Figure-1 and Figure-2 respectively

Table-1 shows the experimental conditions of HAN and hydrazine and results from several experimental studies. In each case, Pu concentration in the organic phase was under 1.2 mg-Pu/ℓ and a DF (decontamination factor) on the order of 10^4 was achieved without regard to the presence of hydrazine.

Figures-1 and 2 show summarized flowsheets and profiles of major parameters such as U and Pu concentration in cases 1 and 3. In these cases, the A/O ratio in the Pu strip bank was adjusted to almost the same value. It was obvious that the "tailing" profile of Pu in the organic phase might result in Pu leakage. Although further improvements in the hydrazine-free partition process might be necessary, this is not viewed as a major problem for LMFBR spent fuel reprocessing. Furthermore, the hydrazine-free partition process also provides additional benefit through its reducing reoxidation ability as well as avoiding formation of unfavorable nitric by-products.

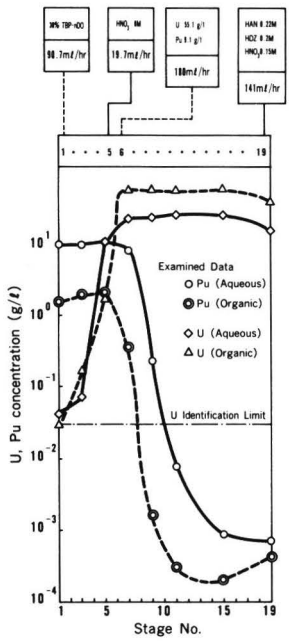


Figure-1 U and Pu extraction profile in partition bank with hydrazine
(After 34Hr from start up)

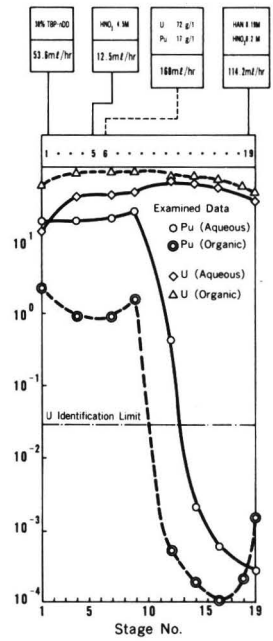


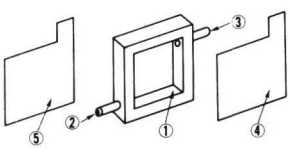
Figure-2 U and Pu extraction profile in partition bank without hydrazine
(After 12Hr from start up)

(2) In-situ Electro-Oxidation

Following partition, Pu must be reoxidized from Pu(Ⅲ) to Pu(Ⅳ) and any accompanied reductant must be decomposed so that the Pu(Ⅳ) can be purified in the next extraction cycle. In this experiment, a small diaphragmless filter-press type electro-oxidation cell with a Pt-coated Ti electrode which has 400cm² of anode and cathode surface area was employed in cold tests (see Figure-3). Batchwise and continuous flow tests were carried out by changing the current density, stream velocity, material component of electrolyte,. Oxidation efficiency, material balance, etc. were determined. The electrolytes used in this test were HAN and hydrazine, and nitric acid acted as a supporting electrolyte. In several cases Ce(Ⅲ) and Fe(Ⅱ) ions were added to simulate Pu(Ⅲ).

Figure-4 shows results from a batchwise test with and without metal ions. In the case of HAN and Hydrazine without the presence of a co-existing metal ion, the oxidation velocity of HAN was relatively slow, ca.0.026 mol-HAN/hr, although under a high anodic current density of 100 mA/cm^2. In tests where metal ions were present, the oxidation velocity of HAN experienced a 10 fold increase to ca.0.25 mol-HAN/hr. This phenomena is easily explained by recognizing that the metal ion behaved as a "mediator" (see Figure-5). As for the metal ion itself, Fe(II) was oxdized easier than Ce(III). HAN was oxdized faster with Ce(III) than with Fe(II).

Figure-6 shows results from a continuous flow test where metal ions were added to the solution and linear velocity was the test parameter. HAN could be oxidized at a higher linear velocity in the presence of Ce(III) than Fe(II). From these results, the electro-oxidation of HAN depended upon the redox potential of the "mediator" metal ion. Thus, the ability of Pu(III) to oxidize HAN/hydrazine in nitric acid could be predicted.



(made of TEFLON)

① Electrolytic cell without diaphragm (20×20×1.5cm)

② Electrolyte inlet

③ Electrolyte outlet

④ Anode(Pt-coated Ti plate) surface area : 400cm^2

⑤ Cathode(Ti plate and Pt-coated Ti plate) surface area : 400cm^2

Figure-3 Electro-Oxidation cell

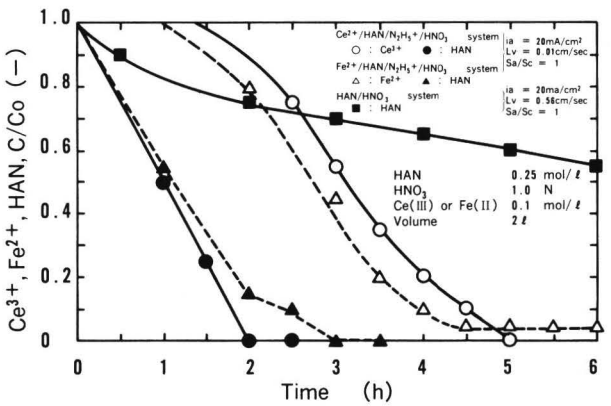


Figure-4 The effect of oxidizing power of mediator (Ce^{3+}, Fe^{2+})on the electro-oxidation rate of HAN

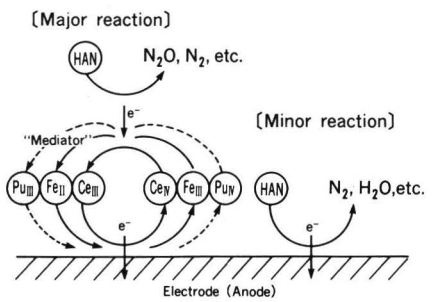


Figure-5 Assumed oxidation paths of HAN in an anodic electrode reaction

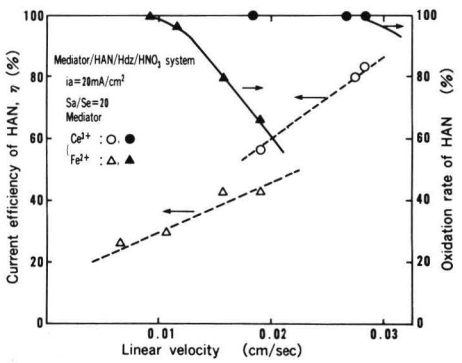


Figure-6 The effect of linear velocity of feed upon the current efficency and oxidation rate of HAN

SALT-FREE SOLVENT REGENERATION

(1) Solvent cleanup by salt-free reagents

There exist a number of salt-free reagents suggested in previous studies[3)4)]. In this experiment, some of them were tested at the same operating conditions. Two kinds of experiments were carried out. One was batchwise tests using a separation funnel and another was continuous flow tests using 3 stages of small mixer-settlers (see figure-7).

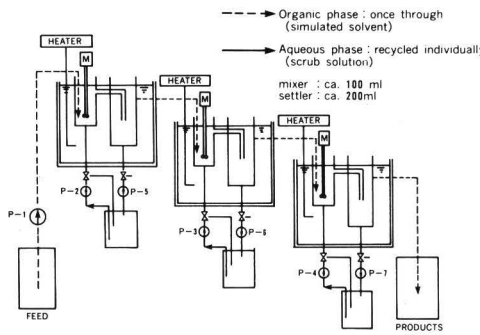


Figure-7 Experimental apparatus (3 stages of mixer-settler)

Figure-8 shows the cleanup efficiency of DBP and Ru from the batchwise tests. The cleanup efficiency of DBP increased as the pH of the chemical reagent increased. To maintain high cleanup efficiency for DBP, the pH of the chemical reagent solution should be kept over 5 for oxalate and tartrate and over 7 for carbonate. Zr and U behaved in almost the same manner as DBP, but Ru showed different behavior. The cleanup efficiency of Ru depended not on the types of complex ion but on only the pH of the chemical reagent; a pH over 7 was indiscriminately necessary for all reagents to maintain high Ru scrubbing efficiency. Based on these results, three candidate scrubbing reagents, hydrazine oxalate, hydrazine carbonate, and TMAO/C, were selected.

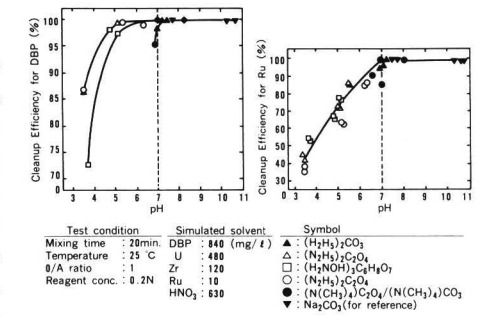


Figure-8 Cleanup efficiency of DBP and Ru in batchwise test

Figure-9 shows typical results from continuous mixer-setter tests. In these tests hydrazine carbonate demonstrated good cleanup efficiency for DBP and Ru (as well as for Zr and U), but there was a considerable amount of interfacial crud formation and build-up. Hydrazine oxalate, on the other hand, maintained good cleanup efficiency for U and Zr as did hydrazine carbonate over a long time period, but cleanup efficiency became poor immediately for DBP and Ru. The degree of crud build-up in tests with hydrazine oxalate was negligible throughout the testing period. TMAO/C also maintained good cleanup efficiency for Ru, but cleanup efficiency became poor for DBP. Although the amount of crud formed in the TMAO/C system was less than that in the hydrazine carbonate system, it could scarcely be ignored when operation continued for a long time.

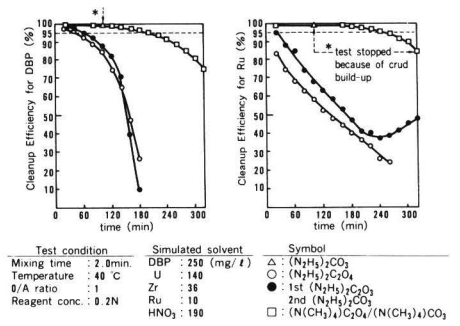


Figure-9 Ru in the 1st stage Mixser-settler Cleanup efficiency of DBP and

(2) Electro-Oxidation of Salt-free Scrubbing Reagents

In this test, the same electro-oxidation cell as described earlier was employed. The electrolyte was made by adding hydrazine nitrate or oxalic acid to nitric acid solution to simulate the scrubbing reagents hydrazine oxalate and hydrazine carbonate. Once hydrazine carbonate was added to nitric acid, it immediately converted to hydrazine nitrate. As for TMAO/C, it was not tested because of its high chemical stabilty.

Table-2 shows typical experimental conditions and results. Hydrazine was decomposed faster than oxalate ion. Each component was decomposed to gas as H_2, N_2, CO_2, O_2 and N_2O. In the electro-oxidation of hydrazine carbonate (nitrate), the formation of hydrogen azide (HN_3) and ammonium ion (NH_4^+) as secondary products occurred.

Figure-10 shows the tendency of NH_4^+ formation. NH_4^+ formation mainly depended on the cathode current density. In our experiment, the amount of NH_4^+ formation was recognized as small. Therefore, it might not be a major problem under the conditions tested.

Based on these test results, the proposed selection of reagents for the 3 stages in the solvent cleanup system were as follows ; 1st stage: Hydrazine oxalate, 2nd stage: Hydrazine carbonate, and 3rd stage: Nitric acid.

Table-2 Experimental conditions and results of electro-oxidation of salt-free reagents

Conditions

Items	Case 1	Case 2	Unit
Electrolyte (before electrolysis)	$N_2H_5NO_3$ 0.25 HNO_3 0.92	$(COOH)_2$ 0.23 $N_2H_5NO_3$ 0.47 HNO_3 0.12	mol/ℓ
Current density (Anode)	25	100	mA/cm²
Linear velocity	0.56	0.56	cm/sec
Volume	2.0	2.0	ℓ
Testing time	4	6.5	hr

Results

Electrolyte (after electrolysis)	$N_2H_5NO_3$ 3.3E-3 HNO_3 1.09 HNO_2 0.02 HN_3 6E-4 NH_4NO_3 0.04	$(COOH)_2$ 9E-3 $N_2H_5NO_3$ <7E-3 HNO_3 0.13 NH_4NO_3 2E-5	mol/ℓ
Gas composition (after 2 hr from start up)	$H_2 > N_2 \gg O_2 > N_2O$	$H_2 > CO_2 \gg N_2 > O_2$	
Temperature rise	+5	+40	℃
Current efficiency and demand for $N_2H_5^+$	99 107	N_2H_4 140~40 $(COOH)_4$ ca. 5	% A＊hr/mol-N_2H_5
Yield of NH_4^+	1.5E-3	ND	mol-NH_4^+/A＊hr
Yield of HN_3	1.5E-4	ND	mol-HN_3/hr

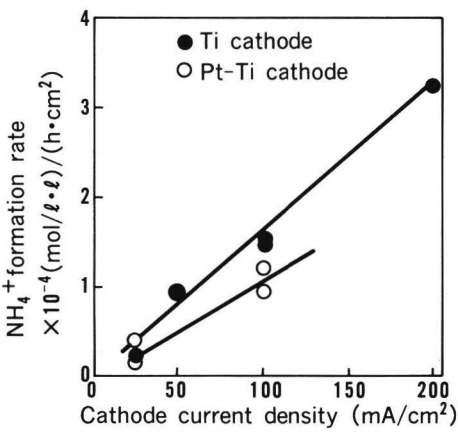


Figure-10 Tendency of NH_4^+ formation in electrooxidation of hydrazine nitrate

CONCLUSIONS

Results from a series of basic expreiments confirmed the feasibility of a Salt-free purex solvent extraction process concept based on application of electro-oxidation as well as electro-reduction processes to an entire purex solvent extraction process.

(1) Partition tests using HAN without hydrazine successfully indicated that similar decontamination factors for Uranium product were obtained compared with tests when hydrazine was present, although slight retention of Pu was noticed at the tail end of the Pu stripping section. Additional investigation might be required even when adapting this process to a centrifugal contactor extraction cycle.

(2) The electro-oxidation behavior of Pu(Ⅲ)/HAN/hydrazine exiting the partition cycle was verified. Although low electro-oxidation rates were observed for pure HAN in nitric acid solution, its oxidation rate accelerated greatly in the presence of metal ions such as Fe and Ce which have a rather high standard redox potential. A similarly high oxidation rate is predicted for Pu. Considering actual application of an electro-oxidation cell to the purex process, centrifugal contactors might provide an ideal interface because both the start-up and shut-down periods when the process solution contains a low concentration of co-existing Pu ion are sufficiently shortened in a centrifugal contactor based system.

(3) Solvent cleanup tests using various types of salt-free reagents were conducted. The scrubbing behavior of DBP, Zr, U and Ru were determined from the pH characteristics of the aqueous phase. Ru scrubbing behavior primarily depended on alkalinity but not on the kind of aqueous phase reagent. As a result, the combination of hydrazine oxalate and hydrazine carbonate gave high scrubbing efficiency which closely corresponded to that in conventional salt-contained reagent tests. If this salt-free solvent cleanup system was applied to the purex process using centrifugal contactors for FBR spent fuel reprocessing, although less solvent degradation could be expected, mixing time dependency on scrubbing efficiency should be verified.

(4) Electrolysis of both hydrazine oxalate and hydrazine carbonate was demonstrated. Decomposition of hydrazine carbonate was easy as previously expected but a considerably high anodic current density was required to obtain quantitative destruction of oxalate ion.

(5) Results from a series of electro-oxidation tests provided the basic information necessary to develop two different functional electrolysis cells for the purex process.

ACKNOWLEDGEMENT

The authors wish to acknowledge the valuable contribution of Dr. J. C. Mailen for significant input as well as the dedication and commitment of the staff of Hitachi Ltd. and Asahi Chemical Industry Co., Ltd. for their service and experimental work.

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Solvent Extraction 1990, T. Sekine (Editor)

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OPERATING EXPERIENCE OF CENTRIFUGAL CONTACTORS USED IN A THIRD PLUTONIUM PURIFICATION CYCLE AT THE MARCOULE REPROCESSING PLANT

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ISEC 90 - KYOTO - (Poster n° °27)

ABSTRACT

Multistage centrifugal contactors of the type ROBATEL LX 208 NSC (SGN-ROBATEL PATENT) are used in a third plutonium cycle at the Marcoule Reprocessing Plant, they have been smooth-running since the commissionning in 1984.
The four centrifugal contactors, totalling 32 stages, are used for Extraction, Scrub and Acidic Strip, and a bank of three flat mixer-settlers is used for plutonium blocking, and soda washing of the solvent.
The plutonium product, the residual activity of which is less than one microcurie per gram, is diluent washed in a bank of three flat mixer-settlers, before been concentrated in a zirconium evaporator to 200 $g.l^{-1}$.

INTRODUCTION

. The process employed in the Marcoule Reprocessing Plant was based, until 1984, on a two cycle 30 % TBP flow sheet. The first cycle (1 CUPu), using mixer-settlers, separates the Plutonium which is fed to a second Plutonium purification and concentration cycle (2 CPu-CPS) using pulsed columns [1] with the solvent of 1 CUPu, the Uranium is fed to a second Uranium cycle using mixer-settlers.

. A third Plutonium cycle (3 CPu) using multistage centrifugal contactors of the type ROBATEL LX 208 NSC (SGN-ROBATEL PATENT) has been designed as an add-on to keep below 1 $\mu Ci.g.Pu^{-1}$ the BETA-GAMMA contamination of the Plutoniun nitrate, arising from spent gas-graphite fuel irradiated to a burn up of up to 6000 $MWd.t^{-1}$, with a cooling time of one year or more.

. The bank of four centrifugal contactors has been in plant service since 1984. Operational experience of six years has been obtained, demonstrating the high degree of reliability of these space efficient contactors.
An outline of the applied extraction process, the extractor equipment and the performance is given here.

EXTRACTION PROCESS AND EQUIPMENT

. The third Plutonium cycle comprises the following operations :
- oxidation of Plutonium (III to IV) by nitrous vapour in a packed column ;

- extraction scrubbing and back extraction in four multistage centrifugal contactors of 8 stages ;
- diluent washing of the Plutonium nitrate product in a first mixer-settler bank of 3 stages ;
- carbonate washing of the unloaded solvent, preceded by one Plutonium blocking stage, in a second mixer-settler bank of 3 stages ;
- concentration of Plutonium nitrate product 20 times in a thermosiphon evaporator.

All the equipments are geometrically safe.

. The chemical flowsheet of the extraction unit is given figure 1. Its main characteristics are :

- a dilution factor of 1,9 between feed and product, due to the diluted acid back-extraction (0,1 - 0,2 N - HNO_3) ;
- the use of U IV in back-extraction (U IV/Pu feed = 0,002) and in a Plutonium blocking stage (U IV/Pu feed = 0,02) in mixer-settler ;
- a large excedent of stages in extraction and back-extraction to allow for transient operation and reduce the occurence of Plutonium leaks.

. The multistage centrifugal contactor, model LX 208 N, SGN-ROBATEL-patented, has been marketed since 1974 and a comprehensive testing program has been undertaken in 1977-1978 in JAPAN by PNC [3].

Its technical advantages, which have guided the choice made for the UP1 - 3 CPu cycle, are as follows [2] :

- critically eversafe ;
- great number of theoretical stages available ;
- wide range of flexibility in capacity ;
- small space required in active cell ;
- low Plutonium and solvent inventory ;
- short start up and shut down times ;
- low volume of flushing effuents.

Its main disadvantage is the risk of plugging, the aqueous feed coming from UP1-2 CPu being non clarified. The model LX 208 NSC was not available with a built-in deplugging device.

. A schematic diagram of the centrifugal contactor model LX 208 NSC (SC, for subcritical) is shown in Fig. 2, giving the main characteristics and typical stage construction with fluid transfer path.

. The layout of the bank of the four centrifugal extractors is shown in Fig. 3, giving the main features.

. Operating characteristics of the centrifugals are as follous :

- rotational speed variable with DC motor : 1800 RPM ;
- centrifugal separation force : 200 à 400 g ;
- dynamic liquid volume : 2,3 l for n° 1, 2, 3 - and 1,95 l for n° 4 ; 10,8 l for the bank ;
- solvent aqueous interface : fixed by the diameters of the weir : for light phase 95 mm for heavy phase 106 or 104 mm ;
- total liquid flow : 20 - 30 $l.h^{-1}$;
- plutonium mass rate : 8 $kg.day^{-1}$;
- temperature : kept below 40°C by appropriate ventilation of the casing of each contactor.

OPERATING EXPERIENCE

The operating experience with the centrifugals has been very satisfactory since the commissionning year, 1984, corresponding to 30.000 hours of running time and 7 metric tons of Plutonium reprocessed.

Equipment Maintenance

. One coupling and one bearing have failed on the driving device. The routine maintenance is lubrication. The vibration monitors (METRAVIB) are useful sensors.

. The inlet pipe carrying washed solvent in the centrifugal n° 1 had to be deplugged a few times, with nitric acid, the origin of the plugging could be deposition of sodium carbonate in the 6 mm ID pipe, entrained in the solvent which is not filtered after solvent washing. There is no built-in deplugging device in the centrifugals which are supposed to be replaced by direct maintenance in case of incurable plugging. The preventive maintenance performed is a biannual rinsing operation between campaigns. The Plutonium holdup of the unit on stream is about 3 kg and the rinsing volume of about 2500 l has a plutonium content of about 40 g, 75 % of which are sent to nitric acide recovery.

Process Performances

. The centrifugals are started up and shut down speedily, the drainage is recycled at the next start up. When shut down, they are flushed for a few hours.

. The control requirements on flow rates, due to the short residence time of less than 30 s per stage, have been met satisfactorily. Fig. 4 gives a comparison between measured and calculated [5] Plutonium concentrations in the solvent ; it shows, notwithstanding the Plutonium drag due to DBP, and a discrepancy in Extraction, that the number of mechanical stages are in excess. A Murphree stage efficiency of 0,93 per stage had been found [4] in uranium cold runs.

Expressed as fraction of Plutonium flux in the feed, 0,002 % is recovered in the alpha blocking stage, 0,001 % is lost in the solvent washing and less than 0,001 % is lost in the raffinate.

. Fission products decontamination factors are the following ones on the average : Zirconium 95 DF = 5 ; Niobium 95 DF = 20 ; Ruthenium-Rhodium 106 DF = 30. Reckoning with the activity arising from the 2nd CPu, the Plutonium product activity is less than 1 $\mu Ci.\beta\tau.(g.Pu)^{-1}$. The fission product activity bound in the washed solvent, 30 % TBP in TPH, is less than 1 $\mu Ci.\beta\tau.(l^{-1})$.

. The solvent holdup is about 60 l, it is replaced once a year, and renewed by make up, the losses being on the average of 0,8 l $(day)^{-1}$: partly due to the temperature rise in the centrifugals ; the heat imput has been modelized, most part of it is due to the friction on the agitating discs.

CONCLUSION

The successful on-going operating experience with multistage centrifugal contactors on the third Plutonium cycle in UP1-FRANCE, added up to the one gained on the third Uranium cycle in UP2-FRANCE, should incite new plant designers to take into consideration these types of compact contactors. When solid accumulation may be a problem, multistage centrifugals of the type used in 3 CU.UP2, which have built-in deplugging device and can be dismantled, are available.

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FIGURES

1. Extraction unit flow sheet
2. Schematic diagram of multistage centrifugal contactor LX 208 NSC
3. Extraction unit layout
4. Plutonium concentration in solvent : measured and calculated profiles

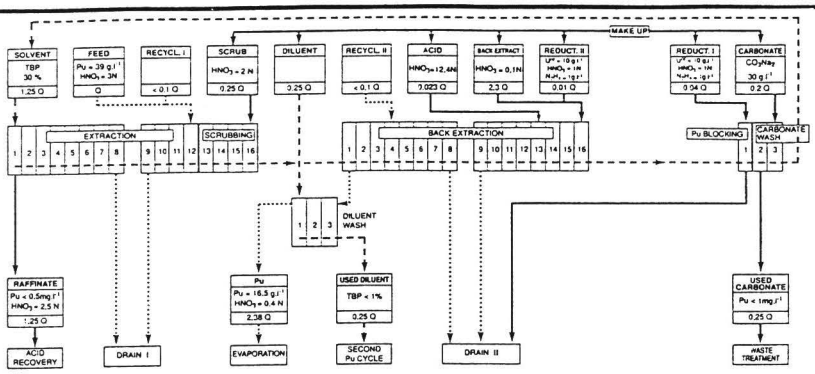
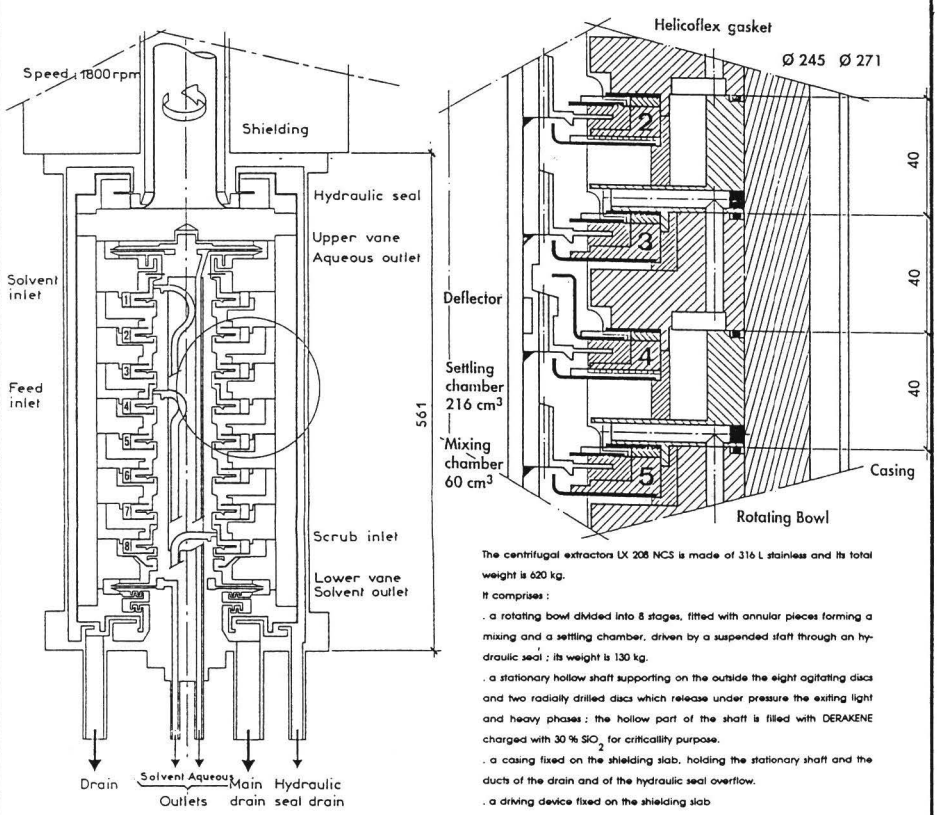


Fig. 1 – EXTRACTION UNIT FLOWSHEET



The centrifugal extractors LX 208 NCS is made of 316 L stainless and its total weight is 620 kg.

It comprises :

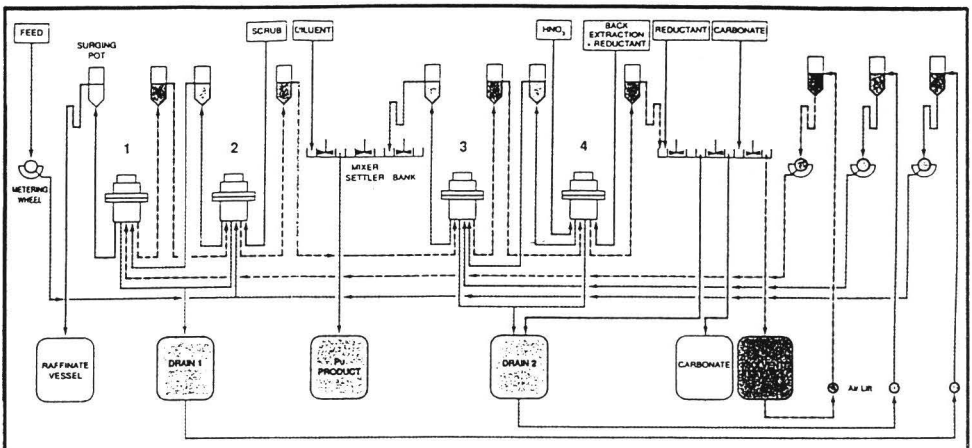
. a rotating bowl divided into 8 stages, fitted with annular pieces forming a mixing and a settling chamber, driven by a suspended staft through an hydraulic seal ; its weight is 130 kg.

. a stationary hollow shaft supporting on the outside the eight agitating discs and two radially drilled discs which release under pressure the exiting light and heavy phases ; the hollow part of the shaft is filled with DERAKENE charged with 30 % SiO_2 for criticality purpose.

. a casing fixed on the shielding slab, holding the stationary shaft and the ducts of the drain and of the hydraulic seal overflow.

. a driving device fixed on the shielding slab

Fig. 2 – SCHEMATIC DIAGRAM : LX 208 NSC – (3 CPu n° 2)



The four centrifugal extractors are set in a square bank on an anti-vibration slab.

The entering phases are gravity fed through inlet ducts forming lutes, the exiting phases flow under pressure to surging pots, equipped with sampling and temperature monitoring. The upper and lower radially drilled discs, which pump the exiting phases out, allow the extractors to be installed at the same level. To limit during start-up the pollution brought by the drainage of the stages at shutdown, the phase exiting by the upper disc has been selected for each extractor.

The nominal rotating speed is 1800 rpm, it allows to meet the constraints of phase separation, hydraulic head, temperature limitation (< 40°C), maintenance of the driving device.

The instrumentation comprises metering wheels on the inlet streams, vibration measures, temperature monitoring of the exiting stream and of the casing.

Fig. 3 – EXTRACTION UNIT LAYOUT

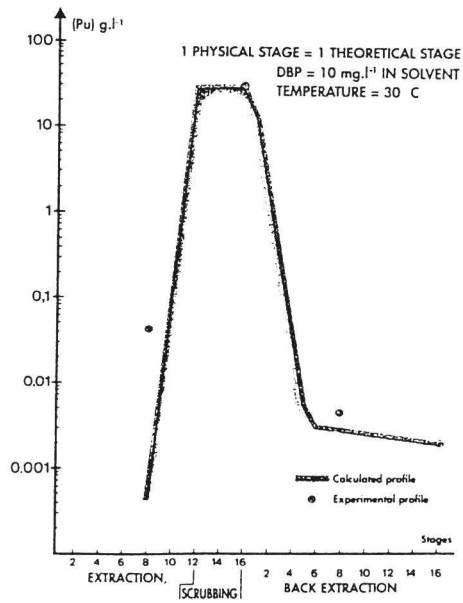


Fig. 4 – PLUTONIUM CONCENTRATION IN SOLVENT
Measured and calculated profiles

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EXTRACTION DYNAMICS OF PULSED COLUMN IN THE PUREX PROCESS

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ABSTRACT

Tanks in series model was applied to describe the flow characteristics of the pulsed column used in the Purex Process. The model has two kinds of parameters, the number of tanks and the volume of each tank, to express the axial dispersion. The parameters were determined from steady-state concentration profiles, then the dynamic behavior of uranium and plutonium in the pulsed column was simulated by this model. The experimental transient response data were obtained on a 4-m-high annular pulsed column with baffle plates in a $UO_2(NO_3)_2$-HNO_3-30% TBP/n-dodecane system. The simulated results were good agreement with the experimental ones.

INTRODUCTION

Several simulation codes for the pulsed column in solvent extraction of nuclear fuel reprocessing have been proposed in order to design the column and to determine the operating conditions (Groenier, 1972 etc.). In practical operation, the dynamic behavior of uranium, plutonium and fission products in the pulsed column must be predicted to control the process safely.

Three typical models; dispersion model, back-mixing model and tanks in series model, have been used to simulate the pulsed column performance at the steady state. The simulation using the dispersion and back-mixing models at the unsteady state is very complex because the axial dispersion coefficients and the back-mixing ones change in the pulsed column. In present work, dynamical simulation for the pulsed column operation was carried out by using of the tanks in series model. The longitudinal change of axial dispersion corresponds to the change of the volume of each tank in this model. The simulation results were compared with the experimental data.

The experimental transient response data were obtained on a 4-m-high annular pulsed column with baffle plates in a $UO_2(NO_3)_2$-HNO_3-30% TBP/n-dodecane system.

MODELING AND SIMULATION

The material balance equations of the tanks in series model are shown as Equations (1), (2) and (3):

$$\phi_x V_i \frac{dx_{i,j}}{dt} = Q_x x_{i-1,j} - Q_x x_{i,j} - K_d a V_i \left(y^*_{i,j} - y_{i,j} \right) \quad (1)$$

$$\phi_y V_i \frac{dy_{i,j}}{dt} = Q_y y_{i+1,j} - Q_y y_{i,j} + K_d a V_i \left(y^*_{i,j} - y_{i,j} \right) \quad (2)$$

$$y^*_{i,j} = m_{i,j} x_{i,j} \quad (3)$$

Distribution coefficients $m_{i,j}$ are expressed as functions of nitrate ion and uncomplexed TBP concentration (Richardson et al., 1975). Overall mass transfer coefficients based on dispersed phase K_d, are calculated using diameter of dispersed droplet which are estimated by operating conditions (Tung et al., 1988). Volume of each tank V_i and the number of tanks are determined by minimizing the difference between the experimental steady-state concentration profiles of uranium and nitric acid in organic phase and calculated ones.

Equations (1) and (2) were rewritten in finite difference form by implicit method and the finite-difference equations were solved by iterative method.

EXPERIMENTAL

A schematic diagram of the experimental apparatus is shown in Fig. 1. The annular pulsed column with two-hundreds of baffle plates is used for uranium extraction. The column made from stainless steel is 4 m long. The inner tube of annular is 89 mm in outside diameter and the outer one is 165 mm in inside diameter. The baffle plates with 23 % free area are made from stainless steel and the plate spacing is 2 cm. Three sampling ports for measuring the organic phase concentration and the dispersed phase holdup are set at 1 m intervals from top of the column. Operating conditions are shown in Table 1.

The experimental transient response curves were obtained by introducing a step change in the aqueous feed solute concentration at the top of the column. Before the step change was carried out, the column was operated with solute free streams in order to reach the hydraulic stability. The organic phases in the column were sampled every 2 minutes. The concentration of uranium and nitric acid were measured by potentiometric titration.

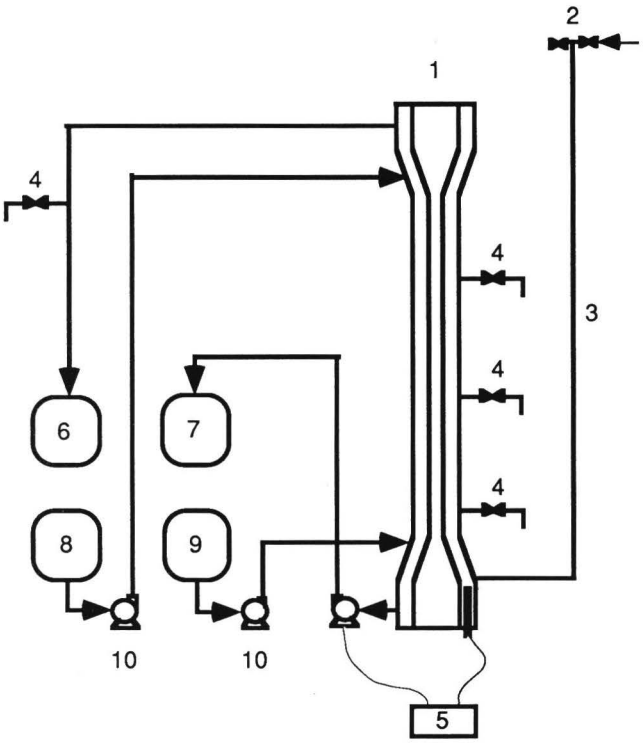


Fig. 1. Schematic diagram of the experimental apparatus
(1, Annular pulsed column with baffle plates; 2, Pulse generator; 3, Pulse leg; 4, Sampling ports; 5, Interface controller; 6, Loaded solvent storage vessel; 7, Raffinate storage vessel; 8, Aqueous feed storage vessel; 9, Organic feed storage vessel; 10, feed pumps)

TABLE 1 Operating conditions

Aqueous phase flow rate, Q_x	20.50	[cm^3/s]
Organic phase flow rate, Q_y	40.83	[cm^3/s]
Aqueous feed concentration, $UO_2(NO_3)_2$	158.5	[g/l]
HNO_3	3.12	[mol/l]
Pulse conditions:		
Frequency	55.00	[cpm]
Amplitude	2.00	[cm]

RESULTS AND DISCUSSION

Figure 2 shows the concentration profiles of uranium and nitric acid in organic phase at the steady state. Dispersed phase holdup was about 5 % through the operation. The number of tanks determined by using this profiles was 9 and the change of tank volume was determined as shown in Fig. 3.

The simulation of dynamic behavior of uranium was carried out by solving Equations (1), (2) and (3) using the parameters determined. Figures 4(a) and (b) show the time change of uranium concentration in the organic phases at the top of the column and the sampling port under 1 m from the top, respectively. The time to reach steady state was about 50 minutes in the experiment. Since the calculated results using these parameters showed good agreement with the experimental ones, this model was adequate to the simulation of extraction dynamics in pulsed column.

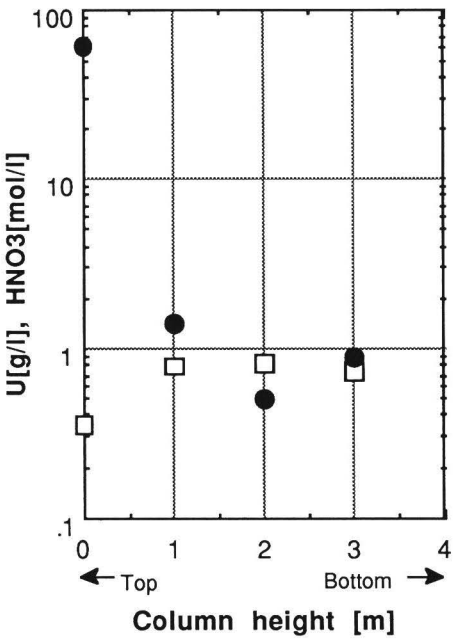


Fig. 2. Organic phase concentration profiles at steady state (●, uranium; □, HNO_3).

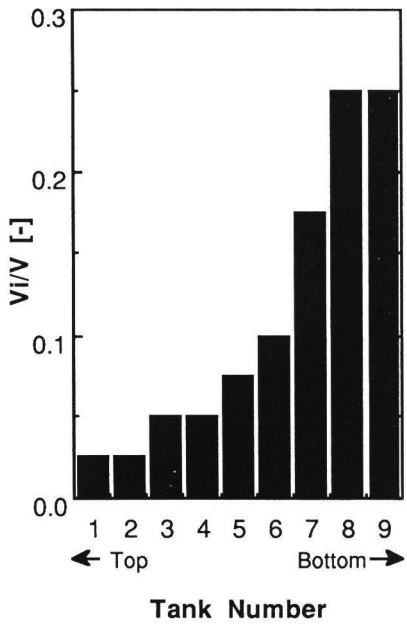


Fig. 3. The volume of each tank.

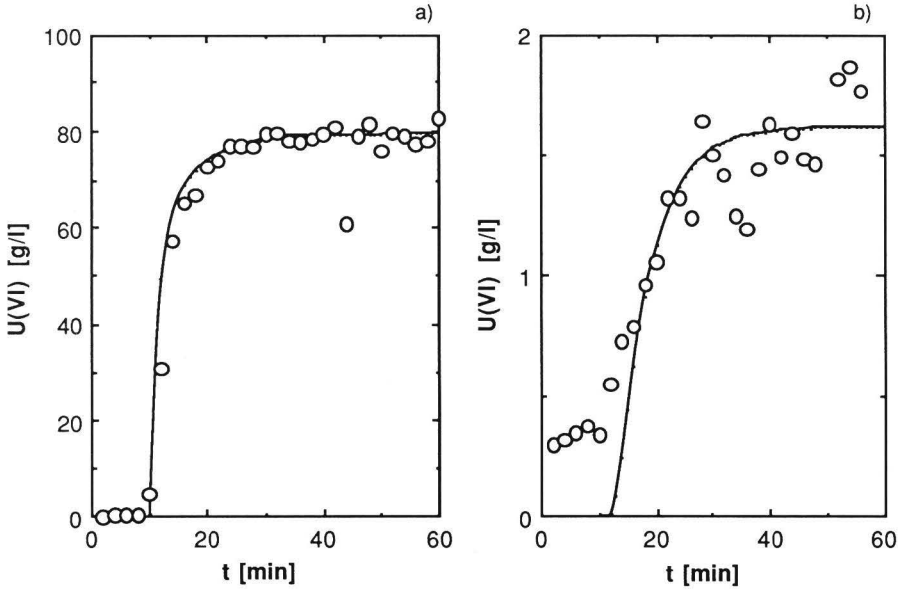


Fig. 4. Comparison of simulated transient response curve with experimental data (O, experimental; --, calculated). (a) organic phase at the top of the column. (b) organic phase at the sampling port under 1 m from the top.

CONCLUSION

The tanks in series model was applied to simulate the extraction dynamics of the pulsed column. The volume of each tank as the parameter was introduced to describe the axial dispersion in this model. This model was applicable to predict the extraction dynamics and is available to process simulation and control.

NOMENCLATURE

a	interfacial area	(cm^2)
K	mass transfer coefficient	(cm/s)
m	distribution coefficient	(-)
Q	flow rate	(cm^3/s)
t	time	(s)
V	volume of tank	(cm^3)
x	aqueous phase concentration	(mol/cm^3)
y	organic phase concentration	(mol/cm^3)
ϕ	fractional holdup	(-)

Superscripts and Subscripts

d	dispersed phase
i	tank

j component
x aqueous phase
y organic phase
* equilibrium

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IMPURITY CARRY-OVER IN LIQUID-LIQUID EXTRACTION CONTACTORS

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ABSTRACT

Impurities are carried over into the organic product from liquid-liquid extraction contactors dissolved either in the organic phase or in aqueous phase entrained in the organic phase. Experiments with pulse plate columns and uranium to simulate the Purex process show that species of low extractability are carried over principally in entrained aqueous phase, which is produced mainly by water rejection from the organic phase when uranium is extracted. The contribution of aqueous phase entrainment to carry-over of the more extractable species is relatively minor.

However, in both cases scrubbing efficiency can be predicted assuming that diffusion controls the rate of mass transfer, directly from the organic phase to the scrub acid in the case of the more extractable species, or mainly from the entrained aqueous phase to the scrub acid via the bulk organic phase in the case of the species of low extractability. A model based on these mechanisms has been developed which enables the sensitivity of scrubbing efficiency to key parameters to be assessed and therefore contactor and flowsheet design to be optimised.

1 INTRODUCTION

Operation of liquid-liquid extraction contactors can give rise to carry-over of impurities, originally dissolved in the aqueous feed, into the organic product. Impurity carry-over can place an undesirable burden on downstream purification and waste treatment processes and therefore it is important to understand the mechanisms which cause carry-over and to determine how it can be controlled and minimised.

This paper describes experiments with pulsed plate columns operated on the system uranyl nitrate (UN)/nitric acid/20% tri-n-butyl phosphate in odourless kerosene (TBP/OK) to study the carry-over of fission product impurities which arise in nuclear fuel reprocessing, i.e.

- Caesium (Cs) and strontium (Sr) which represent the fission products of low extractability
- Bismuth (Bi) to simulate the more extractable species such as cerium (Ce) and ruthenium (Ru).

The experiments have led to the development of a model for fission product scrubbing which is used to identify the key parameters affecting fission product decontamination factors (DF's).

2 EXPERIMENT

The experiments were carried out with compound extract and scrub columns which were operated with the aqueous phase dispersed as shown in Figure 1.

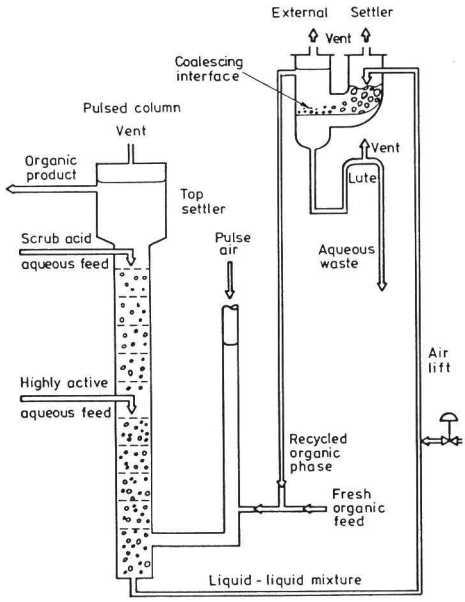


FIG. 1. SCHEME OF A PULSED PLATE COLUMN. (with external settler control of aqueous waste removal)

The columns were operated in the Harwell solvent extraction pilot plant which can evaluate the performance of liquid-liquid extraction contactors with total volumetric throughputs up to 500 $\ell\ h^{-1}$. The plant also has mixer-settlers for on-line washing of the organic raffinate and aqueous product, and an evaporator for concentrating the aqueous product for recycle. The columns were 25, 50 and 100 mm diameter and were fitted with stainless steel nozzle plates and pulsed by compressed air. The height of the extract section was 6 m. After approximately 4 m height for scrubbing, the organic product passed through a top settler, approximately 1 m high and twice the diameter of the plated section, to be disengaged from the aqueous phase and removed from the column.

A mixture of the two liquid phases was removed from the bottom of the column by air lift to an external settler which provides for the aqueous drops a coalescing interface which is hydrodynamically independent of the column and whose position does not require measurement and control.

Approximately 2 g/ℓ each of non-radioactive Cs, Sr and of Bi were added to the aqueous U feed and their concentrations in the organic product were measured by graphite furnace/atomic absorption spectrometry (GF/AAS). Water concentration was measured by Karl Fischer titration and the size distribution of the entrained aqueous drops was measured by a laser spectrometer.

3 RESULTS

3.1 Carry-Over of Impurities

Species of low extractability are carried over predominantly in entrained aqueous phase which previous work by Jenkins (1988) has shown is produced mainly by water rejected from the organic phase when uranium is extracted. The profiles of Cs concentration dissolved and entrained in the organic phase along the column are given in Figure 2 and show that;

- dissolved Cs concentration decreases by more than an order of magnitude to the limit of detection when U is extracted.
- entrained Cs concentration is much higher than the dissolved concentration and peaks at the U feed point, where water is precipitated, before steadily decreasing towards the scrub feed point.

However, the contribution of aqueous phase entrainment to the carry-over of the more extractable species is comparably minor. As Figure 3 shows, the dissolved Bi concentration in the organic phase also decreased by more than an order of magnitude at the U feed point but there was not a detectable difference between the dissolved and total Bi concentrations.

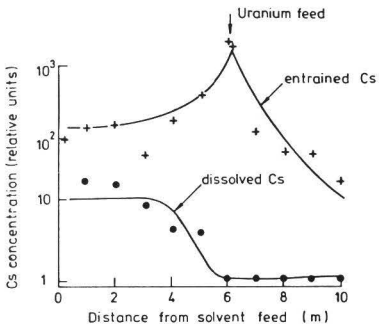


FIG. 2. PROFILES OF Cs CONCENTRATION

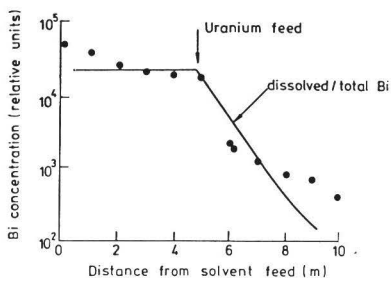


FIG. 3. PROFILE OF Bi CONCENTRATION

Chemically-precipitated drops of water are very small, as shown in Figure 4. Previous work by Jenkins (1989) shows that there are several consequences of this small size;

1) mutual coalescence is infrequent and therefore size does not increase significantly along the scrub section or in the top settler.
2) the precipitated drops are difficult to capture by coalescence with the scrub acid drops.
3) the drops are not efficiently removed by a conventional top settler, as Figure 5 shows.

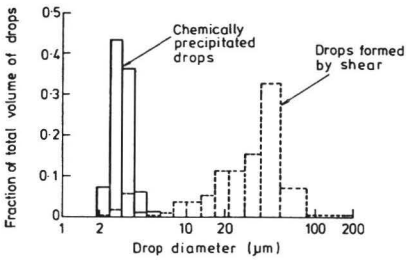


FIG.4. SIZE DISTRIBUTIONS OF ENTRAINED AQUEOUS DROPS

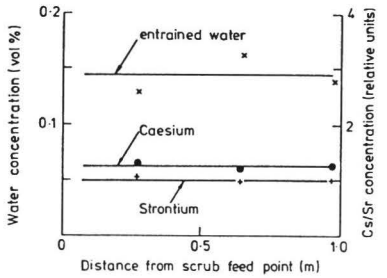


FIG. 5. ENTRAINED WATER, CAESIUM AND STRONTIUM CONCENTRATIONS IN ORGANIC PHASE ALONG TOP SETTLER.

3.2 Theoretical Model

These experimental observations have led to the development of a theoretical model for predicting carry-over of fission products in nuclear fuel reprocessing, but which can also be applied to other liquid-liquid systems where water precipitation from the organic phase gives rise to aqueous phase entrainment. The bases of the model are;

a) The concentration of dissolved water decreases with increasing concentration of the major solutes in the organic phase, and hence increases the yield of precipitated water.

b) The concentration of an impurity dissolved in the organic phase decreases when the major solutes are extracted, the impurities being effectively stripped into the precipitated water.

c) Transfer of impurities from the entrained drops to the scrub acid occurs by diffusion via the bulk organic phase as well as by drop capture.

d) For species of low extractability the mechanisms in c) above are paramount in determining scrubbing efficiency and DF, but for the more extractable species they are minor and scrubbing occurs mainly by diffusion from the organic phase to the scrub acid.

The model divides the column into a number of well-mixed cells and calculates first the profiles of U (and plutonium) and free TBP concentration before carrying out a steady-state mass balance on the fission product species. Important model parameters are;

- **yield of precipitated water 'haze'**, as a fraction of the overall change of dissolved water concentration.
- **haze capture factor**, i.e. the fraction of precipitated water which is captured in each cell.
- **FP distribution coefficients.**

The predicted profiles of Cs and Bi concentration in the organic phase are shown by the solid lines in Figures 2 and 3 and show good agreement with the experimental data points. The results of using the model for a preliminary assessment of the sensitivity of DF to haze yield for three different fission product species, given a constant capture factor, are shown in Figure 6. As expected, the DF for Cs is the most sensitive and indicates very high DF's are potentially achievable if the formation of haze can be suppressed. A similar study of the effect of haze capture factor on DF is given in Figure 7, and shows a similar sensitivity for Cs, with the more extractable species being much less sensitive to capture factor.

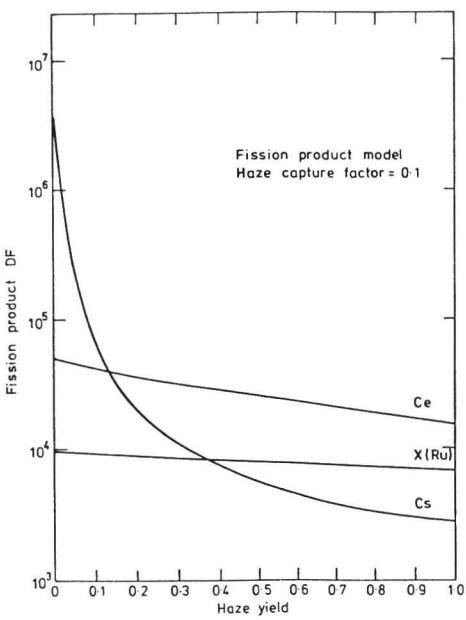


FIG 6 EFFECT OF HAZE YIELD ON FISSION PRODUCT DF.

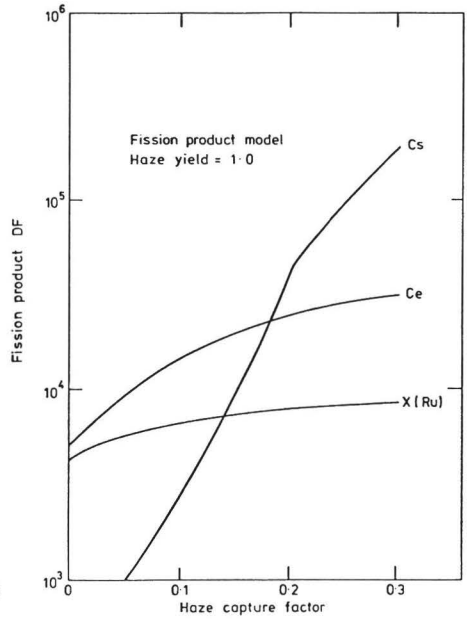


FIG 7. EFFECT OF HAZE CAPTURE FACTOR ON FISSION PRODUCT DF

4 CONCLUSIONS

Carry-over of an impurity in the liquid-liquid extraction process depends on the solubility of the impurity in the organic phase and on its presence in aqueous phase entrained in the organic phase.

A diffusion-based model of the transfer of impurities from the organic phase and from the aqueous drops entrained in the organic phase has been developed. The model can predict scrubbing efficiency for a variety of fission product species. It allows an understanding of the mechanisms underlying fission product behaviour in the scrubbing process and provides a basis for optimising flowsheet conditions and contactor types.

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AXIAL TEMPERATURE PROFILES IN A PULSED COLUMN FOR PUREX PROCESS

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Abstract

It has been shown that axial temperature profiles, due to a reaction heat of uranium extraction, in a pulsed column can be utilized for process control. For the purpose of detecting the uranium extraction zone, the amount of extracted uranium and the hydrodynamic condition as a function of temperature profiles, measurements were made of the temperature profiles using a small pulsed column with " a heat generating section ". The generation of reaction heat was simulated by injecting hot water.

The most effective parameter on the temperature profiles is found to be the heat capacity ratio (Λ). For $\Lambda=1$, the temperature peak appeared at the heating position, while the rapid temperature increase occurred near the heating position for $\Lambda\neq1$.

In the Purex condition, temperature increase of about 5 ℃ was detected and the variation of temperature profile was rapid enough to detect the change of the uranium concentration or the flow rate of the aqueous and organic phases.

It is suggested from this study that the temperature profiles are available for identifying the uranium extraction zone and then useful for the process control.

1 Introduction

In current commercial nuclear fuel reprocessing plants, pulsed columns consisting of both organic solvent and aqueous solution flows in the reverse direction have been used to extract and to scrub uranium and plutonium from solution of spent nuclear fuel.

Most of all uranium and plutonium are usually extracted in relatively narrow parts called "uranium extraction zone" at the top of the column.

During extraction, however, some hydrodynamic disturbances of the solvent and the feed solution occur, and the uranium concentration tends to exceed a saturation level in the solvent at the top of the column, contrary plutonium distribution coefficient becoming smaller. Plutonium once extracted to the solvent at the bottom is consequently re-extracted in the aqueous phase at the top of the column.

This results in an accumulation of plutonium in the column, which is called "Pinching Effect". The Pinching Effect is caused by the uranium extraction zone movement down to the bottom of the column due to saturation of uranium at the top of the column.(Suwa,1989, Tachimori,1986).

Axial temperature profiles induced by the reaction heat of uranium extraction have been observed in commercial scale pulsed columns , which may be available and useful for detecting the position of the uranium extraction zone (Eiben,1985, Okada,1987, Nothaft,1986).

Although a study has been done on direct contact heat exchangers in which two kinds of hot and

cool liquids exchange heat each other (Jacobs,1988), the mechanism of the direct contact heat exchanger with the inside heat source such as a reaction heat is still unknown. Previously, we predicted and found that the most effective parameter on the temperature profiles was the heat capacity ratio (Λ) defined as:

$$\text{Heat capacity ratio}: \quad \Lambda = \frac{(\rho Cu)o}{(\rho Cu)a} \qquad \begin{array}{l} \rho : \text{density } (g/cm^3) \\ C : \text{specific heat } (cal/cm^3/^\circ C) \\ u : \text{flow rate } (cm/s) \end{array} \qquad \begin{array}{l} o : \text{organic phase} \\ a : \text{aqueous phase} \end{array} \qquad (1)$$

by using our calculation code simulating the temperature profiles in a pulsed column with a heat source (Tsukada,1989).

The purposes of this study are to confirm the capability of identifying the uranium extraction zone as a function of the temperature profiles. In this study, we fabricated a small pulsed column equipped with a heat generation section, in which hot water was injected to simulate the reaction heat of uranium extraction. The temperature profiles for various heating condition were determined.

2 Experimental

We used a cylindrical type of pulsed column of 3 m in height and 10 cm in diameter with sieve plates as distributors. We also used deionized water as aqueous phase and 30%TBP-n-dodecane as organic phase.

A schematic diagram of the pulsed column is shown in Fig.1. About 30 pairs of thermocouples were located along the column, and some of them were settled at the inlet and outlet of each phase of aqueous and organic.

This column is sectioned into four parts; two upper parts are 50 cm in height and two lower parts are 100 cm in height. Heat generation by the reaction heat of uranium extraction was simulated by injecting hot water into the column. The hot water injection point is located at the middle of the second

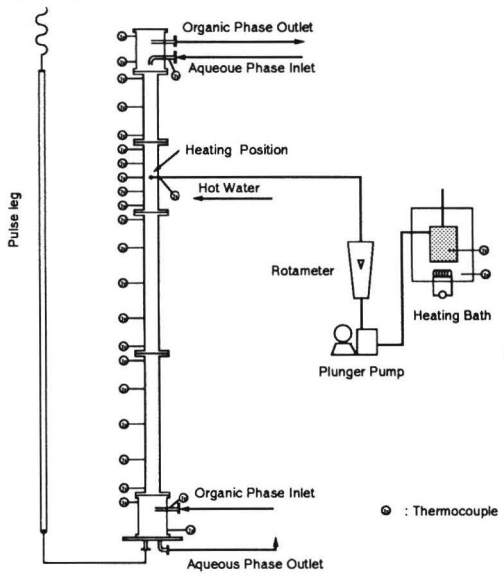


Fig.1. Schematic diagram of the pulsed column for temperature measurement.

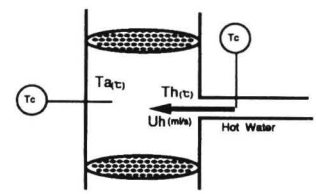


Fig.2. The measurement point near the heating position.

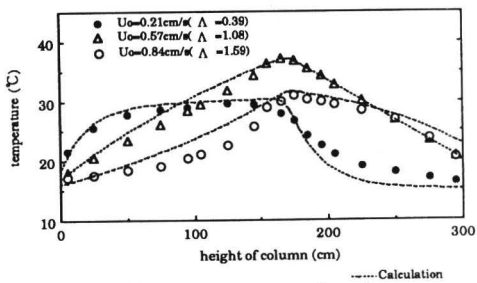


Fig.3. Effect of the heat capacity ratio on the temperature profiles. (Ua=0.21cm/s, Heating at 178cm)

50 cm height column. By changing the position of four columns, we can select the heat generation positions.

The quantity of heat supplied by hot water was estimated by the following equation:

$$Q = (Th-Ta)(\rho C)_a\, Uh \quad (cal/s) \qquad (2)$$

$(\rho C)_a$: Heat capacity (1 cal/cm^3/℃)
Th : temperature of hot water (℃) d
Ta : temperature of fluid at the heating position (℃)
Uh : flow rate of hot water (cc/s)

Hot water warmed to ca. 50 - 85℃ at the heating bath was transported to the column by the plunger pumps through the flow meter. Measurements of temperature were made at the injection point (Th) and at the center of the column diameter near the injection point (Ta), as shown in Fig.2.

Uranium concentration in the feed solution which generates the same heating rate of the hot water is estimated by the following equation:

$$X = \frac{Q\ 1000}{(-\triangle H_R)\ Ua} \quad (gU/l) \qquad (3)$$

$(-\triangle H_R)$: enthalpy of uranium extraction (cal/gU)
Ua : flow rate of aqueous phase (cc/s)

3 Results and Discussion

3.1 Temperature profiles in a direct contact heat exchanger

(1) Effect of the heat capacity ratio

We measured the temperature profiles for various heat capacity ratios in order to ascertain the effect of the heat capacity ratio. The density , the heat capacity of each phase, and the aqueous phase flow rate (Ua=0.21cm/s) were fixed, while the organic phase flow rate was varied (Uo=0.21, 0.57, 0.84cm/s). Fig.3 shows examples of the temperature profiles for the heating position of 175cm in height. Results of calculation by our code are also shown in the same figure.

For an organic phase flow rate of 0.21cm/s corresponding to a heat capacity ratio Λ=0.39, most of the generated heat are carried by the aqueous phase and the temperature profile moves down because the aqueous phase has larger value of heat capacity (ρCu) than that of organic phase.

With increasing the organic flow rate, temperature profiles tend to move toward the top of the column. When the flow rate of the organic phase reaches 0.84 cm/s (Λ=1.59), almost all of heat are carried by the organic phase flow.

The peak temperature reaches the highest value for Λ=1 because the amount of heat carried by each

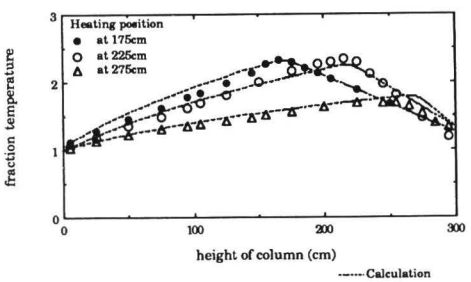


Fig.4. Effect of the heating position on the temperature profiles.
(Ua=0.21cm/s, Ua=0.57cm/s, Λ=1.08)

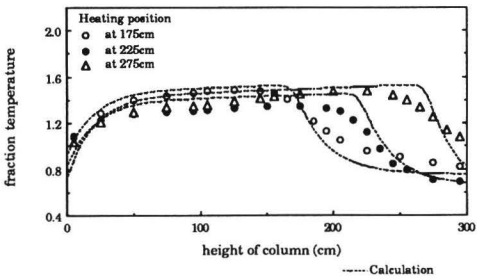


Fig.5. Effect of the heating position on the temperature profiles.
(Ua=0.21cm/s, Ua=0.21cm/s, Λ=0.39)

phase is constant despite of the reverse heat flow. Thus the net heat flow carried by bulk fluid doesn't exist in reason. In this case, the axial thermal diffusivity is the only driving force for heat transfer in the column. In the Letan's(1968) analysis model for the heat transfer in a spray column, the same value of Λ was defined and it was found that the most efficient in heat exchange is for Λ=1.

Because changes in the density (ρ) and heat capacity (C) of each phase are small in an actual operation, the flow rates (u) of both phases are dominant factors for the temperature profiles.

(2) Effect of the heating position

The variation of temperature profiles with various heating positions are shown in the Fig.4 and Fig.5, respectively, for heat capacity ratios of Λ=1 and Λ=0.39. In these figures, the measured temperature is normalized with the feed temperature of organic phase.

When Λ=1 (Fig.4.), each temperature profile has linear slopes and the temperature peak position coincides with the heating position. The maximum peak temperature comes into existence when the heating position is located near the center of the column, and becomes smaller as the heating position moves away from the center.

In the case of the Λ =0.39 (Fig.5.), however, the rapid temperature increase is observed at the heating position and the value of the peak temperature is not affected by the heating position.

From this result, we suggest that the heating position can be detected from the temperature profiles in any case.

3.2 Temperature profiles in a extraction column for the Purex process

(1) Correlation between the peak temperature and the uranium concentration

The temperature profiles in steady state were obtained for various amounts of heat supply at the heating position of 225 cm in height from the bottom settler. The flow rate of the aqueous and organic feed solution were nearly equal in the normal condition (Ua=0.18cm/s, Uo=0.31cm/s).

The temperature increases from the feed temperature of the organic phase are shown in Fig.6, for various uranium concentration in the feed solution corresponding to the amount of heat supply. The correlation between the temperature increase at the peak temperature and the uranium concentration in feed solution is shown in Fig.7, indicating a good linear relation.

In a commercial plant, the temperature increase is assumed to be about 5℃ in the extraction column

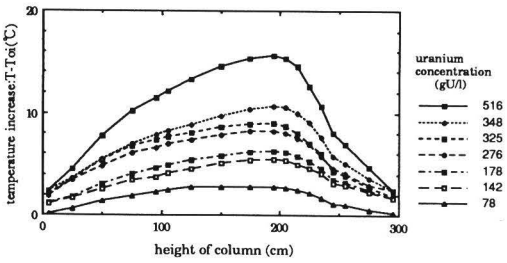


Fig.6. Temperature profiles at steady state for various uranium concentration (Ua=0.18cm/s, Uo=0.31cm/s, Heating at 225cm)

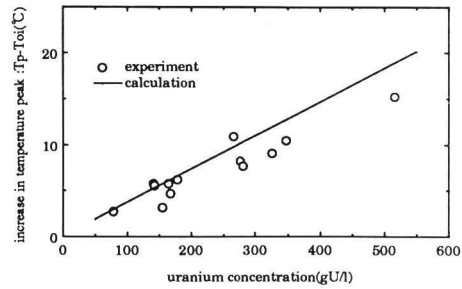


Fig.7. Increase of peak temperature for various uranium concentration. (Ua=0.18cm/s, Uo=0.31cm/s, Heating at 225cm)

because the uranium concentration in feed solution is 150 - 200 gU/L. The increase in the peak temperature seems to be large enough for measurement, which suggests the capability of detecting the uranium extraction zone from the temperature profiles in the commercial plants.

(2) Transient behavior of the temperature profiles

(i)Increase of the heat generation rate

Measurements were made of transient behavior of temperature profiles during increasing the heat generation rate. After the temperature profiles reached steady state, the heat generation rate was doubled (the flow rate of hot water increased twice). The heating position and flow rate of aqueous and organic phases were fixed in the same experimental conditions as the previous experiment.

Fig.8 shows the transient temperature distributions when the experimental condition was adjusted to simulate the uranium concentration increase in the feed solution from 141 gU/L to 276 gU/l. The transient behavior is very rapid and about 60 minutes was needed to reach the next steady state.

It is seen from this figure that the change of the uranium concentration is detectable as a function of the temperature profiles.

(ii)Increase of organic flow rate

Measurements were also made of the transient behavior of the temperature profiles for an abrupt increasing the flow rate of the organic phase twice. After reaching steady state (Ua=0.14cm/s, Uo=0.21cm/s), the flow rate of the organic phase was doubled (Uo=0.42cm/s). In this case, the heat capacity ratio changes from 0.6 to 1.2.

As shown in Fig.9, the shape of the temperature profile becomes gradually steeper, especially during the first 10 minute. This is very rapid because the heat accumulated at the lower part of the column is moved toward the upper part.

As mentioned in chapter 3.1, for an organic flow rate of 0.21 cm/s (Λ=0.6), the generated heat is carried by the aqueous phase. With increasing an organic flow rate (Λ=1.2), the generated heat is carried by the organic phase as shown in Fig.9. When $\Lambda > 1$ like this case, the change in temperature profiles is notable. The transient behavior of the temperature profiles was unchanged so much for the heat capacity ratio Λ ranging between 0.6 and 0.9.

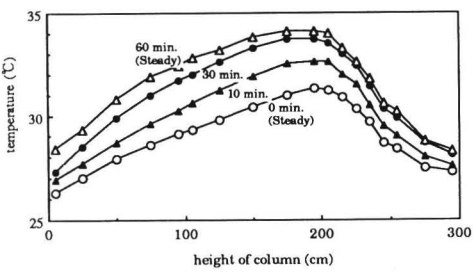


Fig.8. Temperature profiles when heat generation rate is increased. Uh=150cc/min to 300cc/min Uranium constriction 141gU/L to 276gU/L (Ua=0.18cm/s, Uo=0.31cm/s, Heating at 225cm)

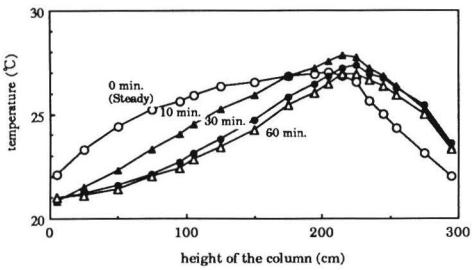


Fig.9. Temperature profiles when organic phase flow rate is increased.
Uo=0.21cm/s to 0.42cm/s (Λ=0.6 to 1.2)
(Ua=0.14cm/s, Heating at 225cm, Uh=150cc/min
:Uranium concentration 208 gU/L)

We can conclude that the change of the flow rate of aqueous or organic phase would be detectable when the flow rate is changed so much as to give the heat capacity ratio of more than unity.

4 Conclusion

Measurements of temperature profiles in a direct-contact heat exchanger with a heat source were made using the small pulsed column with the heating section. The results show that the heat capacity ratio (Λ) is the most effective parameter on the temperature profiles. For the case of $\Lambda=1$, the temperature peak position coincides with the heating position, while rapid temperature increases occurs at the heating position for the case of $\Lambda\neq1$.

The temperature profiles in the the extraction column were also measured under the Purex condition in order to ascertain the capability of utilizing the temperature profiles for the column operation. The temperature increases of about 5℃ at the peak is large enough for detection. The transient behavior of the temperature profiles is rapid enough for detection of the change in the uranium extraction rate and position or the flow rate of the aqueous and organic phase.

It is concluded from this study that the uranium extraction zone and the extraction condition is detectable by measuring the temperature profiles.

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U/Pu SEPARATION IN THE PUREX PROCESS: EXPERIMENTAL COMPARISON OF DIFFERENT PROCEDURES

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ABSTRACT

U/Pu separation in the first cycle of the PUREX process was studied by application of three different procedures in the plutonium test facilities PUTE and MINKA. In PUTE the separation column was operated in the aqueous continuous mode, U(IV) was used as reduction agent for Pu(IV) or the electroreduction process as developed in Karlsruhe was applied. In both cases, uranium scrub of the plutonium product was integrated in the separation column. In MINKA the separation column was operated in the organic continuous mode, but uranium scrub was performed in a second column, which was operated in the aqueous continuous mode. For the U(IV) feed process we found comparable decontamination factors for Pu (1000 to 2000) independent of the operating mode. The Pu-DFs achieved in the electroreduction process were 3 to 5 times higher. After addition of technetium, the Pu-DFs decreased in all operating modes. Technetium separation from the uranium product was better in the aqueous continuous processes which can be explained by a higher Tc(VII) reduction rate in that case. Hydrazine consumption and the formation of HN_3 and NH_4^+ in the three different procedures will be discussed.

INTRODUCTION

In the PUREX process plutonium is separated from uranium in the organic phase (tri-n-butyl phosphate in n-alkane) into which both constituents had been extracted before. For this the tetravalant plutonium is reduced to Pu(III) and then backextracted into an aqueous nitric acid solution which contains hydrazine in order to stabilize the trivalent plutonium. Most of the uranium remains in the organic phase. U(IV) has become generally accepted as reductant; it is either prepared outside the contactor and then supplied into it or, as under the electroreduction method developed in Karlsruhe, prepared in the contactor itself.

When pulsed columns are used as contactor they are normally operated in the aqueous continuous mode. Initially, relatively low separation efficiencies were measured with plutonium decontamination factors of only a few hundreds contrary to the values obtained with mixer-settlers as contactors (Geel et al., 1971; Detilleux and Geens, 1978; Galla and Schmieder, 1987). This has been attributed to the fact that the plutonium rich aqueous phase, entrapped in organic droplets, was transported from the bottom part of the column into the top part. We succeeded in largely avoiding this effect by optimizing the operating conditions, especially the pulsation parameters (Galla et al., 1989).

In Great Britain a process relying on the organic continuous mode of operation was developed with a view to improving the separation efficiency (Philipps, 1985).

In the plutonium test facility PUTE the U/Pu separation process based on the aqueous continuous mode of operation of the column was investigated both with U(IV) prepared outside the column and with electroreduction directly inside the contactor. The organic continuous mode of operation was studied in the MINKA miniature column facility.

TEST FACILITIES

PUTE is an α-shielded test facility which makes up a complete cycle of the PUREX process. Five pulsed sieve plate columns of 6 to 8 m extraction height and inner diameters

between 50 and 90 mm are available as contactors. The throughput is 100 kg heavy metal (U+Pu) per day (Galla et al., 1983).

The column used for U/Pu-separation is made of glass, total height 8.5 m, with the height of the extraction part being 6 m. The column is operated in the aqueous continuous mode and can be used as an electroreduction column. The sieve plates made of titanium (50 mm spacing) serve as the cathode and the platinum coated rod made of hafnium (8 mm diameter) serves as the anode. Fig.1 shows a schematic arrangement of the column with the various media supply modes and discharges.

The MINKA miniature column facility is also an α-shielded test facility comprising four pulsed columns which can be interconnected in a variable way and used for different purposes. All columns are 3.5 m in extraction height and the inner diameter are between 26 and 35 mm. The throughput is 20 kg heavy metal (U+Pu) per day (Schön et al.,1989).

Unlike in PUTE, two separate BX-(U/Pu-separation), BS-columns (U-backwash) were used in the experiments on U/Pu-separation. A schematic of the combined column is shown in Fig. 2.The BX-column is 26 mm in inner diameter and was operated in the organic continuous mode; the BS-column (32 mm inner diameter) was operated in the aqueous continuous mode.

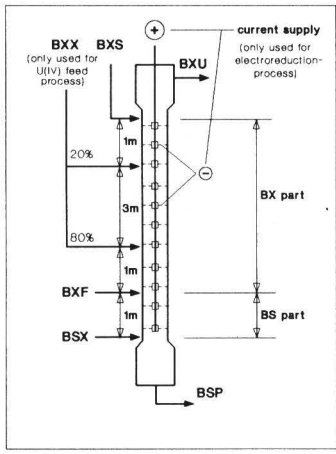


Fig. 1: PUTE BX/BS column

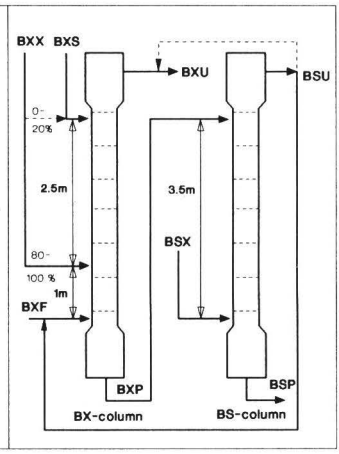


Fig. 2: MINKA BX/BS columns

RESULTS AND DISCUSSION

Both as regards the aqueous continuous mode of operation in PUTE and the organic continuous mode of operation in MINKA, the experiments were performed with a view to the Wackersdorf reprocessing plant (WAW). Therefore, U/Pu-separation was studied especially under the flowsheet conditions applicable to that plant:

BXF : 60-80 gU/l , 0.6-0.8 gPu/l , 40-70 mgTc/l , ~0.1 M HNO_3
BXS : 0.1 M HNO_3 , 0.2 M $N_2H_5^+$
BXX : ~150 gU/l (70 % U(IV)) , 1 M HNO_3 , 0.2 M $N_2H_5^+$
flow ratio o/a in BX : 7.25
flow ratio o/a in BS : 1.0
reductant supplied : 7-times stoichiometry

Some of these flowsheet parameters were subjected to variations in order to study their influence on the separation efficiency, hydrazine degradation, and the formation of byproducts (HN_3 and NH_4^+).

Separation efficiency

The plutonium decontamination factor (DF) is examined in order to be able to assess the separation efficiency of the BX-column (Reactor Handbook, 1961). The results of the individual test runs have been compiled in Fig. 3. The results measured under the WAW flowsheet conditions have been specially marked.

	Flow ratio in BX-column o/a	$[N_2H_5^+]_{BXS}$ [M]	$[Tc]_{BXF}$ [mg/l]	reduction agent Pu (IV) stoichiometric	pulse energy [cm/min]	Pu-DF
U(IV)-feed-process org. continuous	4.7	0.2	50	9	90	200
	4.7	0.2	50	9	105	800
	4.7	0.2	50	9	120	2500
	6.4	0.2	49	7.5	105	300
	7.25	0.2	60	7	135	600
	7.6	0.2	67	9	120	500
U(IV)-feed-process aq. continuous	5.0	0.2	90	7	180	3300
	7.25	0.2	55	7	180	650
	7.25	0.2	41	5	180	850
	7.25	0.2	41	5	240	850
	7.25	0.05	43	7	180	1400
electro-reduction process aq. continuous	5.0	0.2	34	7	180	8600
	5.0	0.035	26	7	180	5700
	5.0	without	12	7	180	2000
	7.25	0.2	40	7	180	2400
	7.25	0.2	37	5	180	3400
two electro-reduction columns	7.25	0.15	13	7	180	507000

Fig. 3: Pu-DFs achieved in PUTE and MINKA BX columns

For the U(IV)-feed process in the aqueous continuous mode of operation of the BX-column approx. the same Pu-DFs were measured as in the organic continuous mode (Pu-DF ~600). The required Pu-DF of >1000 has been achieved under these conditions only by application of the electroreduction method (Pu-DF = 2400). Even Pu-DFs >500,000 were achieved with two series connected electroreduction columns (Galla et al., 1989).

Besides on the WAW flowsheet conditions, the studies of the organic continuous separation process concentrated on the influence of the ratio of flows and of the pulsation parameters on the separation efficiency of the column. As had been expected, the Pu-DFs increased at smaller flow ratios. However, the pulsation energy introduced into the column (expressed here as the product of pulsation frequency and amplitude) exerted a clearly stronger influence on the Pu-DFs. This can be explained from the effect which is clearly visible in the glass column that at low pulsation energies some of the U(IV)-solution feed quickly falls down in the column as stable droplets without any U(IV) available as reductant. By increasing the pulsation energy dispersion of these droplets and hence the U(IV) distribution in the column can be improved which gives higher Pu-DFs. The column, however, has to be operated at pulsation energies of 120 cm/min and more than 90% of its flooding capacity. A further increase in pulsation energy to more than 120 cm/min did not produce a further improvement.

However, the Pu-DF requested for WAW has been attained in the BX-column in the organic continuous mode of operation only after reduction of the flow ratio, even at optimized pulsation energy.

Also in the aqueous continuous mode of operation the separation efficiency has been improved by reduction of the flow ratio both for the U(IV) feed process and for the electroreduction process. A further increase in the pulsation energy of 180 cm/min, optimized at an earlier stage already (Galla et al., 1989), did not exhibit an influence on the Pu-DFs achieved. However, it was possible to improve slightly on the separation efficiency

by reduction of the reductant supply (U(IV) and current, respectively) from seven times stoichiometry to five times stoichiometry. The reduction of the hydrazine required as stabilizer for Pu(III) in the aqueous backextraction solution (BXS) was likewise accompanied by an increase in the Pu-DFs in the U(IV) feed process which is attributable to less salting out of Pu(III) through hydrazine (Schmieder et al., 1981). In the electroreduction process the Pu-DFs obtained reduced slightly but this process can be performed free of hydrazine under specified conditions (Heilgeist et al.,1986; Galla and Schmieder, 1986).

The Tc(VII) fed into the column together with the organic feed solution (BXF) is reduced in all three processes to Tc(IV), and most of it leaves the column together with the aqueous plutonium product. In the organic continuous mode of operation of the BX-column Tc-DFs of 10-30 were attained for the uranium product (BXU), whereas in the aqueous continuous mode and in the presence of hydrazine Tc was separated down to <0.1 mg/l (Tc-DF >200). Only during operation without hydrazine Tc accumulated in the BX-column and the DF for the uranium product was only 6.5 .

Likewise, an influence was found in all three processes of Tc on the Pu-DFs which in the experiments free of Tc had been measured to be higher by the factor 2-4 under the rest of test conditions remaining unchanged. It can be concluded from this finding that Tc exerts an influence on the Pu reduction kinetics (Schön et al., 1990).

Hydrazine degradation and formation of ammonium and hydrazoic acid

Hydrazine is necessary to stabilize trivalent plutonium in the BX/BS-column. It allows nitrite from nitric acid to be distroyed which oxidizes autocatalytically Pu(III) to Pu(IV). Only in electroreduction hydrazine can be renounced at low HNO_3-concentration (<0.7 M in BXP) and temperatures <30 °C because under the latter conditions nitrite does no longer oxidize Pu(III) (Heilgeist et al., 1986) and, as no BXX-solution is fed, no stabilizer is needed for U(IV).

	$[N_2H_5^+]_{BXS}$ [M]	$[Tc]_{BSP}$ [mg/l]	$\Delta N_2H_5^+$ / Pu	ΔHN_3 / Pu	ΔNH_4^+ / Pu	ΔHN_3 / $\Delta N_2H_5^+$	ΔNH_4^+ / $\Delta N_2H_5^+$
U(IV)-feed-process org. continuous	0.2	465	15.8	4.2	5.9	0.27	0.37
	0.2	215	10.9	2.4	3.2	0.22	0.29
	0.2	0	2.0	<2.0	0.07	<1	0.04
U(IV)-feed-process aq. continuous	0.2	450	7.1	2.6	5.3	0.67	0.75
	0.2	280	4.9	2.0	4.4	0.41	0.90
	0.05	310	3.1	1.4	1.1	0.45	0.36
electro-reduction process aq. continuous	0.2	290	5.0	2.0	1.8	0.41	0.37
	0.2	170	3.8	1.7	0.3	0.45	0.08
	0.2	0	2.1	<0.6	0.09	<0.3	0.04
	0.035	130	1.6	1.1	0.3	0.70	0.21
	0	80	-	<0.7	0.15	-	-

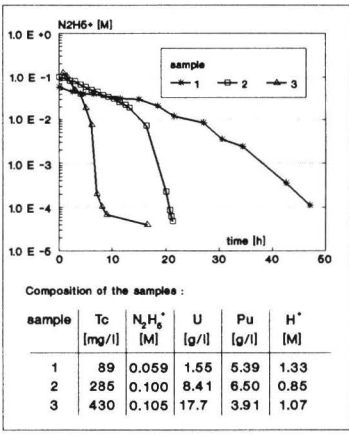
Fig. 4: Hydrazine degradation and formation of ammonium and hydrazoic acid in BX/BS columns

In the absence of Tc about 2 moles $N_2H_5^+$ per mole of plutonium passing the column are consumed in the BX/BS-column, both in the aqueous continuous and organic continuous modes of operation. In the presence of Tc the hydrazine consumption rises conspicuously (Fig. 4) which is attributable to the Tc catalyzed degradation of hydrazine

(Garraway and Wilson, 1984; Vialard and Germain, 1986). The byproducts are ammonium and hydrazoic acid.

Technetium catalysed hydrazine degradation depends primarily on the Tc-concentration and, in addition, on the $N_2H_5^+$, H^+, U and Pu concentrations of the solutions as well as on the temperature (Boukis, 1988; Garraway, 1984). Figure 5 shows the decrease of the $N_2H_5^+$-concentration in some typical BSP-samples with different Tc-contents versus time at room temperature. In all samples an initially exponential decrease of the hydrazine concentration down to a value of about 0.02 M is found. As soon as the latter value is attained the velocity of $N_2H_5^+$-degradation increases heavily.

Figure 6 shows of a total of ten typical BSP samples of different compositions the half-life of hydrazine degradation in the range above 0.02 M plotted versus the Tc-concentration. This gives for the Tc-concentrations in BSP of 300-400 mg/l, typical of LWR-fuel reprocessing, a half-life of hydrazine degradation in the aqueous phase of 3-4 hours which decreases but slowly even with rising Tc-concentration.



Composition of the samples :

sample	Tc [mg/l]	$N_2H_5^+$ [M]	U [g/l]	Pu [g/l]	H^+ [M]
1	89	0.059	1.55	5.39	1.33
2	285	0.100	8.41	6.50	0.85
3	430	0.105	17.7	3.91	1.07

Fig. 5: Hydrazine degradation in typical BSP samples

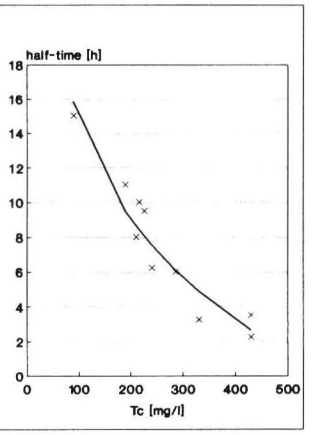


Fig. 6: Half-time of hydrazine degradation in BSP dependent on Tc concentration

In U/Pu-separation in the presence of Tc about twice the amount of hydrazine is degraded in the organic continuous mode of operation, with the other conditions remaining constant, related to the plutonium throughput, compared to the aqueous continuous mode (Fig. 4). It appeared that the degradation of hydrazine besides on the Tc-concentration heavily depends also on the amount of hydrazine used which means that the less hydrazine is supplied the less is consumed. In the aqueous continuous mode of operation the amount of hydrazine supplied was reduced without problems to one quarter (0.05 M in BXS) without producing negative effects on the separation process. It has not been investigated whether also in the organic continuous mode the supply of hydrazine can be minimized.

Also the formation of HN_3, related to the plutonium throughput, is clearly higher in the organic continuous mode of operation than in the aqueous continuous mode.

The formation of ammonium is comparable for the two U(IV) feed processes, i.e. aqueous and organic continuous. In electroreduction only about half the amount of NH_4^+ is formed, part of it originating from nitric acid reduction at the cathode (Heilgeist, 1983).

The rates of formation of HN_3 and NH_4^+ entered in Fig. 4 relate solely to the BX/BS-columns. If one considers the inventories, the often major amounts of HN_3 and NH_4^+

produced during the process of U(IV)-preparation must be taken into account in addition in the U(IV)-feed processes.

SUMMARY

U/Pu-separation in pulsed columns with U(IV) as the reductant were studied experimentally in the aqueous and organic continuous modes of operation as well as with electroreduction applied.

The Pu-DFs obtained are comparable in the U(IV)-feed process under conditions of aqueous and organic continuous modes of operation. In the electroreduction process, with the other conditions remaining unchanged, Pu-DFs higher by a factor of 4 have been measured. This is attributable above all to the highest degree of homogeneity in reductant distribution in this process. The separation of technetium from uranium product is complete in the aqueous continuous processes (Tc-DF >200) whereas in the organic continuous mode an average of 5% of Tc remains in the uranium product. Hydrazine degradation in the BX-column in the presence of Tc is in the organic continuous mode of operation about twice that in the aqueous continuous mode. This is probably due to the higher nitrite inventory in the organic phase and leads to more violent gas production in the organic continuous mode of operation. The rates of formation of HN_3 are higher in the organic continuous mode of operation than in the aqueous continuous mode. Clearly less NH_4^+ is formed in electroreduction compared with the U(IV)-feed processes.

This comparision makes obvious advantages inherent in the electroreduction process which, in addition, calls for the least expenditure in terms of process engineering and features the simplest process control. Technetium does not jeopardize the stability of the U/Pu-separation process provided that it is duly taken into consideration in laying down the flowsheet conditions. However, it contributes to ammonium and hydrazoic acid formation and influences the kinetics of Pu reduction. Therefore, the separation of technetium to the highest possible extent as early as in the HA/HS-zone of the PUREX-process should be aimed at.

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DEVELOPMENT OF ELECTRO-REDUCTION PULSE COLUMN

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ABSTRACT

For the purpose of Pu(Ⅳ) reduction needed for FBR fuel reprocessing, an Electro-Reduction Pulse Column has been under development since 1980 by PNC. As part of this development work, a full scale Uranium test stand was installed in the EDF-Ⅰ and U(Ⅵ) reduction experiments in the aqueous phase were conducted. Experimental data were analyzed mainly to evaluate the reduction performance, and an experimental rate-equation for U(Ⅵ) reduction was derived with the full scale equipment. On the other hand, to evaluate the influence of Scale-Up and/or Scale-Down in radial and axial directions, small scale U(Ⅵ) reduction tests were conducted and analyzed.

INTRODUCTION

For the purpose of Pu(Ⅳ) reduction needed for FBR fuel reprocessing using Pulse Column contactors, an Electro-Reduction Pulse Column has been under development since 1980 by PNC (Power Reactor and Nuclear Fuel Development Corporation). Based on fundamental experiments such as electrode corrosion tests, beaker scale U and Pu reduction tests, and reduction tests in a small scale Electro-Reduction Pulse Column (Ⅰ), a full-scale test stand, the Electro-Reduction Pulse Column (EPC-Ⅱ) which is capable of handling U and radio-isotopes, was installed in the Engineering Development Facility-Ⅰ (EDF-Ⅰ) at TOKAI works in 1983 and U reduction experiments were conducted mainly focusing on reducing properties. Succeeding these developments, an engineering scale Pu test stand was installed in the Plutonium Fuel Development Facility (PFDF) in 1988. After several tests, Pu partitioning tests using an electro-reduction pulse column were started early in this summer.

This paper shows the outline of the development of an Electro-Reduction Pulse Column in PNC.

2 EXPERIMENTS IN FULL-SCALE ELECTRO-REDUCTION PULSE COLUMN

2.1 Test Conditions

To obtain engineering data such as reduction ratio, current efficiency, gas generation property, and electrical characteristics, a full-scale test stand EPC(Ⅱ) was installed. It contains two electro-reduction pulse columns (2m hight× φ 140mm) (Fig.1), one standard pulse column (4m hight × φ 140mm), and support equipment. The column diameter was determined by the assumed capacity of a FBR fuel reprocessing pilot plant (120 ~240 kg/d) but the column length (2m long× 2 columns) was tentatively chosen based on fundamental experimental results.

Adjusted uranium nitrate solution with hydrazine hydrate was fed to the electro-reduction pulse columns connected in series and then pulsation and constant current was supplied. After reaching steady state, uranium solution was sampled every 50 cm along the column height, and U(Ⅵ), U(Ⅳ), HNO_3 and N_2H_4 concentration profiles were determined. During the U(Ⅵ) reduction experiment, gas generation was observed and its generation rate and composition were analyzed. Feed solution flow rate, feed composition, current density, and pulsation were chosen as the experimental variables. Experimental conditions are summarized in Table 1.

2.2 Test Results and Discussion

U(Ⅵ) is reduced to U(Ⅳ) as it flows through the column, and from the test results it appears that U(Ⅵ) reduction ratio reaches a certain saturation point. Under the experimental standard conditions, typical results are as follows : current efficiency 43 %, reduction ratio 31 %, total gas generation rate 98 Nℓ/hr. The generated amount of U(Ⅳ) was comparable to the assumed Pu throughput. U(Ⅵ) reduction rate increases as supplied current increases up to around 150 Amp/column. But beyond that point U(Ⅵ) reduction rate does not increase. In the case of $HNO_3 \geq$ 0.5 N, the U(Ⅵ) reduction rate increases, but this condition causes a cathode corrosion problem and inefficiency of Pu back-extraction in the actual process. In the case of $N_2H_4 \leq$ 0.1 mol/l, the U(Ⅵ) reduction rate decreased.

Concerning the by-product gas, roughly speaking, gas generation rate depends linearly on the supplied current amount. The types and composition of generated gas were as follows : N_2:60 ~90vol %, O_2:0~ 20vol %, H_2:0~ 20vol %, others (N_2O, NO). Explosion risk caused by hydrogen was easily avoided by sweeping by-product gas using air with adequate flow rate.

U(Ⅵ) profiles were analyzed to obtain the experimental rate equation of the U(Ⅵ) to U(Ⅳ) reduction reaction. To describe the reduction rate from the reaction limited step to the diffusion limited step at the cathode surface, eq.(1) is assumed. On the other hand, typical data showed that the U(Ⅵ) reduction ratio reaches a certain saturation point. This means that the re-oxidation of U(Ⅳ) to U(Ⅵ) will occur in this system (a). To simplify the rate equation, the re-oxidation rate is assumed to have a first order dependence on the U(Ⅳ) concentration. Assuming plug flow, eq.(2) is obtained at steady state.

$$\frac{1}{\gamma} = \frac{1}{k1 * C} + \frac{1}{Is / n * F} \qquad (1)$$

where γ : reduction rate of U(VI)
$k1$: diffusion constant
C : concentration of U(VI)
Is : current density
n : electron number
F : Faraday constant

$$\frac{dC}{dz} = \frac{1}{u} \left(-\Omega * \gamma + k2 * (UT - C) \right) \qquad (2)$$

where z : column height
u : flow rate
Ω : cathode surface area
$k2$: re-oxidation constant
UT : U concentration

Integrating eq.(2), the formula from which U(VI) concentration profiles can be derived was obtained. In this formula, k1 and k2 are unknown. A set of experimental constants, k1 and k2, is derived from fitting experimental data which were obtained under the condition of HNO_3: 0.2 N and N_2H_4: 0.2 mol/l. Calculated profiles using this formula with a certain set of k1 and k2 show good agreement with experimental data except for the data obtained at low flow and low U concentration. Fig.2 and Fig.3 show examples of this fitting. These figures show the validity of this analytical procedure, and eq.(2) can simply represent the U(VI) reduction rate in this system.

3 INFLUENCE OF SCALE-UP AND/OR SCALE-DOWN

Current density is not uniform at the cathode surface because of the cathode's complicated configuration. This non-uniformity causes difficulty in scale-up and/or scale-down in radial and axial direction.

Current distribution in radial direction was measured by copper deposition on the cathode surface in H_2SO_4-Cu-H_2O system (with 50mmϕ × 5cm and 140mm ϕ × 5cm electrodes). In the case of a 140mmϕ electrode, the current density at the innner cathode surface is ~10 times as high as that at the outer surface. The current density ratio is around 2 for a 50mmϕ electrode . This uneven distribution of current becomes more conspicuous as the electrode diameter increases, and it leads to a lowering of current efficiency. U(VI) reduction experiments were conducted with different diameter electrodes (50mmϕ , 100mm ϕ and 140mmϕ × 50cm long electrodes) under the same linear velocity of feed solution, pulsation and F/Eq factor (F/Eq=(current supplied)/(current needed to reduce all of the supplied U(VI)). At the same F/Eq factor, the ratio of the U(VI) reduction ratio with 50mm ϕ, 100mm ϕ and 140mmϕ electrodes was 1 : 0.82 : 0.68, respectively (see Fig.4).

On the other hand, current distribution of the EPC(Ⅱ) along with the column height was estimated by the equivalent circuit. It showed that the ratio of the current at the top and bottom of the column was 0.8 with a 2 m long electrode. This ratio would be about 0.6～0.5 when this type of electrode was lengthened to 3 m ～4 m.

4 CONCLUSION

For the purpose of Pu(Ⅳ) reduction needed for FBR fuel reprocessing, an Electro-Reduction Pulse Column has been under development since 1980 by PNC. As part of this development work, a full scale U test stand was installed in the EDF-Ⅰ and U(Ⅵ) reduction experiments in the aqueous phase were conducted. Experimental data were analyzed mainly to evaluate the reduction performance, and an experimental U(Ⅵ) reduction rate equation was derived with the full scale equipment.

On the other hand, to demonstrate Pu partitioning with an electro-reduction pulse column, an engineering scale Pu test stand was installed and Pu tests in the back-extraction system were started early in this summer.

To carry forward the design work of actual Electro-Reduction Pulse Columns, it is necessary to evaluate these different scale experimental results consistently. From this point of view, evaluation of scale-up and/or scale-down factors and revision of the PULCO code (simulation code of the PUREX extraction process in pulse column contactor) are being undertaken.

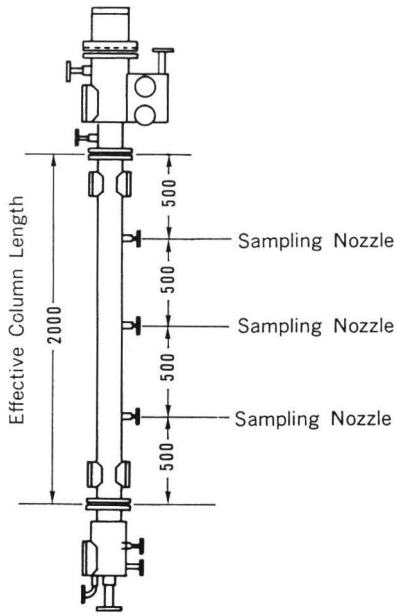
5 References

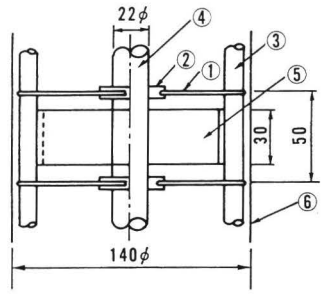
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Table 1 Experimental conditions of U(Ⅵ) to U(Ⅳ) reduction

	Feed Solution				Current(Amp.)		Pulsation (mm× cpm)	
	Flow Rate (ℓ/hr)	Composition			column No.22	column No.23	column No.22	column No.23
		U(Ⅵ) (g/ℓ)	HNO_3 (mol/l)	N_2H_4 (mol/l)				
Experimental Standard Conditions	41.0	50.0	0.20	0.20	171	171	20 × 60	20 × 60
Parametric Study Range	25 ～ 80	15 ～ 80	0.1 ～ 0.9	0.0 ～ 0.4	40 ～ 270	40 ～ 270	0 ～ 20×60	0 ～ 20×60





① Cathode (Sieve Plate)
② Insulator
③ Cathode Supporting Rod
④ Anode
⑤ Additional Cathode Ring Plate
⑥ Shell

Detail Structure of Electrode

Fig.1 Structure of Electro-Reduction Pulse Column (Ⅱ)

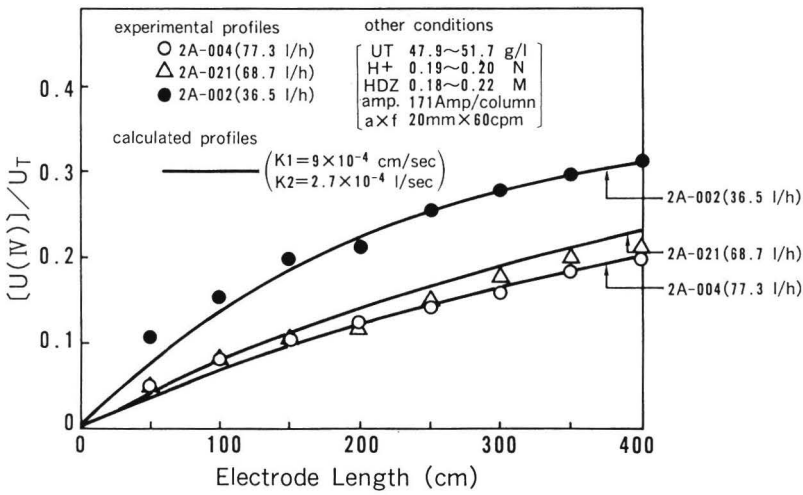


Fig.2 Comparison of Calculated and Experimentally obtained Profiles in various Flow Rates

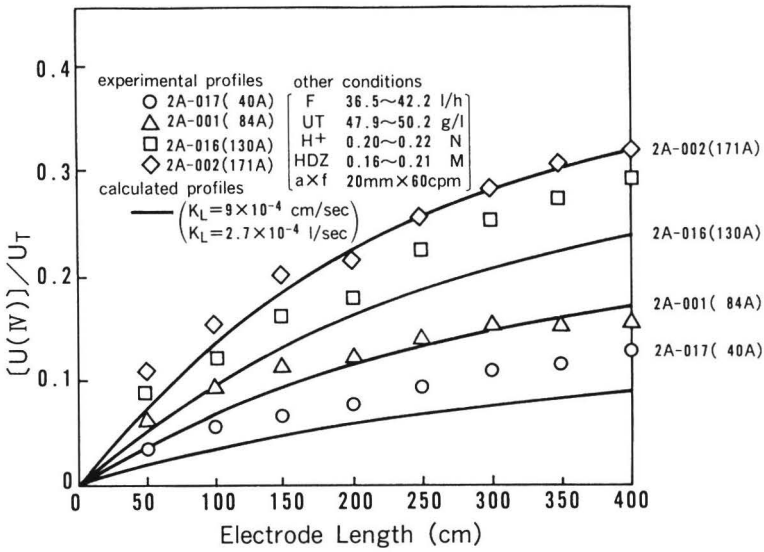


Fig.3 Comparison of Calculated and Experimentally obtained Profiles in various low Current Runs

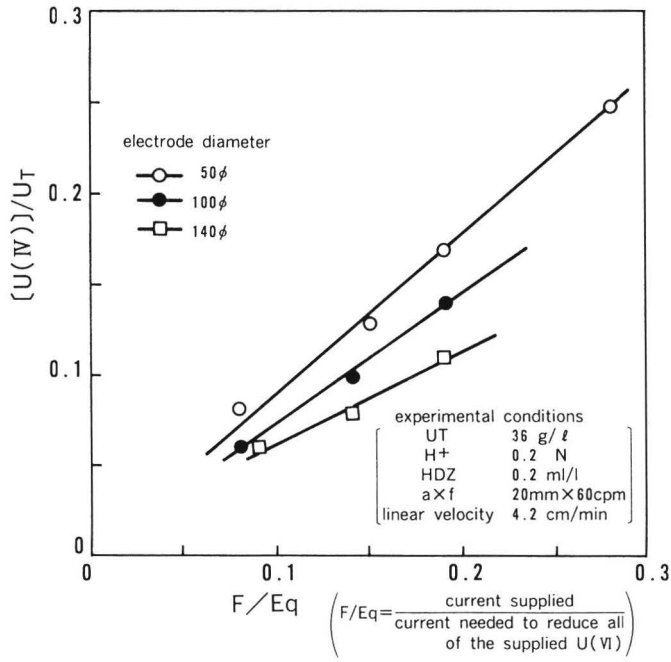


Fig.4 Influence of electrode diameter on the U(VI) reduction reaction

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ELECTROCHEMICAL REDUCTION OF URANIUM IN ORGANIC AND AQUEOUS MIXED PHASES

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ABSTRACT

Electrochemical reduction experiment of uranium was carried out in the mixed phases of 30% TBP+70% n-Dodecane and nitric acid solution. The oxidation state of uranium is very important in the purification process by solvent extraction or precipitation. In the current study, effects of experimental parameters on the electrochemical reduction rate of uranium were quantitatively discussed, and the mutual relationship between reduction rate and mass transfer in a uranium reextraction process was also analyzed.

1. INTRODUCTION

When actinide elements are separated and purified by the solvent extraction or precipitation method, ionic state of each element is very important in separation yield and purification efficiency aspects, etc. Especially, in the case of U/Pu partitioning in the PUREX process, the valence control of uranium is dominant factor in operation of the process. Even if there were many methods to control the ionic state of uranium, the advantages of a uranium electrochemical reduction were reported by earlier publications.[1,2]

In the present study, we extended this work by obtaining the engineering equations for the design and operation of a uranium electrochemical reduction extractor. The reduction kinetic experiment was carried out in a aqueous phase consisting of HNO_3-$UO_3(NO_3)_2$-N_2H_4 and the effect of its reduction rate on uranium reextraction from organic phase to aqueous phase was theoretically analyzed.

2. THEORY

Through the preliminary experiments, it was found that the effect of the organic droplets dispersed in the aqueous phase on electric conductivity of mixed phases was almost negligible. In accordance with the experimental results, the theoretical approach can be represented as two steps; 1)uranium (VI) ion in the organic phase is reextracted to the aqueous phase, and then 2)the reextracted U(VI) ion is electrochemically reduced to U(IV) ion.

2.1 Electroreduction of uranyl ion in aqueous phase

The reduction of uranyl ion and side reactions occur in cathodic chamber consisting of HNO_3-$UO_3(NO_3)_2$-N_2H_4 as follows [3,4] :

$$UO_2^{+2} + 4H^+ + 2e \rightarrow U^{+4} + 2H_2O \qquad Eo = 0.33eV\ (SHE) \qquad (1)$$

$$NO_3^- + 3H^+ + 2e \rightarrow HNO_2 + H_2O \qquad Eo = 0.94eV\ (SHE) \qquad (2)$$

$$2HNO_2 + N_2H_5^+ \rightarrow N_2O + N_2 + H_2O + H^+ \qquad (3)$$

If the uranyl reduction rate on the electrode surface is very slow and its reaction occurs irreversibly, the relation between cathodic potential and current can be

theoretically represented from Bulter-Volmer equation [5] as follows :

$$i = i_o \exp\left(\frac{-\alpha nFE}{RT}\right) \quad (4)$$

For a great many reactions taking place with an appreciable current density, it has been found experimentally that the cathodic potential can be expressed by the following Tafel equation.

$$E = a + b \log i \quad (5)$$

Because the overpotential is a function of experimental condition, electrode material, and the physical state of the electrode surface, constants a and b in eq. (5) must be determined experimentally.

2.2 Relation between electroreduction rate and reextraction rate of uranyl ion in mixed phases

Reextraction of uranyl ion from organic phase to aqueous phase occurs as follows :

$$UO_2(NO_3)_2 \cdot 2TBP \underset{k_b}{\overset{k_f}{=====}} UO_2^{+2} + 2NO_3^- + 2TBP \quad (6)$$

When the above reaction is accompanied with the electroreduction of uranyl ion, the material balance between organic and aqueous phases in terms of U(VI) and U(IV) can be presented as follows :

$$\frac{dC_o}{dt} = k_b A C_A - k_f A C_o \quad (7)$$

$$\frac{dC_A}{dt} = k_f A C_o - k_b A C_A - \frac{dC_B}{dt} \quad (8)$$

$$\frac{dC_B}{dt} = \frac{iS}{nF} = \frac{S}{2.303\,nF} \exp\left(\frac{E-a}{b}\right) \quad (9)$$

$$C_T = C_A + C_B + C_o \quad (10)$$

3. EXPERIMENTS

3.1 Electroreduction of uranium

Fig.1 shows schematically the layout of experimental equipment for the electroreduction of uranium. The cathodic chamber having I.D. of 5.8 cm and height of 10 cm equiped with 4 baffles to maintain homogeneous state was separated from the anodic chamber by the sintered glass diaphram of 5cm diameter. Solution contained into the cathodic chamber was agitated by 6 blades turbine impeller and SCE electrode to measure the half cell potential of the cathode was connected to the nearest position from the cathode through Luggin capillary filled with 3N HNO_3. Cathode and anode were made of Ti plate (Nilaco Co. 99.5% purity) and Pt plate, respectively. And the chemical systems used in this experiment are shown in table 1.

TABLE 1. Chemical systems and those concentrations

Chemicals	HNO_3 (N)	Hydrazine (N)	Uranium (g/l)
Concentration	0.5 - 2.0	0.025 - 0.8	15 - 60

3.2 Reextraction rate of uranium from organic phase to aqueous phase

This experiment was carried out in Lewis cell. The effects of nitric acid and hydrazine concentrations on the distribution coefficient of uranium between two phases were observed and the reextraction rate constant was estimated from experimental results of reextraction rate by using eq. (7). The organic phase used in this experiment was 30% TBP+70% n-Dodecane mixture containing 20-30 g/l uranium, and mixtures of nitric acid (0.5 - 2.0 N HNO_3) and hydrazine (0.025 - 0.8N N_2H_4) were used as an aqueous phase. U(VI) concentration in each phase was measured by spectrophotometer of 414 nm.

4. RESULTS AND DISCUSSION

4.1 Electroreduction of uranyl ion in aqueous phase

The characteristics of uranium reduction were studied by measuring i-E curves at given operating conditions. As shown in Fig.2, the electrode potentials presenting the limiting current were shifted toward the positive side with an increasing of hydrazine concentration. This trend qualitatively agreed with earlier publications [6] studied in aspects of electroreduction mechanisms of uranium and nitric acid. Accordance with those studies, it was found that hydrazine captured the hydrogen ion demanded in uranium reduction. The shifting of the electrode potential results in a gradual increase of the limiting current. When the electrode potential was gradually increased with the same speed, the current at low hydrazine concentration was more steeply changed than the case of high hydrazine concentration.

Fig.3 shows the effect of nitric acid concentration on i-E curves in uranium electroreduction system. Decreasing the nitric acid concentration certainly shifted the electrode potential presenting the limiting current toward the positive side. The current was more steeply changed with an increase of nitric acid concentration.

Consequently, it is suspected that the current efficiency for the uranium reduction will be increased at the low hydrazine concentration and high nitric acid concentration. Unfortunately the effect of uranium concentration on i-E curve was not observed in our experimental range.

When Tafel constants a and b in eq.(5) correlated with nitric acid and hydrazine concentrations under the limiting current, the following equations were obtained.

$$a = 0.45399\,[HNO_3]^{-0.1617} + 0.02442\,\frac{[N_2H_4]}{[HNO_3]} \qquad (11)$$

$$b = 0.13189\,[HNO_3]^{-0.1952} + 0.09568\,\frac{[N_2H_4]}{[HNO_3]} \qquad (12)$$

$$E_{lim} = 0.67044\,[HNO_3]^{-0.2120} + 0.24815\,\frac{[N_2H_4]}{[HNO_3]} \qquad (13)$$

Fig.4 Shows typical curves that i-E curve calculated by using eqs.(5), (11), (12), and (13) compared with experimental i-E curve.

4.2 Relation between reduction rate and reextraction rate in mixed phase

In our preliminary experiments for U(VI) reextraction, it was found that the effect of hydrazine concentration on the distribution coefficient and reextraction rate constant was negligible, and then the empirical correlations of distribution coefficient and rate constant as a function of nitric acid concentration were respectively obtained as follows :

$$D_{U(VI)} = \frac{C_o}{C_A} = \frac{k_b}{k_f} = -0.2803 + 6.2646\,[HNO_3] \qquad [HNO_3] \geq 0.5N \qquad (14)$$

$$k_f = 1.839 \times 10^{-4}\,[HNO_3]^{-0.78} \qquad [HNO_3] \geq 0.5N \qquad (15)$$

In order to observe the relation between reduction rate and reextraction rate of uranyl ion, uranium concentrations, C_o C_A, C_B in a batch reextraction system accompanied with electroreduction of uranyl ion in the aqueous phase were calculated by using eqs. (7)-(15) and those results are shown in Fig.5.

Ra defined as $(-dC_o/dt)/(dC_B/dt)$ was also calculated and shown in Fig.5. This figure is showing 3 cases of $Ra<<1$, $Ra\approx1$, and $Ra>1$. The case of $Ra<<1$ as Fig.5(A) cannot expect the maximum utilization of supplied electricity, while the case of $Ra>1$ as Fig.5(C) will not achieve 100% reduction yield of uranyl ions reextracted from organic phase. Consequantly, the best reduction and reextraction yields can be expected at the condition of $Ra\approx1$. It was also found that the reextraction rate was increased with a decreasing of Ra value.

5. CONCLUSIONS

This work was carried out in a batch reactor with the aim of obtaining the engineering equations for the design and operation of a uranium electrochemical reduction extractor. The following principal results were obtained.

- The electrochemical reduction of uranyl ion was satisfactorily achieved at lower hydrazine concentration and higher nitric acid concentration.
- It was found that the reextraction rate of uranyl ion from organic phase to aqueous phase was accelerated in electrochemical reduction system.
- The optimum operation of the electroreduction extractor was expected at the condition maintaining Ra=1.

Nomenclature

E : Electrode potential (VS. SCE)
Eo : Standard redox potential
R : Gas constant
α : Transfer coefficient
F : Faraday's constant
i_o : Exchange current
i : Current density
$D_{U(VI)}$: Distribution coefficient
C : Uranium concentration
k_f : Forward rate constant
k_b : Backward rate constant
A : Mass transfer area per system volume
S : Electrode surface area per system volume
a,b : Tafel's constants

Subscript

A : U(VI) in aqueous phase
B : U(IV) in aqueous phase
O : U(VI) in organic phase

T : Total

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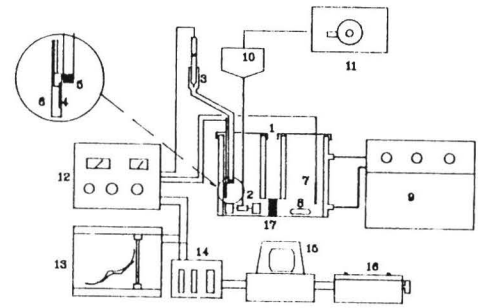


Fig.1 Schematic diagram of experiment.

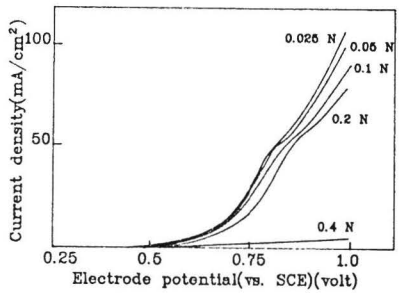


Fig.2 Current density vs. electrode potential at various hydrazine concentrations.

cathodic solution : 0.5 N HNO_3 + 30 g/l U + x N N_2H_4

anodic solution : 1.0 N HNO_3 + 0.5 N N_2H_4

agitation speed : 346 rpm

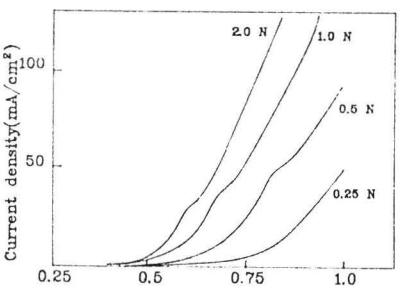


Fig.3 Current density vs. electrode potential at various nitric acid concentrations.

cathodic solution : 30 g/l U + 0.1 N N_2H_4 + x N HNO_3

anodic solution : 1.0 N HNO_3 + 0.5 N N_2H_4

agitation speed : 346 rpm

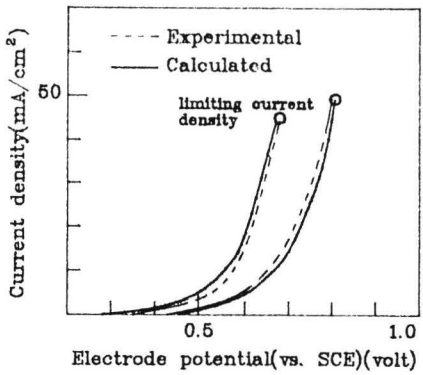


Fig.4 Typical comparison of calculated i–E curve with experimental i–E curve.

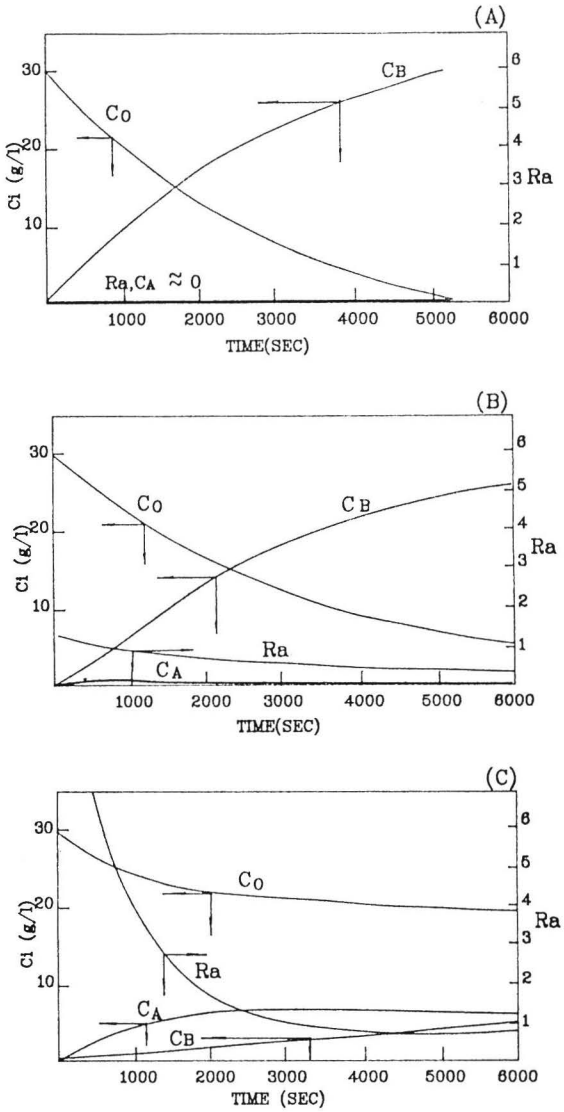


Fig.5 Uranium concentration profile calculated in batch type uranium reextractor accompanied with electroreduction.

(A) : Aqueous phase; 0.5 N HNO_3 + 0.025 N N_2H_4
current density : 48.2 mA/cm^2
(B) : Aqueous phase; 0.5 N HNO_3 + 0.05 N N_2H_4
current density : 49.5 mA/cm^2
(C) : Aqueous phase; 0.5 N HNO_3 + 0.10 N N_2H_4
current density : 50 mA/cm^2

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SCRUBBING EFFECT OF TRITIUM AND RUTHENIUM FROM IRRADIATED ORGANIC SOLVENT

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ABSTRACT

Tritium and ruthenium retention in organic solvent is studied under the condition of Purex process. Experiments simulating the acid scrubbing and alkaline washing were conducted using differently irradiated 30%TBP/nDD solvents. Chemical factors were found to have the marked influence on the tritiation reaction. A new equation is proposed to estimate the tritiation rate of solvent. Ruthenium retention behavior is studied by measuring the concentration change in the batchwise scrubbing and washing.

INTRODUCTION

Basic reagents such as organic solvent, nitric acid and water are recycled as much as possible in order to reduce the amount of waste generated in spent fuel reprocessing process. Some fission products such as tritium and ruthenium have a special affinity with organic compounds in the process. Tritium is chemically exchanged for protium of organic solvent. Ruthenium has a strong affinity with degradated organic compounds. So, these FPs tend to diffuse to down streams of the process and increase the level of radio-activity of the recycled reagents. For the purpose of improving the controllability of these FPs in the process, the influence of irradiation on the specific behavior of these elements are studied by experiments simulating the acid scrubbing and alkaline washing steps using irradiated 30%TBP/nDD solutions.

TRITIUM

1. EXPERIMENTAL

Organic solvents in contact with nitric acid aqueous solution in flasks were irradiated by γ ray of ^{60}Co source or spent fuel rods in a concrete cell of JAERI. MAGNOX spent fuel rods of 5,400 MWd/T burn-up were used for the present study. Tritiated water was used as tritium source. Tritium concentration was analysed by liquid scintillation analyser. In order to eliminate the interference of uranium in tritium analysis, uranium were separated by distillation before the measurement.

2. RESULTS AND DISCUSSION

2.1 Tritiation of Irradiated Solvent by Contacting with Simple Tritiated Nitric Acid Solution

Organic solvent of 30% TBP/nDD under contact with nitric acid aqueous solution was irradiated by γ ray of ^{60}Co source. The irradiated solvent was sampled and contacted with tritiated nitric acid.

Distribution ratios of tritium between the phases were measured. Batchwise acid scrubbing removed most tritium which had been extracted in the organic phase as tritiated water and tritiated nitric acid. However, small amount of tritium was retained in the solvent even after the series of scrubbing.

Tritium distribution ratios decrease by increasing the irradiation dose, because TBP is degradated by irradiation. The tritium retained in solvent after the 5 times 1.5N HNO_3 scrubbing is found to be proportional to the tritium concentration of aqueous phase initially contacted, as shown in Fig.1. The tritium retained in solvent is so stable that it has not been removed even by the 4 times 0.5M Na_2CO_3 washing following the acid scrubbing(Fig.2).

2.2 Organic Species Tritiated

Pure TBP, nDD and mixed 30% TBP/nDD were irradiated separately by 10^7 Gy. The irradiated solvents of pure TBP and nDD were mixed with non-irradiated solvents to make 30% TBP. These solvents were

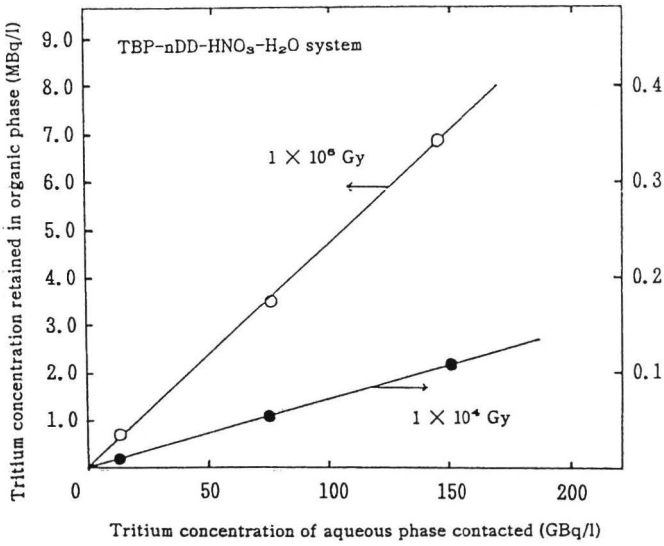


Fig.1 Dependency of tritium concentration retained in organic phase on tritium concentration of aqueous phase contacted (for the cases of solvent irradiated by 10^4 and 10^6 Gy)

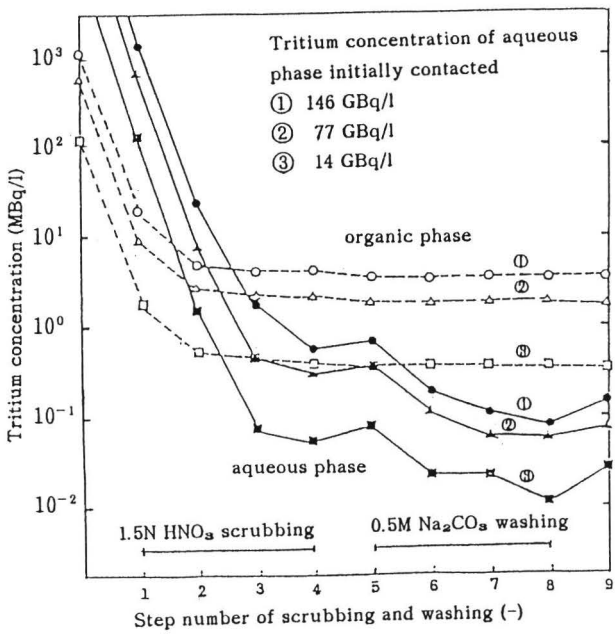


Fig.2 Tritium concentration change by batchwise 1.5N HNO_3 scrubbing and 0.5M Na_2CO_3 washing(The solvent has been irradiated by 10^6 Gy using ^{60}Co source.)

contacted with tritiated nitric acid. Samples taken at each lapse time were scrubbed and washed stepwise by 1.5N HNO_3 and 0.5M Na_2CO_3 in the same way as Fig.2. Figure 3 shows the retained tritium concentrations in organic solvent after the series of scrubbing. Marks △▲ show the mixed solvent of irradiated TBP and non-irradiated nDD. Marks ○● show the mixed solvent of non-irradiated TBP and irradiated nDD. Marks □■ show the irradiated 30%TBP/nDD. The retained tritium were detected more in degradated nDD than in degradated TBP. Most of degradated TBP seems to be removed by the alkaline washing .

Infra-Red spectrums of the irradiated organic solvents show a marked change of the absorption peaks of $>$CO, -O-NO and $>$ C-NO_2. Tritium is considered to be bound chemically in the main structure of organic solvent.

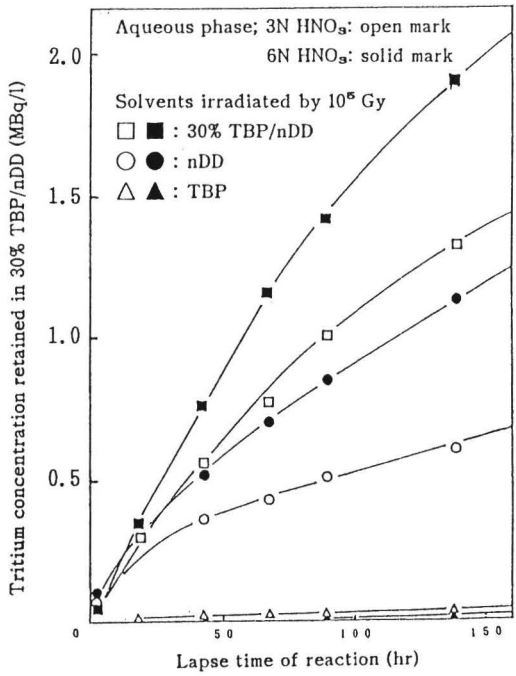


Fig.3 Tritiation reaction of differently irradiated and prepared 30% TBP/nDD

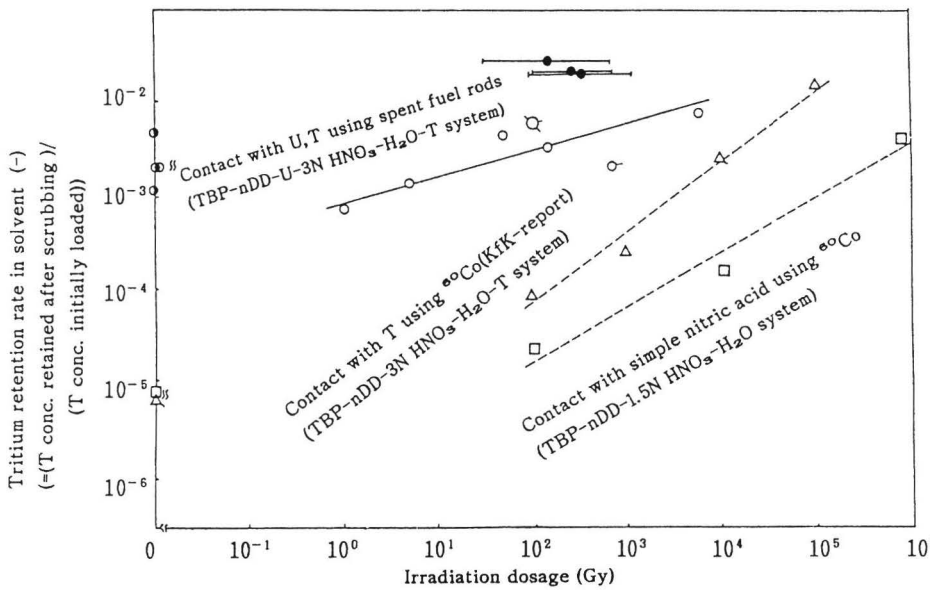


Fig.4 Dependency of irradiation dosage on tritium retention rate in organic solvent.

2.3 Tritiation by Contacting with Uranium Nitric Acid Solution Containing Tritium under γ Ray Irradiation Using Spent Fuel Rods

Solvents of 30% TBP/nDD loaded by uranium 85gU/l and tritium 16～18 MBq/l were irradiated under contact with uranium nitric acid solution. The acidity of uranium aqueous solution is 3N HNO_3 and containing tritium by 4.8 GBq/l. The irradiation was conducted by putting MAGNOX spent fuel rods beside the flasks of the solvent. Dose rate and accumulated dosage were measured by ionization chamber and film dosimeter.

After the irradiation for 2～100 hrs in the concrete cell, solvent samples were withdrawn, scrubbed and washed. Figure 4 shows the data obtained. For comparison, the data obtained by irradiation of ^{60}Co source are also shown for both cases of contact with simple nitric acid solution and of contact with the solution containing tritium. More tritium was retained in the solvent irradiated under contact with uranium nitric acid solution containing tritium than in the solvent under contact with the solution excluding uranium. The data indicates that chemical conditions have the significant influence on the solvent tritiation reaction.

2.4 Equation for Tritiation Rate of Organic Solvent

Tritiation of organic solvent progresses under the influence of chemical condition, even if irradiation is not conducted. In order to estimate the effect of each factor on the tritiation rate, analytical experiments were conducted. The equation for tritiation of the solvent was expressed as follows,

$$\Delta\,[RH_{x-1}T]_o = 169.2 \times (\Delta t + 3.62\times10^{-3}\times I_r^{0.61}) \times \mathrm{Exp}\,(-8{,}100/RT) \times [H]_a \times [T]_o \times [M]_o^{1.42}$$

where $[RH_{x-1}T]$ and $[T]$ are tritium concentrations of organic species and initially loaded, respectively. Ir is irradiation dose(Gy). $[H]$ and $[M]$ are the concentrations of acid and metalic ions(M), respectively. Sufixes a and o mean aqueous and organic phase, respectively. Mark $\triangle$ means difference. Figure 5 shows the influence of metalic ions on the tritiation rate. Uranium affects as a catalyst rather than a radiation source on the tritiation reaction. The data for ^{238}Pu obtained by Sameh et al.(1979) indicate that ^{238}Pu also affects as a catalyst rather than a α source on the reaction.

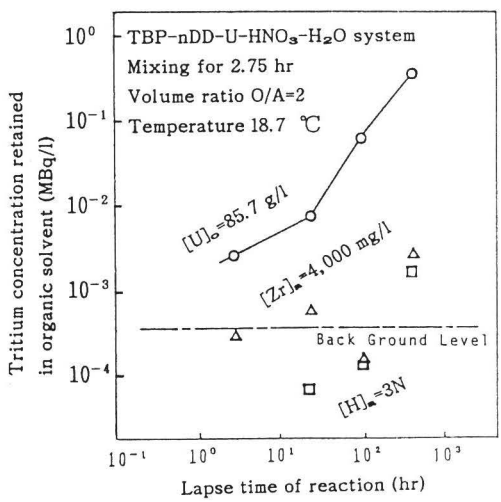


Fig.5 Influence of metal ions on tritiation reaction rate of organic solvent

2.5 Scrubbing Effect by Multi-Stage Mixer-Settler

Tritium scrubbing experiment was conducted using a multi-stage mixer-settler. In advance of the scrubbing experiment, organic solvent of 30% TBP/nDD loaded by uranium 90gU/l and tritium 5.6 MBq/l was irradiated by 10^4 Gy using spent fuel rods under contact with uranyl nitric acid solution. The time for the irradiated solvent preparation before scrubbing had to be shortened as much as possible in order to avoid the progression of solvent tritiation by chemical effects. The total time for the preparation was approximately 48 hrs for the present case.

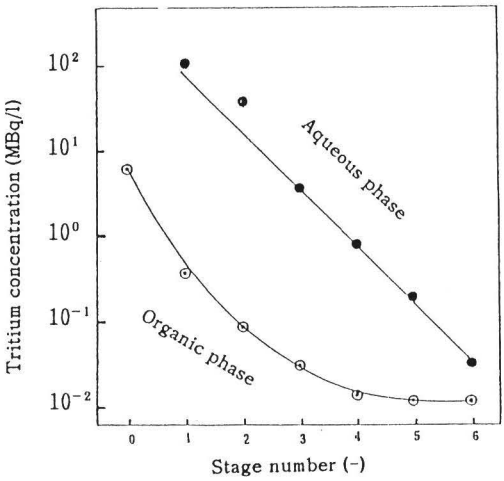


Fig.6 Experimental result of tritium scrubbing by multi-stage mixer-settler with internal recycling of aqueous phase, operated at counter-current flow ratio of O/A=25.

The organic solvent and non-tritiated 1.5N HNO_3 nitric acid solution were contacted in the mixer-settler counter-currently at the flow ratio of O/A=25. Aqueous phase of settler in each stage was recycled to the mixer of the same stage as the settler to improve the scrubbing efficiency. As shown in Fig. 6, tritium concentration in organic phase decreases steadily up to 4th stage, however, leveled off at the following stages. Tritium of 0.002 times the initially loaded was retained in the organic phase.

RUTHENIUM

1. EXPERIMENTAL

Solvents of 30%TBP/nDD was contacted with uranyl nitrate solution of 120 gU/l and 3N-HNO_3 in a flask stirred electrically. A sealed ^{137}Cs as a β ray source was located in the center of the flask. Irradiated solvents was withdrawn periodically. These samples were contacted with uranyl nitrate solution containing ruthenium by 5×10^{-3} M and scrubbed bachwise 3 times by 0.5 M-Na_2CO_3, NaOH and 3N-HNO_3 in series. Ruthenium concentration in both phases was analysed by measuring the radio-activity of ^{106}Rh at 512keV, the daughter of ^{106}Ru.

2. RESULTS AND DISCUSSION

Figure 7 shows the ruthenium concentration change in the batchwise scrubbing and washing. The organic solvent of 30% TBP/nDD had been irradiated by 65 kGy, and contacted with 9M-HNO_3 containing ruthenium for 7 days. Data for the case of non- irradiated solvent are shown for comparison. No differences were observed in the nitric acid scrubbing. Difference appeared in the alkaline washing. Degradated solvent which is not easily washed away into aqueous phase seems to retain ruthenium in the organic phase. Concentration of HDBP was analysed by 1.59 mg/ml in the

solvent.

CONCLUSIONS

Tritium and ruthenium retention in organic solvent was studied using irradiated solvents and the following conclusions were obtained.

(1) Chemical factors along with irradiation dose of γ ray affect markedly on the tritiation reaction of 30% TBP/nDD solvent. A new equation was proposed to estimate the reaction rate.

(2) Tritium is retained more in degradated nDD than in degradated TBP.

(3) Tritium is easily scrubbed using multi-stage contactor. Tritium of lower than 0.002 times the initially loaded is retained in the solvent irradiated by 10 kGy of γ ray.

(4) Little retention of ruthenium was observed in the solvent irradiated by 65 kGy of β ray and contacted with ruthenium for 7 days after the irradiation.

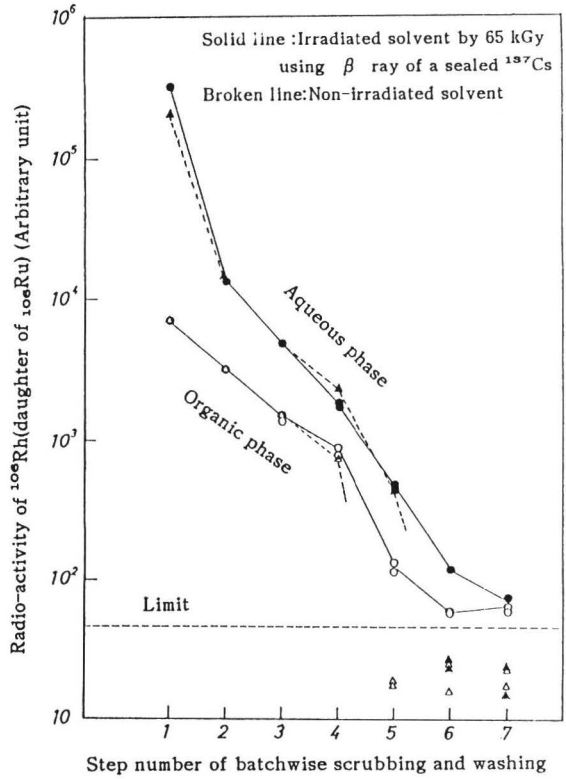


Fig.7 Ruthenium concentration change in the 3 times batchwise acid(3N HNO_3) scrubbing followed by 0.5 M-Na_2CO_3, NaOH and 3N-HNO_3 washing in series.

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RESULTS OF ^{106}Ru AND ^{95}Zr DECONTAMINATION STUDIES IN THE CO-DECONTAMINATION CYCLE OF THE TOKAI REPROCESSING PLANT

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ABSTRACT

The decontamination characteristics of ^{106}Ru and ^{95}Zr in the co-decontamination process of the Tokai Reprocessing Plant were examined based upon the operational data obtained in the hot operation during this decade. The observed ^{106}Ru/ ^{95}Zr behavior showed good agreement with the result of the simulation calculation by MIXSET to which calculational method was incorporated for determining the distribution ratio of Ru and Zr. Both revealed to have quite high decontamination factors at the co-decontamination process, however, rather low scrubbing efficiency was found at the scrub bank than the calculation. This can possibly be attributed to the contaminated entrainment remaining in the scrubbed organic phase.

INTRODUCTION

^{106}Ru and ^{95}Zr are two FP nuclides that are difficult to be eliminated from uranium and plutonium, and these sometimes require a careful examination in the flowsheet design of the PUREX extraction process.[1] Their complex formation or polymerization in the nitric acid solution is quite complicated, which sometimes makes us confused in understanding their behavior in the actual plant process. Therefore, it is important to know how it behaved in the reprocessing process under actual operation. In the Tokai Reprocessing Plant (TRP) which has been under hot operation since 1977, examination on the behavior of some noticeable nuclides were carried out by investigating the samples taken from the process under operation.

2 MEASUREMENTS CARRIED OUT

The behavior of ^{106}Ru and ^{95}Zr throughout the extraction cycles of TRP was investigated by taking samples from some key-process-points that can give us reliable mass balance. Samples were analyzed by gamma-spectrometry. For determining the distribution of Ru, both ^{106}Ru and ^{103}Ru were examined. The

examination of ^{95}Zr was carried out when shortly-cooled spent fuels(ca. 330 days) were reprocessed. In order to see the extraction profile of these two nuclides in the extraction bank of the co-decontamination cycle, samples were taken from several stages throughout the bank at the same time.

3 RESULTS OF THE MEASUREMENTS

Fig.1 shows the outline of the flowsheet of the co-decontamination cycle with the observed distribution balance of ^{106}Ru and ^{95}Zr. It was found that as low as 0.02% of Ru and 0.4% of Zr was distributed to the loaded solvent. At the strip bank, they were more evenly distributed between the product stream and scrubbed solvent.

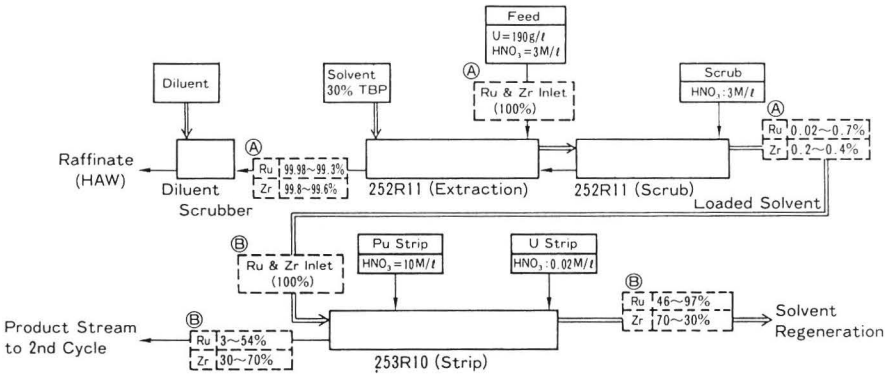


Fig.1 Observed Distribution Balance of Ru and Zr in the Co-decontamination Cycle of the Tokai Reprocessing Plant

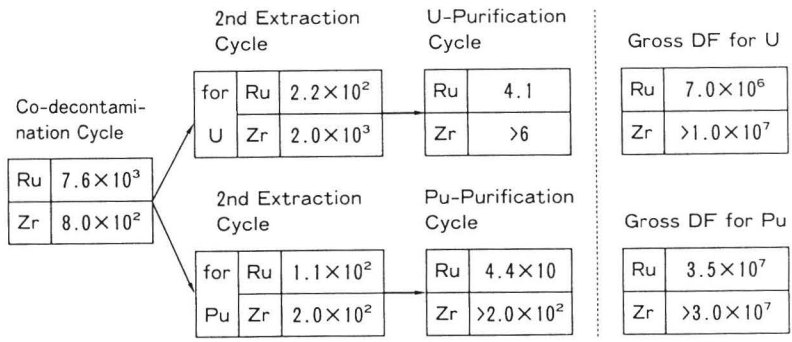


Fig. 2 Decontamination Factors for Ru and Zr Observed in the Extraction Process

Fig.2 shows the decontamination factors(DF) observed for consecutive extraction cycles. The gross DFs for both nuclides are satisfactorily high, and this partly owes to the rather high DF at the co-decontamination cycle.

4 CALCULATION OF THE EXTRACTION OF Ru AND Zr

Simulation calculation to explain the observed distribution of Ru and Zr was performed with the calculational procedures shown in Fig.3. The distribution ratio of extractable complex of Ru(tri-nitrato nitrosylruthenium) under the coexistence of U, Pu and HNO_3 was calculated using apparent extraction equilibrium constant that was obtained from the published distribution data[2] for the HNO_3-TBP extraction system. The apparent constant K was obtained as a function of free nitrate ion concentration in the aqueous phase to express the experimental distribution ratio with the free TBP concentration in the organic phase. Other less extractable complexes(e.g.di-nitrato nitrosylruthenium) were treated as non-extractable because of their small contribution to the extracted amount. The distribution ratio for Zr was calculated with L.Rozen's equation.[3] Their distribution ratios were calculated with the free TBP and free nitrate ion concentration that was obtained as the result of the extraction calculation for U, Pu and HNO_3. These distribution ratio were applied to the REVISED.MIXSET[4] to calculate their profiles.

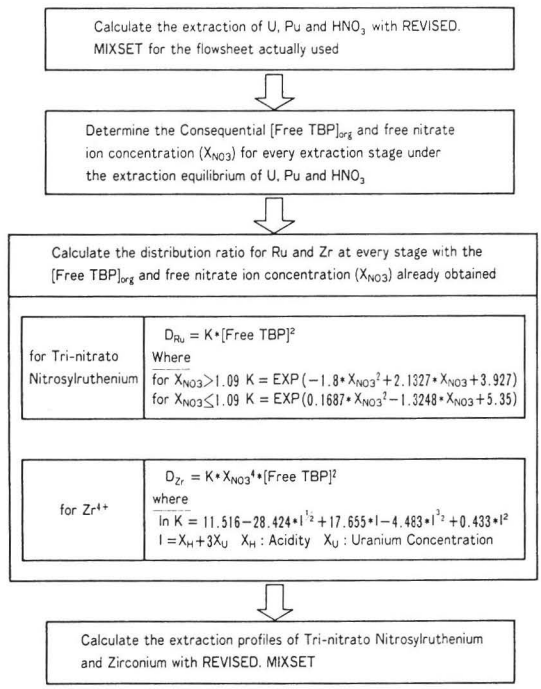


Fig. 3 Calculational Procedures for the extraction of Tri-nitrato nitrosylruthenium and Zr^{4+} using REVISED. MIXSET

5 RESULTS AND DISCUSSIONS

5.1 Extraction Profiles

Fig.4 Shows the calculated extraction profiles of Ru and Zr under the flowsheet actually taken when their distribution behavior was examined. The content of the extractable tri-nitrato nitrosylruthenium in the feed solution was assumed to be 3% as described below. Both Ru and Zr have a slight

accumulation at the extraction part of the bank. For Zr profile, assumption with 80% of stage efficiency gave more agreeable calculation result with the observed points. This is attributed to the slow scrubbing reaction of Zr. In both cases of Ru and Zr, it was found that the observed concentration in the organic outlet is quite higher than the calculated value. This phenomena is described below.

5.2 Estimated Content of Tri-nitrato nitrosylruthenium in the Feed

The calculation for tri-nitrato nitrosylruthenium provided quite higher distribution ratio at the feeding stage than that was actually observed. This can be attributed to the existence of non-extractable species in the feed. Lower content of extractable tri-nitrato nitrosylruthenium makes the apparent distribution ratio lower, which well explains the low observed distribution ratio. It was found that assumption with 3% of tri-nitrato nitrosylruthenium content in the feed explains the observed ditribution ratio well. This number seems rather lower than that is generally expected for the equilibrated uranyl nitrate solution having the same acidity. This unexpectedly low content of extractable species of Ru is one of the reasons of high decontamination result of Ru at the co-decontamination cycle.

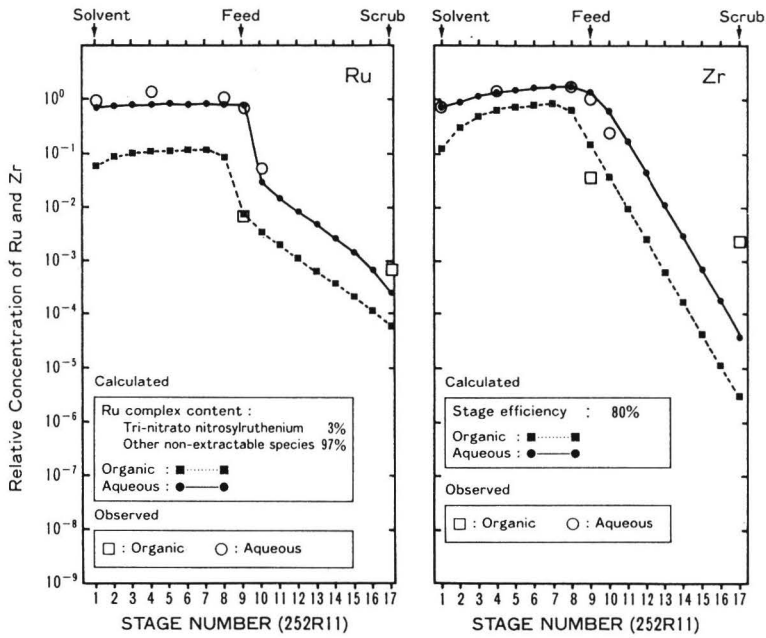


Fig. 4 Extraction Profiles of Ru and Zr at the Extraction Bank of the Co-decontamination Cycle

5.3 Distribution Balance of Ru and Zr in the Co-decontamination Cycle

Table 1 shows the comparison of the distribution balances that were observed and calculated. The distribution between raffinate and loaded solvent gives comparably good agreement. The distribution between the product stream(effluent) and solvent(this goes to the solvent-regeneration process) does not give good agreement in the comparison of the calculated and the observed. Higher observed distribution of Ru to the product stream than the calculation may be attributed to the formation of the less-nitrated complexes during the stripping reaction with very diluted nitric acid. Nitrosylruthenium complex is likely to form less-nitrated(mono-, di- or non-nitrato)complex in propotion to the decrease of the nitrate ion concentration. The low nitric acid concentration(ca. 0.1 M/l at max.) in the aqueous phase of the strip bank allows the tri-nitrato complex to be converted to less-nitrated complexes that are less extractable. The higher observed distribution of Zr to the solvent than the calculation can possibly be attributed to the existence of the degradation product of TBP. The Di-Buthyl Phosphate(DBP) forms strong complex with tetravalent cations like Zr^{4+} that allows some Zr to remain in the scrubbed solvent. The concentration of DBP usually detected in the solvent outlet stage of the strip bank ranges <20～100 ppm. However, we could not find any quantitative explanation between the Zr remainder in the solvent and the DBP concentration.

5.4 Scrubbing Efficiency at the Scrub Bank

Table 2 shows the observed scrubbing efficiency for Ru and Zr at the scrub part of the bank. The Ru is scrubbed up to 1/9.7 of the organic inlet while this was 1/12 for Zr. These observed values seem lower than the calculated efficiency, which suggests us the possibility of the existence of the organic-preferring material. For Zr, the formation of DBP complex seems to be the most

Extraction Bank		Fraction to Raffinate	Fraction to Loaded Solvent
Ru	Calculated (1)	99.99 %	0.01 %
	Observed	99.3～99.98 %	0.7～0.02 %
Zr	Calculated	Approximately 100 %	5.4×10^{-4} %
	Observed	99.6～99.8 %	0.4～0.2 %

Strip Bank		Fraction to Prduct	Fraction to Solvent
Ru	Calculated (2)	10.4 %	89.6 %
	Observed	2.8～54.1 %	97.2～45.9 %
Zr	Calculated	Approximately 100 %	Approximately 0 %
	Observed	30～70 %	70～30 %

(1) Calculated for the mixture of 3 % of Tri-nitrato Nitrosylruthenium and 97 % of other non-extractable species.
(2) Calculated for Tri-nitrato Nitrosylruthenium.

Table 1 Comparison between calculated and observed distribution balance of Ru and Zr at the Co-decontamination Cycle

probable cause as is seen above. There is no explicit explanation for the Ru remainder in the organic solution but the entrainment of the aqueous solution or radiocolloidal impurity that remained in the organic solution. The fine particles of undissolved residue of rare metal element containing ^{106}Ru as a main radioactive nuclide can be another possible cause. What should be noted in Table 2 is the scrubbing efficiency of the ^{137}Cs, ^{134}Cs and ^{144}Ce. These nuclides have much lower extractability than Tri-nitrato nitrosylruthenium or Zr^{4+}, and these must have much higher scrubbing efficiency according to the extraction equilibrium with TBP. This also suggests the possibility of the existence of entrainment effect that controls the maximum DF achievable in such type of process.

Nuclides	R1109-Org(μCi/ℓ)	R1117-Org(μCi/ℓ)	Ratio (R1109/R1107)
Ru-106	8.0×10	8.5	9.4
Ru-103	1.7	1.7×10^{-1}	10.0
Zr-95	6.7×10^{1}	5.6	12.0
Ce-144	2.4×10	6.6×10^{-1}	36.4
Cs-137	1.0	2.9×10^{-2}	34.5
Cs-134	7.2×10^{-1}	2.0×10^{-2}	36.0

R1109 : Feeding Stage of Extraction Bank
R1117 : Loaded Solvent Outlet Stage of Scrub Bank

Table 2 Observed Scrubbing Efficiency for Ru and Zr at the Scrub Bank of Co-decontamination Cycle

6 CONCLUSION

The extraction behavior of Ru and Zr at the co-decontamination cycle of the Tokai Reprocessing Plant was examined with the process data. Extraction calculation of Ru and Zr using REVISED.MIXSET was carried out and showed good agreement with the observed behavior. A further examination on the stage efficiency of the Zr at the scrub bank will be needed. The observed low scrubbing efficiency at the scrub bank is possibly attributed to the organic-preferring entrainment or fines. A further investigation will be needed for this effect.

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INTERPHASE MASS TRANSFER COEFFICIENT OF NEPTUNYL ION IN THE PUREX SYSTEM

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ABSTRACT

Single droplets of neptunyl nitrate solution were formed in a glass column filled with 30-volume % TBP/normal dodecane to evaluate the mass transfer coefficient. Neptunium was adjusted to hexavalent state by electrolytic oxidation and held in this state by potassium dichromate. Mass transfer coefficients of neptunyl ions were obtained as a functional of feed concentration, column height and droplet diameter by measuring the neptunyl nitrate concentrations in the feed and the effluent. The mass transfer coefficients were correlated by a set of dimensionless groups of parameters. The highest value of the mass transfer coefficients was observed at droplet diameter of 0.37 cm for the neptunyl ion. For reference, mass transfer coefficients of uranyl ion and nitric acid were estimated by similar experiments.

I. INTRODUCTION

Many researchers[1,6-8] have studied mass transfer coefficients by single droplet experiments in order to obtain design parameters of extraction columns.

In the feed solution of pulsed columns in reprocessing plants, the neptunium ion state is often quoted to be a mixture of two valence states Np(V) and Np(VI) and the behaviour of the neptunium ion is reported to be very complicated due to their different affinity for the organic extractant[2]. Because the hexavalent neptunium has the highest affinity to 30-volume % TBP diluted in normal dodecane, neptunium was adjusted to the hexavalent state by electrolytic oxidation and held by potassium dichromate.

In the present study, single droplets of neptunyl nitrate were formed in the small column of the solvent of 30-volume % TBP diluted in normal dodecane. Mass transfer coefficients were obtained by measuring the solute concentration change between the feed and the effluent. The overall mass transfer coefficient K_R from an aqueous droplet to the surrounding organic phase can be calculated from the equation (1).

$$K_R = \ln (C_2/C_1)/ A\ t_c \quad (1)$$

where t_c is the contact time of falling droplet, C_1 and C_2 are the solute concentrations in the feed and in the effluent, respectively. A is the surface area of mass transfer per unit volume of droplets.

The experimental data are correlated by the equation composed of dimensionless groups of the parameters.

$$K_R/U = k'' (H/d_p)^a (R_e)^b (C/\rho_a)^c \quad (2)$$

where k", a, b, c are constants, U is the velocities of falling droplets, R_e is Reynold's number.

II. EXPERIMENTAL

II.1. Equipment

The equipment employed is shown in Fig.1. The aqueous feed of neptunyl nitrate was supplied through a nozzle at the top of extraction column by a microtube pump. The column was made of glass with a water jacket to keep the temperature constant at 25 ± 1°C.

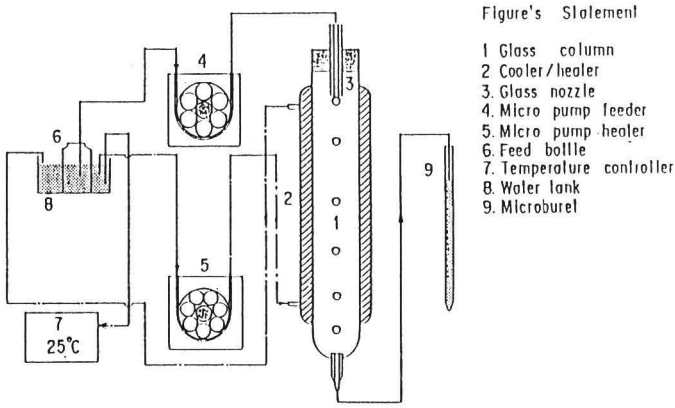


Fig.1 : Experimental apparatus

The internal diameter of the column is 25 mm. The nozzle is made of glass and placed at the top of the column and fitted with a silicone rubber cap. The inside diameter of the nozzle is in the range of 0.4 to 4.5 mm and the outlet diameter is from 6.0 to 7.0 mm. The effluent solution was collected in a microburet. The height of the microburet was adjusted so that the interface between aqueous and organic phases was always kept at a given

level from the bottom of the column. The capillary used for the feed and effluent tubing is made of plyethylene of 0.1 mm in internal diameter.

II.2. Procedure

For the first step, the column was filled with the solvent of 30-volume % TBP diluted in normal dodecane and warmed up to 25±1 °C with circulating water. Then, the neptunyl nitrate in nitric acid solution was fed to the column. The experimental conditions are summarized in Table 1. The droplet diameter was estimated by dividing the feed flowrate by number of droplets generated at the nozzle per minute. The neptunium concentrations in samples were analysed by gamma spectrometry. The concentrations of $UO_2(NO_3)_2$ and nitric acid were analysed by titration. The physical properties necessary to calculate Eq. (2) were referred in references[4]. In order to make the effect of droplet formation and coalescence negligible, the column height was determined to be higher than 9 cm from the assessment of the experimental data on the relation between the $\ln(C_2/C_1)$ and the contact time.

TABLE 1. EXPERIMENTAL CONDITIONS

Flowrate (F)	:	12 cm^3/hr (constant)
Column height*1(H)	:	9. 15.5, 19, 25. 30 , 35 cm
Solvent	:	30% TBP diluted in normal dodecane
Feed concentration of		
Neptunium nitrate*2(C)	:	65 - 350 mg/l
Uranium nitrate*2(C)	:	250 g/l
Temperature	:	25 ± 1 °C

*1. The distance from the top of the nozzle to the bottom of the column

*2. The feed concentration of nitric acid was kept at 3N throughout the experiment

III. RESULTS

III.1. Effect of droplet diameter on the velocity of falling droplets

Figure 2 shows the velocity of falling droplets plotted against the diameter. The result shows that the velocity is independent of droplet diameter in the range of the present experimental condition.

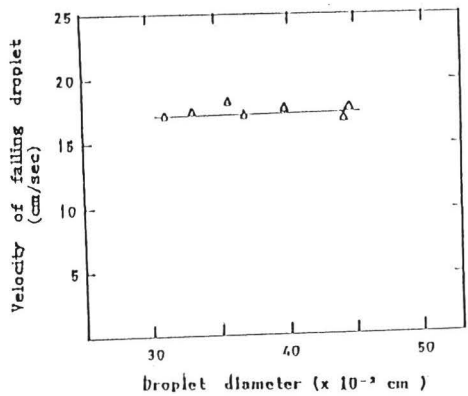


Fig.2: Dependency of the velocity of falling droplet on the diameter at 25°C

III.2. Evaluation of Mass Transfer Coefficient

Mass transfer coefficient during the fall of droplet can be estimated from the slope of the line which correlates $\ln(C_2/C_1)$ and the contact time, since the inter-phase mass transfer of neptunium ions during the droplets formation at nozzle and the coalescence at outlet is considered to be constant for the different column heights.

The experiment was conducted to evaluate the effect of column height H on the mass transfer coefficient. From the slope of the correlation between $\log(K_R/U)$ and $\log(H/d_p)$, the power a of the dimensionless group H/d_p in Eq.(2) was evaluated to be -1.4 by the least square method.

Similar methods were applied to evaluate the effect of concentration of neptunyl nitrate on mass transfer coefficient. The power c of the dimensionless group of C/ρ_a was 0.61.

Several experiments were made to evaluate the effect of droplet diameter d_p on mass transfer coefficients. Figure 3 shows the relation between the mass transfer coefficient and droplet diameter. From the slope of the correlation between $\log\{(K_R/U)(C/\rho_a)^{-0.61}(H/d_p)^{1.4}\}$ and $\log(R_e)$ the power of Re was estimated to be 17 for d_p in the range of 0.31 to 0.37 cm and -6.5 in the range of 0.37 to 0.45 cm, respectively.

The mass transfer coefficients are expressed by equations (3) and (4), for d_p in the range of 0.31 to 0.37 cm and in the range of 0.37 to 0.45 cm, respectively.

$$K_R/U = 1.2 \times 10^{-44}(C/\rho_a)^{0.61}(H/d_p)^{-1.4}(R_e)^{17} \quad (3)$$

$$K_R/U = 6.2 \times 10^{19}(C/\rho_a)^{0.61}(H/d_p)^{-1.4}(R_e)^{-6.5} \quad (4)$$

IV. DISCUSSION

Figure 2 shows that the velocity of falling droplet is independent of the droplet diameter for the present experimental condition. The velocity is 17.5 cm/sec. In our previous study it was indicate that the velocity of the droplets increased by increasing the diameter up to 0.26 cm[8], however, leveled off at the larger droplet size than 0.26 cm. Value of the leveled off velocity depends on the physical properties.

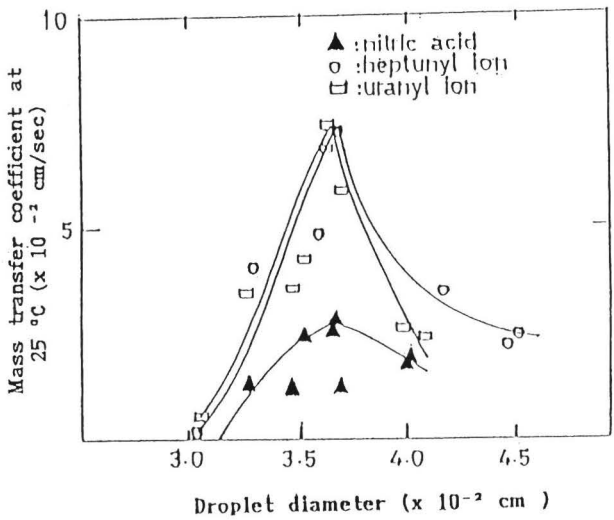


Fig.3 : Dependency of K_R on droplet diameter.

Figure 3 shows the dependency of mass transfer coefficient on droplet diameter. Mass transfer coefficient is observed to increase sharply with the increase of diameter up to a certain diameter and then decreases beyond that diameter. Similar tendency was observed in the case of uranyl and nitric acid ions. This behaviour is considered to be due to the oscillaion and internal circulation within the droplet. Schroeder and Kintner[9] reported that oscillation increases the rate of heat and mass transfer between the moving droplets and the surrounding fluid. The circulation velocity inside the droplet has been observed by Horton, et al.[3]. They reported that the rate of interphase mass transfer in such circulation systems is larger by twice the rate in an equivalent non-circulating system. After the mass transfer coefficient reached to the maximum value, it then decreased in the present study. The optimum range of droplet sizes which gives the maximum mass transfer coefficients is in the range from 0.35 to 0.39 cm.

V. CONCLUSION

The correlations between the mass transfer coefficient with H/d_p, C/ρ_a and R_e have been obtained for neptunyl ions-nitric acid as the aqueous phase and 30-volume % TBP diluted in normal dodecane as the organic phase. The neptunyl concentraion in the feed solution were changed in the range of 65 to 350 mg/l while the concentration of nitric acid was kept at 3 N throughout the experiment. The correlations are differently expressed by Eq.(3) and Eq.(4), depending on the range of droplet diameter. A critical diameter exists around 0.37 cm. In the smaller range, mass transfer coefficient sharply increases with the increase of droplet diameter, while, in the larger range, mass transfer coefficient decreases with the increase of the diameter.

For reference, mass transfer coefficient of uranyl ions and nitric acid were also evaluated by similar experiments. The dependency of mass transfer coefficient on droplet diameter for uranyl nitrate and nitric acid is similar to that for neptunyl nitrate.

The optimum range of droplet size which gives the maximum mass transfer coefficient is around 0.35 to 0.39 cm.

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STUDY OF THE COMPLEXES OF Np(V) WITH SOME ORGANIC LIGANDS BY SOLVENT EXTRACTION

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ABSTRACT

The complex formation of Np(V) with some aliphatic dicarboxylates (oxalate, malonate, succinate, adipate), hydroxycarboxylates (L-malate, tartrate, citrate) and aromatic carboxylates (salicylate, m-hydroxybenzoate, phthalate, α-picolinate, α-furoate) has been studied by the solvent extraction method using thenoyltrifluoroacetone and 1,10-phenanthroline in isoamyl alcohol. The stability of the complexes is discussed in connection with the structure of the organic ligands.

1 INTRODUCTION

Solution chemistry of neptunium has received much attention in recent years since ^{237}Np in radioactive wastes will have a long-term radiological toxicity in the human environment. Since this element most probably exists as a quinquevalent state in oxic neutral solutions, the study of the complex formation of Np(V) in aqueous solutions is very important for the understanding of the behavior of this element in natural water.

In our previous studies (Inoue and Tochiyama, 1983, 1985a,b), the formation constants of Np(V) complexes with some organic ligands (hydroxycarboxylates, dicarboxylates, aminocarboxylates) and inorganic ligands (carbonate, fluoride, sulfate, phosphate) have been obtained by the solvent extraction method using thenoyltrifluoroacetone (TTA) and 1,10-phenanthroline (phen). However, the later study (Stout et al., 1989) on the dicarboxylate complexes has shown that our values were consistently lower than those obtained by spectrophotometry.

This disagreement induced us to reevaluate the reliability of the solvent extraction method for the determination of the stability constants. After checking various factors in the extraction procedure, we investigated the complexation of Np(V) with the following ligands, which have characteristic structures common in naturally occurring organic substances such as humic or fulvic acids;

(a) aliphatic dicarboxylates; $HO_2C(CH_2)_nCO_2H$ (n=0,1,2,4),

(b) hydroxycarboxylates; tartrate, L-malate, citrate,

(c) aromatic carboxylates; phthalate, salicylate, α-furoate, α-picolinate.

2 EXPERIMENTAL PROCEDURE

^{239}Np tracer was prepared by milking from ^{243}Am by the method of Sill (1966) and adjusted to the quinquevalent state by evaporation to dryness and dissolution in water (Inoue and Tochiyama, 1977). In the standard procedure, the ^{239}Np tracer was first extracted into an isoamyl alcohol (i-AmOH) solution containing TTA and phen. A 4-ml portion of this organic solution was then shaken for 15 min at 25 °C in a glass tube with the same volume of aqueous solution containing a variable concentration of complexing agent, 1M $NaClO_4$, and buffer reagents (a proper mixture of 0.1M of 2-morpholinoethanesulfonic acid (MES) and tris(hydroxymethyl)aminomethane (THAM)). After phase separation, γ-activity of each phase and pH of the aqueous phase were measured to give the distribution ratio and equilibrium pH.

3 CALCULATION OF STABILITY CONSTANTS

Distribution ratio D of Np(V) in the presence of a complexing agent (L) can be expressed by

$$D = [MTnB]_o/([M]+\Sigma[MT_n]+\Sigma[ML_n]) = D_0/(1+\Sigma\beta_n{}^T[T]^n+\Sigma\beta_n[L]^n) \quad (1)$$

where $D_0=[MTnB]_o/[M]$, $\beta_n{}^T=[MT_n]/[M][T]^n$, $\beta_n=[ML_n]/[M][L]^n$; and M, HT, B denote NpO_2^+, TTA and phen, respectively (for simplicity, charges are omitted). The ligand concentration [L] was calculated from the total concentration of the organic acid and its dissociation constants. In the calculation, distribution of the acid into the organic phase was neglected because the organic acids used are hydrophilic and mostly in the dissociated form under the conditions used. The term $\Sigma\beta_n{}^T[T]^n$ for the complex formation of Np(V) with TTA was calculated by using $\log\beta_1{}^T=2.89$, $\log\beta_2{}^T=5.48$ and $[T]=C_{TTA}/(K_{DR}[H]/K_a+[H]/K_a+1)$, where $pK_a=6.53$, $\log K_{DR}=1.83$ for i-AmOH. This term was less than 0.01 under all the conditions studied.

The optimum set of the values of $\log D_0$ and $\log\beta_n$ was obtained by a nonlinear least-squares fitting, which minimizes the sum of the squares of the residuals between logD's observed experimentally and calculated by eqn.(1).

4 RESULTS AND DISCUSSION

4.1 Extraction System for Determination of Stability Constants

In order to assess the possible sources of errors inherent in the present solvent extraction method, the distribution of Np(V) in the absence of complexing agent was examined as a function of pH by forward and backward extraction, with i-AmOH and methylisobutyl ketone (MIBK). Fig. 1 shows that the distribution ratios obtained by forward extraction are discernibly lower than those by backward extraction for these solvents. The same distribution

TABLE 1

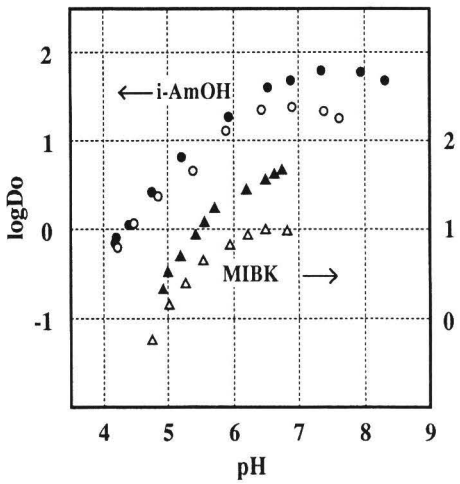
Stability constants of Np(V) with various carboxylates.

Ligand(acid form)	pK_a(μ=1.0)(a)	$\log\beta_1$	$\log\beta_2$
oxalate $(COOH)_2$	1.04,3.55	3.71 ± 0.02	6.15 ± 0.02
		3.53 ± 0.04	6.12 ± 0.05 (b)
malonate $HOOCCH_2COOH$	2.60,5.07	2.62 ± 0.02	4.22 ± 0.02
		2.51 ± 0.01	4.17 ± 0.02 (b)
succinate $HOOC(CH_2)_2COOH$	3.97,5.11	1.45 ± 0.06	2.43 ± 0.05
		1.51 ± 0.02	2.14 ± 0.09 (b)
adipate $HOOC(CH_2)_4COOH$	4.26,4.94	1.22 ± 0.03	2.05 ± 0.03
L-malate $HOOCCH(OH)CH_2COOH$	3.16,4.44	1.66 ± 0.03	2.69 ± 0.02
tartrate $[CH(OH)COOH]_2$	2.86,4.10	1.46 ± 0.01	2.11 ± 0.02
citrate $HOOCCH_2C(OH)(COOH)CH_2COOH$	2.80,4.08,5.33	(unknown side reaction)	
salicylate $o\text{-}C_6H_4(OH)COOH$	2.80	(0.84)	
m-hydroxybenzoate $m\text{-}C_6H_4(OH)COOH$	3.96	(0.88)	
phthalate $o\text{-}C_6H_4(COOH)_2$	2.67,4.73	(1.59)	
α-picolinate $\alpha\text{-}C_5H_4NCOOH$	0.86,5.17	3.53 ± 0.03	6.01 ± 0.03
α-furoate $\alpha\text{-}C_4H_4OCOOH$	3.02	<1.0	

μ=1.0($NaClO_4$),25°C, $C_{TTA}=10^{-3}$M(pH≃5)/10^{-4}M(pH≃7), $C_{phen}=2\times10^{-2}$M in i-AmOH
(a)Martell and Smith (1977,1989).
(b)by spectrophotometry, μ=1.0,23°C,pcH=6.14, Stout et al.(1989).

ratio was observed for varying the shaking time from 5 to 40 min. Repeated experiments by the use of the different milking batches of ^{239}Np solutions showed that the reproducibility was somewhat poorer in the forward extraction than in the backward extraction. The result suggests that a small amount of unextractable neptunium species might be introduced during milking as a result of unfavorable reactions such as redox reaction, sorption on a small amount of colloidal particles, and hydrolysis. Fig. 2 shows that the forward extraction procedure gives lower logβ values than the backward extraction. In order to avoid this unfavorable effect, we decided to use backward extraction here.

Fig. 3 shows the difference between i-AmOH and MIBK in the backward extraction. In the MIBK system, unexpected higher distribution ratios were observed at higher concentrations of the ligands, especially with oxalate. Since this deviation cannot be explained by eqn.(1), some unknown side reactions such as redox reaction are considered to occur, probably owing to the coexistence of MIBK and the ligand. In this connection, i-AmOH is preferred as an organic solvent. It should be noted, however, that the shape of logD vs. log[L] curve must be carefully examined even with i-AmOH, because



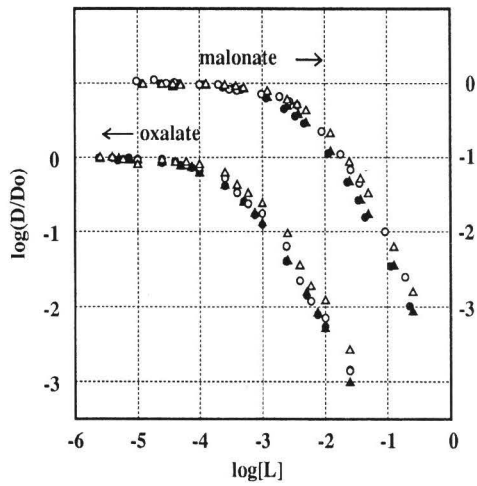
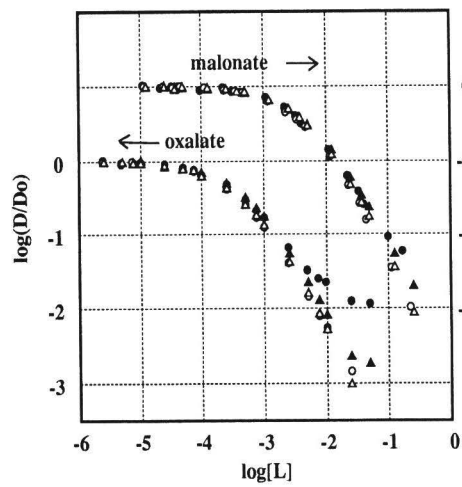


Fig. 1(left). Variation of $\log D_0$ with pH in forward(○,△) and backward(●,▲) extraction.
○ ● : i-AmOH, $C_{TTA}=1\times10^{-3}$M, $C_{phen}=2\times10^{-2}$M.
△ ▲ : MIBK, $C_{TTA}=2\times10^{-2}$M, $C_{phen}=2\times10^{-2}$M.

Fig. 2(right). Variation of $\log(D/D_0)$ with log[L] in forward(○,△) and backward(●,▲) extraction with i-AmOH.
$C_{TTA}=1\times10^{-3}$M(○,●), 1×10^{-4}M(△,▲); $C_{phen}=1\times10^{-2}$M(○,△), 2×10^{-2}M(●,▲)
pH= oxalate : 5.80(○), 5.80(●), 7.61-7.69(△), 7.17-7.38(▲);
malonate: 5.60(○), 6.10(●), 7.40-7.52(△), 7.69-8.02(▲).



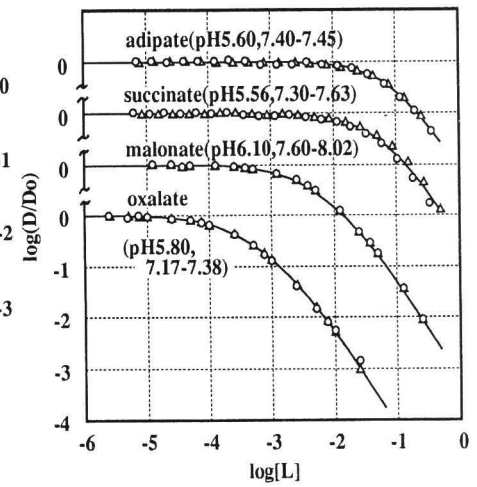


Fig. 3(left). Variation of $\log(D/D_0)$ with log[L] in backward extraction with i-AmOH(○,△) and MIBK(●,▲).
$C_{TTA}=1\times10^{-3}$M(○), 1×10^{-4}M(△), 2×10^{-2}M(●), 1×10^{-2}M(▲); $C_{phen}=2\times10^{-2}$M.
pH= oxalate: 5.80(○), 5.60(●), 7.17-7.38(△), 7.14-7.31(▲);
malonate: 6.10(○), 5.80(●), 7.60-8.02(△), 7.25-7.52(▲)

Fig. 4(right). Complex formation with aliphatic dicarboxylates.
pH = 5-6(○), 7-8(△).

we do not know much about the nature of the organic solvent with which the ligand is liable to induce this kind of reaction.

In our previous work, forward extraction was adopted for organic ligands(Inoue and Tochiyama, 1983), while backward one for inorganic ligands (Inoue and Tochiyama, 1985a,b). Thus, we have decided to reinvestigate the complex formation with organic ligands by using backward extraction with i-AmOH since logβ values in our previous paper might be lower than true values by 0.2-0.4 in the worst case.

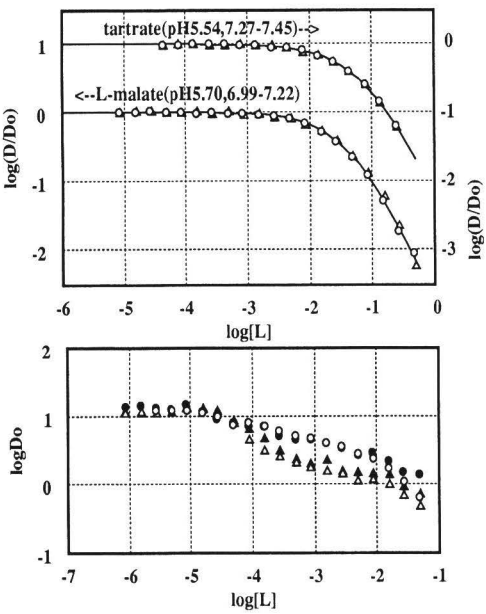
4.2 Complex Formation of Np(V) with Organic Ligands

(i)Aliphatic dicarboxylates. Fig. 4 shows the plots of $\log(D/D_0)$ vs. log[L] for aliphatic dicarboxylates. Stability constants thus obtained are listed in Table 1. These values are in fair agreement with those reported by Stout et al. (1989). The stability of aliphatic dicarboxylate complexes appears to be controlled mainly by the stability of the chelate ring, since the stability decreases with increasing the number of carbon atoms between two carboxyl groups in the ligand in spite of the increase in the basicity (ΣpK_a).

(ii)Hydroxycarboxylates. Fig. 5 shows the plots of $\log(D/D_0)$ vs. log[L] for L-malate and tartrate, where one or two methylene hydrogens in succinate are replaced by hydroxyl groups. Although the presence of hydroxyl groups causes a decrease in the basicity of the ligand, the stability of the complex is in the order, succinate < L-malate > tartrate. Therefore, hydroxyl groups are considered to have some small stabilizing effect in these complexes, which may be balanced with the effect of the basicity change to give the observed stability sequence.

Fig. 6 shows the result on citrate, which has three carboxylates and one hydroxyl group in the molecule. The shape of the curve clearly indicates that a certain side reaction exerts influence in this case. Considering together with the result on oxalate-MIBK system, it is probable that in certain organic solvents, strongly complexing polycarboxylates are prone to induce some unknown reaction of Np(V).

(iii)Aromatic carboxylates. Fig. 7 shows the plots of $\log(D/D_0)$ vs. log[L] for aromatic carboxylates. Owing to the solubility limits of the ligands, only limited information was obtained. The resonance stabilizing effect of aromatic π-electron seems small in o- and m-hydroxybenzoates, although the effect is noticed in a phthalate complex (phthalate forms more stable complex than succinate in spite of its smaller ΣpK_a). It is interesting to see that the heterocyclic oxygen in α-furoate has little effect in the stabilization of the carboxylate complex, while the nitrogen atom in α-picolinate greatly raises the stability.



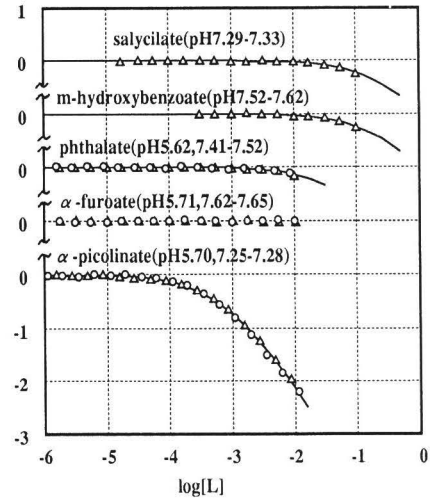


Fig. 5(left,top). Complex formation with hydroxycarboxylates.
pH=5-6(○), 7-8(△).
Fig. 6(left,bottom). Variation of $\log D_0$ with $\log[\text{citrate}^{-3}]$
○△: 15 min shaking, pH=5.70(○), 7.42-7.48(△)
●▲: 5 min shaking, pH=5.55(●), 7.18-7.22(▲)
Fig. 7(right). Complex formation with aromatic carboxylates.
pH=5-6(○), 7-8(△).

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PROCESS STUDY ON NEPTUNIUM SEPARATION USING SALT-FREE REDUCTIVE REAGENT

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ABSTRACT

Neptunium separation process from product organic stream of co-decontamination step is studied using salt-free reductive reagents which can be decomposed to gases and water. Neptunium should be selectively reduced from Np(VI) to Np(V) in the process. Kinetic data were obtained for the reaction by n- and iso-butyraldehydes. Iso-butyraldehyde was found to have higher reaction rate and lower selectivity than n-butyraldehyde. The reaction rate at T=283 to 323° K is described by the following equation:

$-d[Np(VI)]/dt=k\cdot[Np(VI)]\cdot[iso\text{-}C_3H_7CHO]_o\cdot[H^+]$, where $k= 3.1\times10^6\exp(-4.1\times10^3/T)M^{-2}\cdot min^{-1}$. A scheme for the reaction is newly proposed to explain the data.

A chemical flow sheet study was conducted using a miniature mixer-settler of 16 stages. About 90% of Np, which was extracted by 30vol% tri-n-butyl-phosphate/n-dodecane solvent with uranium, was reduced and stripped by 3M HNO_3 aqueous solution containing 3vol% n-butyraldehyde.

1 INTRODUCTION

The control of neptunium ^{237}Np(α-emitter, half life:2.14 x 10^4 y) in the fuel cycle is important to avoid the diffusion of this nuclide in the environment[1]. About 750g of Np per ton of uranium are produced in a thermal nuclear power reactor under the condition of 3.3% enrichment,33,000 MWD/t burn up, 150 days post irradiation decay[2]. Np tends to diffuse in the process of fuel reprocessing due to the extractable tetravalent Np(IV) and hexavalent Np(VI) ions in the system of tri-n-butyl phosphate(TBP) diluted with saturated hydrocarbon diluent(e.g. n-dodecane(nDD)) and nitric acid[3]. Inextractable Np(V) is said to be stable in the dissolver solution of highly concentrated nitrous acid(>10^{-3} M). Major part of Np is oxidized to Np(VI) by nitrous ions in the co-decontamination step and extracted to the organic solvent along with U(VI) and Pu(IV). In the U/Pu partition step, Np(VI) is reduced to Np(IV) or Np(V) by a reductant for Pu(IV) such as hydroxylamine and U(IV). So Np is distributed to the U and the Pu purification cycles. Stripping the Np from the organic solvent before U/Pu partition step is considered to be favourable to avoid the diffusion into the down streams.

A process to separate Np before U/Pu partition step is studied using salt-free reagents which can be decomposed to gases and water for the present study. Np should be reduced from Np(VI) to Np(V) selectively in the presence of U(VI) and Pu(IV) in the process. Preliminary experiment was conducted to compare the reduction rate of Np(VI) by several reagents, aldehydes and alcohols[4]. The results showed that butyraldehyde, which had been proposed as a Np reductive reagent by Kolarik[5], had several advantages of the higher reduction rate and a more favourable redox potential to reduce Np(VI) selectively. Redox potential of butyraldehyde is about 0.8V(vs SCE) at 298° K and 3M HNO_3. The potential is much higher than the standard redox potential of U(VI)/U(IV) system, higher than

that of Pu(IV)/Pu(Ⅲ) system and lower than that of Np(VI)/Np(V) system.

A kinetic study and a chemical flow sheet study were conducted in order to test the feasibility of Np separation using a salt-free butyraldehyde before U/Pu partition. In the kinetic study, fundamental data were obtained on the reduction rate of Np(VI) to Np(V) by n- and iso-butyraldehydes in nitric acid solution. In the chemical flow sheet study, Np separation was demonstrated with a miniature mixer-settler using nitric acid solution containing U and Np.

2 EXPERIMENTAL

Oxide of ^{237}Np purchased from Radiochemical Centre, Amersham, was used for the present study. The NpO_2 was dissolved in 3M nitric acid solution with heating by an IR lamp. The valency was adjusted to Np(VI) by an electrolytic cell with platinum electrodes.

The Np(VI) solution was put into a stirred optical cell with a stopper(light path:1cm) of absorption spectrophotometer. The reaction was started by adding a reductive reagent into the cell. The concentration change of reaction product Np(V) was detected at 983nm, which is the primary absorption peak of Np(V). The amount of reductive reagent was more than ten times the amount stoichiometrically required. The temperature was kept at constant using a thermostat. The reduction rate of Np(VI) in the organic phase of a 30vol%TBP and 70vol%nDD mixture was measured in the same way.

A miniature mixer-settler of 16 stages was operated at room temperature for the chemical flow sheet study. The flow sheet consists of two steps:the U・Np extraction step of 8 stages and the Np/U separation step of 8 stages. Each volume of the mixer and settler is 6 ml and 17 ml, respectively. Simulated feed solution was made by mixing uranyl nitrate solution and the Np(VI) nitrate solution adjusted in the above-mentioned procedure. The solvent of 30vol%TBP/nDD and 3M nitric acid solution containing 3vol% n-butyraldehyde were fed countercurrently into the contactor.

Purchased reagents such as n- and iso-butyraldehydes, TBP and nDD were used without any special pretreatment. Concentrations of U and nitric acid were analysed by alkalimetric titration. A gamma-counter and a spectrophotometer were used to analyse Np concentration. Concentration of Nitrous ion was spectrophotochemically analysed by using chromogenic reagents.

3 RESULTS

3.1. Kinetic study of Np(VI) reduction

Reduction rate of Np(VI) is shown in Fig.1. Np(VI) was reduced by iso-butyraldehyde at several nitric acid solutions in the range of 0.75-6.0M. The reaction began immediately after the addition of butyraldehyde. The reduction rate of iso-butyraldehyde is much higher than that of n-butyraldehyde in the range of the present conditions. The reduction from Np(VI) to Np(V) was completely finished in 3 minutes in the case of iso-butyraldehyde. Np(IV) was not detected by the spectrophotometer in the first 60 minutes. The rate of further reduction from Np(V) to Np(IV), involving the break of Np-O bonds, was measured by less than one fifth the rate of the reduction from Np(VI) to Np(V). This means that butyraldehyde is effective to reduce Np(VI) to Np(V) and to keep the pentavalent state of Np in the separation process.

Figure 1 shows that the reaction rate is first-order in respect of [Np(VI)] under these conditions.

Apparent rate constant k_o is estimated based on the following equation.

$$d[Np(V)]/dt=-d[Np(VI)]/dt=k_o \cdot [Np(VI)], \quad (1)$$

where [Np(VI)] is Np(VI) concentration at the time t. The values of log k_o were arranged as each function of $\log[H^+]_o$ and $\log[C_3H_7CHO]_o$ as shown in Fig.2 and Fig.3, respectively. Sodium nitrate was used to control the ionic strength of the solution. Big differences of log k_o are observed between n- and iso-butyraldehydes. The values of the slope are about 1.0 for both n- and iso-butyraldehydes. From these results, the rate equation is expressed by

$$-d[Np(VI)/dt=k_1 \cdot [Np(VI)] \cdot [C_3H_7CHO]_o \cdot [H^+] \quad (2)$$

The scheme of the reduction reaction of simple metal ion system does not explain the increase of the reduction rate proportional to acidity as shown in Fig.2.

The observed kinetic data can be explained by the following reaction scheme, by analogy with the scheme of the oxidation of butyraldehydes by vanadium(VO_2^+) in acidic media[6].

Enolisation of butyraldehyde

$$C_3H_7CHO \xrightarrow{H^+} C_3H_6CHOH \quad (3)$$

Complex formation between the enol and NpO_2^{2+}

$$C_3H_6CHOH + NpO_2^{2+} \rightarrow (C_3H_6CH\text{-}O\text{-}Np(=O)\text{-}OH)^{2+} \quad (4)$$

Enolisation of the complex

$$(C_3H_6CH\text{-}O\text{-}Np(=O)\text{-}OH)^{2+} + H^+ \rightarrow (C_3H_6CH\text{-}O\text{-}Np\text{-}(OH)_2)^{3+} \quad (5)$$

Decomposition of the complex(rate-determining step)

$$(C_3H_6CH\text{-}O\text{-}Np\text{-}(OH)_2)^{3+} \xrightarrow{slow} \cdot C_3H_6CHO + (HO\text{-}Np\text{-}(OH)_2)^{3+} \quad (6)$$

$$(HO\text{-}Np\text{-}(OH)_2)^{3+} \rightarrow NpO_2^+ + 2H^+ \quad (7)$$

$$\cdot C_3H_6CHO + H_2O \rightarrow C_3H_7COOH + \cdot H \quad (8)$$

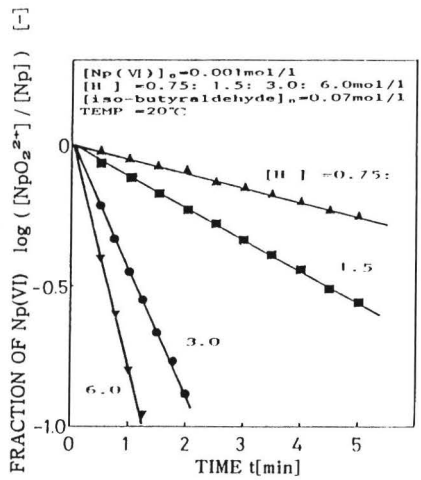


Fig.1 Effect of acidity on the reduction of Np(VI) in aqueous solution by iso-butyraldehyde.

By plotting the logarithm of the rate constant k_1 of Eq.(2) against the inverse of the absolute temperature, the apparent activation energy ΔE of iso-butyraldehyde was estimated to be 34 J/mol, nearly the same as that of n-butyraldehyde. The rate constant of iso-butyraldehyde is much bigger than that of n-butyraldehyde. The big difference of the Np(VI) reduction rates between n- and iso-butyraldehydes is considered to be due to the different steric structure between these butyraldehydes.

The reduction rate is expressed by the equation for each butyraldehyde:

$$-d[Np(VI)]/dt=k_2 \cdot [Np(VI)] \cdot [iso\text{-}C_3H_7CHO]_o \cdot [H^+], \quad (9)$$

$$-d[Np(VI)]/dt=k_3 \cdot [Np(VI)] \cdot [n\text{-}C_3H_7CHO]_o \cdot [H^+], \quad (10)$$

where $k_2=3.1 \times 10^6 \exp(-4.1 \times 10^3/T)$ $M^{-2} \cdot min^{-1}$ and $k_3=7.3 \times 10^3 \exp(-3.4 \times 10^3/T)$ $M^{-2} \cdot min^{-1}$. The reduction rate of Np(VI) by iso-butyraldehyde is nearly equal to the rate of Np(VI) reduction by U(IV) and HAN at the concentration of 0.001M reductive reagent and 3M HNO_3 at 298° K.

Because nitrous ion is known to work as a redox reagent for Np in Purex process, concentration of

nitrous ion was analysed in the aqueous solution for the present experiment. The concentration is in the range of 10^{-6} to 10^{-5} M, very low compared with concentrations of Np and butyraldehydes. So the influence of nitrous ion on Np(VI) reduction rate is considered to be very small. The influence of U(VI) on the Np(VI) reduction rate was also confirmed to be very small by the experiment at the concentration lower than 50g/l and negligible in the Np/U separation step.

In the Np separation step, it is required that only Np(VI) is reduced to Np(V) selectively in the presence of Pu(IV) and U(VI) ions. Possibility of the reduction from Pu(IV) to Pu(Ⅲ) was tested by adding excess amount of butyraldehyde in the 30vol%TBP/nDD-3M HNO_3 binary phase system. Concentration change of Pu in the aqueous phase measured by α-counting is shown in Fig.4. No reduction of Pu(IV) to Pu(Ⅲ) was observed in the case of n-butyraldehyde, however, slow reduction was observed in the case of iso-butyraldehyde. The reduction rate of Pu(IV) by iso-butyraldehyde is lower than that of Np(VI).

The reduction rate of Np(VI) in 30vol% TBP/nDD solvent was measured to be by far lower than in aqueous solution under the same condition. The reduction progresses mainly in the aqueous phase.

Experiment was conducted to measure the off-gas composition of decomposed butyraldehydes in nitric acid solution. More than 90% of iso-butyraldehyde in the nitric acid solution was decomposed in less than 60 minutes by bubbling air. About 90% of decomposition products was gases: CO_2, CO, C_3H_8 and C_3H_6. The rest was relatively stable organic compounds which could be decomposed by electrolysis.

3.2. Chemical flow sheet study on Np separation process

A flow sheet as shown in Fig.5 was studied to test the feasibility of Np separation using n-butyraldehyde in the first cycle. The reductant has the higher selectivity but lower reaction rate of Np(VI) reduction than iso-butyraldehyde.

Concentrations of U, Np and nitric acid are shown in Fig.5. The simulated feed solution containing U(VI) by 200g/l, Np by 78mg/l and 3.1 M nitric acid is fed at stage 8 of the miniature mixer-settler. The valency of Np in the feed solution was analysed to be Np(V) by 20% and Np(VI) by 80%. The 30vol%TBP/nDD solvent is fed at stage 1. The Np scrub solution of 3.0vol% n-butyraldehyde in 3.1M nitric acid is fed at stage 16. The Np product stream leaves the contactor from stage 9. Each flow ratio (O/A) of solvent to aqueous solution is 1.7 in the U・Np extraction step and 4.6 in the Np/U separation step. The O/A ratio of U・Np extraction step was determined to obtain high U loading in the organic stream. The solvent was actually loaded by 100g-U/l in the U・Np extraction step and left the process from stage 16 at a concentration of 99.3g-U/l. About 6% of U loaded in the U・Np extraction step was stripped by the scrub solution in the following Np/U separation step. This indicates that a certain amount of Pu must be stripped by the scrub solution along with U and Np in the real case of U-Pu-Np system, according to the distribution equilibrium of Pu. The loss of U and Pu cannot be neglected. So a recovery step of U and Pu from the Np product solution should be followed in order to obtain a purified Np target for production of ^{238}Pu by neutron irradiation. About 90% of Np fed into the process was scrubbed as the Np product in the Np/U separation step. About 3% of Np leaked to the raffinate. Approximately 85% of the Np(V) in the feed solution seems to be oxidized by nitrous ion in the U・Np extraction step, while 15% of the Np(V) left to the raffinate.

Separation factor of Np in the process was about 13.5, where the separation factor is defined as the concentration ratio of Np to U in the feed solution at stage 8 divided by the Np to U ratio in the Np product solution at stage 9. The separation factor can be improved by optimizing the process condition: concentrations of n- and iso- butyraldehydes and nitric acid, temperature, residence time and the number of stages. The leak of Np into the raffinate can be reduced by adding nitrous acid to oxidize more Np(V) to Np(VI) in the U・Np extraction step.

Distribution data of butyraldehydes were measured as a function of TBP concentration in the range of 0-60 vol% at 3M HNO_3 in aqueous phase at 298° K. Distribution ratio increases in proportion to TBP concentration for both butyraldehydes. The slope of the extraction curve is about 2. These data are in favor of the following extraction formula:

$$C_3H_7CHO_{Aq.} + 2TBP_{Org.} \rightarrow C_3H_7CHO \cdot 2TBP_{Org.} \quad (11)$$

This means that most of n-butyraldehyde fed into the process at stage 16 was extracted and left with the solvent. Butyraldehydes should be fed into the U loading solvent at stage 9 instead of stage 16 in order to be contacted effectively with Np(VI).

4 CONCLUSIONS

A neptunium separation process from the product organic stream of co-decontamination step was studied using salt-free reagents which can be decomposed to gases and water. Kinetic data were obtained for the Np(VI) reduction to Np(V) by the proposed n- and iso-butyraldehydes as reductants.

A scheme for the reaction is newly proposed to explain the data. Iso- butyraldehyde was found to have a higher reaction rate and lower selectivity than n-butyraldehyde. Equations to estimate the reaction rate were proposed for n- and iso-butyraldehydes.

A chemical flow sheet study was conducted using a miniature mixer-settler of 16 stages. About 90% of Np extracted in the product stream along with uranium was separated from U by 3M HNO_3 aqueous solution containing 3vol%n-butyraldehyde. About 6% of U fed into the process was scrubbed into the Np product.

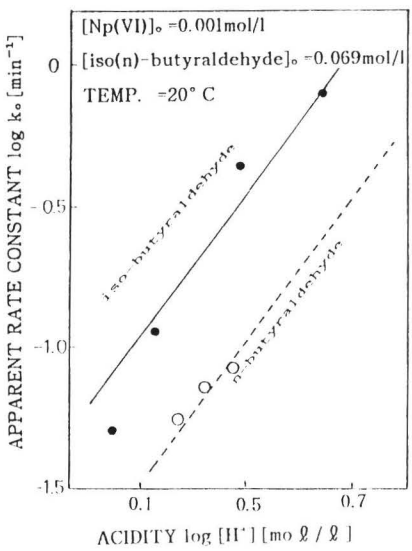


Fig.2 Variation of apparent first order rate constant with acidity.

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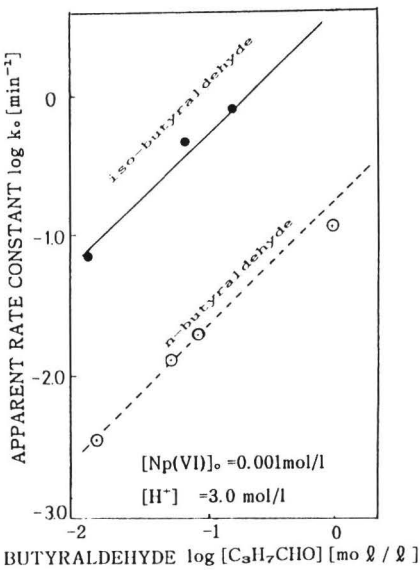


Fig.3 Variation of apparent first order rate constant with butyraldehyde.

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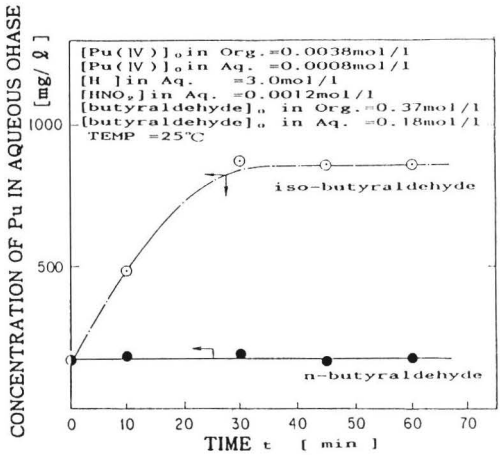
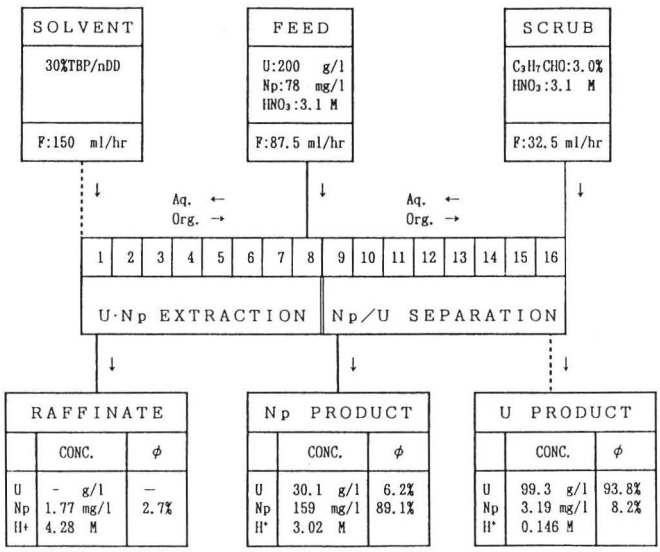


Fig.4 Time dependence of concentration of Pu in aqueous phase with reduction reaction of Pu(IV) by butyraldehydes.



φ[%]:Fraction of U and Np distributed to U and Np products and the raffinate.

Fig.5 Distribution data of Np, U and HNO_3 in the chemical flowsheet study.

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A Study on the Interfacial CRUD Formation in the Purex Process.

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ABSTRACT

A.IDEGAMI ,H.SUGAI ,C.TANAKA ,M.OZAWA* ,Y.KISHIMOTO* ,S.HAYASHI* SMM. , *PNC. A Study on the Interfacial CRUD Formation in the Purex Process.

In this study , more fundamental experiments and quantitative discussion on the crud using mainly platinum group elements (Pd etc.) have been carried out. The roles of the fine dispersed metal particles on the crud formation and the properties of crud stability are discussed.

1 INTRODUCTION

In the Purex process of solvent extraction for reprocessing spent nuclear fuels , an operational disturbance is caused by the formation of the third phase. We usually call it "crud". It tends to be accumulated at the interface between the aqueous phase and the organic phase.

In order to examine the origin of the crud , many studies have already been done. Some of them resulted in an adsorption of residual fine particles (Baetsle et al.,1974; Boudry et al.,1974; Gonda et al.,1982), others a chemical interaction giving rise to precipitates which cause the crud formation.(Huppert et al.,1974; Zimmer et al.,1984)

In this study , fundamental experiments and quantitative discussion using mainly platinum group elements (Pd etc.) have been carried out. The roles of the fine dispersed metal particles on the crud formation and the properties of stabilities are discussed.

2 EXPERIMENTAL

2.1 Materials

Using dispersed elements were two types of Pd (mean diameter: 0.2 μm , 0.8 μm) , Ru (16.4 μm) , two types of Al_2O_3 (2.1 μm ,44.7 μm) and simulated insoluble residues (3.1 μm , composition Ru:60.5w% , Mo:18.5w% , Rh:9.87w% , Pd:10.6w%)

2.2 Procedures

The organic phase was 30 vol% TBP diluted by n-dodecane. The aqueous phase were prepared by adding fine solids into an aqueous HNO_3 solution with required concentration. Those solids were dispersed by ultrasonic wave about ten minutes before shaking. The solution which consisted of aqueous phase (50cc) and organic phase (50cc) was vigorously shook for ten minutes. After shaking the mixture was kept standing in a measuring cylinder and emulsion thickness was measured with time.

3 RESULTS AND DISCUSSION

3.1. Crud formation tests

(i) Boundary concentration. In order to survey the boundary concentration of fine dispersed solids in the water phase for stabilizing emulsion , various systems of component and concentration have been done.

Figure 1 shows the change of emulsion thickness with time by metal (Pd) concentration. Average particle size of palladium is 0.8 μm and aqueous HNO_3 concentration is adjusted at 3M before shaking. The higher the palladium particle concentration is, the more delayable the coalescence is observed. When the palladium concentration is higher than 5g/l , stabilized emulsion is observed. Those emulsion are stable after several hours. The results of other components are similar except Al_2O_3.

Table 1 shows that various solids have the boundary concentration for stabilizing emulsion. It exceeds approximately 5g/l in the water phase. Those emulsion observed in this study are considered to be the oil in water (O/W) type from dyeing method except Al_2O_3. This emulsion type conforms well to the experience obtained in the reprocessing plant.(Gonda et al.,1982)

Under the boundary concentration (5g/l), the emulsion is not stabilized but the delay of coalescence is observed.

(ii) Particle size. Figure 2 shows the change of emulsion thickness with time by metal particle sizes (Pd: 0.2 μm ,0.8 μm). The emulsion of fine particle (0.2 μm) is more stable than that of another one (0.8 μm). It is considered that when the metal particle concentration is the same , the finer the dispersed solid is , the more stable the emulsion forms. When the particle concentration is near the boundary concentration, this property is remarkable.

TABLE 1

Boundary concentration of metal particles for stabilizing emulsions.

component	perticle size(μm)	concentration (g/l)	crud type	crud formation
Pd.	0.2	> 5	O/W	stable crud
		5 > Pd. > 1		unstable crud
	0.8	1 >		no crud
Ru.	16.4	> 5	O/W	stable crud
		5 > Ru. > 1		unstable crud
		1 >		no crud
Al.	2.1,44.7	1 ~ 10	W/O	no crud
simulated insoluble residues (Ru,Mo,Rh, Pd)	3.1	3 ~ 5	O/W	stable crud
		3~5> alloy >1		unstable crud
		1 >		no crud

(iii) HNO_3 concentration. Figure 3 shows the effect of HNO_3 concentration in the aqueous phase. The lower the HNO_3 concentration is , the more stable the emulsion forms. In the case of HNO_3 concentration is free , the most stable emulsion forms in this study. It is suggested that the large electrolytic dissociation in the water phase prevents the formation of crud.

(iv) Uranium containing. These experiments have been done in the systems without and with uranium. Figure 4 shows the effect of uranium contained on the crud formation. Uranium concentration is similar to feed solution in the codecontamination step in the Purex process. The metal dispersed particles are also simulated the insoluble residues. The boundary concentration of stabilized emulsion is almost the same , but the volume is tend to be increased by uranium containing. It means that the higher the viscosity of continuous phase which is the water phase in O/W emulsion is , the more stable the emulsion forms.

3.2 Prevention tests and demulsification test

Table 2 shows the results of prevention tests and demulsification test.

(i) Prevention tests. In this study various methods of crud prevention have been done. The most effective method is control of metal particle concentration in the feed aqueous phase by filtration. At three filter conditions (0.1μm , 1.0μm , 5.0μm) there is no crud formation.

Figure 5 shows that the volume of stabilized emulsion is reduced by the addition of reforming liquid (2-ethylhexanol). The adding volume is 20 vol% for organic phase.

(ii) Demulsification test. In order to break the stabilized emulsion, the electrochemical treatment is carried out. D.C. 20 KV of 100 Hz is applied between two electrodes about ten minutes. In this test demulsification of emulsion is observed, but the amount is a little.

TABLE 2

Results of the prevention tests and demulsification tests.

methods	condition	component	crud formation
filtration	filter condition 0.1 1.0 μm 5.0	Pd. 0.2μm 5 g/l	no crud
heating	temperature 50 75 ℃	Pd. 0.2μm 10 g/l	reduced the amount of crud
velocity of stirring	200 ~ 400 rpm	Pd. 0.2μm 5 g/l	stable crud
reforming liquid	1 ~ 10 (for organic phase)	simulated insolble residues 3.1μm 5 g/l	reduced the amount of crud (about 1/2)
electric treatment	20 KV 100 Hz	Pd. 0.2μm 10 g/l	no effect

4 CONCLUSION

The major conclusions drawn from this study are following :

(1) The boundary concentration of metal particles for stabilizing emulsion exceeds approximately 5g/l in the water phase. And when the concentration is lower than 5g/l the emulsion is not stabilized but the delay of coalescence is observed.

(2) The finer the dispersed solid and the lower the HNO_3 concentration are, the more stable the emulsion forms.

(3) In the system of uranium containing, the emulsion is more stable than that of uranium free.

(4) For prevention tests of the stabilized emulsion, it is confirmed that the control of metal particle concentration is effective.

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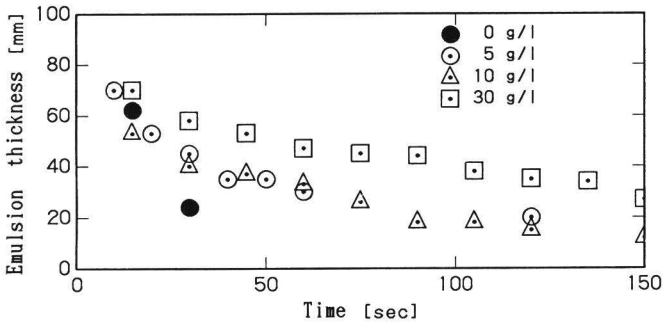


Fig.1 Change of emulsion thickness with time by metal particles (Pd.) concentration. (particle size 0.8 μm HNO3 3N)

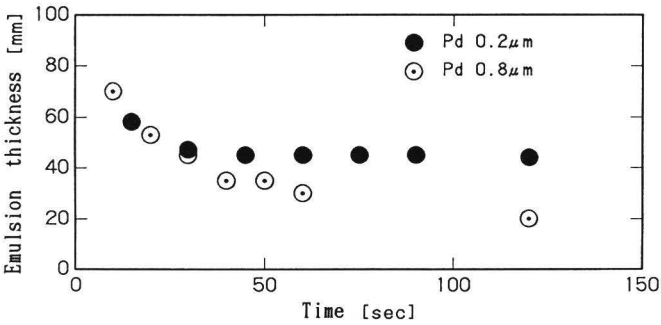


Fig.2 Change of emulsion thickness with time by metal particle size. (Pd. 5g/l , HNO3 3N)

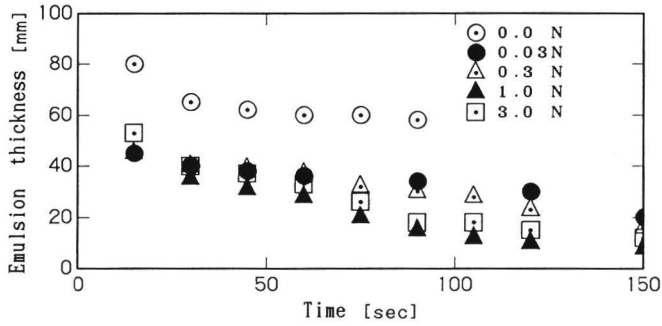


Fig.3 Change of emulsion thickness with time by HNO3 concentration. (Pd. 10g/l , particle size 0.8 μm)

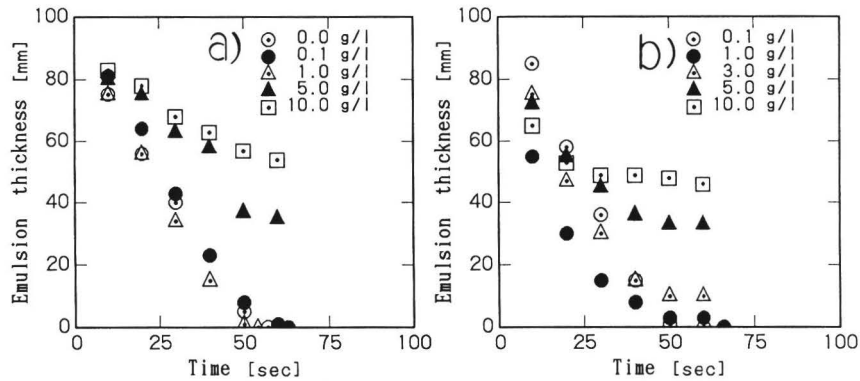


Fig.4 The effect of uranium containing on the crud formation. a:U 208.9g/l b: U free (simulated insoluble residues , HNO3 3N)

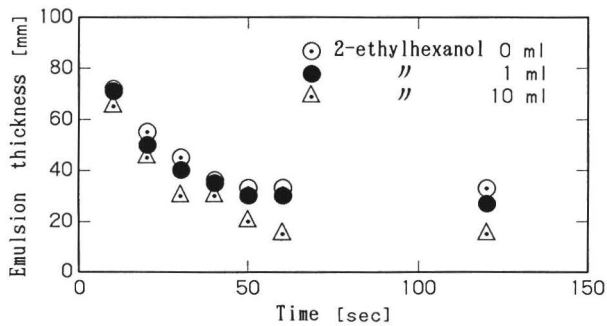


Fig.5 The effect of reforming liquid for the crud prevention. (simulated insoluble residues 5g/l HNO3 3N)

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STUDY ON HYDRODYNAMICS OF PULSED PLATE COLUMNS BY COMPUTER CODE DYNAC

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ABSTRACT

Empirical correlations of axial mixing, mean size and travel velocity of droplet swarms in pulsed plate columns were incorporated into a computer model DYNAC. This model is provided with a sub-model to describe the dynamic variations of droplet holdup profile during hydrodynamic transients. Good agreement has been attained between experimental and simulated fraction of droplet holdup during steady and transient operations. The role of in-process variables is discussed, and the profiles of solutes and temperature under ordinary and off-standard conditions are also presented.

1 INTRODUCTION

Pulsed counter-current differential extractors have been generally applied to the Purex processes in the reprocessing of the irradiated nuclear fuels. In this type of contactors, the hydrodynamic variables have great influence on the fluid residence and mass transfer. Moreover, the hydrodynamics and chemical kinetics have complex interactions between them. Thus,the knowledge of the internal physical phenomena is essential to estimate the column performance. The present paper describes the hydrodynamics and chemical kinetics in the Purex pulsed columns. Subsequently, the applicability of the numerical model to the analysis of the pulsed columns is discussed.

2 DESCRIPTION OF DYNAC

The simulation model DYNAC(Nabeshima and Tanaka,1989) has been developed to predict the detailed behavior of an entire Purex solvent extraction cycle composed of pulsed columns. This code has been provided with various correlations of the hydrodynamic process variables. The mean size of droplets(d_{32}) is expressed by a function of pulse agitation and plate geometry. The principal features of the hydrodynamic model are described in the following sections.

2.1 Hydrodynamics

(i) Longitudinal mixing. The liquid flow inside the pulsed columns deviates from the ideal plug-flow by the liquid re-mixing

which reduces the concentration gradients of solutes along a column. Thus, the mixing changes strongly the residence time distribution of the fluid, even when the apparent holdup fraction remained unchanged. The longitudinal mixing ratio(q) is formulated by the pulse amplitude(a), frequency(f), column diameter(D_c) and the local values of the in-process variables, i.e. the holdup fraction(ϕ) and the superficial velocity(F) of the fluid:

$$q = 0.248 \{1 - 15\exp(-D_c)\} a^{0.304} f^{0.162} \phi / F^{1.51}, \quad (1)$$

(ii) Droplet residence. The settling velocity of drop swarms changes the holdup fraction directly. Hence, both the throughput capacity and extraction efficiency are greatly influenced by the hydrodynamic variables through the variation of the fluid residence time distribution and interphase contact area.

In most of the previous study, the droplet holdup fraction was expressed by a function of the operating variables, the column geometry,and the liquid physical properties. In addition, neither the axial distribution nor its time-dependent variation was considered. The slip velocity however makes it possible to convert the settling velocity into the holdup of droplets and vice versa. Eq.(2) makes it possible to compute the holdup from the pulsation intensity (P), the plate number (N_p) and the local values of the process quantities, i.e. the superficial velocity of the liquids and the holdup fraction of the droplets.

$$V = k \exp\{ -0.150(P - 1.0)^2 \} (1-\phi_d)^{1.2} \xi^{-0.317} \{1 + \exp(-0.060N_p)\}, \quad (2)$$

k=5.23(aqu. phase cont.), 3.83(org. phase cont.),

$\xi = \eta_d / \eta_c$,

$$\eta_c = \eta_{c,o}\{1 + 2.5\phi \left(\frac{\xi_o + 2/5}{\xi_o + 1} \right)\}, \quad \phi = \phi_d/(1-\phi_d).$$

The prediction accuracy of the droplet holdup has been significantly improved by introducing the viscosity ratio($\xi = \eta_d / \eta_c$,) into the settling velocity. Thus the selection of the continuous and dispersed phase affects the droplet holdup.

2.2 Transfer kinetics

The transfer kinetics the other integral part of the understanding of the column behavior. The distribution coefficient controls the limiting extent of the interphase solute transfer. This factor is expressed by the empirical function of the total nitrate concentration in the acid phase and temperature.

On the other hand, the mass transfer coefficients control the rate of the transport. The empirical expression(Petrich,1980) has been confirmed useful to estimate the overall transfer coeffi-

cients of U(IV), U(VI) and Pu(IV), since the expression implies the contribution of not only the chemical kinetics but also the eddy diffusion.

3 FUNDAMENTAL MODEL EQUATIONS

The backflow and dispersion models have been shown equivalent in a certain occasion, however, the stagewise model expresses the longitudinal mixing as the exchange of bulk fluids between neighboring stages. Thus the non-uniform distribution of droplets along the column height causes the liquid mixing. Hence, the liquid flow inside the contactor can be described appropriately, particularly during hydrodynamic transients. In the DYNAC,most of the in-process variables are varied along the column axis.

The axial profiles of the droplet holdup and its dynamic variations are established by applying all the hydrodynamic correlations and the physical properties of the liquids to a set of balance equations. The volumetric holdup of the droplets in a typical stage(i) under solvent continuous mode is described by the following differential equation:

$$\frac{dH_i}{dt} = A_{f,i} + A_{i-1} - A_i + A_{b,i-1} - 2A_{b,i} + A_{b,i+1} - A_{b,i}, \quad (3)$$

A, A_b and A_f are the volumetric flow rate of the aqueous main, inter-stage and feed streams, respectively. The inter-stage mixing is assumed to be zero at the two end stages, where the top and bottom settlers are placed. These decanters have also been modeled by a series of complete mixing cells. Equation(3) can be applied to the operation in the aqueous phase continuous mode by replacing the variables.

The balance of the solutes in each stage is expressed likewise including the terms of the solute transfer kinetics and Redox reactions of uranium and plutonium involved. Furthermore, the heat balance is obtained by the summation of the fluid convection between neighboring stages, the generation of the extraction enthalpy, and the radiation losses to the environment. The longitudinal profiles of the fluid density and viscosity are also computed using the solute concentration and temperature.

4 PULSED COLUMN BEHAVIOR

4.1 Fluid residence behavior

Small-sized extraction(HA) and scrub(HS) columns were operated to confirm the numerical prediction using HNO_3-U(VI)-30%TBP/n-dodecane. The steady-state values of the experimental holdup fraction of droplets agreed satisfactorily with the prediction within a few percent difference(Fig. 1). The increase of the feed flow rate of the dispersed phase increased its fraction almost

linearly. Furthermore, both predicted and measured values have a same trend to increase consistently with the continuous phase flow rate. This phenomenon is due to the hindering action of the continuous phase to hold back the settling drops.

The predicted step-response in start-up also agreed well with the experimental data with respect to the time required for the drops to travel through the column and to the steady-state droplet fraction. In addition, the temporary increase of the droplet amount in the initial period was also reproduced numerically. Hence, the DYNAC has been proved effective to analyze the residence characteristics of fluids during steady and transient operations.

4.2 Solute transfer behavior

The HA-HS column connection was first operated under the base conditions(Table 1 and Fig. 2). After the system reached steady operation, the flow rate of the HAF inlet stream was increased stepwise first by 15% and followed by 26%. Figure 3 demonstrates an excellent agreement between the computed and measured profiles of solutes and temperature.

The temperature profile is important in the prediction of the extractor performance, since the distribution and transfer rates are affected by temperature and vice versa. Under the base condition, temperature peak(38°C) appeared at about 1.0 m below the HA column top. By the 15% increase of the HAF inlet stream, both the profiles of U(VI) and temperature shifted downward by 0.5 m. At the same time, the maximum temperature increased by 5 degrees. This is because that the transfer flux of U(VI) was increased and the outflow of heat was reduced: the high temperature zone descended to the middle of the HA column. Further increase of the HAF by 26% led to the intensive accumulation of U(VI) in the HA-HS contactors.

TABLE 1

Equipment geometry of HA-HS pulsed columns.

Column	
Effective height	3 m (HA), 2 m (HS)
Diameter	3.5 cm
Internals	Sieve plates
Perforation diameter	0.3 cm
Fractional free area	0.23
Plate spacing	5.0 cm
Pulse intensity	1.66 cm/s
Continuous phase	Organic

4.3 Effects of hydrodynamics on mass transfer

It was demonstrated numerically that the droplet velocity and axial mixing influence the uranium mass transfer significantly: the former is due to the change of the droplet holdup fraction,

and the latter due to that of the convective re-mixing of fluids. Thus the importance of these variables are apparent in the prediction of solute profiles.

5 CONCLUSIONS

The computer simulation model DYNAC has reproduced successfully the dynamic variation of the longitudinal profiles of the dispersed phase holdup during steady and transient operations. Besides, the axial profiles of the solutes and temperature were in good agreement with the experimental data under both ordinary and off-standard conditions.

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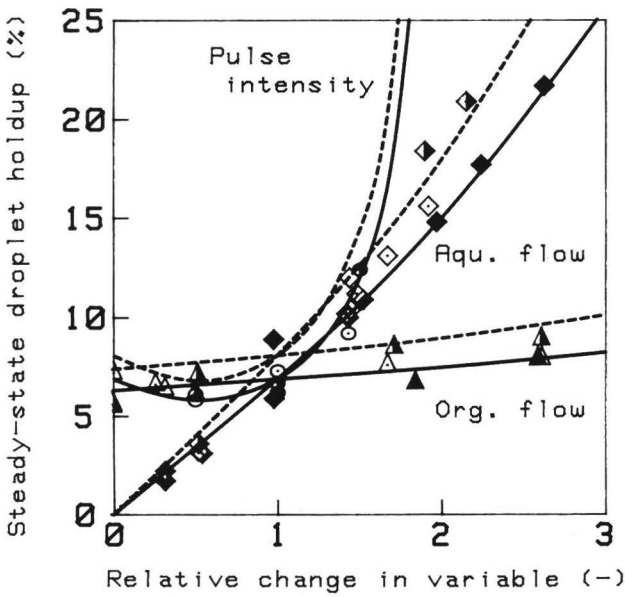


Fig. 1. Comparison between measured and predicted values of steady-state droplet holdup for organic phase continuous operation with sieve-plate column. Open, half-closed and closed keys denote U(VI) concentration of 0, 40 and 80 g/l, respectively.

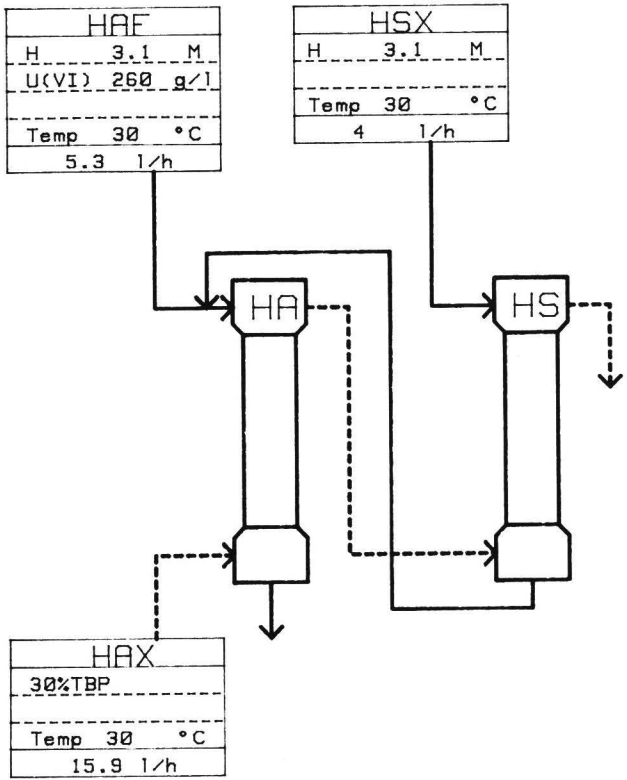


Fig. 2. Standard operating conditions. (Environmental temp.: 17.3 °C)

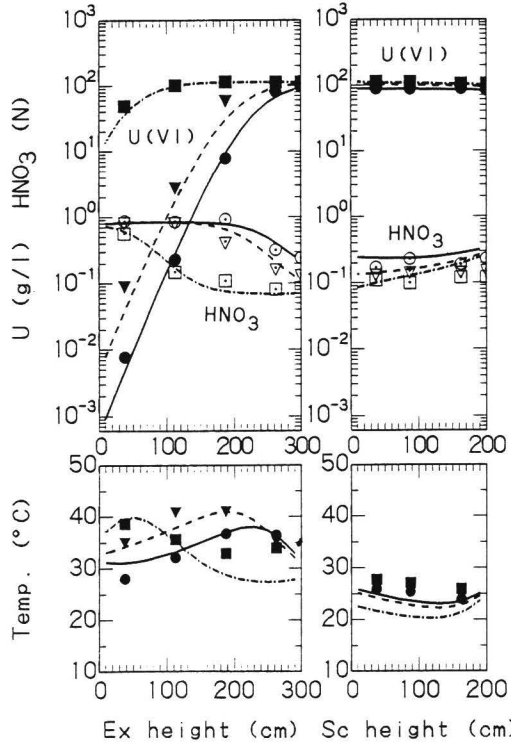


Fig. 3. Comparison between predicted and measured profiles of U(VI) and HNO_3 concentration along HA-HS columns under base and off-standard conditions (Circles, triangles and squares denote values under base, 15% and 26% increase of of HAF flow rate, respectively.)

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REACTION MODEL FOR THE EXTRACTION OF URANIUM (VI) FROM NITRIC ACID AND HYDROCHLORIC ACID SOLUTIONS WITH BIS(2-ETHYLHEXYL) PHOSPHORIC ACID

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ABSTRACT
Extractions of uranium(VI) from nitric acid and hydrochloric acid (both denoted as HA) solutions with Bis(2-ethylhexyl)phosphoric acid (denoted as HR) show a downward and then an upward variations of the uranium(VI) distribution ratio, D_u, with the increasing acidity of the aqueous phase. A reaction model comprising the ion-exchange reaction froming UO_2R_2 and the solvation reaction forming $(UO_2R_2)_r(HR)_2(HA)_s$, with values of r and s depend on U(VI) loading and acidity, was proposed to elucidate the equilibrium behavior consistently. The upward variation of D_u with the increasing acidity was elucidated with the solvation reaction between $UO_2R_2(HR)_2$ and HA. This reaction is insignificant at low acidity, but it is important at high acidity. The HA solvated product was verified evidently with proton NMR technique.

1 Introduction

Extractions of uranium(VI) from nitric acid solutions with bis(2-ethylhexyl)phosphoric acid , HDEHP, has peculiar equilibrium behaviors as shown in Fig. 1. At low acidity, the distribution ratio of uranium(VI), D_u, decreases with the increasing acidity of the aqueous phase, then, turns to increase with the acidity at the moderate high range, and drops again at the vicinity range of saturated acidity. Variations of D_u with the aqueous phase acidity in the HDEHP-U(VI)-HCl extraction system is shown in Fig. 2, which shows a similiar pattern as that of Fig.1, except that the concave extreme is located at higher acidity and no more downward variation of D_u with the aqueous phase acidity is observed at the vicinity range of saturated acidity.

Previous studies found that the extraction reaction occurring at low acidity can be adequately described as

$$UO_2^{2+} + \overline{H_2R_2} = \overline{UO_2R_2} + 2H^+ \qquad (1)$$

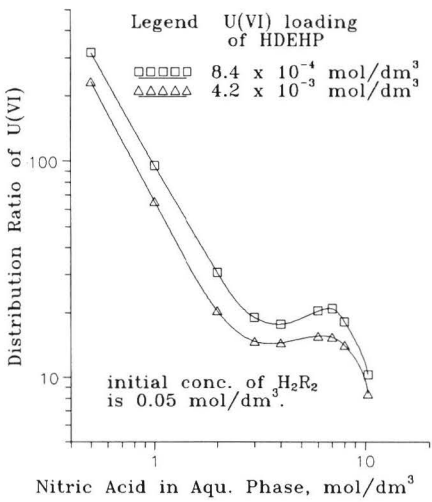


Fig. 1 Variations of D_u with C_{HNO_3} under different U(VI) loadings of HDEHP.

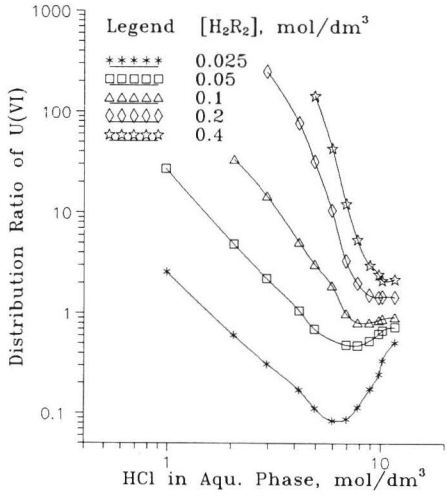


Fig. 2 Variations of D_U with C_{HCl} under various initial concentrations of HDEHP.

Where the upperbars denote organic species. In the presence of excess HDEHP, $\overline{UO_2R_2}$ is solvated by $\overline{H_2R_2}$ as follows:

$$\overline{UO_2R_2} + \overline{H_2R_2} = \overline{UO_2R_2(HR)_2} \quad (2)$$

Several models were proposed to describe the reaction occurring at high acidity. The solvation model by Sato (1963) was similiar to the solvation reaction between TBP and uranyl nitrate, it was expressed as

$$UO_2^{2+} + 2\,NO_3^- + \overline{H_2R_2} = \overline{UO_2(NO_3)_2(HR)_2} \quad (3)$$

This model was inconsistent with the experimental result of Rozen et al. (1971), who showed that the distribution ratio of uranium(VI) is not proportional to the second power of the concentration of nitrate ion in the aqueous phase. An ion exchange-solvation model was proposed by Rozen et al. as

$$UO_2^{2+} + NO_3^- + 2\,\overline{H_2R_2} = \overline{UO_2NO_3(HR_2)(HR)_2} + H^+ \quad (4)$$

This model was inconsistent with that observed by Huang and Huang (1987), who showed that all the nitrate ligand in the uranium(VI)-loaded HDEHP is that of nitric acid using the proton NMR technique, and that the product formed in the absence of nitric acid contains no nitrate ligand, regardless of the presence of other nitrate in the aqueous phase. A model including ion exchange

reaction forming $\overline{UO_2R_2}$ and the solvation of $\overline{UO_2R_2}$ by HDEHP and HNO_3 was proposed by Huang and Huang (1987), i.e.

$$UO_2^{2+} + 2\,\overline{H_2R_2} + HNO_3 = \overline{UO_2R_2(HR)_2(HNO_3)} + 2\,H^+ \quad (5)$$

$$2\,UO_2^{2+} + 2\,\overline{H_2R_2} + HNO_3 = \overline{(UO_2R_2)_2(HNO_3)} + 2\,H^+ \quad (6)$$

$$UO_2^{2+} + \overline{H_2R_2} + 2\,HNO_3 = \overline{UO_2R_2(HNO_3)_2} + 2\,H^+ \quad (7)$$

The extent to which these reactions proceed depends on the concentrations of uranyl nitrate and nitric acid in the aqueous phase. Reactions (5) and (6) are important for low and high uranium(VI) loadings, respectively, as the concentration of nitric acid in the aqueous phase exceeds 1 mol/dm^3; reaction (7) is responsible for the complete saturation of uranium(VI) and nitric acid in HDEHP. This model describes the equilibrium behavior consistently. Kinetics of the extraction was also elaborated (Huang and Huang, 1988) according to this model. In the present paper, principles of the model are used to elucidate the equilibrium behavior of the extraction from hydrochloric acid.

2 Experimental

2.1 Reagents

HDEHP used is a product of Mobile Oil Co., U.S.A., it was purified following the method described by McDowell et al. (1976). CCl_4 used as the diluent of HDEHP is a GR grade reagent of E. Merck Co.; Uranyl chloride was prepared by dissolving uranium trioxide of high purity in hydrochloric acid and recrystallizing.

2.2 Measurements

Equilibra of uranium(VI) and hydrochloric acid between phases were performed by stirring CCl_4 solutions of HDEHP and aqueous solutions containing various concentrations of uranyl chloride and hydrochloric acid in beakers for at least 30 min at 25 $\pm$ 0.2°C, then, the phases were separated by centrifuging. Concentrations of uranium(VI) and HCl in the aqueous and organic phases were determined with the procedures described by Huang and Huang (1987). Hydrogen NMR spectra of the organic phase were recorded with a Bruker NMR spectrometer having a max. frequency of 300 MHz.

3 RESULTS AND DISCUSSIONS

3.1 Effects of the aqueous phase acidity

In the HCl-UO_2Cl_2-HDEHP extraction system, as shown in Fig. 2,

the value of D_u is disproportional to the second power of the aqueous phase acidity at low HDEHP concentration and low aqueous phase acidity, indicating that the reaction occurring at these conditions is consistent with eq (1). The upward variation of D_u with the aqueous phase acidity occurs at where the aqueous phase contains 6 to 10 mol/dm^3 HCl depends on the concentration of HDEHP. According to the model, the following solvation reaction is responsible for this variation, i.e.

$$UO_2^{2+} + n\ HCl + 2\ \overline{H_2R_2} = \overline{UO_2R_2(HR)_2(HCl)_n} + 2\ H^+ \qquad (8)$$

The solvated hydrochloric acid can be easily removed from the organic phase by washing with water and can be titrated readily. The solvated HCl thus determined includes that resulted from the reaction

$$2\ HCl + p\ \overline{H_2R_2} = 2\ \overline{(HR)_p(HCl)} \qquad (9)$$

where p was found to be 1-3 (Zelikman and Nerezov, 1967). The value of n can thus be determined from the molar ratio of the solvated HCl to uranium(VI) in the organic phase, provided that reaction (8) is dominant. As shown in Fig. 3, when the extraction was done with an

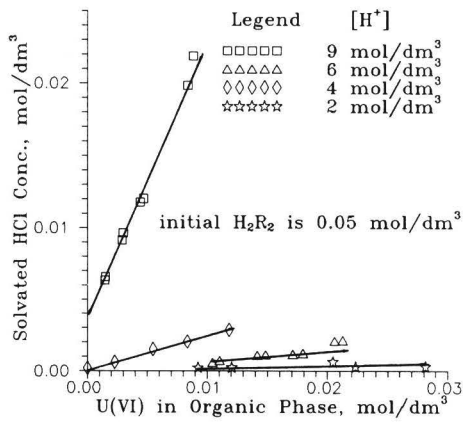


Fig. 3 Uranium(VI) Conc. vs. Solvated HCl Conc. in Organic Phase under various Aqueous Phase Acidity.

aqueous phase containing 9 mol/dm^3 HCl, this molar ratio was found to be 2. Because reaction (8) is dominant at this acidity, it is suggested that the value of n equals 2. According to the law of mass action, reaction (8) gives the expression of D_u as

$$D_u = K\Gamma_{UCl}^{3}[Cl^-][\overline{H_2R_2}]^2/\{\Gamma_{HCl}^{2}[H^+]\} \quad (10)$$

where Γ_{UCl} and Γ_{HCl} are the mean activity coefficients of uranyl chloride and hydrochloric acid in the aqueous phase, respectively; K is the product of the equilibrium constant and the activity coefficients of the organic species involved. Since that $[Cl^-]=[H^+]$ and the ratio of Γ_{UCl} to Γ_{HCl} is nearly constant for dilute solutions of uranyl chloride, so, eq. (10) calls for D_u to be proportional to Γ_{UCl} under constant concentration of HDEHP. Because Γ_{UCl} increases with the concentration of HCl, consequently, D_u increases with the acidity of the aqueous phase while reaction (8) is dominant. As the aqueous phase contains < 6 mol/dm^3 HCl, Fig. 3 shows that the solvated HCl is almost independent of the concentration of uranium(VI) in the organic phase. This is in agreement with the principle of the present model, i.e, the upward variation of D_u with the aqueous phase acidity is due to reaction (8). Accordingly, the slopes of the lines in Fig. 3 indicate the importance of reaction (8).

3.2 Effects of the concentrations of HDEHP and U(VI)

The strong effect of the concentration of HDEHP on D_u can be observed from Fig. 2. The higher the concentration of HDEHP used, the higher the inverse order of D_u with respect to the aqueous phase acidity obtained at low acidity. Higher inverse order than the second was found in the figure for the extraction with organic phases containing dimeric HDEHP more than 0.1 mol/dm^3. It was observed in the experiment that the viscosity of the organic phase increases with the concentration of HDEHP, indicating that the extent of polymerization of the U(VI)-HDEHP complex increases with its concentration. The polymerization reaction of the complex is

$$m\ UO_2^{2+} + m\ \overline{H_2R_2} = \overline{(UO_2R_2)_m} + 2m\ H^+ \quad (11)$$

this reaction calls for the value of D_u to be inversely proportional to the 2m-th power of $[H^+]$ in the aqueous phase. As shown in Fig. 2, the value of m depneding on the concentration of the U(VI)-HDEHP complex is larger than 1, for the extraction with the organic phase containing dimeric HDEHP more than 0.1 mol/dm^3. The degree of polymerization of the U(VI) complex is obviously much higher than that obtained from the extraction from nitric acid solution. This is due to that nitric acid has higher solvation power than hydrochloric acid with HDEHP, thus, the organic phase obtained in the extraction from nitric acid solution contains more solvated nitric acid, which

has high polarity, and thus polymerization is obstructed. Reaction (8) is depressed by reaction (11) and vanishes gradually with the increase of the degree of polymerization, and so does the upward variation of D_u with the aqueous phase acidity as being shown in Fig. 2.

3.3 NMR measurements

The proton NMR spectra of the organic phase in the extractrion from both solutions were measured. In the U(VI)-HDEHP-HNO_3 extraction system, two proton resonance peaks representing the presence of the solvated HNO_3 were found, i.e., a downfield peak represents the presence of the solvated nitric acid in the complexes such as $\overline{HR(HNO_3)}$ and $\overline{UO_2R_2(HR)_2(HNO_3)}$, and an upfield peak indicates solvated nitric acid in the complexes such as $\overline{UO_2R_2(HNO_3)}$ and $\overline{UO_2R_2(HNO_3)_2}$. The total proton integral intensity of these two peaks increases with the total concentration of the solvated nitric acid in the organic phase, indicating that the NMR behavior is consistent with the proposed model. In the U(VI)-HDEHP-HCl extraction system, the resulting products including $\overline{(HR)_p(HCl)}$ and $\overline{UO_2R_2(H_2R_2)(HCl)_2}$ contain only outer-sphere solvated HCl molecules, which gave only one proton resonance peak. This peak is also assigned to the resonance of the hydroxyl hydrogen of HDEHP, for its intensity also increases with the concentration of the hydroxyl hydrogen. The intensity of this peak is not affected by reaction (8), because the total concentration of the proton represented by the peak, including those in the solvated HCl and that in the hydroxyl group of HDEHP, is constant during the occurrence of reaction (8).

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STUDY ON ACCUMULATION OF U(IV) IN EXTRACTION-SCRUB COLUMNS OF 30 VOL% TBP-n·DODECANE-U(VI)-HNO_3 SYSTEM

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ABSTRACT

An accumulation behavior of U(IV) was studied for the Purex co-decontamination cycle under the standard and off-standard flowsheet conditions. The experiments were carried out with two small pulsed columns. In an attempt to simulate the transient behavior of the solutes in the pulsed columns, an equilibrium stage model, EXTRA-M code, was modified to fit the experimental results of the pulsed columns. The fitting parameters were holdup, stage numbers, and distribution coefficients in EXTRA-M code. A good agreement between the experiments and the calculation was achieved by the fitting procedures.

1 INTRODUCTION

A recycle accumulation of plutonium in a counter-current extractor of Purex process may occur under off-standard conditions: a decrease of organic solvent flow rate, an increase of high active feed flow rate, a decrease of scrub acidity, and so on (Poczynajlo, 1979; Petrich, 1988, 1989; Schön, 1989). They cause a high-loading of U(VI) in the organic solvent.

With mixer-settler, an experimental study on the recycle accumulation had been performed by using U(IV) as a substitute of Pu(IV) for the Purex co-decontamination cycle (Tachimori, 1988, 1989). The present experiments were carried out with two small pulsed columns to investigate simulated parameters which regulate accumulation of U(IV) in pulsed columns: pseudo-equilibrium system. The concentration profiles of the solutes in the pulsed columns were compared with calculated ones by EXTRA-M code(Tachimori, 1988, 1989), an equilibrium stage model (EQ-model). A fitting to the experimental results was done by varying parameter values: dispersed phase holdup, stage volume, number of stage and distribution ratios (D_r). Finally the experimental results were simulated by using the code with determined parameter values.

2 EXPERIMENTAL

2.1 Pulsed columns and operation

The pulsed columns (I.D. 2.5 cm, H. 230 cm) for extraction and scrubbing equip with 46 cm spaced sampling devices for pure organic and mixed phases and thermistors for temperature measurement (Fig.1). Each column was operated in an organic continuous mode by a mechanical pulsator. The flowsheet conditions shown in Fig.1 were changed abruptly after concentrations of the components except U(IV) reached a steady state (about 5 hours after the normal operation). The conditions changed are:

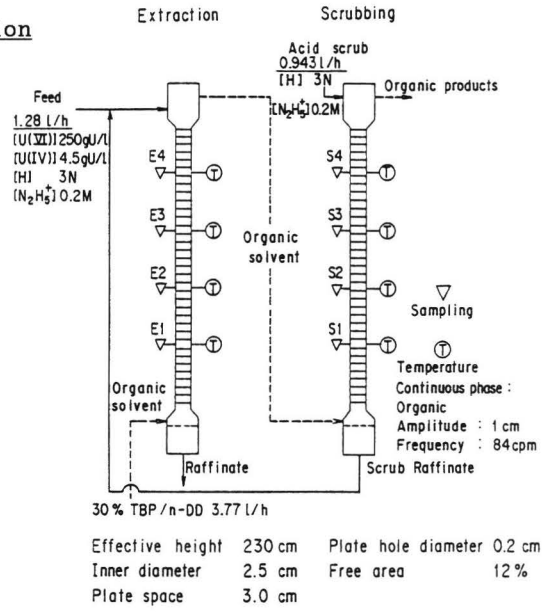


Fig. 1 Arrangement of two pulsed columns for extraction and scrubbing.

(a) 18 % decrease in solvent flow rate, and

(b) decrease in scrub acidity from 3 M to 0.5 M.

2.2 Chemical analysis

To determine concentrations of U(IV), U(VI) and HNO_3, several milliliter solutions of continuous phase were periodically sampled during the experiment. Free HNO_3 in the sample solution was determined alkalimetrically with NaOH solution after masking U(IV) and U(VI) with NaF and $(NH_4)_2SO_4$, respectively. Uranium(VI) was determined by titration of acid which freed from dissociation of UO_2SO_4 after adding H_2O_2. Uranium(IV) was determined by complexometric titration with EDTA using Xylenol Orange as an indicator.

3 RESULTS AND DISCUSSION

(i) Experimental results. Figures 2 and 3 show concentration profiles of U(IV) and U(VI) in the organic phase for the reduction in solvent flow rate and scrub acidity, respectively. It is seen that U(IV) accumulated not only after changing conditions but also during the standard operation. The maximum concentration

of U(IV) was observed in front of the high concentration zone of U(VI) in the organic phase. After the decrease in solvent flow rate, the high organic U(VI) zone expanded toward solvent inlet direction with time as seen in Fig. 2, and U(IV)-peak appeared at the high-U(VI) front. The maximum temperature rise occurred also near the high-U(VI) front (see Fig. 4).

In case of the reduced scrub acidity, the high-U(VI) front proceeded more slowly to solvent inlet direction with slow increase of peak concentration of U(IV) as seen in Fig. 3.

(ii) Fitting procedures. The pseudo-equilibrium distribution characteristics of the pulsed columns differ from that of mixer-settlers. Therefore, to simulate the transient behavior of the solutes in the pulsed columns, parameter values in EXTRA-M code were adjusted to agree with the experimental results of U(IV)- and U(VI)-accumulations. Procedures are as follows.

(a) Total volume and holdup value of the EQ model were fixed equivalent to those of the pulsed columns.

(b) Stage number of the EQ model in extraction and scrub section was determined by comparing calculated concentration

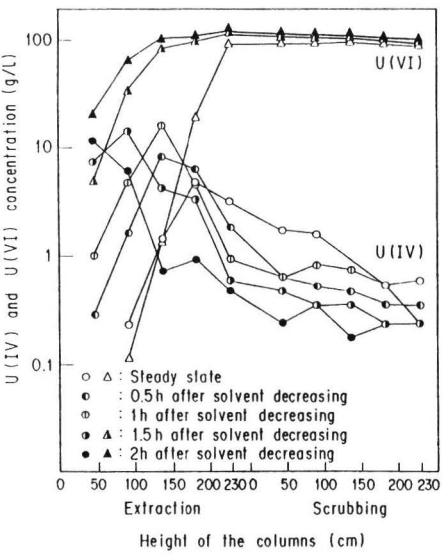


Fig. 2 Change of U(IV) and U(VI) profiles in organic phase with time by 18% decrease of solvent flow rate from the standard flow sheet.
Holdup(%) extraction : 6.5
scrubbing : 3.1

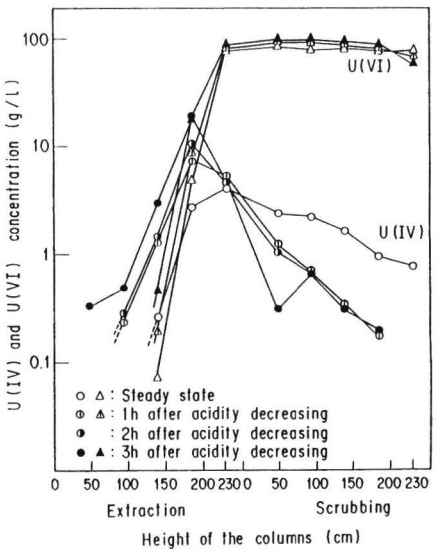


Fig. 3 Change of U(IV) and U(VI) profiles in organic phase with time by decrease of scrub acidity 3 M to 0.5 M.
Holdup(%) extraction : 5.5
scrubbing : 3.8

profiles with experimental ones in standard condition. Particularly, on view of leakage rate, U(IV) and U(VI) concentrations at the organic outlet stage in scrub section should agree with the experimental.

(c) D_r, U(IV), U(VI) and HNO_3 should be changed from data in equilibrium to those in pseudo-equilibrium for fitting to the experimental transient behavior.

Figure 5 shows the dependence of U(IV) profiles of the organic phase on D_r of U(IV) as a function of number of stages in the scrub section. Values of n in Fig.5 are factors multiplied to the distribution coefficient (D_c) of U(IV). The leak rate of U(IV) and U(VI) from the organic outlet increases with decrease of stage number in the scrub section. Besides, with increase of n for U(IV), i.e., a higher D_r value, the leak of U(IV) from the organic outlet increases and conse-

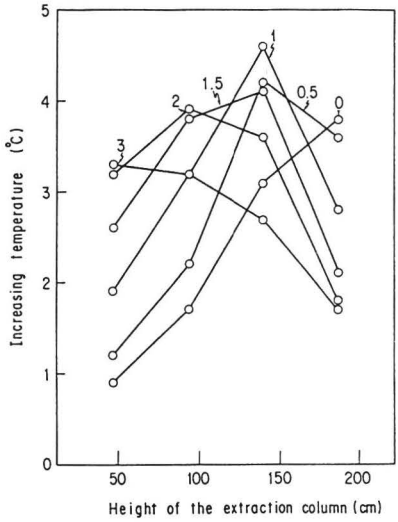


Fig. 4 Change of temperature profiles during extraction. Numerals on the figure show time after solvent decrease.

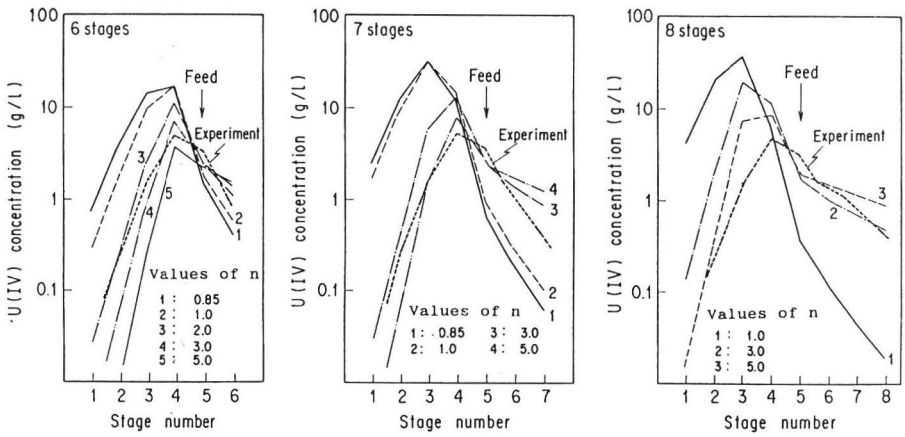


Fig. 5 Dependence of U(IV) profiles in the organic phase on scrubbing stage number and U(IV) distribution ratio in EXTRA-M code. The flow sheet conditions were in the standard operation.

TABLE 1

Characteristics of the EQ model corresponding to the pulsed column used.

Fitted parameter		Value
Effective volume		4.06 1
Holdup		Experimental value
Extraction stage		5
Scrubbing stage		2
Distribution ratio	U(VI):	Dc x 0.85
	U(IV):	Dc x 3.0
	HNO_3:	Dc x 3.0

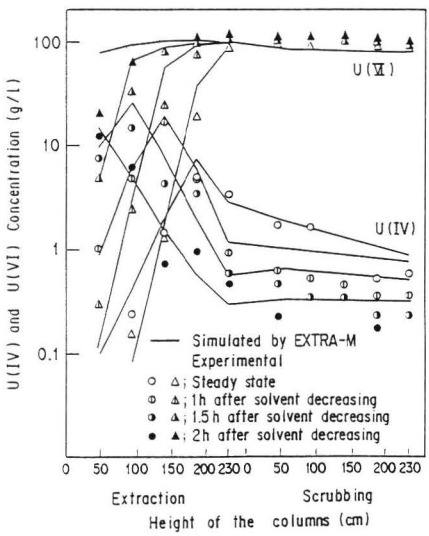


Fig. 6 Comparison of the transient behavior of concentration profiles of U(IV) and U(VI) in the organic phase with time under 18% decrease of solvent flow rate.

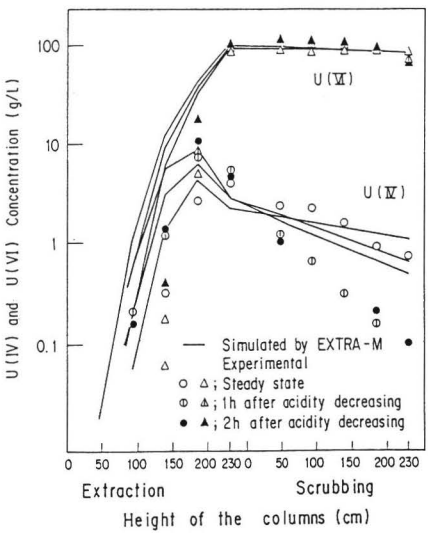


Fig. 7 Comparison of the transient behavior of concentration profiles of U(IV) and U(VI) in the organic phase with time under decrease of scrub acidity from 3 M to 0.5 M.

quently accumulation of U(IV) was depressed. The progress speed of the high-U(VI) front during off-standard operation depends also on D_r of U(VI). The value of n determined from the experiments were 0.8-1.1 for U(VI), 2-4 for U(IV), and 2-4 for HNO_3.

(iii) Results of simulation. Based on these findings and procedures described above, the values of n for U(IV), U(VI) and HNO_3, and number of stages were determined for the EQ model corresponding to the pulsed column used. Characteristics of the model are shown in TABLE 1. The stage number of scrub section is less than that of our expectation. The very small stage number

obtained for the scrub column could be ascribed to an inefficiency of stripping U(IV) from the continuous organic phase to the dispersed aqueous phase. Simulation of the transient experiment with the pulsed columns was performed with the EQ model of EXTRA-M code on 18% decrease of the solvent flow and reduction in scrub acidity . Concentration profiles of U(IV) and U(VI) by the experiment (symbols) and the calculation (lines) are shown in Fig. 6 and Fig. 7. The figures indicate that the agreements between the experiment and the calculation are satisfactory in the rates of both accumulations of U(IV) and the progress of the high-U(VI) front. The explanation of the parameter values obtained needs further study.

4 CONCLUSIONS

The EQ model, EXTRA-M code, by the parameter fitting method was modified to analyze the behaviors of U(IV) and U(VI) in the pulsed columns. Findings by the model obtained were as follows.

(1) A good agreement in concentration profiles of U(IV) and U(VI) and transient characteristics of U(IV)-U(VI) were obtained between calculation by the EQ model and the experiment.

(2) Distribution ratios, which are different from those in equilibrium, are necessary to a pulsed column, and more experimental data of distribution of the solutes in a pulsed column are needed.

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CONCEPTUAL STUDY FOR A COMPUTER-AIDED EXTRACTION-STATUS DIAGNOSTIC SYSTEM FOR THE Pu-U PARTITION CYCLE OF THE TOKAI REPROCESSING PLANT

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ABSTRACT

The computer aided system that automatically diagnoses the status of the extraction process is under development in the Tokai Reprocessing Plant(TRP). The second extraction cycle of TRP was chosen as the base model of the conceptual design of the system, and basic logic flow for the diagnosis-making was basically established. The combination of the CCT(Cause Consequence Tree) and the determination of the extraction profile change by the indication pattern of in-line monitors(Table-Treatment) was found to be the best way for the automatic diagnosis and the cause identification of the anomaly.

INTRODUCTION

The operators of the PUREX extraction process are required to have deep understanding on the normal/abnormal status of the process with its complicated cause-consequence relation. This is particularly required for the case of abnormal events because of a proper decision and corrective operation is necessary within a restricted time. The cause identification of the events is also important for recovering the process. In the actual plant, highly trained operators having much experience usually make the diagnosis with his extensive knowledge. However, there may be some cases when veteran operator gets confused, or misjudge is made that finally affects the plant efficiency. The development of this system was started for the purpose of automatizing the diagnosis on the operation of the extraction process and of decreasing the dependence to the veterans. The system is expected to provide some guidance to the operators, to watch the process, and to be used as a so-called "Expert System". The conceptual study was finished and the basic logic structure was established as described below.

2 FUNCTIONS REQUIED FOR THE SYSTEM

Fig.1 shows the outline of the second extraction cycle(partition process) of the TRP. Mixersettlers are used for all extraction banks. This process was chosen as the model process of the "Extraction Status Diagnosis System(ESDS)" because of its important role to separate the U and Pu and of its complicated process response to various causes. At the very beginning stage of the development, the functions expected to the system was categorized. Fig.2 provides the categorized functions. The system has to stand on 4 different status of the process(normal, abnormal, manual shutdown and post-trip), and to do main three roles(Monitoring, Diagnosis and Guidance). The most difficult role is the diagnosis because it has to find the anomaly, to find the cause and to predict the influence that used to be done by veterans. The computer has to have knowledge and some kinds of intelligence as the veteran operators do.

3 METHOD OF THE DIAGNOSIS ON THE EXTRACTION STATUS

Anomaly that occurs in the extraction process can be divided into two categories, one which can be detected by an ordinary instrument system(Category 1) and another which can not be detected by it(Category 2). The former contains change in the flowrate, liquid level, temperature, pressure etc. The anomaly in Category 1 can be quickly detected with a certain entry-node to be set on the logged process data. As a result of a detailed examinations on every considerable anomaly, it was convinced that the cause of these disturbances can be well identified by a CCT(Cause Consequence Tree). CCT that

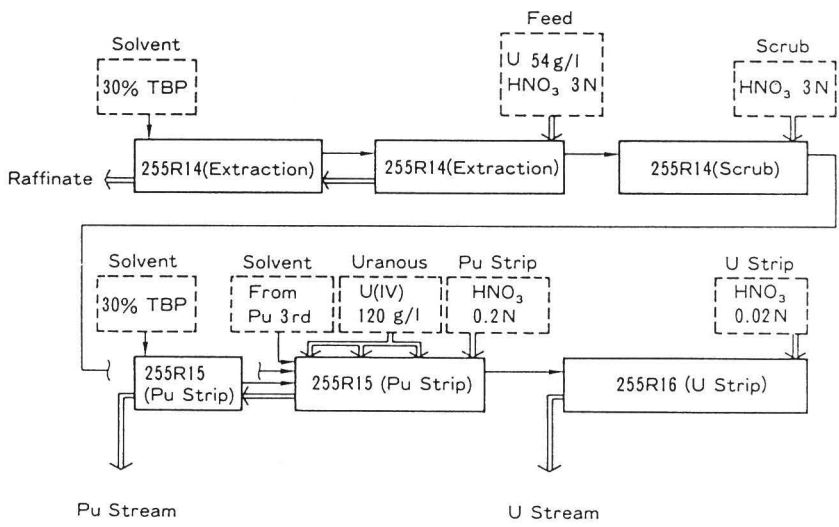


Fig. 1. The outline of second extraction cycle(partition process) of the TRP.

covers entire process was established with Fault Tree analysis on every not small event.

Category 2 contains concentration change in the feed solution or reagents fed to the extractors. Currently, these are checked by a periodical sampling/analysis, but they are not real-time and we can not perfectly deny the possibility of human mistake in the sampling/analysis. The mal-functioning of the instrument is also treated as this category because it can not be detected when it does not raise any anomaly-like indication. This is typical in the case that the indication seems perfectly normal with a faulse output while the real physical status is already abnormal. Because the occurrence of this category can not be detected, the status change of the extraction must be detected as quickly as possible. If the consequential change in the extraction status(profile change) is recognized by a computer at its early stage and the different pattern of the status change can be attributed to a particular cause, the cause identification is also possible. By examining the mal-operation response of the extractors, we found that the in-line monitors gives quite distinguishable appearance with various causes. Therefore, the cause of the disturbance can be identified by comparing the observed status-change pattern with the standard pattern of various events which are previously put in a computer as a knowlege. The calculational treatment is called "Table-Treatment" and this can also be used for the post-event diagnosis for the Category 1.

Consequently, the second extraction cycle was found to be well diagnosed by the combination of CCT and Table-Treatment.

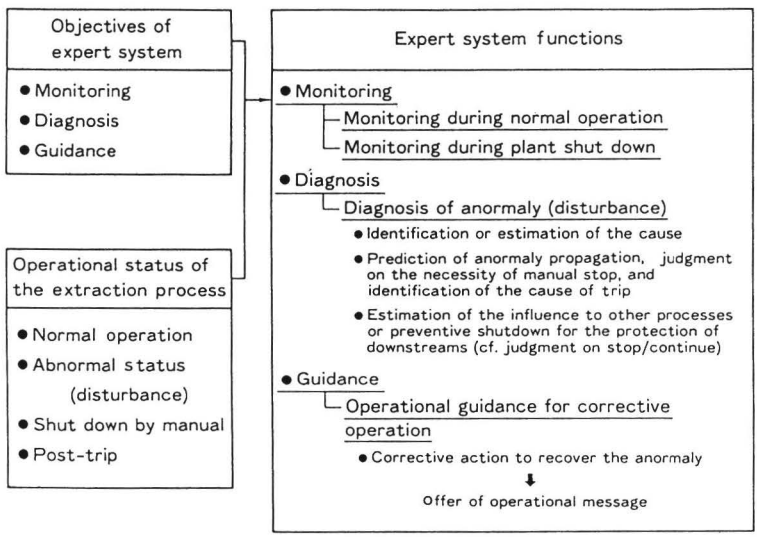


Fig. 2. Functions expected for the extraction status diagnostic(expert) system.

4 ANOMALY ANALYSIS AND TABLE-TREATMENT

4.1 Anomaly Analysis

In order to establish the knowledge base(Table) of the extractor's dynamic response on various disturbances in the operational parameters, we used extraction simulation code REVISED.MIXSET. A number of calculations were carried out with different types of the disturbance in the concentration and flow rate of the fed solution, and the dynamic change of the extraction profile of Pu, U and nitric acid were carefully examined.

4.2 Examination on the Appearance to the In-line Monitors

The change of the Pu concentration in the extraction bank is monitored with neutron-monitors placed at some stages. Because the n-monitor counts the neutrons emitted from both organic and aqueous phase, slight change in one phase can not be detected, which means the profile change of Pu may have an obscure appearance to the monitors. We simulated their counts(cpm) by summing the neutron emission rate in both phases using the Pu concentration result obtained by MIXSET.

The U concentration in the aqueous phase is monitored with density meter. However, because the density is defined as the combination with the nitric acid concentration, U concentration change can not singly be detected. The density in the aqueous phase was calculated using the equation of uranyl nitrate solution with the Uranium and nitric acid concentration obtained by MIXSET. As a trigger level of the detection of the change in the indication of in-line monitors, $2*(N(cpm))^{1/2}$ for n-monitor and 0.01 for density meter were applied. Changes greater than these threshold can be recognized as a

Categories of abnormal events	Detection methods	Results	Diagnosis methods	Prediction of further influence
Events that are detectable by ordinary instrument Example : disturbance in flowrate, temperature, liquid level	Direct monitoring by ordinary instrument (flowrate, etc) Periodically check if the indication is exceeding the entry node value	●Changes in instrument indication (entry node) ↓ ●Alarm : ON ↓ ●Protection : ON	CCT logic ↓ Identification of cause	Based on the analysis with Rev. MIXSET code
Events that are not detectable by ordinary instrument Example : ① material concentration in fed solutions U, Pu, HNO_3 concentration ② Failure of the instrument that seems normal on the indication	Monitoring of consequential concentration change in extractor (U, Pu) ↓ n-monitor, density monitor α-monitor	●Changes in the Concentration profile in extractor (should be found in early stage)	Table treatment ↓ Find the change of the indication of various inline-monitors and recognize it as a pattern ↓ Compare the observed pattern with the standard patterns for various types of events	

Fig. 3. Detection and diagnosis methods for abnormality in the extraction systems.

significant change if proper noise filtration is applied.

Fig.4 gives an example of the anomaly calculation. The neutron monitors that exceeds $2*N^{1/2}$ at a certain time are marked and the pattern of the marked monitors changes as the dynamic change of the profile proceeds. This is because there is a delay in the appearance on different stages. Thereafter, when it achieves a certain unique pattern that can be identified from the ones made by any other cause at proper time, this pattern can be registered as the standard pattern of this cause. Actually detected pattern during the plant operation will be compared with this standard pattern, and if they coincide, the cause of the actual event is diagnosed to be the standard's one. Some typical cases of different cause were examined, and they revealed to show quite different patterns. Fig.5 shows the 5 typically different

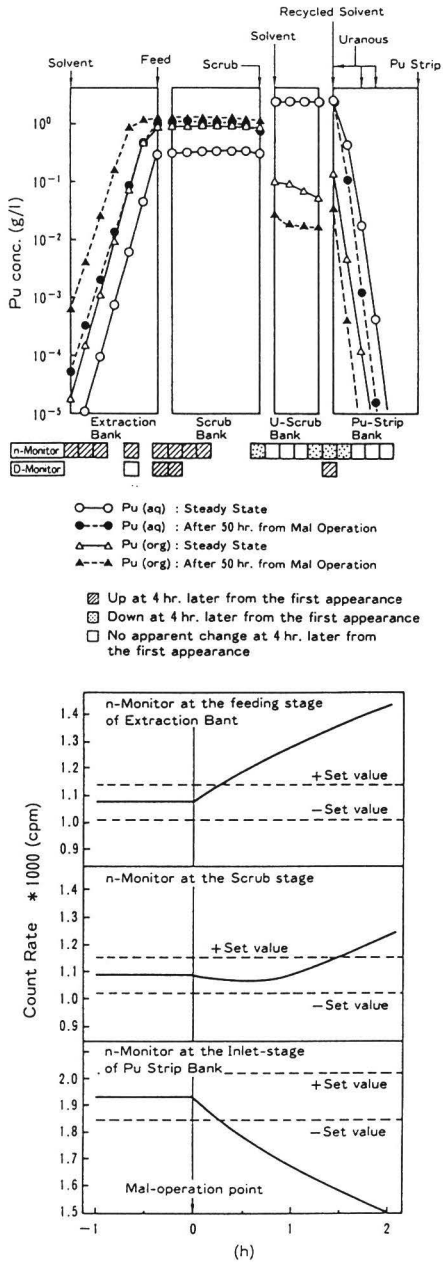


Fig. 4. Mal operation case :
decrease of solvent feed rate to extraction bank.

cases. The increase/decrease of the counts of the n-monitors shows different patterns as the time passes after the first trigger. Because the mixersettler has rather slow response, there are some stages that take more than 5 hours to exceed the threshold value. However, because at earlier stage there are no other cases that show same pattern, these fives can be distiguished at 1 hour later from the first appearance. The change of the neutron emission rate due to the change of the isotopic ratio(change of the burn-up) was found to be clearly separated from the anomaly.

CONCLUSION

Conceptual design of the ESDS was performed, and it was revealed that the extraction status of the bank can be monitored with the Table-Treatment for in-line monitor's appearance. It was convinced that cause identification for the anomaly can be done with the combination of CCT and the Table-Treatment. More detailed examination on other events together with the magnitude of the disturbance will be required.

ACKNOWLEDGMENT

We are gratefull to the experts of the AI(Artificial Intelligence) development of MITSUBISHI HEAVY INDUSTRIES, Ltd. and MITSUBISHI ATOMIC POWER INDUSTRIES, Inc. for their contribution to this study.

No.	Events	Variation of concentration at each bank																						
		U by density meter				Pu by neutron monitor																		
		1412	1414	1415	1505	1408	1409	1410	1412	1414	1415	1416	1417	1421	1501	1502	1503	1504	1505	1506	1507	1508	1509
1	decrease of H⁺ conc. in scrub											>20 ↑ >18	15.5 ↑ 13.5	3.0 ↑ 1.0						2.0 ↓ T			
2	increase of feed rate								0.5 ↑ T	1.0 ↑ 0.5	1.0 ↑ 0.5	1.5 ↑ 1.0	2.0 ↑ 1.5	3.5 ↑ 3.0	6.0 ↑ 5.5	6.0 ↑ 5.5	5.5 ↑ 5.0	5.5 ↑ 5.0	5.5 ↑ 5.0	3.5 ↓ 3.0			
3	decrease of U (IV) conc.																			1.5 ↑ T	4.0 ↑ 2.5		
4	decrease of H⁺ conc. in strip																			7.5 ↓ T			
5	decrease of solvent feed rate		1.0 ↑ 0.5	2.0 ↑ 1.5	4.5 ↑ 4.0	4.5 ↑ 4.0	2.0 ↑ 1.5	1.0 ↑ 0.5	0.5 ↑ T	0.5 ↑ T	1.0 ↑ 0.5	1.5 ↑ 1.0	2.5 ↑ 2.0	2.0 ↓ 1.5					0.5 ↓ T	0.5 ↓ T	3.0 ↓ 2.5		

: can be detected at 1 hour later from the first appearance

↑, ↓ : Upward and Downward deviation from standard with the time after the occurrence (Top) and the time after the first appearance. (Bottom)

Pu ; $N \pm 2N^{1/2}$ (N=Standard count rate (cpm))

U : $M \pm 0.01$ (M=Standard density (g/cm^3))

T (Trigger) : the first appearance

Fig. 5. Example of the Table-Treatment on in-line monitor's appearance.

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SEPARATION OF THE ACTINIDES Pa, Th, U, Np AND TPE INCLUDING Md BY EXTRACTION METHODS

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ABSTRACT
In the radiochemical investigations of the nuclear reactions induced by accelerated heavy ions a selective separation of reaction products is necessary. For this purpose extraction with trioctylphosphine oxide (TOPO) and di(2-ethylhexyl) orthophosphoric acid (HDEHP) can be successfully used. New data on the extraction behaviour of Pa, Th, U, Np and transplutonium elements (TPE) in complex forming and salting-out agents are shown. The obtained results were used in the extraction chromatographic version for the purification of TPE from other actinides. A single-cycle separation process in the case of TOPO and a two-step process using HDEHP give a high degree of actinide separation and their purification from most fission products.

INTRODUCTION

In recent years nuclear reactions of heavy ions with heavy actinide targets were extensively used at JINR, Dubna. These studies were carried out for the synthesis of new heavy elements. The cross sections of nuclear reactions can be determined from the yield of transplutonium elements (TPE). For this purpose the actinides must be separated with high separation factors from the target or from the catcher, and also from a great quantity of radioactive isotopes representing the elements from radium to plutonium and fission products. The yields of these nuclides are quite low because of small formation cross sections in the nuclear reactions. The cross section decreases by a factor of about $> 10^4$ in going from ^{237}U to ^{246}Cf and by a factor of $> 10^8$ for elements from U to TPE $\geq$ Es (Oganessian 1987). That means that the concentration of actinides in the catcher material after irradiation decreases in the same order. Hence there arises the problem of the separating a few atoms of Md, Fm, Es and of a great number of atoms of Cm, Am, Pu, Np, U, Pa, Th from macroquantities of Cu, Al or other catcher materials. It is necessary to perform separations with considerable yields and with high separation factors. The degrece of TPE purification must reach about 10^{10}. We recommend for this purpose extraction chromatographic methods with trioctylphosphine oxide (TOPO) or HDEHP. In addition to our earlier papers (Gorski, 1989, Hussonnois, et al. 1989) we are reporting here the conditions for the extraction and reextraction of the light actinides Pa, Th, U, Np. The obtained results were used in improved extraction chromatographic versions for the purification of TPE and their separation from Pa, Th, U, Np.

2 EXPERIMENTAL

The extraction experiments were carried out as described earlier (Gorski, 1988). The 0.005–0.4 $mol \cdot l^{-1}$ solutions of TOPO in benzene and 0.1 $mol \cdot l^{-1}$ HDEHP in toluene were used as extractants. ^{231}Th, ^{233}Pa, ^{237}U, ^{239}Np, ^{241}Am, ^{244}Cm, ^{249}Cf, ^{256}Fm and ^{256}Md were used as radiotracers for the actinides. ^{256}Fm and ^{256}Md were obtained from a transfer reaction by irradiating ^{249}Bk with ^{22}Ne. Md was separated from Fm by cation exchange (Gorski et al., submitted for publication). ^{239}Np was separated from ^{243}Am by extraction chromatography with HDEHP, Np was purified from small residues of Am by anion exchange on Dow 1x8 and transfered by hydrazine in 8M HNO_3 or $NaNO_2$ in conc. HCl to Np(IV) or Np(VI) respectively. The distribution coefficients for Np(IV) and Np(VI) in the systems of HCl/HF and $H_2C_2O_4$ were determined by reextraction from 0.1M HDEHP in toluene. ^{231}Th and ^{237}U were obtained by γ-irradiation of $Th(NO_3)_4$ or $UO_2(NO_3)_2$ using the "microtron MT-25". The concentrations of Th and U in the extraction experiments were $7.7\ 10^{-4}$ $mol \cdot l^{-1}$ and $8.0\ 10^{-4}$ $mol \cdot l^{-1}$ respectively.

3 RESULTS

A high selectivity of TPE and REE extraction with TOPO towards fission products and other elements is reached when strong complexing agents, such as diethylenetriaminepentaacetate (DTPA) and lactic acid are added. For the selection of optimal conditions for TPE, REE, Pa, Th, U and Np separation the extraction by TOPO has been studied. The results of the extraction of some lanthanids and TPE by TOPO from DTPA solutions in lactic acid containing $Cu(NO_3)_2$, $Al(NO_3)_3$ or $Ni(NO_3)_2$ as salting-out agents are presented in Fig. 1. The dependence of the REE has a maximum for Sm while higher distribution coefficients (K_d) are

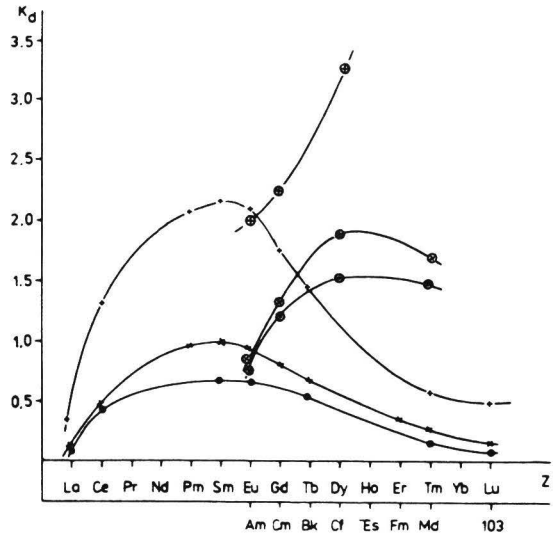


Fig. 1. Distribution ratios for lanthanides (+x•) and actinides (⊕ ⊗ ⊙) as a function of the atomic number aqueous phase: 0.07M DTPA, 1M lact.ac., 0.3M HNO_3,
(+ ⊕) 0.5M $Al(NO_3)_2$
(x ⊗) 0.5M $Cu(NO_3)_2$
(• ⊙) 0.5M $Ni(NO_3)_2$
organic phase: 0.1M TOPO in benzene

characteristic for all TPE in comparison with the lanthanides. In addition the maximum for the actinides is shifted in the direction of larger atomic numbers. The plot of lg K_d versus lg [TOPO] for REE, and actinides has the form of a straight line excluding Pa (Fig. 2) with an angle coefficient equal to 3, demonstrating the same extraction mechanism for these elements, resulting in the formation of trisolvates. This is true for Pa for a limited range of TOPO concentrations. The influence of the salting-out agent concentration on the extraction of actinides was studied separately. The extraction efficiency increases in the order TPE < Np < Pa < Th < U. The optimal copper concentration is about 1 mol·l^{-1} $Cu(NO_3)_2$. Under these conditions the actinides may be separated from most of the fission products and from other elements (Hf, Bi) which are practically not extracted. Using the high distribution coefficients of the lighter actinides in solutions of 7M HCl the TPE may be purified from Pa, Th and U by the extraction chromatographic technique. For the separation of U, Th and Pa from each other their elution from the TOPO column was investigated using the following agents: 0.05M - 0.3M HF, 2M - 6M H_3PO_4, 0.1M - 0.5M $H_2C_2O_4$, 1M - 2M $(NH_4)_2CO_3$, 2M - 4M H_2SO_4. From the obtained results the separation conditions were chosen as shown in Fig. 3.

A second method we used for the actinide separation is the extraction chromatography with HDEHP. Taking into account that Th, Pa, Np and U are extracted by HDEHP in a wide concentration range of HCl or HNO_3 these actinides can be easily

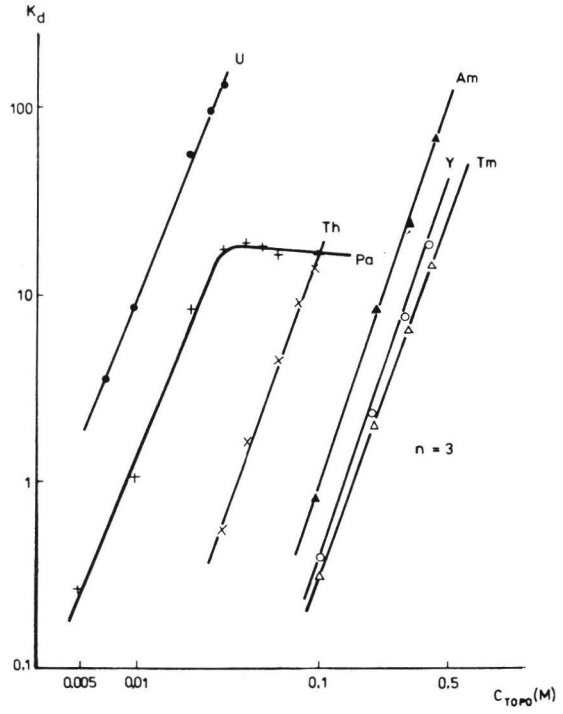


Fig. 2. Distribution ratios for actinides as a function of the analytical concentration of the extractant, aqueous phase:
0.07M DTPA, 1M lact.ac.
Am, Y, Tm: 1M $Cu(NO_3)_2$
Th: 0.1M $Cu(NO_3)_2$
U, Pa: 0.05M $Cu(NO_3)_2$

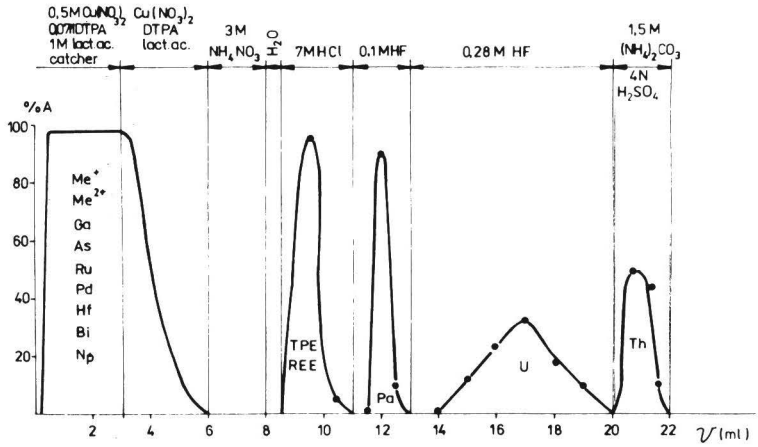


Fig. 3. Elution curves of group separation of TPE from Pa, U, Th, column: 20% TOPO/EP-60 (3x60 mm)

separated from the TPE. After the sorption of all actinides on a HDEHP - column from diluted HCl the TPE are usually eluted by 6M HCl. In this case, however, the TPE fraction is impurified by Np, because under these conditions Np exists as a mixture of Np(V), (IV), (VI). Therefore it is reasonable to realise a two - step separation process. In the first step we separated U and TPE from the lighter actinides, which were sorbed on a HDEHP column from concentrated HCl. For the selection of separation conditions of Np, Pa and Th we investigated their extraction and reextraction by HDEHP using solutions of HF/HCl, $H_2C_2O_4$ and H_3PO_4. The obtained results are shown in Fig. 4-6. It is seen (Fig.4) that Pa and Np can be easily reextracted by a mixture of HCl/HF but their separation would be difficult. Thus we used a diluted solution of $H_2C_2O_4$ for the selective elution of Np (Fig.5) after which Pa may be eluted by 0.2M HF or 9M HCl/0.5M HF or 0.4M $H_2C_2O_4$. At last we eluted Th by 4M H_3PO_4 (Fig. 6) or 1M $H_2C_2O_4$. In a second step the TPE are purified from U and from most of the fission products. The HCl effluent from the first column was evaporated to dryness. The residue was taken up in a solution of 0.1M HNO_3 and transferred to a HDEHP column. After washing with 0.1M HNO_3 for the separation of the catcher material (Cu) and the fission products two fractions of TPE were eluted by 0.4M HNO_3 (Am-Bk) and 4M HNO_3 (Cf-Md). The distribution coefficients of Md and Fm extraction by 0.1M HDEHP in toluene were determined separately. At C_{HNO_3}=0.5M we obtained K_{dFm}=2 and K_{dMd}=13. Finally U was eluated from the column by conc.HCl.

CONCLUSIONS

The results have shown that a one-cycle separation process - using TOPO as an extractant - can give a high degree of TPE purification from most of the fission

products, lighter actinides and catcher or target material. On the basis of the extraction properties of U, Th, Pa, Np and TPE by HDEHP a two-step separation scheme is recommended for this system. The described methods were used for the separation of Cf–Fm from the mixture of isotopes of elements produced in $^{238}U + ^{18}O$ and other reactions with a Cu or Al catcher.

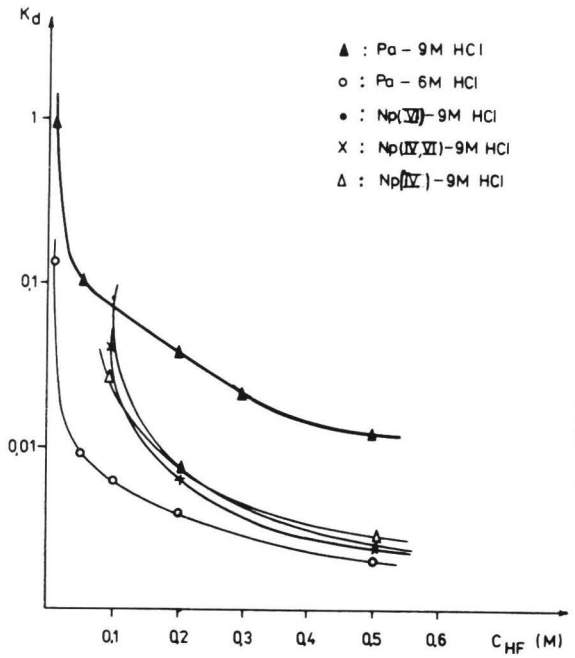


Fig. 4. Distribution ratios of Pa and Np in dependence on C_{HF}, organic phase: 0.1M HDEHP in toluene

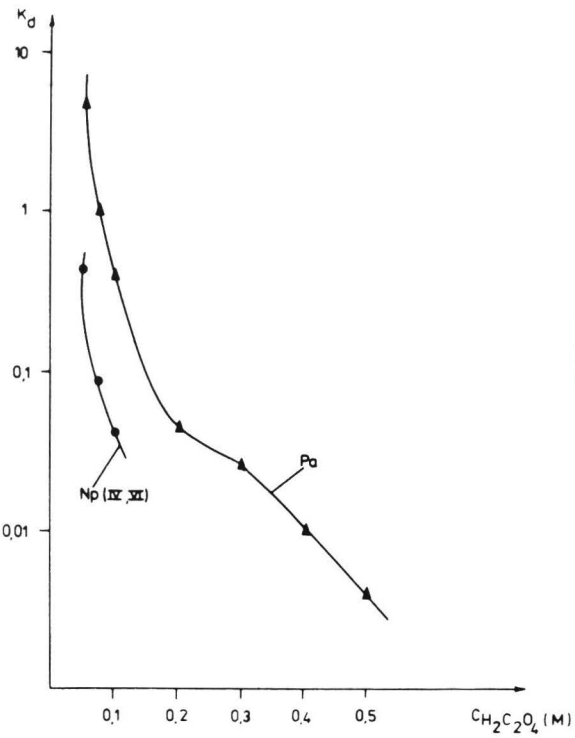


Fig. 5. Distribution ratios of Pa and Np in dependence on $C_{H_2C_2O_4}$, organic phase: 0.1M HDEHP in toluene

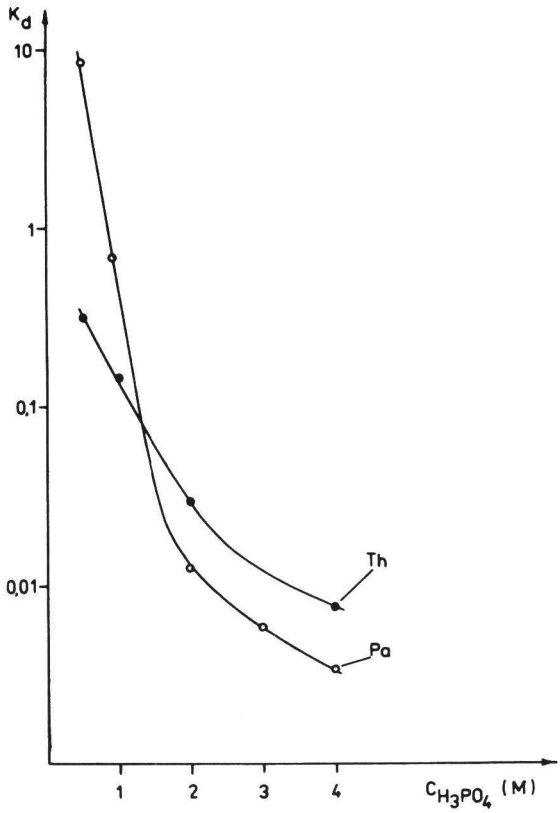


Fig. 6. Distribution ratios of Pa and Th in dependence on $C_{H_3PO_4}$, organic phase: 0.1M HDEHP in toluene

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APPLICATION OF CENTRIFUGAL PARTITION CHROMATOGRAPHY TO SEPARATION OF ACTINIDES AND LANTHANIDES IN TBP EXTRACTION SYSTEM

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ABSTRACT

Centrifugal partition chromatography (CPC) has been applied to separation of actinides and lanthanides. The first application is separation of Nd(III), U(IV) and U(VI), which was successfully performed in about 1 hour by selecting 30% TBP-n·dodecane as the stationary phase and 0.3 M HNO_3-0.05 M hydrazine as the mobile phase. The second application is separation of lanthanides in TBP-n·dodecane(-CCl_4) and HNO_3-$LiNO_3$. The separation properties of lanthanides were improved by salting-out effect of $LiNO_3$ under appropriate operation condition of the CPC device.

1 INTRODUCTION

A new separation technique besed on centrifugal liquid-liquid partition chromatography (CPC) was developed by Murayama et al.(1982). The technique has been used mainly as analytical and preparative means of organic substances. Recently, Araki et al.(1985) and Akiba et al.(1988) have applied it to separation of inorganic substances, such as alkali and lanthanide elements. The authors have a plan to apply it to recovery and purification of useful elements in nuclear spent fuels.

Merits of CPC are as follows: 1) effective separation is expected due to high theoretical plate numbers; 2) macroamounts of chemical species can be purified due to liquid-liquid extraction; 3) relatively rapid separation is performed by centrifugal force, so that degradation of organic solvent by radiation is minimized; 4) many extraction data reported are available for the CPC technique.

The present paper deals with separations of actinides and lanthanides in TBP extraction system by use of the CPC device. Emphasis has been placed on a control method of specific gravity of the stationary phase to gain high salting-out effect of $LiNO_3$ in the lanthanide separation and to operate stably the CPC device.

2 EXPERIMENTAL

2.1 Separation procedure

Figure 1 shows the CPC separation system for this study. The CPC device used was Model CPC LLN (Sanki Engineering Ltd.) which equipped with 6 partition cartridges. One cartridge was composed of 400 microcells. An organic stationary phase (TBP and its diluent) was previously held in the partition cells, and an aqueous mobile phase (nitrate solution) was supplied by a pump into the stationary phase at 25°C. Rotational speed of the rotor was 800 to 1200 rpm. Sample solution was charged from a sample injector to the partition cells and then developed chromatographically by supplying the aqueous phase.

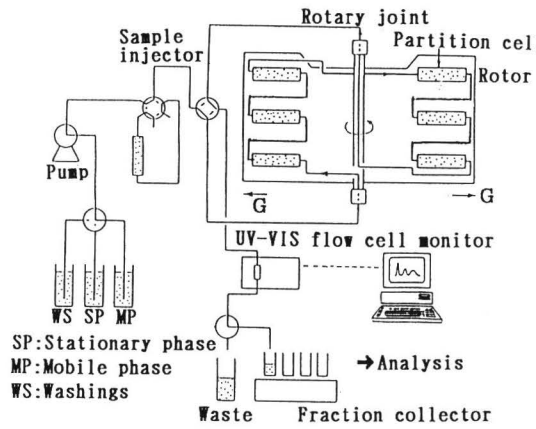


Fig.1 Schematic CPC separation system.

Effluent from the CPC device was monitored by a flow cell type photodiode array UV-VIS detector (SPD-M6A: Shimadzu Co.) at 380 to 670 nm, and then taken in a fraction collector to determine the concentration of separated elements.

2.2 Determination of the rotational speed and difference of specific gravity between the two phases

Control of the rotational speed and specific gravity of both the phases is neccessary for determining the optimum operation conditions. The rotational speed a (rpm) is expressed by the following equation:

$$a^2 = 3.06 \cdot 10^3 \cdot P / |d_m - d_s| \qquad (1)$$

where P is the pump pressure (kgf/cm^2), d_m specific gravity of the mobile phase and d_s specific gravity of the stationary phase. The equation was derived from the balance of centrifugal force and the pressure. The higher rotational speed will be preferable for improved separation (Akiba et al., 1988), but it produces the higher pressure which is undesirable for the stable operation. It is therefore meaningful to determine the difference of specific

gravity between the two phases.

2.3 Analysis

An ICP emission spectrometer (UOP-2: Kyotokouken Ltd.) was used for analysis of lanthanides, Cu and Ba in the solutions. A well-type Ge detector (GWL-80230: ORTEC Ltd.) was also used for determination of U concentration by measurement of 186 keV gamma-ray of ^{235}U. The detection limit was about 0.05 g·^{nat}U/l.

3 RESULTS AND DISCUSSION

3.1 Separation of actinides

The actinide separation was successfully performed in the system of 30% TBP-n·dodecane and 0.3 M HNO_3-0.05 M N_2H_4. Hydrazine, N_2H_4, was added as stabilizer for U(IV). Figure 2 shows a chromatogram of Nd(III), U(IV) and U(VI). Neodium(III) was used as a substitute of actinide(III). Composition of the sample solution (2.5 ml) was as follows; HNO_3: 1.3 M, Nd(III): 13.6 g/l, U(IV): 13.7 g/l and U(VI): 50.0 g/l. In this system, Distribution coefficients (Kd) of Nd(III) was very low, and those of U(IV) and U(VI) were obtained to be 0.18 and 1.10, respectively. Uranium(IV) and U(VI) were eluted separately in about 1 hour. Differing from usual column chromatography, CPC favorably performs separation of species with such low Kd values.

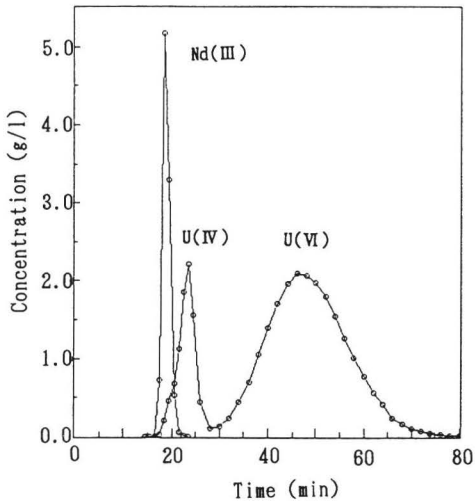


Fig.2 Chromatogram of Nd(III), U(IV) and U(VI) at 800 rpm and at 3 ml/min. Mobile phase: 0.3 M HNO_3-0.05 M N_2H_4, stationary phase: 30% TBP-n·dodecane.

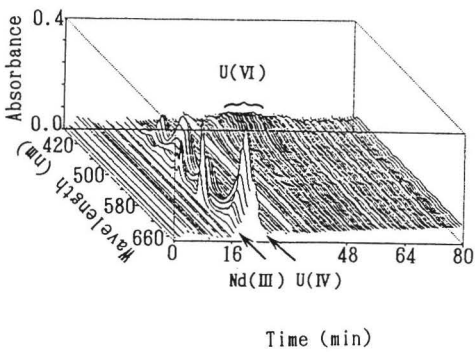


Fig.3 Result of photometric monitoring by the flow-cell type UV-VIS detector.

Figure 3 shows a scanning spectrum of photometric monitoring in the above separation

by the flow-cell type UV-VIS detector, which enables quantitative and qualitative monitoring of the effluent from the partition cells.

3.2 Separation of lanthanides

Separation factors (α) of lanthanides in TBP-HNO_3 extraction system increase with increase of HNO_3 (Scargill et al., 1957). Since the use of concentrated HNO_3 is difficult for this CPC device, $LiNO_3$ was used as a salting-out reagent.

Figure 4 shows chromatograms of Cu, Pr and Eu in 1, 2 and 3 M $LiNO_3$ solutions containing about 1 M HNO_3 at a flow rate of 3 ml/min. To adjust specific gravity of the

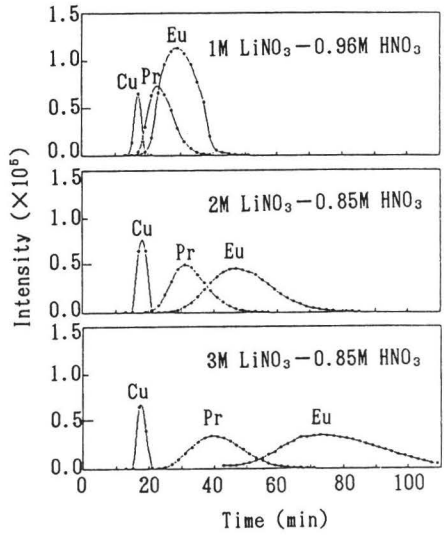


Fig.4 Chromatograms of Cu, Pr and Eu in 1, 2 and 3 M of $LiNO_3$ solutions containing about 1 M HNO_3 at 800 rpm and at 3 ml/min.
Stationary phase:70% TBP-n·dodecane, sample solution(2 ml): Cu; 1.2 g/l, Pr; 15 g/l, Eu; 57 g/l.

TABLE 1

Summary of separation properties and operation conditions

Mobil phase	[$LiNO_3$] (M) [HNO_3] (M)	1.0 0.98	2.0 0.85	3.0 0.85	5.0 1.0
Stationary phase	[TBP] (%) [n·dodecane](%) [CCl_4] (%)	70 30 —			30 28 42
K_d	Pr Eu	0.19 0.39	0.43 0.98	0.76 1.85	0.12 0.63
N	Pr Eu	31 25	27 23	22 23	490 180
α	Eu/Pr	2.0	2.3	2.4	5.1
R	Eu/Pr	0.32	0.54	0.70	2.0
Flow rate (ml/min)		3.0			1.5
Pressure (kgf/cm^2)		ca.34	ca.39	ca.45	ca.20
Rotational speed (rpm)		800			1200

stationary phase, 70% TBP-n·dodecane was selected. Copper was used for correcting the retention time. The separation properties and operation conditions are summarized in TABLE 1. With an increase in concentration of $LiNO_3$, the K_d values increased several times. The α values increased a little while theoretical plate numbers (N) were almost constant. Consequently, resolutions (R) were improved by the salting-out effect.

To obtain higher salting-out effect with increase of $LiNO_3$, specific gravity of the organic stationary phase must also increase considerably for not exceeding a limited pressure. Figure 5 shows a typical chromatogram for improved separation of Ba, Pr and Eu in 5 M $LiNO_3$-1 M HNO_3 and 30% TBP-28% n·dodecane-42% CCl_4 at 1.5 ml/min and at 1200 rpm. Barium was used for the same role as Cu, since Cu was retained in such concentrated nitrate solution. Both α and N values increased and excellent R was obtained (see TABLE 1).

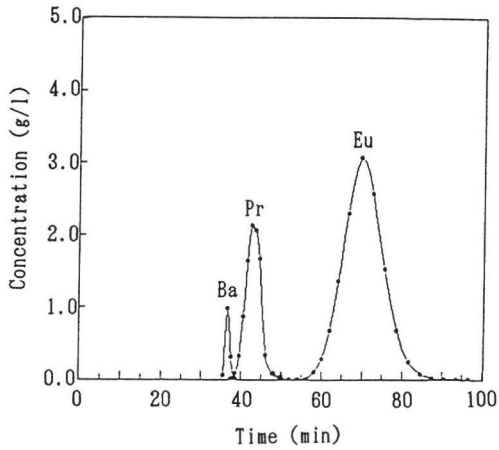


Fig.5 Chromatogram of Ba, Pr and Eu in 5 M $LiNO_3$-1 M HNO_3 at 1.5 ml/min and at 1200 rpm.
Mobile phase: 5 M $LiNO_3$-1 M HNO_3, stationary phase: 30% TBP-28% n·dodecane-42% CCl_4, sample solution(2 ml): Ba; 1.2 g/l, Pr; 15 g/l, Eu; 57 g/l.

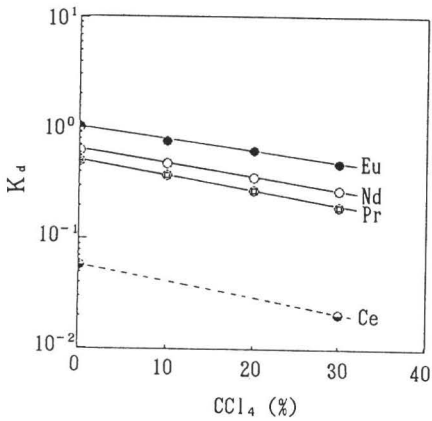


Fig.6 Effect of the volume ratio of CCl_4 diluent on K_d of some lanthanides in 2 M $LiNO_3$-1 M HNO_3 solution.

Decrease of TBP content seemed to produce poor separation, but increase of the $LiNO_3$ concentration and decrease of flow rate contributed to the improved separation. The higher rotational

speed (1200 rpm) may also enlarge the N values because dropsize of the mobile phase in the partition cell decreases (Akiba et al., 1988). The value of $|d_m-d_s|$ was controlled to be 0.043 by adding a heavier diluent, CCl_4 (d: 1.6). From the equation (1), the pump pressure obtains to be 20 kgf/cm^2, which well agreed with the observed value. Operation at such lower pump pressure could avoid the leak of the mobile phase.

In the last, effect of the diluent CCl_4 on the separation properties should be considered. Figure 6 shows effect of the volume ratio of CCl_4 on K_d of some lanthanides. The values were determined by a batch method. The increase in the ratio of CCl_4 to TBP-n·dodecane decreased the K_d values but increased the α values between Pr and Eu.

4 CONCLUSIONS

This study is in progress, and the present findings are as follows:

a) The separation of macroamounts of actinides in TBP system was carried out by use of the CPC device in about 1 hour.

b) In the lanthanide separation with TBP, the separation factor between lanthanides was increased by salting-out effect of $LiNO_3$.

c) Not only the higher salting-out effect but also stable operation of the CPC device were attained by controlling the specific gravity of the organic stationary phase.

d) In about unity or below unity of K_d values, effective separation was favorably performed by CPC.

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APPLICATIONS OF EXTRACTION CHROMATOGRAPHY IN THE BIFUNCTIONAL EXTRACTANT-NITRIC ACID SYSTEM FOR SEPARATION OF ACTINIDES IN NUCLEAR FUEL CYCLE

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ABSTRACT

Bifunctional organophosphorus compounds, dihexyl-N,N-diethylcarbamoylmethylphosphonate(CMP) and octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide(CMPO), have a high selectivity for the extraction of actinides and lanthanides from nitric acid. The extraction chromatography in the bifunctional extractant-nitric acid system has then been studied for removal and recovery of actinides and for analytical separation of actinides and fission products. In the present work, the distribution coefficients of Am(III), Pu(IV) and U(VI) between HNO_3 and TBP-CMP/XAD-4 or TBP-CMPO/XAD-4 resin were measured and compared with those for anion and cation exchange resins. The results show that these resins containing the bifunctional extractants are more effective than the ion exchange resins for removing the actinides from nitric acid. On the other hand, the elution behavior of Np(V), Am(III), Cm(III) and fission products on CMP/XAD-4 column was also studied. The results show that Np(V) and fission products except lanthanides are effectively separated from trivalent actinides and lanthanides using only nitric acid.

1 INTRODUCTION

The various nitric acid solutions containing actinides are generated from many stages of nuclear fuel cycle. The separation, removal and recovery of the actinides from the waste solution have been an important problem in view of radioactive waste management. Bifunctional organophosphorus compounds, dihexyl-N,N-diethylcarbamoylmethylphosphonate(CMP) and octyl(phenyl)-N,N-diisobutylcalbamoylmethylphosphine oxide(CMPO), extract trivalent actinides as well as tetra- and hexavalent actinides from moderately concentrated nitric acid (Horwitz et al., 1983). Application of extraction chromatography with the bifunctional extractants, in the presence of TBP as a modifier, has then been studied for the removal and recovery of tri-, tetra- and hexavalent actinides from nitric acid. On the other hand, the CMP solvent extraction data of trivalent actinides and lanthanides suggest the possibility of mutual separation of these elements using only

nitric acid (Horwitz et al., 1981). Application of extraction chromatography in the CMP-HNO_3 system has also been studied for the analytical separation of the actinides and fission products. The present paper deals with the comparative studies of TBP-CMP/XAD-4 and TBP-CMPO/XAD-4 resins with anion and cation exchange resins on the removal and recovery of Am(III), Pu(IV) and U(VI), and the elution studies of Np(V), Am(III), Cm(III) and fission products on CMP/XAD-4 column.

2 EXPERIMENTAL

2.1 Materials

CMP, obtained from Occidental Chemical Corp., New York, was used without additional purification. CMPO, obtained from M&T Chemicals, Inc., New Jersey, was purified by hydrolysis with 6 M HCl and washing with 0.5 M NaOH and water. TBP, obtained from Koso Chemical Co., Tokyo, was purified by washing with 5 % Na_2CO_3 and water. Amberlite XAD-4, supplied as 20-50 mesh beads from Rohm and Haas Co., USA, was used as a support material of extractants. The preparation procedure of extractant loaded XAD-4 resin was described in the previous report (Akatsu et al., 1990). The 50 wt%(1 g of extractant/g XAD-4 resin) resins in 20-50 mesh or 100-130 mesh were used for batch or column experiments, respectively.

Radioactive tracers such as ^{233}U, ^{237}Np, ^{239}Pu, ^{241}Am and ^{244}Cm were used in the experiments. Fission products(^{90}Sr-Y, ^{137}Cs, ^{144}Ce-Pr and ^{147}Pm etc.) were prepared from uranium dioxide irradiated in Japan Research Reactor 4 (JRR-4).

2.2 Batch distribution experiments

From the radiometric analysis of aqueous phase, the distribution coefficient D as defined by Eq.(1) was calculated

$$D = \frac{C_0 - C}{C} \cdot \frac{V}{M} \quad (ml/g) \qquad (1)$$

where C_0: initial concentration of a metal ion in the aqueous phase, C: equilibrium concentration of the metal ion in the aqueous phase, V: volume of the aqueous phase (ml), M: mass of the extractant/XAD-4 or ion exchange resin (g).

2.3 Column experiments

Slurry packing procedure was adopted for the column preparation. Temperature of the column was held constant by a water

jacket with circulating thermostat. The eluent was supplied by a micro-tube pump and the flow rate was held constant. Fractions of 1.0 ml volume were collected by an automated fraction collector, and the element in each fraction was determined by the radiometric analysis.

3 RESULTS AND DISCUSSION

3.1 Application of TBP-CMP/XAD-4 and TBP-CMPO/XAD-4 resins for removal and recovery of actinides

(i) Distribution coefficients of Am(III), Pu(IV) and U(VI).

Figures 1 and 2 show the distribution coefficients of Am(III), Pu(IV) and U(VI) between HNO_3 and 50 wt% TBP-CMP/XAD-4 and TBP-CMPO/XAD-4 resins, respectively. The tetravalent plutonium was prepared by the addition of 0.001 M $NaNO_2$ at the batch distribution experiments. The distribution coefficients of all three actinides for the TBP-CMP/XAD-4 resin increased with increasing HNO_3 concentration. The higher distribution coefficients of the actinides for the TBP-CMPO/XAD-4 resin were observed in the wide range of HNO_3 concentration. The effect of CMP or CMPO addition on the extraction of the actinides was the greatest for Am(III).

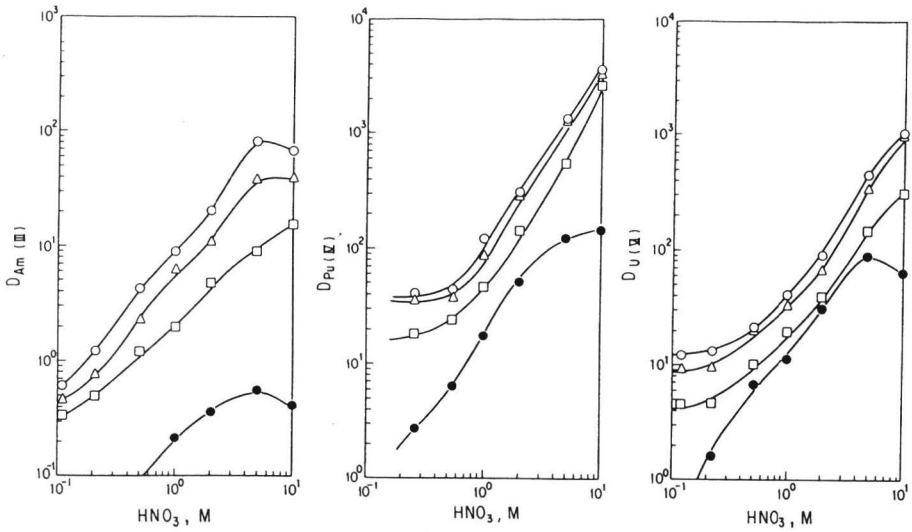


Fig. 1 Distribution coefficients of Am(III), Pu(IV) and U(VI) between HNO_3 and 50 wt% TBP-CMP/XAD-4 resin; ●, 1.88 M TBP; □, 1.25 M TBP-0.46 M CMP; △, 0.63 M TBP-0.92 M CMP; ○, 1.38 M CMP; M, mol/kg resin; 25°C.

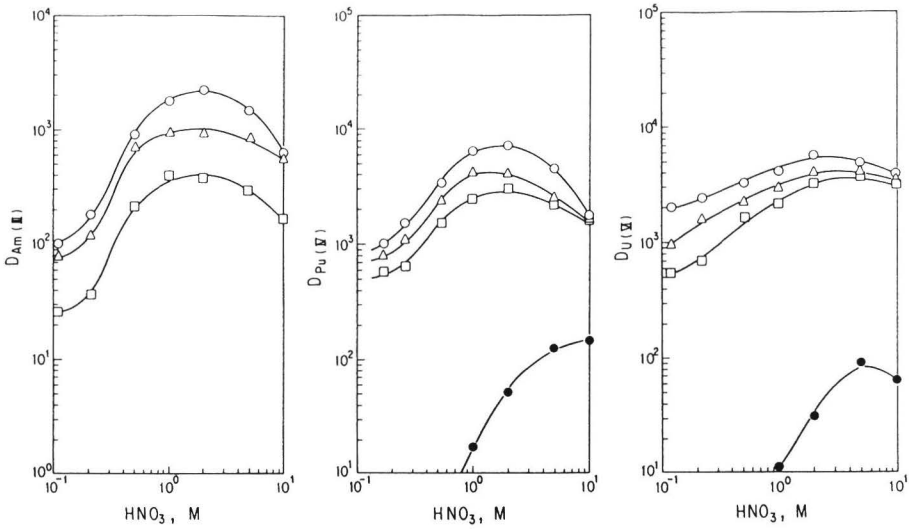


Fig. 2 Distribution coefficients of Am(III), Pu(IV) and U(VI) between HNO_3 and 50 wt% TBP-CMPO/XAD-4 resin; ●, 1.88 M TBP; □, 1.25 M TBP-0.41 M CMPO; △, 0.63 M TBP-0.82 M CMPO; ○, 1.23 M CMPO ;M, mol/kg resin; 25 °C.

A distinct synergistic interaction of the bifunctional extractant and TBP was not observed in both the TBP-CMP and TBP-CMPO systems. These results show that the TBP-CMP/XAD-4 resin makes it possible to extract tri-, tetra- and hexavalent actinides at higher concentration of HNO_3 and to recover the extracted actinides by dilute HNO_3. On the other hand, although the TBP-CMPO/XAD-4 resin is a powerful resin for the removal of the actinides from HNO_3, the use of complexing agents might be required for back extraction of the actinides from the resin at low concentration of HNO_3.

(ii) Comparison with anion and cation exchange resins.

The distribution coefficients of Am(III), Pu(IV) and U(VI) between HNO_3 and Dowex 1-X8 and 50W-X8 were also measured to compare with the results of the TBP-CMP/XAD-4 and TBP-CMPO/XAD-4 resins. The distribution coefficients obtained with the anion exchange resin (Dowex 1-X8) were more than 10^2 for Pu(IV) at above 3 M HNO_3, however those for Am(III) and U(VI) were less than 10^2 and 10^1 in the range of 0.1 and 10 M HNO_3, respectively. On the other hand, the higher distribution coefficients D were

obtained with the cation exchange resin (Dowex 50W-X8) at low concentration of HNO_3, that is, $D>10^3$ for Am(III) and Pu(IV) at below 1.5 M HNO_3 and $D>10^2$ for U(VI) at below 0.5 M HNO_3. These results show that the cation exchange resin has a high ability for the removal of the actinides at low concentration of HNO_3, while the anion exchange resin does not have the ability except for Pu(IV).

3.2 Application of CMP/XAD-4 column for analytical separation of actinides and fission products

(i) Effect of temperature, flow rate and HNO_3 concentration.

In order to determine the conditions of column operation for actual separation of actinides and fission products, the effect of temperature of column, flow rate and HNO_3 concentration of eluent on the distribution coefficient, separation factor and resolution was studied by using Np(V), Am(III) and Cm(III). The separation factor is expressed as a ratio of the distribution coefficients. The resolution, which represents the degree of separation of two peaks in an elution chromatogram, is defined by

$$R = \frac{V_2 - V_1}{W_1 + W_2} \qquad (2)$$

where V is the total retention volume and W is the width of elution peak at the 1/e concentration of solute to the maximum. The results suggest that the CMP/XAD-4 column operation is more effective for slower flow rate of eluent and higher temperature of the column at a fixed HNO_3 concentration and that the resolution increases with increasing HNO_3 concentration, while the separation factor is held constant.

(ii) Separation of Np(V), Am(III), Cm(III) and fission products.

On the basis of the experimental results, the elution curves of Np(V), Am(III), Cm(III) and fission products were measured at the optimum condition and are shown in Fig. 3. The results indicate that Np(V) and the fission products except lanthanides are effectively separated from trivalent actinides and lanthanides, that the trivalent actinides and lanthanides can be separated roughly from each other by using only HNO_3 and that the order of the distribution coefficients is Ce>Am>Pm>Cm>>Sr>Np>Cs.

4 CONCLUSIONS AND FUTURE WORK

The TBP-CMP/XAD-4 and TBP-CMPO/XAD-4 resins were more effec-

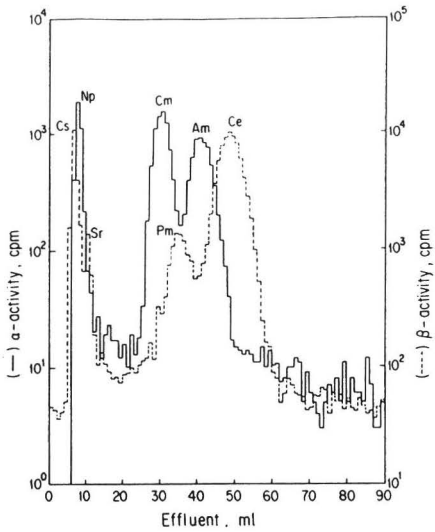


Fig. 3 Elution curves of Np, Am, Cm and fission products; Column bed, 6 mmϕx270 mm; Resin, 4.0 g of 50 wt% CMP/XAD-4; Eluent, 1.5 M HNO_3; Flow rate, 0.020 ml/cm^2min; Temperature, 40°C.

tive than the ion exchange resins for removing tri-, tetra- and hexavalent actinides from moderately concentrated HNO_3. The metal ion loading capacity of the resin and the recovery of the actinides from the resin should be studied by both batch and column experiments.

Chromatographic separation of Np(V), Am(III), Cm(III) and fission products by the CMP/XAD-4 column was carried out by using only HNO_3 without other complexing agents. The extraction chromatography in the CMP- or CMPO-HCl and CMPO-HNO_3 with complexing agent systems should also be studied for more selective separation of the actinides from fission products and from each other.

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PURIFICATION OF URANIUM FROM ZIRCONIUM USING MIXER-SETTLER UNIT

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Abstract

Uuranium solution was used as a scrubbing agent for the purification of uranium from zirconium using 16-stages mixer-settler unit. The different parameters affecting decontamination of uranium extracted by 30% TBP solution diluted by Misrsol-K oderless kerosene were studied. These parameters include uranium feed concentrations and nitric acid molarities at phase ratio 1:1 organic to aqueous solutions. At optimum conditions, more than 90% of the original zirconium concentration in the organic feed uranium solution was scrubbed out into the aqueous phase.

INTRODUCTION

Among the most troublesome elements which interfere in reprocessing of irradiated fuel elements is zirconium.

In the past three decades, an intensive work was carried out in the area of purification of uranium from fission products (Benedict et al,1981; Flagg, 1961; Schulz, 1987; McKibben, 1984).

Kim et al (1982) used organic solvents of Alamine 336 and TBP diluted in dodecane for the separation of uranium from zirconium and other impurities in acid media by liquid-liquid extraction. Uranium can be completely separated from cerium, lanthanum, yttrium, barium, strontium and iron in any concentration of nitric acid but zirconium in the limited acidity of 2-3M nitric acid with TBP-dodecane as an extractant. Pai et al (1982) studied the extraction, scrubbing and stripping behaviour of uranium , zirconium and ruthenium with di-n-hexyl and di-n-octyl sulfoxides in Solvesso-100 and tri-n-butyl phosphate (TBP) in Shell Sol-T irradiated by various gamma doses (0-169 Mrads).

Rozen et al (1977) described a mathematical model of extraction process in the mixer-settlers for a simple step process and extraction complicated with chemical reactions. Sraier et al (1978) described a laboratory plant for the nuclear fuel reprocessing, the initial radioactive solutions for the extraction experiments were obtained by selective nitric acid leaching of the core containing UO_2, followed by eight extraction runs. Different variants of the first cycle of the regeneration process were tested. The effects of the flow rate of the phases, the phase composition, the type of reducing agent, its excess, and the solvent degradation on uranium and plutonium purification from the fission products was satisfactory in all cases (DF=10^3 to 10^5). The uranium product of the first cycle was primarily contaminated with Zr^{95}/Nb^{95} fission products.

Experimental

1. Chemicals

The main chemicals used in this work were AR grade; uranyl nitrate, zirconium nitrate, TBP diluted in Misrsol-K diluent, stannous chloride, ammonium thiocyanate, nitric acid and Alizarine red-S.

2. Instrumentation

A " Shimadzu " type (P/N 204-04550) UV-visible double beam recording spectrophotometer was used for colourimetric determination of uranium and zirconium. All extraction-scrubbing runs were carried out using Cyrano type 16-stages mixer-settler banks of dimensions 395x90x90 mm and mixer volume of 6 ml and settler volume of 17 ml.

3. PROCEDURES

3.1 Batch Equilibrium Extraction

Batch experiments were carried out to study the different parameters affecting the extraction of uranium and zirconium nitrate having different concentration by vigorous shaking with equal volumes of TBP concentrations diluted by Misrsol-K diluent for 30 minutes to reach equilibrium.

3.2 Counter-Current Extraction

In all counter-current extraction runs the flow rates of the feed solution and the organic solvent were 180 ml/h. Organic phase used was 30% TBP diluted in Misrsol-K. Sampling were taken from the 16 stages at the end of each run for the analysis of nitric acid, uranium and/or zirconium. Other operating conditions for each run are given in the results and discussion.

RESULTS AND DISCUSSION

1. Batch Experiments

The effect of uranyl nitrate concentrations on the extraction of zirconium nitrate (2g/L) from different nitric acid concentrations by 30% TBP/Misrsol-K was investigated. The obtained results are given in figures 1-2. The effect of uranium nitrate at different nitric acid concentrations is given in Fig. 1. From this figure, it is clear that by increasing uranium concentrations from 10-250g/L, the distribution of uranium decreased exponentially. Increasing nitric acid molarities up to 3M increased the D values of uranium. Similar behaviour was also observed for the extraction of zirconium under the same conditions, Fig.2.

To investigate the possible scrubbing of zirconium from the organic phase containing uranium and zirconium by different uranium concentrations, an organic bearing solutions containing uranium and zirconium were first prepared from corresponding aqueous nitric acid solutions of different molarities having 65 g/L U together with 2g/L Zr. These solutions were then contacted with uranyl nitrate solutions of different concentrations in certain nitric acid molarities (1,2 and 3M HNO_3). The concentrations of uranium and zirconium were determined after

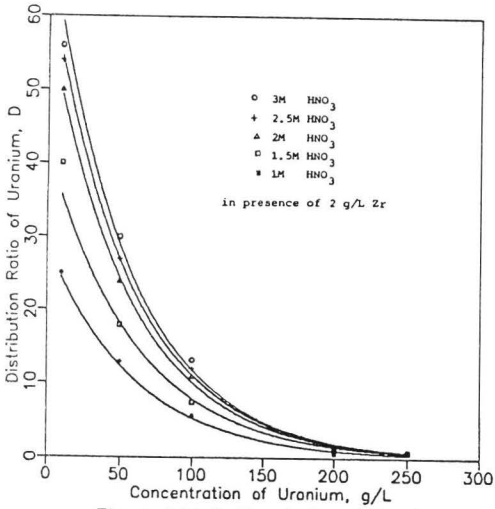


Fig. 1. Distribution Ratio of Uranium at Different Nitric Acid Concentrations

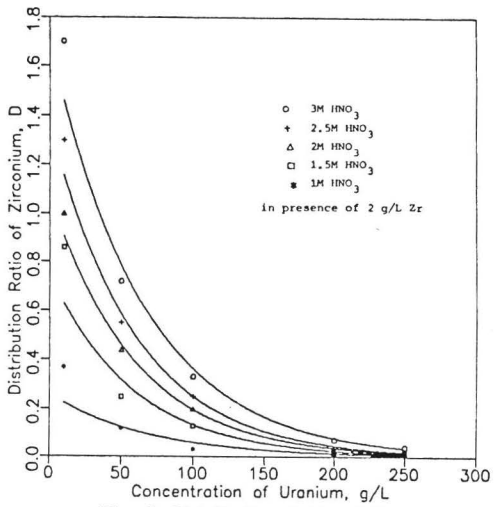


Fig. 2. Distribution Ratio of Zirconium at Different Nitric Acid Concentrations

equilibration and given in Fig. 3-5, as function of initial uranium concentrations in the aqueous phase. A general behaviour of these batch scrubbing experiments is the linear increase of uranium loading in the organic phase with increasing uranium concentration in the aqueous phase. For zirconium, it is found that up to around 40 g/L of uranium in the aqueous phase (scrubbing solution) no change in zirconium content in the organic phase was observed, Fig.3-5. Increasing uranium concentration in the aqueous phase a sharp decrease in zirconium content in the organic phase was attained. For one batch scrubbing step, a decontamination factor of more than 3, 4 and 2.5 could be achieved from 1M, 2M and 3M HNO_3 aqueous solutions, respectively.

2.Counter-Current Extraction-Scrubbing Runs

Prior to scrubbing run, uranium-zirconium run by the 16 stages mixer-settler unit was carried out using a feed solution of 1M HNO_3 containing 60 g/L uranium together with 2 g/L zirconium at a flow-rate of 180 ml/h. The organic solvent used was 30% TBP/Misrsol-K at the same feeding flow-rate. After steady state conditions, the extract contained 55 g/L uranium and 200 mg/L zirconium. Zirconium in the organic phase was then scrubbed in the mixer-settler by scrubbing solution of 1M HNO_3 containing 50 g/L uranium at a flow-rate of 180 ml/h for both phases. The conditions for zirconium scrubbing run is given in Table.1. From this Table, it is clear that, while the uranium concentration in the organic extract increased from 55 to about 91 g/L, yet the concentration of zirconium in the raffinate was found to equal 180 mg/L. This shows that zirconium in the organic extract decreased by about 90% after scrubbing with uranium aqueous solution using 16 stages mixer-settler unit.

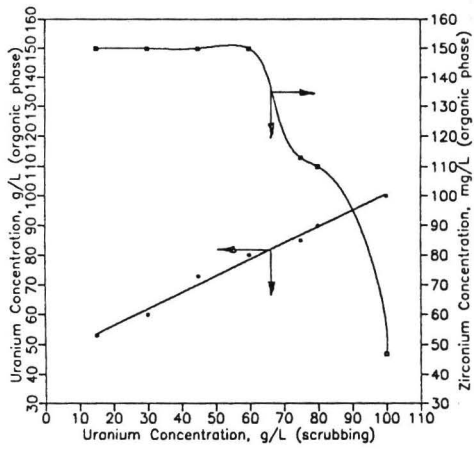


Fig. 3. Scrubbing of Zirconioum at 1M HNO_3

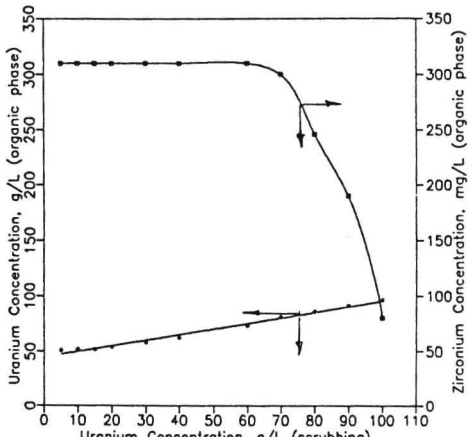


Fig. 4. Scrubbing of Zirconium at 2M HNO_3

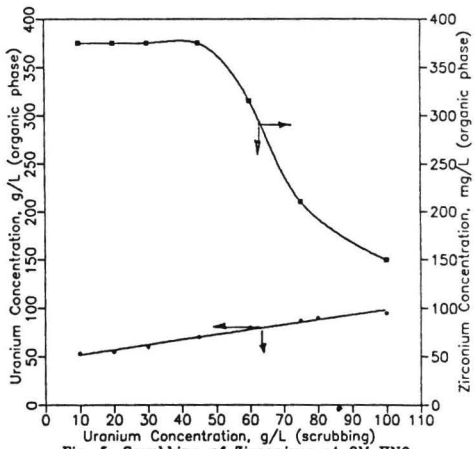
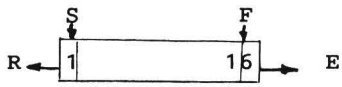


Fig. 5. Scrubbing of Zirconium at 3M HNO_3

In conclusion, it is rather feasible to purify uranium from zirconium in TBP extract by scrubbing solutions containing uranium using mixer-settler counter-current units. Optimization of the counter-current scrubbing processes is still under investigations.

TABLE 1
Conditions of Zirconium Scrubbing Run

Conditions	Data
1. Type of feeding	
2. Duration of the run, hours	14
3. Impeller speed, r.p.m	1600
4. Temperature	25±2°C
5. No. of actual stages	16
6. Flow-rates, ml/h -aqueous feed containing 50 g/L of uranium, 1M HNO_3	180
-organic phase : 55 g/L of uranium + 200 mg/L of zirconium	180
7. -Extract: U g/L	91
HNO_3	0.30 M
-Raffinate Zr mg/L	180
HNO_3	1.05 M

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PERFORMANCE OF THE FEED-RATE CONTROL SYSTEM FOR THE URANOUS NITRATE SOLUTION OPERATED IN TOKAI REPROCESSING PLANT

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ABSTRACT

Five-year performance of the unique flow-rate control system for the feed of uranous nitrate in Tokai Reprocessing Plant is presented. This system has a computer controlled automatic-batchwise flow detection mechanism and can cover wide range of the feed rate from 0.2 l/h to 18 l/h. The flow rate is determined by repeated fill-dump manner with aflow-rate-determination tube controlled by a computer. The resulting flowrate convergence was found to be quite well even at the very low feed rate, and it allowed the U-impurity of the Pu product to be greatly improved in this 5-year hot operation.

INTRODUCTION

In the extraction process of Tokai Reprocessing Plant(TRP), hydrazine stabilized uranous nitrate solution is used as a reducing regent for the separation of plutonium from uranium. The uranous nitrate solution is produced in an electrolysis cell and fed into the partition cycle, the pulutonium purification cycle and the uranium purification cycle. The feed-rate of uranous solution has to be kept within a proper range to keep the product specification. Accurate and stable feed is required especially when the throughput of plutonium tends to change. The turning point of the spent fuel specification and the plutonium flush-out operation are the typical cases when sophisticated feed rate control is required. This system was developed to overcome the unsteadiness and difficulty in the control of the previous system using conventional pump technology. A new technology using micro-computer control developed by Chiyoda Chemical Engineer & Construction Co. Ltd. was applied to this system.

2 MECHANISM AND FUNCTIONS OF THE SYSTEM

2.1 Structure of the system

Fig. 1 shows the outline of this system. The notable feature required to this system was to cover the wide range of the feed-rate of uranous nitrate solution with considerably high accuracy. In order to enhance the accuracy of the planger pump, binary control on the stroke and the frequency of the electric power supply was adapted.

In addition, a feed back control was adapted to ensure the high stability in the low flowrate region. Because an accurate and reliable flowrate determination for the wide flow range(0.15 l/h ~ 18 l/h) was impossible with the conventional flowmeters, "automatic batchwise flowrate measurement technique" was developed and applied.

As can be seen in Fig.1, this system consists of one central micro-computer, eight operator's boards and eight pairs of measurement tube and planger pump. The central computer manages all of the controls and calculations, that allows the operator not to have to do anything, except for plugging in a set-value on the boards.

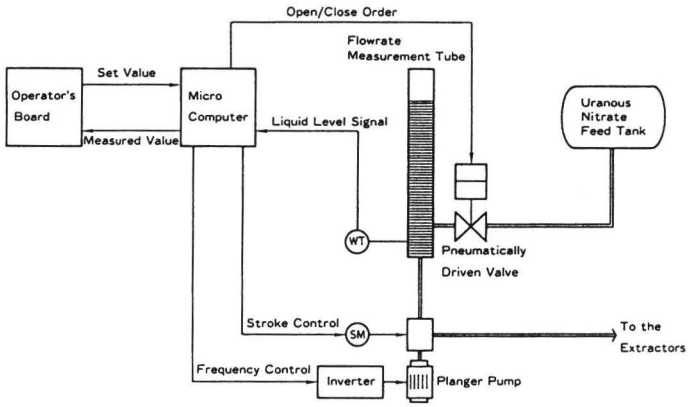


Fig. 1 Outline of Feed-Rate Control System for Uranous Nitrate System

2.2 Binary Control of the Pump

For facilitating accurate low flowrate, the pumps are binarily controlled on their stroke and frequency of the electric power. By lowering the frequency of the electric power with an inverter (i.e. rotation of motor), very low flowrate can be achieved with rather high stroke that ensures high accuracy. Fig.2 shows the flowrate range that can be covered by this system. The size of the pump-head was chosen to adjust the required flowrate range for eight independent feed lines. The computer reads the set value that is plugged in by the operators on the operator's board and determines the best combination of the frequency and stroke. This enables the system cover to wide range of the flowrate.

2.3 Automatic Batchwise Flowrate Measuremernt

Fig.3 shows the sequence of automatic flowrate measurement performed by the central microcomputer. The liquid is filled to the flowrate measurement tube up to a certain level, and after closing the valve of the tank feed line, the liquid is pumped out from the measurement tube. The liquid level in the tube is periodically read with the weight transmitter to calculate the decrease rate (flowrate) by the computer. The calculation of the flowrate is done with a least square method, which enhances the accuracy of the flowrate determination. If the liquid level of the tube reaches to the lowest level, the inlet valve is opened to fill it again, and this sequence is automatically repeated. A best time span for one batch measurement is selected for different flowrate.

2.4 Logic flow of the Control

Fig.4 shows the sequential flow of the control. The set value on the operator's board is periodically read by the computer and the best combination of the frequency and stroke is chosen. The first batchwise flowrate measurement starts and the measured flowrate is displayed on

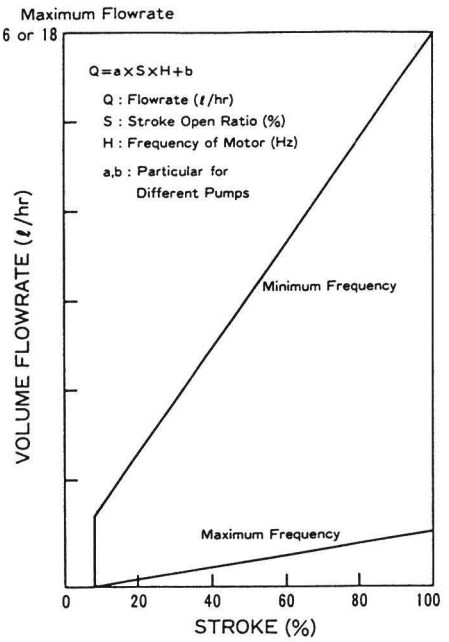


Fig. 2 Flow Range Covered by the Combination of Planger Stroke and Motor Rotation

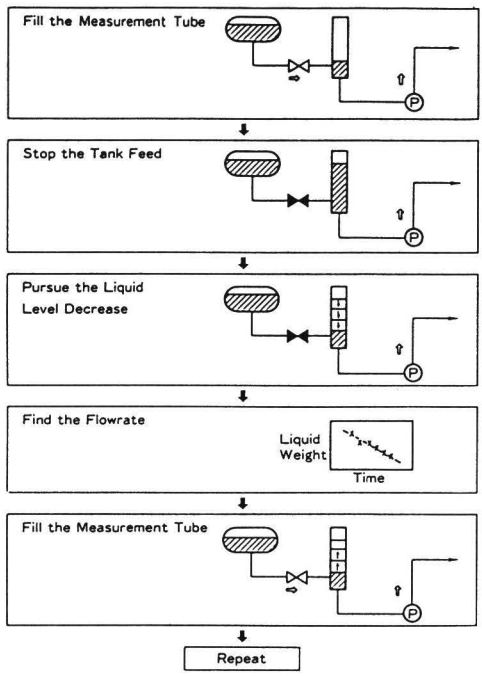


Fig. 3 Sequence of Automatic Batchwise Flowrate Measurement

the operator's boards. After getting the measured value, the deviation between the set and observed flowrate is calculated and fine correction on the frequency is carried out to compensate the deviation. Fine control on the frequency is continued on every measurement batch. In order to avoid a haunting or divergence, a proper corrective parameters are set for the convergence.

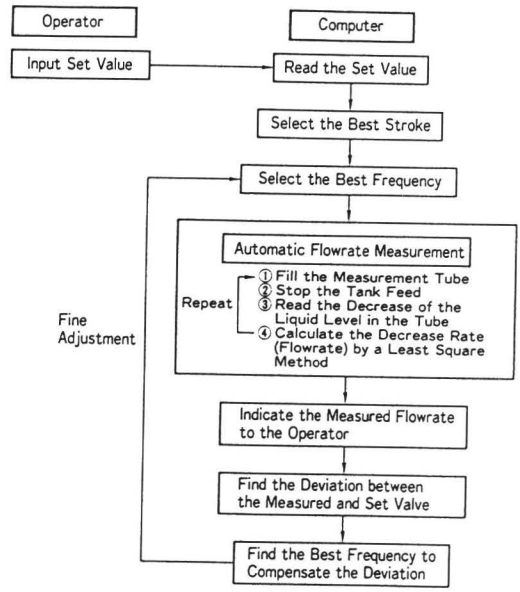


Fig. 4 Control Flow of "Feed-Rate Control System for Uranous Nitrate Solution"

3. PERFORMANCE OF THIS SYSTEM

3.1 Flowrate convergence

Fig.5 shows the observed convergence of the measured flowrate to the set value. Because of the feed-back control on the frequency, initial deviation to the set value decreases as the number of batchwise flowrate measurements proceeds. The deviation for the flowrate greater than 2 l/h is already less than 2% at the first measurement, which means that the first selection of the stroke and frequency is proper and that the selected pair of parameters gives very accurate response to the set value. The deviation of the flowrate 0.15 l/h is large at the first measurement, it converges to less than 2% at the third measurement. It owes to a proper fine-adjustment of the frequency.

Fig.6 represents the example of the flowrate fluctuation observed during continous hot operation. It can be seen that the fluctuation for large flowrate(8 and 17 l/h) is always less than 2 %. The fluctuation of the low flowrate(0.9 l/h) sometimes exceeds 4%, but converges to less than 2% with increasing number of batch measurements. These convergences are satisfactorily good to the required accuracy.

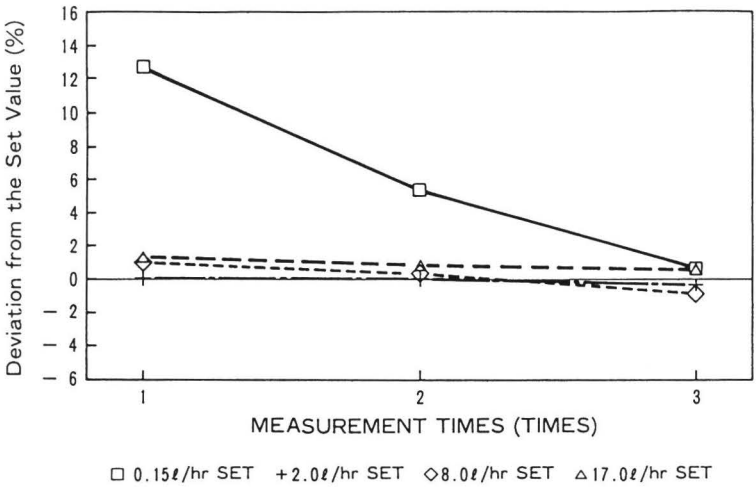


Fig. 5 Convergence of the Experimental Flowrate to the Set Value

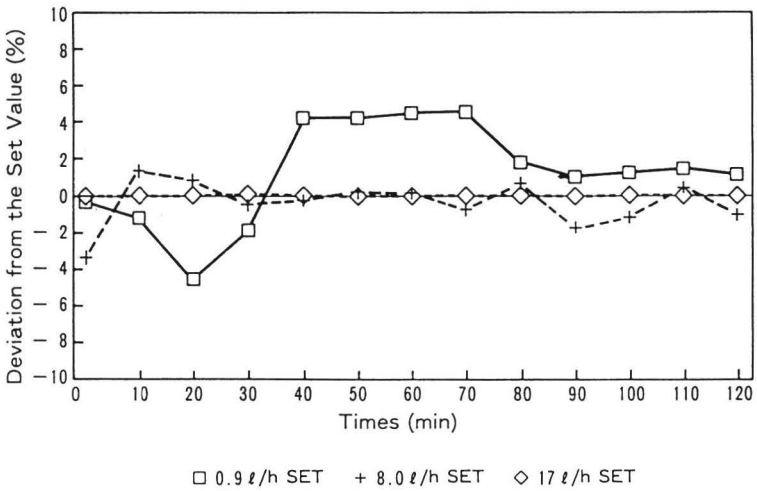


Fig. 6 Flowrate Fluctuation Observed during Continuous Operation

3.2 Improvement to the Products Specification

Some noticeable improvements were achieved to the specification of the Pu product by the use of this system. Before installing this system to the process in TRP in 1985, the uranous nitrate solution was over-fed to avoid the unexpected undercut of the

minimun necessary flowrate. This was likely to increase the U-impurity in the Pu product. The outstanding improvement in the accuracy and stability in the flowrate allowed the operator to apply minimum required flowrate. The improvement can be seen in the comparison of the U-impurity between before and after the installation of the system. Fig.7 shows the example of the U-impurity data actually observed in 1982 (before the installation of the system) and 1987(after the installation).

It can be seen that frequency of the high U-impurity is reduced by the use of this system. It is also notable that the consumption of the uranous nitrate solution was reduced by this system. This system has been operated for longer than 20000 hrs without any significant trouble, which testified its reliability and toughness.

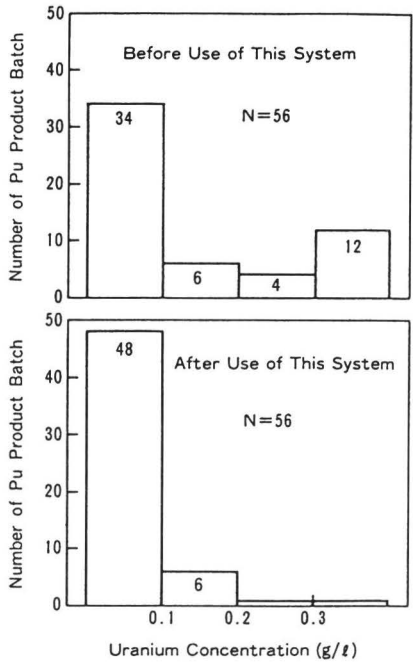


Fig. 7 Uranium Impurities of the Plutonium Products of Tokai Reprocessing Plant (Before and After Use of this system)

4. CONCLUSION

An advanced feed-rate control system for the uranous nitrate solution was developed and applied to Tokai Reprocessing Plant. The accuracy and stability of the flowrate that was achieved by the binary control of the pump and batchwise flowrate measurement made an improvement to the process operation of Tokai Reprocessing Plant. This system can be applied to the similar process in other reprocessing plants.

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THE REMOVAL OF THORIUM ISOTOPES FROM A WASTE ACIDIC LIQUOR

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ABSTRACT

A solvent extraction route for the removal of thorium isotopes from a waste acidic liquor has been explored. Solvents containing either nitrogen or phosphorus functional groups were initially examined and equilibrium curves constructed. The influence of acidity, temperature and composition of feed liquor on the efficiency of thorium extraction is reported. The most successful solvent, TOPO, was further evaluated and the problems of upscaling the process are explained.

INTRODUCTION

A solvent extraction circuit, employing tri-n-butyl phosphate dissolved in a suitable diluent, is used by uranium ore concentrate (UOC) refiners to purify and recover uranium. A crude concentrated uranyl nitrate liquor is produced by dissolving UOCs in a slight excess of nitric acid prior to the solvent extraction purification circuit. In the latter, uranium partitions into the solvent phase whilst all other cations, such as sodium, magnesium, aluminium, iron and thorium isotopes which are also present in UOCs, remain in the aqueous phase and are hence discarded in the raffinate. The radionuclides present in the raffinate in addition to trace quantities of uranium are naturally occurring thorium 232 and uranium daughters thorium 230, thorium 234 and protactinium 234. Their concentrations in the raffinate can range from a few thousand parts per million to less than one part per billion. A typical composition of raffinate is reported in Table 1.

The work described in this paper relates to the recovery of the radionuclides, specifically the thorium isotopes from the aqueous raffinate.

PROCESS SPECIFICATION

A process specification was produced prior to any development work being undertaken. Some of the major technical criteria of this specification are reported -

(i) the process should be versatile and capable of accommodating significant variations in the raffinate composition and volumetric arising.

(ii) a thorium removal efficiency from raffinate of >99% was required under all conditions.

(iii) a significant volume reduction in the quantity of aqueous backwash liquor compared with the original raffinate feed was required.

(iv) the thorium should be finally presented in a solid form.

TABLE 1

Typical Composition of Raffinate

Element	Composition
Nitrate	~120 g/l
Sulphate	5 g/l
Fluoride	2 g/l
Sodium	5000 ppm
Potassium	300 ppm
Magnesium	400 ppm
Calcium	600 ppm
Aluminium	700 ppm
Iron	800 ppm
Thorium	800 ppm
Free Nitric Acid	~60 g/l

SOLVENTS SELECTED FOR ASSESSMENT

Various solvents had been identified in earlier work aimed at the development of a process for the removal of thorium from solids (Rushton 1985, White et al 1961, Deqian, 1980). In addition to these solvents, others were identified from a literature search (Tedesco et al 1966, De, 1970). The thorium extraction efficiencies of ten solvents were measured. 0.1M solutions of these extractants in odourless kerosene (OK) were contacted with an equal volume of raffinate containing 440 ppm thorium and ~70 g/l free nitric acid for ten minutes. After phase separation the phases were analysed for thorium content and the extraction efficiencies determined. These solvents and their measured thorium extraction efficiencies are reported in Table 2.

These initial trials showed that the four solvents with the highest extraction efficiencies and therefore the greatest potential to achieve the target figure were -

TOPO
D2EHPA
HEH(EHP)
and Cyanex 923 (a mixture of trialkyl phosphine oxides, including TOPO).

However, as Cyanex 923 was still under development by the manufacturer and was not available in commercial quantities, this solvent was excluded from further investigations.

TABLE 2

Solvents and their thorium extraction efficiencies
0.1M solvent in OK (batch studies - single contact)

Solvent	% Th Extraction
Tri-n-octylphosphine oxide (TOPO)	99.9
Di-2-ethyl hexylphosphoric acid (D2EHPA)	99.8
Dibutyl phosphonate (DBBP)	39.0
bis-2-ethylhexyl phosphite (bis2EHP)	50.5
Hexyl ethyl Hexyl (ethylhexyl phosphite) (HEH(EHP))	95.6
Trioctylamine (TOA)	44.3
Amberlite LA2 (an unspecified secondary amine)	37.3
Aliquat 336 (an unspecified quaternary ammonium salt)	43.5
Tributyl phosphate (TBP)	34.5
Cyanex 923 (a mixture of trialkyl phosphine oxides)	99.6

Other factors which also influenced the selection of TOPO, D2EHPA and HEH(EHP) were -

(i) the compatibility of the solvent with nitric acid

(ii) low solvent losses to the aqueous stream

(iii) commercial availability of the solvent

(iv) the need to minimise plant inventory, eg solvents which did not require a clean-up facility

(v) the compatibility with upstream operations

(vi) solvent costs

To substantiate the selection of these three solvents, equilibrium curves were constructed from batch experimental data in the conventional manner. The results for TOPO/OK systems are presented graphically in Figure 1 which indicates that TOPO at all concentrations tested could be effectively used to remove thorium from raffinate in a continuous counter-current solvent extraction plant.

The equilibrium curves produced for the other two solvents showed that -

(i) for equivalent molarities of solvent in odourless kerosene, D2EHPA was equally as effective as TOPO.

(ii) the construction of a continuous thorium solvent extraction plant would be impractical for HEH(EHP) as the equilibrium curve approached the origin along the aqueous axis rather than the organic axis.

Although further evaluation of both TOPO and D2EHPA was necessary, only the additional data collected for TOPO systems are reported in this paper.

The influence of aqueous phase acidity and temperature were examined to validate the versatility of the solvent to process fluctuations. Experimental data for a 0.1M TOPO/cyclohexane system showed that increasing the acidity (nitric acid) of the aqueous phase, which contained ~4000 ppm thorium, from one to three molar reduced the thorium distribution value (K_{Th}) from 36 to 11. This behaviour was expected as nitric acid is generally coextracted as HNO_3 . TOPO with the thorium nitrate - TOPO adduct ($Th(NO_3)_4$. 2 TOPO. A similar decrease in the K_{Th} value ie from 36 to 14 was also measured if the temperature of the 4000 ppm Th/1M nitric acid system was increased from 25°C to 60°C.

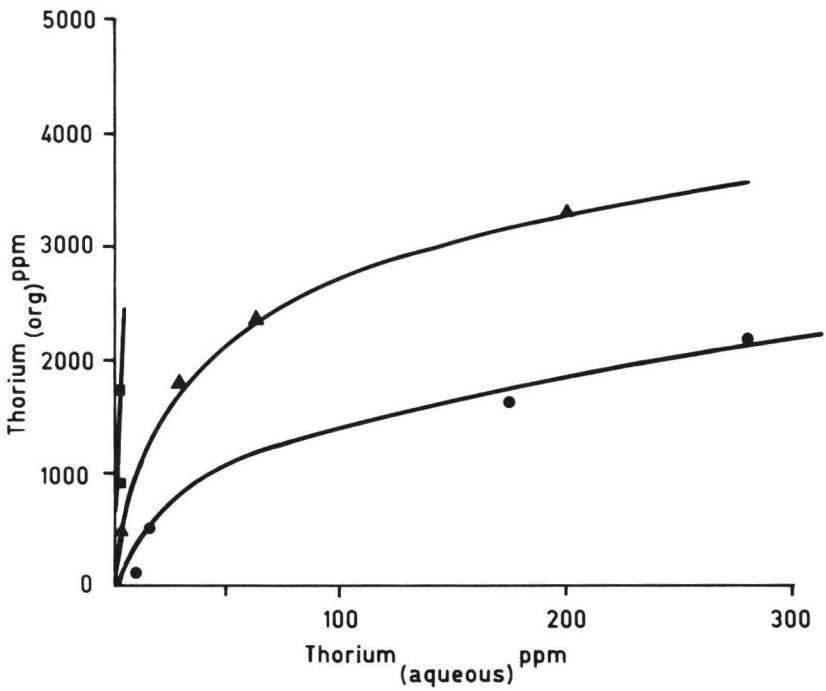


FIGURE 1 THORIUM EQUILIBRIUM CURVES FOR TOPO/OK SYSTEMS AT AMBIENT TEMPERATURE.

● 0·05M TOPO/OK
▲ 0·10M TOPO/OK
■ 0·25M TOPO/OK

The selectivity of TOPO for thorium in preference to ferric iron, aluminium and magnesium was also examined and the results are reported in Table 3.

TABLE 3
Thorium Selectivity Ratios for 0.1M TOPO/cyclohexane

Free Acidity of Aqueous phase M HNO_3	Temperature °C	Thorium Selectivity Ratios (10^3) Fe	Al	Mg
1	25	32	8.3	49
	60	7.6	3.4	20
3	25	4.9	2.4	13
	60	3.2	1.2	6.9

Previous published data indicated that iron (iii), aluminium and magnesium nitrates are not extracted by TOPO from 1M nitric acid solutions. However, this study revealed that these metals are extracted albeit in trace quantities. Typical K values for these metals were of the order 10^{-3} with aluminium the most extractable and magnesium the least.

The co-extraction of nitric acid with thorium nitrate influenced the selection of a back extractant for the recovery of thorium from the loaded solvent. Several potential back extraction reagents were examined, initially using a batch procedure. Some of these reagents and the corresponding results are reported in Table 4.

TABLE 4
Thorium Back Extraction Efficiencies

Back Extraction Liquor	% Th removed from the solvent
0.1M EDTA	80
1.0M Tri-potassium citrate	86
1.0M Tartaric acid	18
3.0M Sulphuric acid	89
1.0M Sulphuric acid	83
0.3M Sulphuric acid	78
1.0M Na_2SO_4/1.0M H_2SO_4	91
2.0M K_2CO_3	85

In an attempt to overcome the adverse effect of nitric acid in the solvent on the thorium back extraction stage, a water scrub stage was considered. Batch studies indicated that the back extraction efficiency for the 0.3M H_2SO_4 system could be increased by means of a solvent water scrub from 78% to 94%. An alternative approach to a water scrub stage was considered to be the use of a buffered back extraction liquor. Consequently, a 1M Na_2SO_4 solution was tested in comparison with 1M H_2SO_4. The measured back extraction

efficiencies were 71% and 83% respectively. The 'low-cost' back extraction liquors were further evaluated using a 10-stage laboratory size mixer-settler unit. Problems with phase disengagement were observed with low ionic strength and/or low acidity systems. Ultimately a 4M potassium carbonate solution was selected.

Resulting from the initial batch studies and a series of continuous counter-current trials using a twenty stage laboratory size mixer settler unit a process flowsheet was produced.

This flowsheet was ultimately validated at pilot plant scale with an aqueous feed throughput of ~100 l/hr generating a back extraction liquor of ~1 l/hr (Rushton, 1989). The following extraction efficiencies were achieved for the corresponding conditions (Table 5).

TABLE 5

Pilot-Plant Data

Raffinate Thorium Content ppm	Solvent to Aqueous Ratio		Thorium Extraction Efficiencies (%)		Thorium Content of Back Extraction Liquor ppm
	Forward	Back	Forward	Back	
165	1:10	10:1	99.5	99.9	12690
1125	1:3.5	10:1	99.9	99.9	30290
1210	1:3.5	10:1	99.8	99.8	32580
905	1:5	10:1	99.9	99.7	34810

Both the laboratory and pilot-plant continuous studies revealed the following potential problems which would need to be addressed in the design of an upscaled facility.

(i) control of process parameters due to significant variation in the thorium content of the raffinate.

(ii) crystallisation of potassium nitrate in the back extraction liquor.

(iii) shielding requirements of the equipment.

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PUREX PROCESS IMPROVEMENTS FOR THE UP3 SPENT FUEL REPROCESSING PLANT AT LA HAGUE, FRANCE.

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CLAUDE BERNARD, PIERRE MIQUEL, SGN, France
ALAIN LEUDET, CEA, Fontenay-aux-Roses, France

ABSTRACT

The UP3 reprocessing plant commissioned for active operation in November 1989 features numerous innovations both for the process flowsheet and the associated equipment. These innovations yielded positive results following initial active testing and are of considerable interest for solvent extraction specialists.

This paper describes the main improvements introduced for the extraction cycles used to separate and purify uranium and plutonium. Specifically, these improvements include : adaptation of the first extraction cycle flowsheet for technetium decontamination and tritium confinement ; solvent purification process based on distillation, a key element in the solvent system ; flowsheets adapted for maximum recycling of liquid organic and mineral streams (solvent or nitric acid) ; use of annular or cylindrical pulsed columns with high-efficiency packing.

INTRODUCTION

UP3 is a completely new reprocessing plant commissioned for active operation in November 1989 for the extraction part (the head end of UP3 will enter active operation in August 1990). It is designed to reprocess 800t/year of spent LWR fuel, including total waste management and packaging for final disposal.

This plant, operated by Cogema, was designed and built by SGN on the basis of process developments performed by the French Atomic Energy Commission (CEA). In fact, UP3 basically implements the same proven process as UP2-400, which has reprocessed about 3 000 t of spent LWR fuel to date. A number of changes have, however, been made to improve performance, to reduce the volume of waste, to meet the radioactive release restrictions, and to satisfy the highest safety conditions.

One of the main changes is probably the implementation of a continuous rotary dissolver in the UP3 head end, but the solvent extraction process also features numerous improvements.

1 PROCESS IMPROVEMENTS

UP3 employs an improved Purex process comprising a first U and Pu codecontamination cycle with U/Pu partition, followed by two purification cycles for U and for Pu.

All the aqueous streams leaving the extraction units are diluent washed . The organic streams (mixed 30 % TBP and diluent) leaving the cycles are successively treated with sodium carbonate and caustic soda. The excess of solvent is distilled to recycle TBP and diluent to the extraction cycles and to eliminale most of the impurities.

Plutonium barriers are placed before solvent regeneration units on the Pu-rich cycles.

1.1 First cycle extraction/scrubbing flowsheet

The main function of this part of the cycle is to extract uranium and plutonium with TBP and to scrub the solvent loaded with entrained fission products.

The first cycle flowsheet of UP3 (Fig. 1) has two separate scrubbing sections, the first one for the main fission products and the second one specifically for Tc.

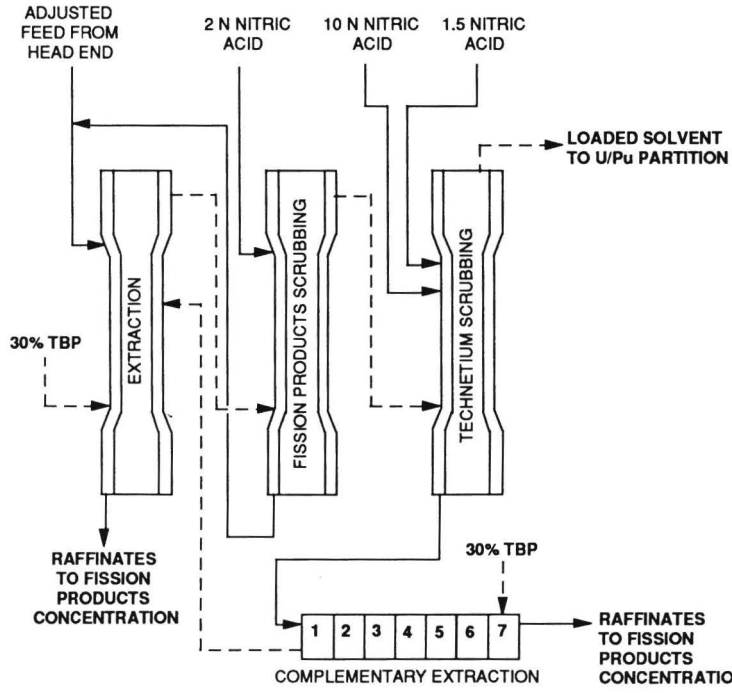


Fig. 1 First cycle extraction/scrubbing flowsheet

Technetium, which is a low specific activity fission product, is undesirable in the step of Pu reductive stripping by uranous nitrate stabilized with hydrazine : technetium, acting as a catalyst increases the consumption of hydrazine. Consequently, a specific scrubbing, using concentrated nitric acid (4 to 5 N) is applied to strip the technetium. In this system, zirconium is firstly stripped at 2 N acidity before stripping Tc at high acidity, thus avoiding the formation of the Zr/Tc complex that is highly extractible in the solvent.

A complementary extraction is combined with this scrubbing to extract the uranium and plutonium stripped in technetium scrubbing and to recycle them to the main extraction.

In addition, the Trilex flow sheet is applied in UP3 by performing a tritium scrubbing in the first cycle FP scrubber. The use of low tritiated recovered acid in this column helps to confine the tritium in the high activity part of the plant (head end, first cycle, HA waste).

1.2 Management of organic effluents

To secure optimized operation of the process, care is taken to remove the TBP dissolved or entrained in the aqueous streams from the extraction cycles. This removal is easily achieved by washing these aqueous streams with pure diluent using either pulsed columns or mixer-settlers.

At the outlet of these washing operations, the diluent streams are small and are all combined with the solvent streams of the corresponding extraction operations, to avoid specific additional treatments. As a result, the organic phase holdup increases and its TBP content decreases, making it necessary to re-adjust the TBP content of the solvent. It is therefore also necessary to withdraw the excess solvent in each extraction cycle.

The excess solvent is treated by distillation, primarily to recover pure diluent and concentrated TBP for recycle purposes. In addition, solvent distillation ensures the decontamination of the processed solvent, as well as the elimination of heavy degradation products of the solvent, which are at least partly responsible of the loss of selectivity of the irradiated solvent. This process is operated :

- at reduced pressure to keep the solvent at moderate temperature,
- with thin-film evaporators to limit residence time.

The equipment includes (Fig. 2) :

- preliminary dilute acid scrubbing to remove any inorganic salts remaining in the solvent,
- dehydration by distillation under reduced pressure,
- an evaporation system wich evaporates (and decontaminates) the solvent and

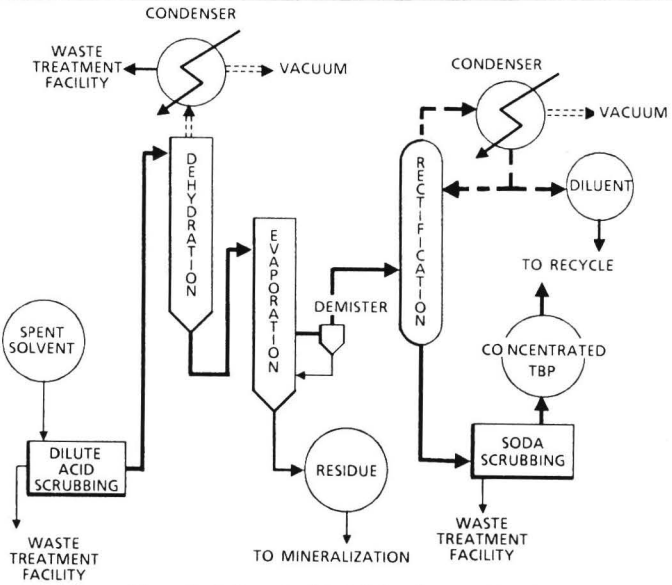


Fig. 2 Solvent distillation process

produces an active residue of less than 5 % of the initial stream. The composition of this residue is mainly TBP (over 90 %) and heavy degradation products,

- a rectification tower, which fractionates the distillates into two parts : pure diluent and concentrated TBP (> 80 %),
- soda scrubbing of the concentrated TBP.

The results anticipated from the use of this distillation unit include control of organic waste volume , less contamination of the plant solvent, and consequently, improved process efficiency and longer solvent life.

The latest operating results have demonstrated the validity of the process. In particular, the aptitude of the recovered products to recycling is now proved.

2 EQUIPMENT DEVELOPMENT

2.1 Pulsed columns

This process uses pulsed columns and mixer-settlers. The major novelty of UP3 is the use of annular pulsed columns in the first extraction cycle, and the use of baffle plates in these columns and in the cylindrical pulsed columns of the Pu purification cycles.

It is well known that the use of conventional sieve trays in pulsed columns can lead to malfunctions (that are often serious and sometimes prohibitive) : in the absence of specific arrangements, the use of such packings in large-diameter columns induces channeling which considerably lower the efficiency of the operation.

Furthermore, changes in the wettability characteristics of the trays towards a pronounced organophilic state seriously alter the hydraulic as well as the chemical performance of the pulsed columns in aqueous continuous operation.

To overcome these drawbacks, adequate arrangements are necessary in the geometric characteristics of the internals (insertion of distributors such as louver plates) or in its operating procedures (systematic action to restore the initial organophobic state of the trays). However, this complicates the design and significantly disturbs the operation of industrial units.

The CEA has investigated the operation of pulsed columns with non-perforated plates (baffle plates) from the laboratory scale to the prototype. On completion of this major development work conducted in conditions representative of those of the Purex process, it was demonstrated that the use of such packings offers a radical solution to the problems observed with sieve trays. The use of baffle trays in large-sized annular columns helps to eliminate the channeling observed with sieve trays (and increased by the annular geometry). The value of the HETS was thus reduced from about 8 m (with sieve trays alone) to less than 1 m (with baffle plates) for standard operating conditions. Furthermore, tests conducted on the pilot scale with Teflon-coated packings (highly organophilic, limiting the expected changes in the wettability characteristics in industrial operation) showed that, for aqueous continuous operation :

- performance is very poor and often unacceptable (considerably reduced capacity) with sieve trays,
- performance with baffle plates is good and very close to that observed for organophobic trays : these packings thus procure operation that is not significantly affected by the wettability of the trays.

The use of baffle plates thus offers a highly attractive alternative to conventional packings. This helps to solve two major problems associated with sieve trays, and also offers a number of other related advantages (ability to convey cruds and solids, ...).

2.2 Slab mixer-settlers

This equipment was developed to perform the plutonium barrier function in the plutonium purification cycles.

This function is performed in mixer-settlers of reduced height to make them geometrically safe, and wide enough to handle large throughputs. The elimination of residual traces of Pu complexed by TPB degradation products is carried out by reductive stripping with uranous nitrate.

To achieve maximum efficiency, these mixer-settlers are of the pump-mix type and operate in a continuous organic phase, with internal recycle of the aqueous phase from the settler to the corresponding mixer.

3 PROCESS CONTROL

Control of the extraction units of UP3, in pulsed columns and mixer-settlers, has been the subject of intensive research and pilot-plant tests. It also benefits from the cumulative operating experience of UP1 and UP2-400.

The installation of a distributed microprocessor control system helped to implement fully automatic control of the hydraulic operation of the facilities (startup, steady-state conditions, change in operating conditions, shutdown).

This automation enables the operator to devote himself wholly to monitoring the extraction process itself. He is effectively aided in this task by the installation of suitable instrumentation.

This includes :

- density and column weight measurements, temperature measurements, which are useful for monitoring uranium extraction.
- neutron measurements which are useful for monitoring plutonium extraction.

In-line analyzers specially developed for the reprocessing industry also enable the operator to monitor the decontamination factor and plutonium residual content in the unloaded aqueous and organic streams.

4 CONCLUSION

The Purex process used in UP3 has been considerably improved to boost its performance in terms of capacity and flexibility, to enhance safety, and to avoid generation of waste. The main innovations consist of the following :

- The use of geometrically-safe pulsed columns equipped with disc-rings or baffle plates, which are unaffected by ageing and fouling;
- The application of in-line solvent distillation at reduced pressure in thin-film evaporators;
- The use of plutonium barriers to obtain Pu leakage lower than previously achieved.

The progressive implementation of this process since November 1989, by using a feed dissolved and predecontaminated by UP2-400, served to reprocess 100 t of uranium from fuels irradiated to 20,000/ 30,000 MW day/t, as well as about 760 kg of Pu, by adjusting the reprocessing rate from 2.3 to 5.2 t of uranium per day according to a preset programme.

Overall decontamination performance is excellent and the process produces finished products with a purity far better than the required specifications.

The organic effluent treatment has distilled about 500 m3 of 30 % TBP without any problem, and regularly delivered TBP and diluent within the requisite purity, recycled in the process without any difficulty.

The alpha emitters content in waste is well below the design values.

This first campaign augurs well for the future of UP3. It represents an absolutely outstanding result for specialists in solvent extraction, who know that the Purex process was applied for the first time at Hanford in the fifties, and that nearly 40 years had to elapse before it could be put to optimal use in a commercial reprocessing plant.

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EXTRACTANTS FOR ACTINIDES

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ABSTRACT

Nikiforov A.S. and Rozen A.M., 1990. Instead of TBP the extractants have been developed to improve (to exclude the second organic phase formation, decrease aqueous phase solubility) the first reprocessing cycle for fuel (particularly U-Pu) and affinage operations. Triisoamylphosphate (TIAP) and diisobutylisooctylphosphate (DIBIOP) are suggested, wich are compatible with plutonium at any concentration. For the deep actinide extraction from wastes arylsubstituted diphosphine dioxides and carbamoylphosphinoxides are suggested.The extractants have been successfully tested on 10C GW.day/t burn up fuel reprocessing.

This paper deals with the solution of two problems. The first one is to develop an extractant - a substituent of TBP to improve the first cycle reprocessing of fuel (particularly U-Pu) and for affinage operations. The second task is to develop an extractant for the deep actinide extraction from radiochemical wastes.

Begin with the former item. As is known all over the world the extraction process of NPP spent fuel regeneration uses TBP. This is an excellent extractant. It effectively extracts U and Pu ; under moderately altered conditions stripping is possible. However, it has some disadvantages. The major one is the limited solubility of Pu-TBP disolvate in a diluent of a saturated hydrocarbon type. At room temperature for 30% TBP it is slightly more than 30 g/l Pu. Therefore, at high Pu concentrations mixed uranium--plutonium fuel reprocessing entails the danger of a second organic phase formation and an impermissible disturbance of an extraction process. Besides, TBP has relatively high solubility in an aqueous phase which during affinage may result in product contamination with phosphorus.

Therefore, the task was to develop an extractant close in its extraction ability (EA) to TBP but free from the TBP disadvantages: Pu and Th complexes must be compatible with saturated hydrocarbons, and the solubility in water must be one order less.

The problem was solved using the earlier investigation results (Rozen at al. 1964, 1965, 1968, 1976, 1988) which established the relation between the extraction ability of organic monodentatic compounds and their structure. An alteration of the

chemical nature of substituents in an extractant molecule was found to result in profound changes of extraction ability, i.e., distribution coefficients or extraction constants K_{extr}. In the phosphate (RO_3PO - phosphine oxides R_3PO series when one ether group RO is replaced by alkyl one R the uranium and plutonium extraction constants are increased by a factor of 50, that of americium - by a factor of 17. On the contrary, a change in the hydrocarbon chain affects the extraction very little (fig.1). Correspondingly it was decided not to change the substituent chemical nature (i.e., to use trialkyl phosphates) but to optimize the hydrocarbon chain. To improve the compatibility with diluents and to lower the solubility in the aqueous phase the chain should be elongated and the isostructure should be used. The properties of some trialkyl phosphates were investigated, the total chain length n_c was varied from 12 (TBP, TiBP) to 21 (Triheptyl P) (Rozen, Nikiforov et al., 1982-85). As a result, instead of TBP with its 12 carbon atoms triisoamyl phosphate (TIAP) with 15 and diisobutylisooctyl phosphate (DIBIOP) with 16 carbon atoms were recommended. The use of triisoamyl phosphate solves the problem of plutonium extraction from concentrated solutions as a third phase does not form if the extractant is fully saturated with plutonium. If one goes to DIBIOP, i.e., the hydrocarbon chain is elongated for one more atom, the formation of the second organic phase with thorium nitrate is eliminated (fig. 2). As is needed, the distribution coefficients differ little from those for TBP (fig. 3) and the separation rates are close (fig. 4) (Rozen, Nikiforov 1984).

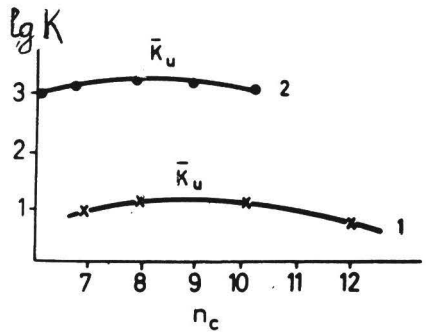


Fig. 1. Effect of n_c
1 - amines
2 - phosphonates

The virtue of both the extractants is also one order lower solubility in the aqueous phase which reduces the product contamination with phosphorus (clearly under condition of a mechanical entrainment elimination).

The recommended extractants - TIAP and DIBIOP - were successfully tested with high burn-up (100 GW.day/t) short cooled (in some cases 3 months) fuels, correspondingly the solution activity was up to 10^3 Ci/l (Nikiforov, Zakharkin, Rozen, Renard, 1988). The extractant damage was obviated through the use of centrifugal extractors with the little phase contact time of 2-3 s on extraction and wash-

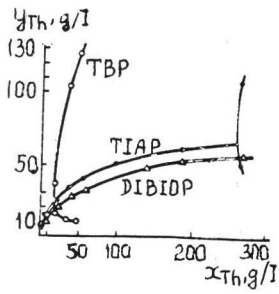


Fig.2. Isotherms of Th extraction with 30% TBP, 33% TIAP, 35% DIBIOP in tetradecane

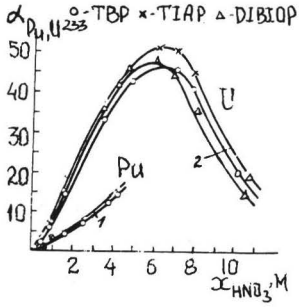


Fig.3. α Pu(IV) and U(VI) vs aqueous phase acidity (for extractant concentrations see fig.2)

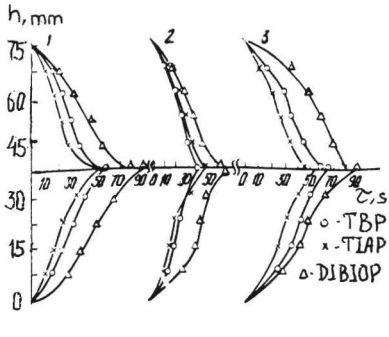


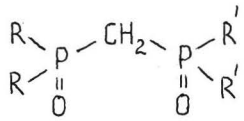
Fig.4. Emulsion layer height vs settling time. 1-HNO_3, 3 M; 2-300 g/l U(VI)+3 M HNO_3; 3-5% Na_2CO_3

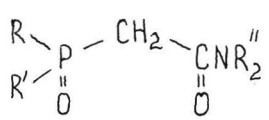
ing , 5-6 s - on reductive stripping. Commercial testing in VVER spent fuel reprocessing was also successful.

Thus, the task of the solvent extraction reprocessing of high burn-up fuel containing a high amount of Pu and F.P. is being successfully solved.

Let's now discuss the problems of a deep extraction of transplutonium elements from extraction process raffinates. This aim can be achieved if adequately powerful extractants are used. However, monodentatic organophosphorus compounds, even most powerful ones - phosphine oxides (TBPO, TOPO) are little suitable here. If the use of TBP requires a salting out agent to be introduced, phosphine oxides effectively extract americium but only at the low acidity; to use them the solution must be neutralized. This is due to the nitric acid competition for a free extractant - the nitric acid extraction constant is rather high (K_H=20) while the free extractant concentration is inversely proportional to K_H.

The problem was successfully solved using bidentatic organophosphorus extractants - diphosphine dioxides (a) and carbamoyl phosphine oxides (b) with the general formulae

a) 

b) 

(below they are abbreviated to 2R2R' (a) and RR'/R'' (b).

For practical purposes compounds with tolyl substituents - 4 tol and 2 tol 2 Ph dioxides that are most powerful extractants

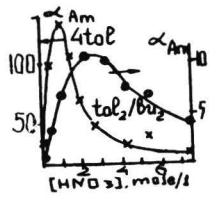


Fig.5. α_{Am} vs HNO_3(0.3 mole/l extractants in trichlorobenzene, in aqueous phase - 10 g/l REE)

and carbomoyl phosphine oxide tol_2/bu_2 were recommended (Rozen, Nikolotova, Kartasheva 1979, 1988).

For 4 tol the nitric acid extraction constant is 2.5 that is one order lower than for TBPO or TOPO, its competition ability is weakened and the americium distribution coefficients increase through both an increase of the free extractant concentration and the bidentate coordination (to both oxygens of the extractant), fig. 5. The efficiency of both the recommended compounds is significantly increased due to the anomalous aryl strengthening effect revealed in 1975 (Rozen et al., 1975, 1977, 1986, 1988).

The essence of this interesting phenomenon is such. The metal-extractant complexes are the stronger the higher is the basisity of an extractant or, which is the same, the higher is the electron donor ability of a functional atom, phosphoryl oxygen in case of organophosphorus compounds.

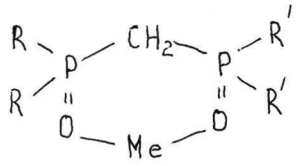
The donor ability of this oxygen depends on the properties of the substituents R in a $R_1R_2R_3PO$ extractant molecule and first of all on their electronegativity X_R. The more electronegative is the substituent the more powerfully does it "pull off" the electron density from oxygen the lower are the basisity and donor ability of a compound (Rozen et al., 1964, 1966, 1976; Rozen 1968, 1988).

$$\lg K_{ex} = A - B \sum X = a + bpK$$

where A, B, a, b are constants for this reaction series.

Alkyl groups $R=C_nH_{2n+1}$ have the lowest electronegativity (X_R is equal to approximately 2). Therefore, phosphine oxides R_3PO have the highest extraction ability. The ether RO (X_{RO}=2.5) and phenyl (X_{Ph}= 2.35) groups are more electronegative than the alkyl ones; and their introduction into an extractant molecule always decreases extraction, e.g., one phenyl group introduced decreases the americium extraction by a factor of 7. The same effect was expected for bidentatic organophosphorus compounds, e.g., diphosphine dioxides. Indeed, on extraction of nitric acid coordinated monodentatically, i.e., to one of oxygens, the phenyl groups lowered the extraction by a factor of 4 (Rozen, Berkman 1976). It appears that everything is all right. But on extraction of americium and other actinides when the coordination

becomes bidentatic, i.e., a 6-membered cycle is formed and closed to the metal, the phenyl, tolyl and other aryl substituents increase distribution coefficients (Rozen et al.,1975-1988), fig. 6.



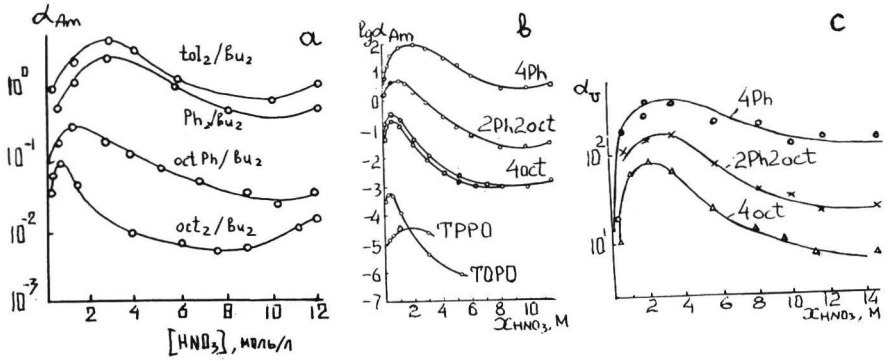


Fig.6. Influence of aryl substituents on extraction of Am with carbamoyl phosphine oxides (a), of Am (b) and U(VI) (c) with disphosphine dioxides

The extractant basisity is lowered but, none the less, the actinide extraction grows and this was called the anomalous aryl strengthening of complexes. One should differentiate between the true AAS when both the distribution coefficients and the extraction constants grow (actinides and lanthanides III) and the visible AAS when only the distribution coefficients grow but the extraction constants are decreased (U(VI), Pu(IV), fig. 7).

The cause of the AAS phenomenon is: the electron density is delocalized from the phenyl rings to the 6-membered cycle of the complex and the entropy grows on complex formation (Rozen at al. 1975, 1977, 1986; Rozen 1988).

However, it is important for practical purposes that the electronegative aryl groups while forcing the actinide extraction simultaneously, as they should do, inhibit the nitric acid extraction, thus, a double gain is attained, see fig.6, the americium distribution coefficients increase by 3-4 orders. As a result, a deep actinide extraction becomes possible from solutions of essentially any acidity without any conditioning (see fig. 5).

Due to the high extraction ability of diphosphine dioxides and carbamoyl phosphine oxides the process developments entail difficulties due to the required suppression of fission product (zirconium, technetium and oth.) extraction. However, the difficulties are sur-

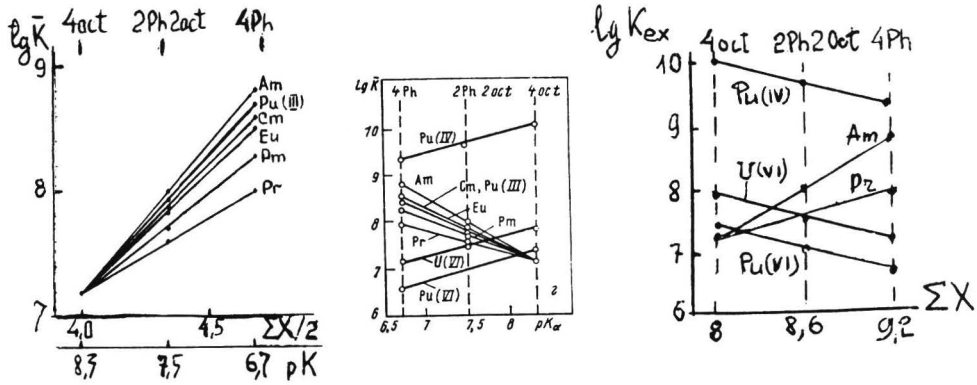


Fig.7. Diphosphine dioxide extraction constants vs electronegativity sum and basisity

mountable, e.g., with complexones. The mentioned extractants were tested in reprocessing burn-up (100 GW.day/t)fuel.

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THE BEHAVIOUR OF DECOMPOSITION PRODUCTS OF HYDRAZINE IN PUREX PROCESS

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ABSTRACT
Zilberman, B.Ya., Lelyuk, G.A., Mashkin, A.N. and Fedorov, Yu.S., 1990. The behaviour of decomposition products of hydrazine in Purex process.

The radiation decomposition of hydrazine and its oxidation by nitric acid in the presence of Tc and Pu (III) as catalysts under Purex process conditions result in the formation of HN_3, NH_4NO_3 and gaseous products. The difference in the processes of catalytic oxidation in aqueous (one-phase) and two-phase systems, the influence of HN_3 on redox interactions and extraction of uranium, plutonium and neptunium are considered. In a real process HN_3 is formed in the zone of plutonium stripping and passes through the first cycle due to high distribution coefficients in the presence of uranium. HN_3 is removed with carbonate wash solution; this makes difficult its reuse and utilization of uranium-containing portions. In the flowsheet with recycle of extract after the washing of plutonium strip solution to U, Pu, Np extractor, HN_3 initiates interphase palladium precipitation and deteriorates Np extraction because of Np (VI) reduction.

INTRODUCTION

Hydrazine nitrate is widely used in Purex process, particularly at partition of uranium and plutonium. The most part of hydrazine is oxidized under the operation conditions. Among the decomposition products of hydrazine, hydrazoic acid (HN_3) is a serious hazard because of its volatility and explosivity of the acid and its salts.

It is known that HN_3 has high distribution coefficients into 30 % TBP (Kelmers and Browning, 1977). However there are no systematic data on its accumulation, distribution and interaction with some elements in Purex process.

2 EXPERIMENTAL

Experimental procedure is described thoroughly in earlier communications (Zilberman et al., 1988a, 1988b).

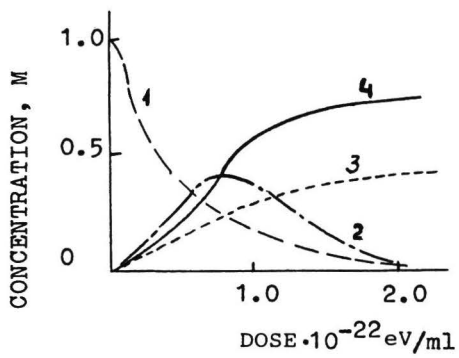
3 RESULTS AND DISCUSSION

3.1 Oxidation of hydrazine in nitric acid

Under γ-irradiation of 1 M hydrazine nitrate in 2 M HNO_3, N_2 and NH_4^+ are, formed while hydrazoic acid is an intermediate product with maximum accumulation of 0.35 M per 1 M hydrazine decomposed (Fig. 1). The ultimate aqueous solution contains 0.32 M of ammonium nitrate per 1 M of hydrazine; the other portion of nitrogen from hydrazine is liberated in gaseous form, mainly as nitrogen.

The oxidation of hydrazine by nitric acid proceeds similarly in the presence of pertechnetate-ion (Fig. 2) as a catalyst. This process depends slightly on HNO_3 concentration in the region of 1 - 3 M, but is hindered by further increase of HNO_3 concentration. With increasing amount of TcO_4^-, the process of hydrazine decomposition is accelerated. Such catalytic oxidation of hydrazine by nitric acid is characterized by the fact, that no complete decomposition of HN_3 and hydrazine takes place.

If the final system is blown by nitrogen or contacted with extractant (30 % TBP in dodecane), the hindered process will be restarted (Fig. 3). Moreover, HN_3 and hydrazine are decomposed completely (in the presence of catalyst) when contacting with organic phase (Fig. 2) and in the presence of plutonium (Zilberman et al., 1988b).



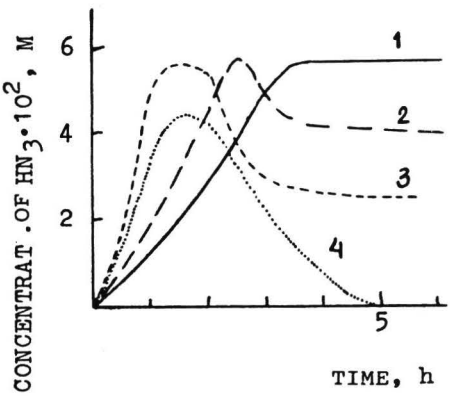


Fig. 1. Radiation-chemical decomposition of hydrazine and yield of decomposition products. Feed solution: 1.0 M $N_2H_5NO_3$, 2.0 M HNO_3. 1 - $N_2H_5NO_3$; 2 - HN_3 ; 3 - NH_4^+; 4 - nitrogen.

Fig. 2. Yield of HN_3 on oxidation of hydrazine in nitric acid solution. Feed solution: 0.36 M $N_2H_5NO_3$, 2.0 M HNO_3; Tc, M: 1 - $5.1 \cdot 10^{-4}$; 2 - $1.01 \cdot 10^{-3}$; 3,4 - $2.02 \cdot 10^{-3}$ (4 - two phase system).

3.2. The behaviour of HN_3 in extraction systems

HN_3 is known to form a monosolvate $HN_3 \cdot TBP$ (Kelmers and Browning, 1977) and has high distribution coefficients on extraction into 30 % TBP from nitric acid solutions with low concentration. Extraction constant is equal to 9 in the range of nitric acid concentrations 0.5 - 6.0 M. Uranyl nitrate forms a coloured complex in the absence of nitric acid (Sherif and Awad, 1961), but the experiments have shown (Fig. 4) that such complex is not formed at concentrations of nitric acid above 0.4 - 0.5 M and the extraction process of HN_3 into 30 % TBP may be described as competition of uranium and HN_3 for extractant (Zilberman et al., 1989).

Increase of HN_3 concentration in feed aqueous solution leads to decreasing the distribution coefficients of tetravalent Pu, Np and U (Zilberman et al., 1988b). This is connected with the competition for free TBP. Such effect is observed in wide region of HNO_3 concentrations (0.2 - 3 M). At the same time HN_3 reduces Np (IV) to Np (V) (Fig. 5) and Ce (IV) to Ce (III), i.e. reacts with one-electron transfer oxidants the oxred potential of which is higher than 1.1 V. These reactions occur not only in aqueous solutions, but also in two-phase systems in the extraction process.

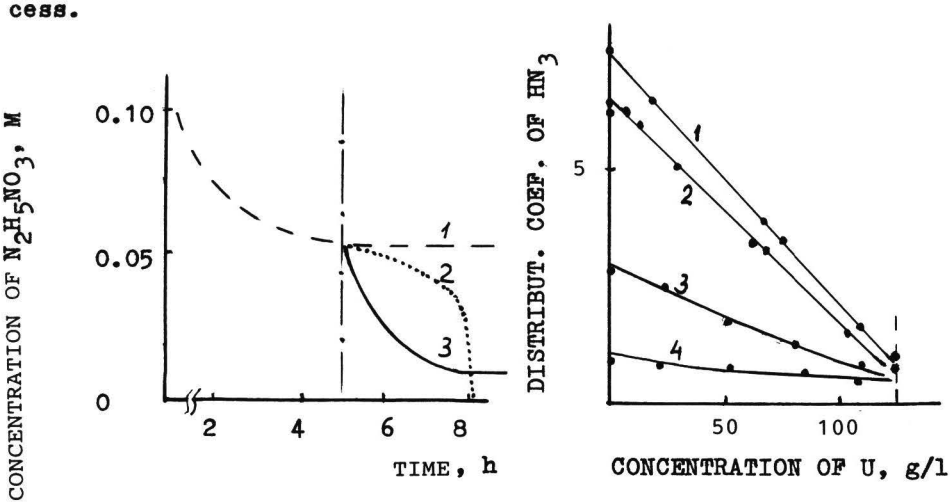


Fig. 3. Variation of $N_2H_5NO_3$ concentration in the steady system. 1 - reference system ($N_2H_5NO_3$ feed - 1 M); 2 - system with HN_3 removal; 3 - system with initial concentration of $N_2H_5NO_3$ = 0.053 M.

Fig. 4. Extraction of HN_3 into 30 % TBP in dodecane depending on U concentration in organic phase. Concentrations of HNO_3, M: 1 - 0.5; 2 - 1.0; 3 - 3.0; 4 - 6.2.

HN_3 forms only one compound with palladium - low soluble palladium azide $Pd(N_3)_2$. With the minimum excess of HN_3 in aqueous phase the solubility of $Pd(N_3)_2$ is 10^{-5} M at concentrations of nitric acid up to 6 M. When contacting palladium-containing aqueous phase with organic phase which contains HN_3, the extraction usual nitric acid media. However such picture is observed up to silubility level of palladium azide in organic phase which is equal to $3 \cdot 10^{-3}$ M.

The behaviour of palladium in two-phase aqueous-organic system in the presence of HN_3 is rather complex. With increasing HN_3/Pd ratio, the extraction of palladium into TBP increases, while its solubility in aqueous phase decreases and palladium azide precipitate falls out irrespective of nitric acid concentration (Fig. 6). The precipitates are accumulated at interphase and present obstacles to the operation of different contactors. In the course of time in the absence of HN_3, the precipitates are decomposed partly by dissolution, partly with formation of metallic palladium.

3.3 The behaviour of HN_3 in Purex process

The complexity of the observed formation, interaction and decomposition of HN_3 leads us to a conclusion that a special series of pilot tests on real solutions of LWR fuel with burn-up

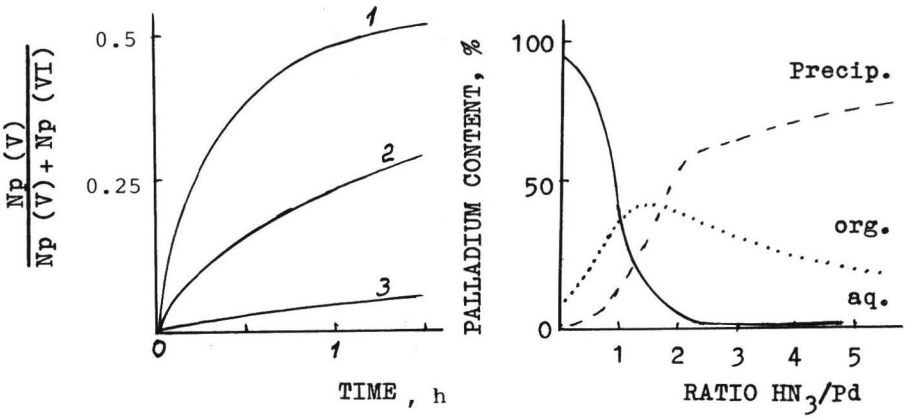


Fig. 5. Reduction of Np (VI) to Np (V) by HN_3 at 20 °C. Feed solution: 1 M HNO_3, $2 \cdot 10^{-3}$ M Np (VI) HN_3, M: 1 - 0; 2 - 0.023; 3 - 0.116.

Fig. 6. Distribution of palladium in the system: 30 % TBP - HN_3 HNO_3. Concentrations: HNO_3 - 2 M, Pd - $7 \cdot 10^{-3}$ M.

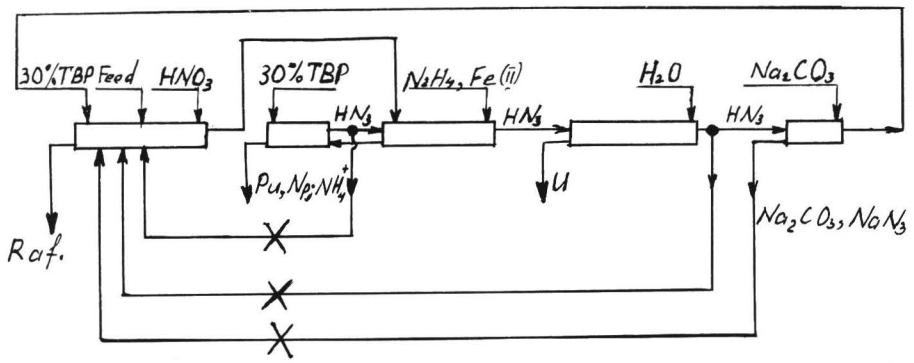


Fig. 7. Flowsheet of the I cycle of Purex process.

32 - 38 GW·d/t are needed. Mixer settlers were used as extraction equipment. Versions of technological flowsheet are shown on Fig. 7.

The concentration profile of components (N_2H_4, HN_3, Tc, Pu) was primarily studied on plutonium stripping with ferrous nitrate. It was established that the main accumulation of HN_3 took place just in organic back-wash zone (Fig. 8).

The process is disturbed while recycling the extract from this zone to the middle of head extraction battery. Neptunium makes its appearance in raffinate and palladium is vanishing

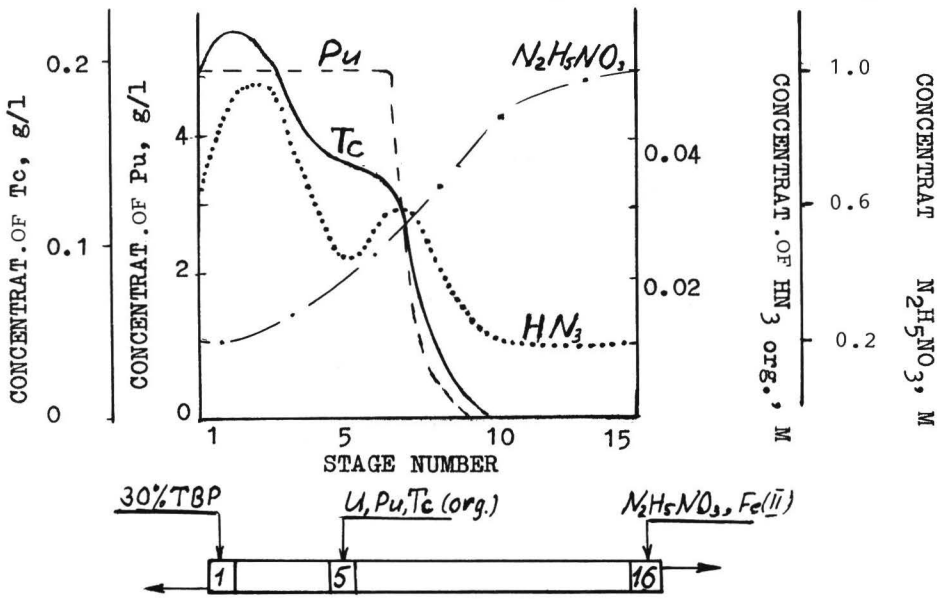


Fig. 8. Concentration profile of different components in apparatus for plutonium stripping.

TABLE

Content of palladium and neptunium in extract and raffinate respectively under the different operation conditions

Pd content in extract (mg/l)		Np content in raffinate (mg/l)	
1.5 ± 0.4 (a)	10.0 ± 1.7 (b)	0.03 ± 0 (a)	10.8 ± 2.6 (b)

(a) Flowsheet of standard Purex process.
(b) Flowsheet with recycle of extractant.

(Table). The inverse picture is observed in extract, i.e. neptunium is lost while palladium enters the reduction plutonium stripping. The distribution of technetium is not disturbed. Hydrodynamic violations of the process owing to precipitation of palladium azide occur in the course of time.

It is known that HN_3 in the routine Purex process follows organic phase up to carbonate scrubbing and then removed from the extraction system. The concentration of azide-ion in carbonate solution under investigation was 2 g/l. In the real process this value is more by a factor of 1.5 - 2. So, no partial recycle of extractant into the first extractor can be tolerated without carbonate scrubbing, even if degradation of extractant is small (for example in centrifugal extractors). The recycle of uranium-containing carbonate scrub solution is also to be excluded.

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5. KINETICS AND INTERFACIAL PHENOMENA

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INTERFACIAL PHENOMENA IN EXTRACTION SYSTEMS

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ABSTRACT
Szymanowski, J., 1990. Interfacial phenomena in extraction systems.

The interfacial properties of extractants at liquid/liquid interfaces are discussed and interpreted in the view of metal extraction kinetics.

INTRODUCTION

The importance of the interphase in each heterogenous process, including metal extraction, is obvious. Depending upon hydrodynamic conditions and the relative rate of the chemical process the extraction can be controlled by mass transfer or chemical kinetics. It can proceed in the bulk of the aqueous phase and/or in the aqueous film near the interface. The width of this film can change significantly depending upon the experimental conditions, i.e. hydrodynamics and reagent concentrations. Under very good hydrodynamic conditions and high concentrations of metal ions in the aqueous phase reaction can proceed at the interface or in a very narrow aqueous film near the interface, even in the case of hydrophilic extractants. The probability that the reaction occurs at the interface and/or in a narrow aqueous film increases with the increase of extractant hydrophobicity, as a result of its decreasing solubility in the aqueous phase.

2 EXTRACTANTS AS AMPHIPHILIC SUBSTANCES

Almost all types of hydrophobic extractants of metals have an amphiphilic character, as a result of the presence of a long hydrophobic group or groups, usually an alkyl chain, and some characteristic hydrophilic fragments which usually are chemically active and react with considered metals. These hydrophilic groups are bonded directly with hydrophobic hydrocarbon chains or an aromatic ring is used as the intermediate link.

Due to this, extractants are interfacially active, i.e. adsorb at the hydrocarbon/water interfaces and decrease the interfacial

tension. Depending upon hydrophobicity they can be dissolved in the organic phase, aqueous phase or partitioned between these two phases. The change of hydrophobicity also efffects their interfacial properties including the decrease of interfacial tension, interfacial population and the location in adsorption layer.

Extractant hydrophobicity depends upon several parameters characterizing the both phases considered. Acidic and basic extractants can dissociate or to be protonated at appropriate pH forming ionic species which, due to higher hydration in an aqueous phase and/or at a liquid/liquid interface, become more hydrophilic.

$$LH = L^- + H^+ \qquad \text{or} \qquad LH + H^+ = LH_2^+ \qquad (1,2)$$

In organic solvents extractant molecules can be solvated with

$$LH + nS = LH*nS \qquad (3)$$

diluent molecules. It also occurs at liquid/liquid interfaces where mixed adsorption layers are formed. They contain various amounts of diluent and extractant molecules become more hydrophobic.

All parameters which effect these processes and the hydration of polar groups may change extractant hydrophobicity. The structure of adsorption monolayer and extractant interfacial properties may be changed by acidity of the aqueous phase, temperature, electrolyte content and the type and composition of the organic phase. The hydration of the polar groups, especially ionic ones, decreases with the increase of temperature and electrolyte content, and extractant becomes more hydrophobic. The same effect is observed as aromatic hydrocarbons are used instead of aliphatic ones as diluents or in some cases as the length of aliphatic hydrocarbons decreases. Thus, depending upon measurement conditions quite different interfacial parameters, including interfacial tension, surface excess and molecular area, composition, width and elasticity of the interfacial monolayer may be obtained.

Apart extractant molecules other surface active substances are usually present in extraction systems. These substances may be added to modify the extraction strength and/or to prohibit the third phase formation, as in the case of alkylphenols, alcohols and esters. They can be added to accelerate the extraction rate as in the case of trialkyl amine added to dialkyl sulphide or LIX 63 present in LIX 64N. Some interfacially active substances are formed during extractant synthesis and they can be in equilibrium with extractant molecules, e.g. Z-isomers of 2-hydroxy-5-alkylbenzophenone oximes and/or α-acyloin oximes. Small amounts of surface

active impurities can be also present in commercial diluents.

These interfacially active substances can effect both the static and dynamic interfacial properties of extractants. The partition and adsorption of both extractant molecules and these additional surface active substances must be taken under consideration. These second substances, although present in small amounts, compete with extractant molecules in adsorption process and decrease the interfacial surface area which can be occupied by extractant molecules. Thus, the extraction rate decrease can be observed. However, as these substances are more hydrophilic than extractant then they are better dissolved in the aqueous phase and, as adsorbed, they can penetrate the aqueous phase more deeper with their hydrophilic heads than hydrophobic extractants. Thus, they can act as accelerators. However, they alone or with extractant can also form some products which can accumulate at the interface blocking it and retarding extraction, as probably in the case of nickel extraction with α-acyloin oxime (LIX 63) and carboxylic acids (Flett, 1975).

The use of the neutron reflection technique gives some possibility to study the structure of the interface, including the location and distribution of various molecules. We think that the development of this technique can give important informations upon the behaviour of hydrophobic extractants at the interface and upon the mechanism of metal extraction.

Various surface active substances can also retard extractant adsorption and the structure of the adsorption layer may change. At first in micro- and miliseconds the adsorption of a less surface active component quickly occurs, which is then slowly replaced by a stronger surfactant (Miller, 1979). Due to this, adsorption of extractant occurs slowly and a plateau can be observed as the relation: interfacial tension versus logarithm of adsorption time is considered. The diffusities calculated from this relation are smaller than those expected.

The generally accepted physical model of adsorption kinetics consists of two processes. In the first step the diffusion of molecules to the subsurface takes place. In the second step these molecules are transfered from the sublayer to the diffusion layer. Thus, they change from the soluted state into the adsorbed one. Depending upon the relative ratio of these steps the adsorption can be controlled by diffusion, $v(diff) < v(trans)$, kinetics, $v(diff) > v(trans)$ or both by diffusion and kinetics, $v(diff) = v(trans)$.

Mysels (1970, 1973) and Lunkenheimer and Miller (1982) found

that in some cases the adsorption of amphiphilic substances is very slow. Van Hunsel (1986) observed it only for adsorption of surfactants dissolved in the hydrocarbon phase and explained it by some slow rearrangement in the adsorption layer, connected probably with the hydration of polar groups with water molecules. Lunkenheimer and Miller (1982) suggest that this slow adsorption is caused by the presence of other surface active substances.

Although the phenomena of slow adsorption at hydrocarbon/water interfaces is not explained, the role of surface active impurities is obvious. In actual extraction systems which almost always contain some surface active modifiers and/or impurities the effect of these additional substances upon extractant adsorption in equilibrium and in un-steady state must be considered. The complex studies of the dynamics of extractant adsorption in various extraction systems would be worth to carry out. The measurement of the shape of liquid meniscili interface is recommended both for equilibrium and dynamic measurements. A video image profile digitizer can be used to transform a drop profile directly into a microcomputer. The method is fast enough to take about 20 or even more images per second and a change of interfacial tension with time and responces of the interface to disturbances can be registered. The method is applicable to relaxations of liquid/liquid interfaces.

In some extraction systems containing amine or sulphonic type extractants micelles or reversed micelles can be formed in the aqueous or organic phase, but never simultaneously in both phases. They can increase both the metal extraction and extraction rate, decrease extraction pH and change the composition of extracted species, as a result of reagent accumulation in micelles. Thus, solubilization can be also important in extraction. This phenomena can be very significant as micelles are formed by additionaly added surface active substances. Water can be also solubilized in the organic phase by reversed micelles.

Less polar hydrophobic extractants which are not protonated and do not dissociate in the aqueous phase do not form micelles in the aqueous phase. In the organic phase they can associate. However, the degree of association is rather small and the formation of the reversed micelles is not observed.

In some special cases microemulsions can be formed giving possibilities of very quick extraction, even in the case of extremely slow processes, demonstrated for gallium and nickel

(Bauer, 1983). In these systems very rapid transfer of metal ions between the water phase and microemulsion is observed.

3 INTERFACIAL TENSION

One of the important parameters characterizing the interfacial phenomena is the equilibrium interfacial tension. In extraction systems the ring method, Wilhelmy plate method and the drop method were usually used. The ring method is the most popular because the measurements are simple and commercial tensiometers are accessible. However, according to Lunkenheimer (1982) their designs are often not correct and when used by a non-experienced person dubious results can be obtained. The Wilhelmy plate and drop methods are more accurate, although in this last case great attention must be paid to obtain equilibrium values. The most accurate results are now obtained by the drop shape method. The spinning drop method is recommended for the measurement of ultra low interfacial tensions which are observed in microemulsion systems.

The interfacial tension isotherm has a specific character. In the region of low concentration interfacial tension decreases weakly, and the relationship γ vs ln c is convex. The interfacial population of molecules adsorbed at the interface increases and the molecular area decreases. When the concentration further increases the interfacial tension falls according to a linear relation. In this region adsorbed molecules are close-packed in the monolayer and the molecular area is constant. For higher concentrations the break point may be observed and then the interfacial tension stops to change with extractant concentration. The micelles are formed and the concentration at the break point is called as critical micelle concentration. However, the region of critical micelle concentration is usually not achieved in extraction systems.

Such a well defined adsorption isotherm is obtained only for pure compounds. The linear part of the isotherm and the sharp break point may disappear for contaminated compounds. Moreover the interfacial tension may then change above cmc and even increase.

A disappearance of the linear part of γ vs ln c isotherm can be also caused by extractant association, very often dimerization, in the organic phase. In such a case the monomer concentration in the organic phase should be considered. Thus, the association constant should be known. This is inconvenient because different values of association constant are obtained using various methods. Moreover values obtained for extractant solutions are usually higher than

those determined in extraction systems where the organic phase is saturated with water which compete in hydrogen bond formation.

In the colloid and interface science it is now generally accepted that only well defined substances can be used for the surface and/or interfacial activity studies. Lukenheimer (1987) proposed the special method of purification of organic substances used for surface activity studies. Using a multiple depression and expansion of the air/water interface followed by the automatic sucking of the interfacial layers after each step of expansion an appropriate purity could be obtained.

In the case of the interfacial tension measurements the highly active impurities can be removed by their preextraction with an aqueous solution but this is reasonable only for very hydrophobic extractants, which partition between both phases can be neglected.

Up to now, so well purified extractants were not used. Thus, the interpretation of the obtained results is uncertain.

As a criterion of compounds/solvents purity, one can propose the interfacial tension measurements in very diluted systems. In this case the interfacial tension isotherm should increase towards the interfacial tension value characteristic for the pure system. Each shift from this expected value towards lower interfacal tensions proves the presence of undesired surface active impurities.

The interfacial activity of extractant can be characterized by adsorption efficiency defined by i) the minimum bulk concentration required to produce a saturated interface, ii) extractant concentration required for an appropriate decrease of interfacial tension and/or iii) by the interfacial tension corresponding to appropriate concentration. Adsorption effectiveness is another characteristic parameter. It can be defined by the lowest interfacial tension possible to obtain in the considered extraction system or by the highest extractant interfacial concentration.

It is difficult to recommend the most positive measures of these parameters. The concentration required for interface saturation depends upon the method of its estimation. Due to extractant partition the concentration in one phase, e.g. organic one, should be considered and the interfacial tension isotherms presented as γ vs ln c_o or γ vs c_o.

Effect of partition upon extractant efficiency can be significant and different in homologous series for less hydrophobic compounds. The interfacial concentration also depends upon the method of its determination.

4 INTERFACIAL CONCENTRATION

The interfacial tension data can be used to estimate the equilibrium interfacial surface population. In works concerning the solvent extraction of metals usually the Gibbs isotherm is used $\Gamma = -1/RT\ d\gamma/d(\ln c)$, where Γ stands for the surface excess. The surface excess is much higher than the bulk concentration and one can assume that it is equal to the surface concentration.

The maximum gradient $d\gamma/d(\ln c)$ can be obtained from the linear part of the interfacial tension isotherm γ vs ln c. It is also possible to differentiate the relationship γ vs c by a graphical or numerical method. However, it is troublesome and connected with high errors, especially in the region of low concentrations. At higher extractant concentration an explicit maximum of surface excess may be obtained. Due to this, the region of higher concentration is not interpreted and the surface excess at maximum is considered as the value determined for the saturated interface.

Differentiating the curve γ vs c a higher surface excess value at saturation is obtained in comparison to that one obtained by linear approximation of relation γ vs ln c. Depending upon the range of considered concentrations this difference can amount up to 30% (Szymanowski and Prochaska, 1987).

Various isotherms or empiric equations can be used to match the interfacial tension isotherms and to compute the term $d\gamma/dc$.

In our works (Szymanowski et al, 1987 - 1990) we used:

- the Szyszkowski isotherm described by the following function:

$$\gamma = \gamma_o[1 - B \ln (\frac{c}{A} + 1)] \qquad (4)$$

where A and B are constants and γ_o is the interfacial tension in system which does not contain extractant (c=0). This isotherm is equivalent to equation (5) used by Japaneses when $B = \Gamma^{\infty}RT$, $A = 1/K$ and Γ/Γ^{∞} is given by the Langmuir isotherm, $\Gamma = \Gamma^{\infty} * Kc/(Kc+1)$.

$$\gamma = \gamma_o + RT\Gamma^{\infty} \ln (1 - \Gamma/\Gamma^{\infty}) \qquad (5)$$

- the Frumkin isotherm.

$$\gamma = \gamma_o[1 - B \ln (c/A + 1) - A'(c/A + c)^2] \qquad (6)$$

A' coefficient takes into account the interactions between adsorbed molecules and this isotherm is recommended for ionic amphiphilic substances. For nonionics A' coefficient is few orders lower than A and the use of the the Szyszkowski isotherm is sufficient.

- the semi-empirical Temkin isotherm, given by equation (9):

$$\log c + K_T = \frac{B_T}{RT} \Pi^{0.5} \qquad (7)$$

where K_T, and B_T are the constants and $\Pi = \gamma_o - \gamma$.

- the logarithmic polynomial of the third order:

$$\gamma = a_1(\ln c)^3 + a_2(\ln c)^2 + a_3 \ln c + a_4 \qquad (8)$$

where a_1, a_2, a_3 and a_4 are the constants.

- the spline function which consists of polynomials glued on small subranges (Bogacki et al, 1988).

Each of these functions can be used to match the interfacial tension. The matching is usually good although sometimes deviations are observed for the Temkin isotherm. The errors of model are small and increase in the order: spline < polynomial < Frumkin = Szyszkowski < Temkin. The matching is much better for individual model compounds than for commercial extractants.

By differentiating these equations and introducing the term $d\gamma/dc$ into the Gibbs isotherm appropriate relations for the surface excess can be directly computed. An appropriate computer program on a IBM PC microcomputer was described (Prochaska et al, 1989).

Surface excess isotherms computed according to the various equations exhibit somewhat different character. The characteristic feature for Szyszkowski and Frumkin isotherms is a very rapid increase of the estimated surface excess, already in the region of very low concentration, and the quick achievement of the plateau characteristic for the saturated interface.

The surface excess computed according to the Temkin isotherm increases monotonously but with a lower rate, and the region of the constant surface excess is usually not obtained.

The character of the surface excess isotherms computed according to the spline functions and the polynomial depends upon the type of extraction system considered, i.e. the type of solvent, and the type and hydrophilicity of extractant. For hydroxyoximes and amine derivatives in systems containing a non-solvating diluent, e.g. octane, explicit maxima of the surface excess were obtained for low extractant concentrations. They can be used to estimate the activity of extractant in the organic phase (Szymanowski and Alejski, 1990) or extractant association degree (Szymanowski, Bauer et al. 1989). In this last case the Gibbs isotherm is presented in the form $\Gamma = -z/RT \; d\gamma/d(\ln c)$.

The use of equations 4 - 8 is not only convenient for surface excess calculation. The adsorption coefficients have some important physicochemical meaning and can characterize extractants and inform upon the character of the interface.

It is obvious that similar values of B coefficient in the Szyszkowski isotherm were obtained for LIX 65N dissolved in various diluents and that much higher values of A coefficient were obtained in systems containing aliphatic hydrocarbons in comparison to those containing alkanes and methylcyclohexane (Szymanowski et al, 1990). However, in system containing Escaid 100 the A coefficient was similar to those obtained as toluene and Solvesso 150 were used as diluents. Thus, although Escaid 100 in arguements relating to bulk properties of solvents is treated as being of largely aliphatic character (it contains only 20% aromatics), the interface has an aromatic character due to the preconcentration of aromatics.

The adsorption coefficients can be also used to determine free energy of adsorption both organic and aqueous phase.

5 STRUCTURE AND INTERFACIAL ACTIVITY

We found the following orders of the interfacial tension activity for 2-hydroxy-5-alkylbenzophenone (E) and (Z) oximes, 2-hydroxy-5-alkylbenzophenones and 4-alkylphenols (Szymanowski and Prochaska, 1988a,b) in systems containing toluene $C_1 > C_2 > t\text{-}C_4 > t\text{-}C_8 > t\text{-}C_9$, where C_i denotes the length and the structure of the alkyl. A similar order was obtained for carboxylic acids containing from 5 to 16 carbon atoms in their molecules, for 4-alkylphenylamines containing from 6 to 16 carbon atoms in their alkyl (Wiśniewski, 1990) (benzene as a diluent), and for aminoether alcohols, $[R(OCH_2CH_2)_2]_2NCH_2CH_2OH$, containing 4, 6 and 8 carbon atoms in each alkyl (Szymanowski and Prochaska, 1989b).

Thus, in systems containing an aromatic diluent the surface activity increases as the length of the alkyl decreases. Compounds having a branched hydrocarbon chain are much less surface active than their normal homologoues having straight alkyls.

Some deviations from these rules were observed. For 2-hydroxy-5-alkylbenzaldehyde oxime the following order of the interfacial activity was observed (xylene was used as diluent): $C_2 < t\text{-}C_4 < t\text{-}C_8 < n\text{-}C_4 < n\text{-}C_8 < n\text{-}C_{12}$ (Stępniak-Biniakiewicz, 1990).

Aminooligooxyethylene ethers, $[(ROCH_2CH_2O)_2]_2N(CH_2CH_2O)_3R$, exhibit much higher interfacial activity (toluene as diluent) than aminoether alcohols, $[R(OCH_2CH_2)_2]_2NCH_2CH_2OH$. The effect of the alkyl length is relatively weak, and the interfacial activity changes according to the atypical order: $C_4 > C_8 > C_6$, probably due to the special configuration of these compounds at the interface. The presence of three oxyethylene groups permits this chain to bend in

such a way that the third alkyl group moves towards the two other alkyls and interacts with them (Szymanowski and Prochaska, 1989b). Due to this, the molecules acquire an amphiphilic character having hydrophilic groups on one side and the hydrophobic alkyls on the other side of the molecules.

In systems containing non-solvating diluents, e.g. aliphatic hydrocarbons, an opposite order of the interfacial activity is observed. For systems containing octane the following order of the interfacial activity was obtained for 2-hydroxy-5-alkylbenzophenone (E) and (Z) oximes, 2-hydroxybenzophenones and 4-alkylphenols: $n\text{-}C_8 > t\text{-}C_4 > C_2 > C_1 > t\text{-}C_8 > t\text{-}C_9$. It was also found that the interfacial activity of carboxylic acids increases as the length of the straight alkyl increases from C_5 to C_{16}. A similar order of the interfacial activity was demonstrated for 2-hydroxy-5-alkylbenzaldehyde oximes having from 2 to 12 carbon atoms in their straight alkyls. Thus, in systems containing aliphatic hydrocarbons as diluents the effects of the alkyl length and alkyl chain branching are different. It seems that the effect of branching is stronger than the effect of the alkyl length. As a result, compounds having a long strongly branched alkyl can exhibit weaker interfacial activity than their analogs with a short straight alkyl. In this case the following order of the interfacial activity was obtained: $t\text{-}C_8 < C_2 < t\text{-}C_4 < n\text{-}C_4 < n\text{-}C_6 < n\text{-}C_{12}$, where $t\text{-}C_8$ stands for 1,1,3,3-tetramethylbutyl group.

Interfacial activity of hydrophobic extractants also depends upon the location of hydrophobic hydrocarbon chains. Positional isomers can exhibit quite different interfacial activities, i.e. 1-(2'-hydroxy-5'-nonylphenyl)-ethanone oxime decreases the interfacial tension more effectively than 1-(2'-hydroxy-5'-methylphenyl)-decanone oxime.

6 INTERFACIAL ACTIVITY AND EXTRACTION RATE

The relationship between metal extraction rate and the interfacial activity is much more comprehensive than it was previously suspected. The rate of copper extraction by various hydroxyoximes always increases as their hydrophobicity decreases. A similar order of hydroxyoxime interfacial activity is observed only in systems containing solvating aromatic diluents. In systems containing aliphatic hydrocarbons the order of the interfacial activity is opposite to that of the reaction rates.

The rate of palladium (II) extraction with 4-alkylphenylamines exibits maximum for compounds having 10-12 carbon atoms in their alkyls (Wiśniewski, 1990). These compounds exhibit the best adsorption at the interface.

Thus, only in some systems the the highest extraction rates are obtained for extractants having the strongest interfacial activity. This proves the complexity of the problem and suggests that the interfacial activity is only one of several important parameters influencing the rate of metal extraction with hydrophobic extractants. More data are necessary to obtain better information upon the effect of extractant structure on its interfacial activity, the kinetics and the mechanism of metal extraction.

Our mathematical and physicochemical approach to this problem was presented in our previous works (Szymanowski et al, 1987-1990). They demonstrate that the interfacial tension data support only such a version of the interfacial process, in which the extractant molecules are preadsorbed at the interface. These adsorbed molecules react at the interface with the metal ions in a quick step, and in the rate determining step occuring in the aqueous film near the interface the intermediate 1:1 complex reacts with an extractant molecule present in the aqueous layers. However, the interfacial tension data do not give any evidence that metal extraction with hydrophobic extractants occurs according to the interfacial mechanism.

7 ACKNOWLEDGEMENT

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INTERFACIAL REACTION IN METAL EXTRACTION WITH CHELATING AGENTS

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ABSTRACT

The metal complex formation at liquid-liquid interface was measured using the stopped flow relaxation method for the microemulsion system including Cu(II), benzoylacetone and Aerosol-OT. The interfacial reaction is, in appearance, similar to the reaction processes in aqueous phase. The rate of Cu(II) extraction with benzoylacetone was discussed by focussing on the interfacial reaction.

1 INTRODUCTION

In solvent extraction of metals, the reaction to yield metal complexes can proceed in three domains; the aqueous stagnant film near the interface, the aqueous bulk phase, and the interface itself. The metal solvent extraction process is described in terms of the solvent ligand flow, whose equivalent circuit is shown in Fig.1. The solvent in the organic bulk phase is transferred to the interface by diffusing through the organic stagnant film and then reacts with metal through three routes. The neutral metal complex is back-extracted to the original organic phase. The resistances of each step, R's, have been formulated elsewhere (Harada et al. 1986).

One of the most important systems, where the extraction is controlled by the reaction processes, is the metal extraction with chelating agents. The key factor determining the main reaction location for metal complex formation is the distribution of chelating agents to the aqueous phase. When the agent is soluble in the aqueous phase, the metal complex is mainly formed in the aqueous stagnant film and/or the aqueous bulk phase. The interface itself is also important as providing the reaction location of complex formation. When the chelating agents are less soluble in the aqueous phase, the interfacial reaction mainly takes place [Flett, et al., 1973, Komasawa et al., 1980, Harada et al., 1989].

The reaction process in homogeneous phase can be experimentally elucidated by some method such as relaxation technique. If the rates are determined, the resistances, R_f, $\vec{R}_f$, $\overleftarrow{R}_f$ and R_b, shown in Fig.1 can be estimated theoretically at present. Whereas, the interfacial process is difficult to be understood due to lack of direct method of observation.

In this work, we discuss some characteristics of the interfacial reaction concerning classical chelating agent, benzoylacetone. First, the nature of the inter-

facial reaction is discussed based on the experimental result on the reaction in reversed microemulsion system. Secondly, the role of interfacial reaction in the copper extraction is discussed using the above result.

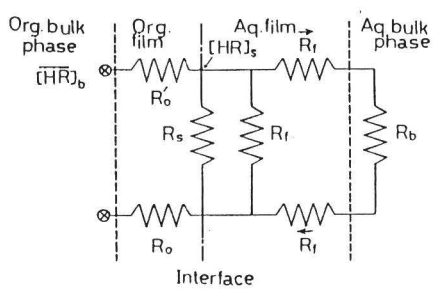
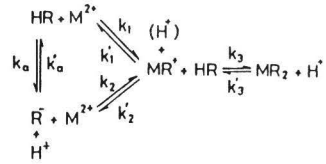


Fig.1 Equivalent circuit of extraction



k_1=2000 $dm^3/mols$,
k_a=81 s^{-1}, k_a' =1.5x10^{10} $dm^3/mols$
k_2=1.1x10^9 $dm^3/mols$

Fig.2 Reaction processes in aqueous phase

2 KINETICS OF INTERFACIAL REACTION

The kinetics of Cu(II) complex formation in aqueous phase has been extensively studied for classical β-diketones, e.g., benzoylacetone (Harada et al, 1983a) The reaction scheme is shown in Fig.2. The rate of CuR^+ formation,

$$r_{CuR}=k_{eff}([HR]-[H^+][CuR^+]/K[Cu^{2+}])$$
$$k_{eff} = k_1[Cu^{2+}]+k_a/(1+k'_a[H^+]/k_2[Cu^{2+}]), \quad (1)$$

determines the formation of the neutral complex, CuR_2. Here, [ ] represents the concentration. Benzoylacetone is composed of enol- and keto-forms, but only enol-form is taken into account, because the reaction processes concerned with keto form are much slower than those of enol-form.

In order to elucidate the role of the interfacial reaction, we must select a system in which the interfacial area to volume ratio is extraordinarily large. Such case is realized in reversed microemulsion system of W/O type. In this system, we can apply the relaxation method of the stopped flow type to observing the reaction course of the complex formation. The microemulsion system, sodium di-2ethylhexyl sulfosuccinate(AOT)/n-heptane/aqueous solution with $NaClO_4$ and Cu^{2+} was used for the relaxation experiment. The microemulsion phase involving benzoylacetone and $NaClO_4$ aqueous solution was instanteneously mixed with the microemulsion which contained $CuClO_4$ in $NaClO_4$ aqueous solution and was free from benzoylacetone. The absorbance at wave length 360nm was observed to detect the copper complexes. The experiment was performed at the condition, $V_w[Cu^{2+}]_i \gg V_o[\overline{HR}]_i$ and 25°C. Here, $[Cu^{2+}]$ and V_w are the mean concentration of copper ion in the water pools of the microemulsion droplets and the volume of the water pools. $[\overline{HR}]$ and V_o are the HR-concentration in n-heptane phase and its volume. The overbar represents the species in the oil phase.

The subscript i represents the initial state. It was confirmed that the time course of the absorbance change was of linear process. From this, the overall reaction constant k_{ov} is determined.

The production rate of the copper complex is described by Eq.(2),if the reactions in the water pools of the microemulsion droplets control the complex formation.

$$V_w d[CuR^+]/dt+V_o d[\overline{CuR_2}]/dt=V_w k_{eff}([HR]-[H^+][CuR^+]/K[Cu^{2+}]) \quad (2)$$

Mass balance of the ligand group is approximated by Eq.(3),because HR dissolved in the water pool is low enough to be neglected.

$$V_w[CuR^+]+V_o(2[\overline{CuR_2}]+[\overline{HR}])\cong V_o C_R \quad (3)$$

Here, C_R is the total concentration of the ligand group which is equal to the concentration initially charged to the oil phase. The equilibrium absorbances observed in the relaxation experiments at constant $[\overline{HR}]_i$ increased as $[Cu^{2+}]_i$ increased,approaching a saturated value. This result means that $V_w[CuR^+] >> 2V_o[\overline{CuR_2}]$. From Eqs.(2) and (3), the overall rate constant for CuR^+ formation is written as

$$k_{ov}=[(V_w/V_o)k_{eff}/P_{HR}](E_s/E), P_{HR}=[\overline{HR}]/[HR] \text{ at equilibrium} \quad (4)$$

E is the equilibrium absorbance and E_s is the saturated absorbance. The k_{ov} values observed are independent of $[\overline{AOT}]$ and are proportional to (V_w/V_o). Figure 3 shows the $k_{ov}(V_o/V_w)(E/E_s)$ values against $[Cu^{2+}]_i$. The dotted curve is calculated from Eq.(4) with the rate constants which has been determined in the experiment for the homogeneous reaction in the aqueous phase. The calculated value is much smaller than the observed ones,suggesting the importance of the interfacial reaction.

Strong electrostatic potential near the interface is imposed in the water pool of a microemulsion droplet due to presence of charged wall comprizing of anionic AOT. The Debye's screening length is 4 to 5 Å. Then, almost all Cu^{2+} are localized near the periphery of the droplet.A benzoylacetone molecule outside the droplet thrusts its polar head group in Cu-rich shell zone due to thermal fluctuation(see Fig.4). The contribution of the reaction in this shell to the overall reaction is described as

$$A\delta k_s\ [HR]^*[Cu^{2+}]_{eff} = V_w k_s [HR]^*[Cu^{2+}] \quad (5)$$

if the reaction in reverse direction is neglected. Here, A is the total area of water pools and δ is the length of benzoylacetone head group,which is nearly equal to the Debye's length. $[Cu^{2+}]_{eff}$ is the effective concentration in the water pool shell zone,i.e., $V_w[Cu^{2+}]/(A\delta)$, $[Cu^{2+}]$being the mean concentration in the water pool. $[HR]^*$ is the HR-concentration in the shell zone.

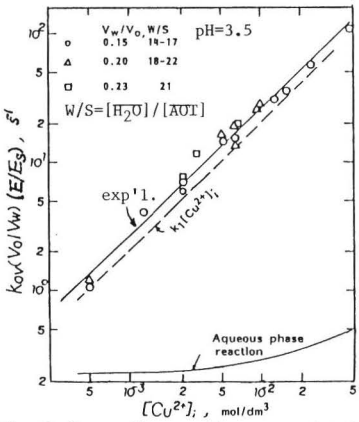


Fig.3 Overall reaction constant of complex formation in micro-emulsion system

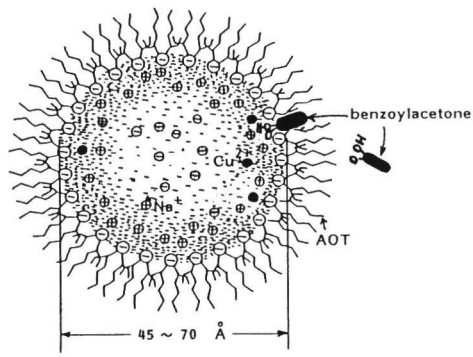


Fig.4 Illustration of the ion distribution in a microemulsion droplet

Using Eq.(5), the overall reaction rate constant is described as

$$k_{ov} = (k_s F[Cu^{2+}] + k_{eff}/P_{HR})(V_w/V_o)(E_s/E) \quad (6)$$

$$F = [HR]^*/[\overline{HR}] \quad (7)$$

Note that the overall reaction rate is proportional to V_w/V_o, in contrast with the case of usual interfacial reaction, where the rate is proportional to A/V_o.

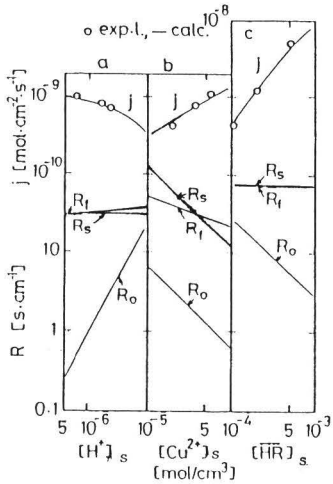
The experimental results shown in Fig.3 are fitted by Eq.(6) with

$$k_s F = 2800\ dm^3 mol^{-1} s^{-1} \quad (8)$$

The water structure near the periphery of a microemulsion droplet is destroyed due to broken hydrogen bonds between water molecules. The lower polarity and dielectric constant of these water molecules possibly lower the HR-dissociation near the periphery. Then, the direct reaction between the anchored HR of undissociated form and Cu^{2+} may dominate the CuR^+ formation, i.e., the reaction rate constant k_s takes similar value to k_1. The k_1 value is $2000 dm^3 mol^{-1} s^{-1}$ in aqueous solution and is close to Eq.(8) if assuming F=1. It is, therefore, concluded that the interfacial reaction is, in appearance, similar to that in a homogeneous phase.

3 EXTRACTION RATE OF Cu(II)

The rate of Cu(II) extraction with benzoylacetone in benzene solution has been measured using the Lewis cell [Harada et al., 1983b]. Some of the experimental results are shown in Fig.5. The resistances R_f, $\vec{R}_f$, $\overleftarrow{R}_f$, and R_b can be evaluated with the aids of the kinetic data of complex formation in aqueous phase. The mass transfer resistances R_o and R_o' werealso determined from mass transfer experiment. Among these, the important resistances to be considered



a : $[Cu^{2+}]_s = 3.75 \times 10^{-5}$
$[\overline{HR}]_s = 4.7 \times 10^{-5}$
b : $[H^+]_s = 1.35 \times 10^{-6}$
$[\overline{HR}]_s = 4.7 \times 10^{-5}$
c : $[H^+]_s = 6.0 \times 10^{-6}$
$[Cu^{2+}]_s = 1.9 \times 10^{-5}$
unit: in mol/cm³

Fig.5 Cu(II) extraction rates in benzoylacetone/benzene system. Data are taken from Reference (Harada et al., 1983b)

were found to be R_f and R_o. These resistances are also shown in Fig.5. The extraction rate can be described in terms of these resistances[Harada, et al, 1986]:

$$j = [P_{HR}(R+R_o)]^{-1}\left([\overline{HR}]_s - \frac{[\overline{CuR_2}]_b[H^+]_s^2}{K_{ex}[\overline{HR}]_s[Cu^{2+}]_s^2}\right) \tag{9}$$

$$1/R = 1/R_f + 1/R_s,\quad 1/(P_{HR}R_s) = (\delta F)\quad k_s[Cu^{2+}]_s,$$

$$R_f = (1+\tilde{K}^{-1})\coth\zeta\ /(k_w\zeta\ ),\ k_w\zeta = [k_{eff}D(1+\tilde{K}^{-1})]^{1/2} \tag{10}$$

$$\tilde{K} = K[Cu^{2+}]_s/[H^+]_s$$

$$1/(P_{HR}R_o) = k_o K_{ex}[\overline{HR}]_s[Cu^{2+}]_s/[H^+]_s$$

Here, k_o and k_w represent the mass transfer coefficients in the organic and aqueous phases. D is the diffusion coefficient in the aqueous phase , and K_{ex} the overall extraction constant. The subscripts s and b represent the values at the interface and in the bulk phase. The observed extraction rates are not explained by considering the resistances, R_o and R_f, only, suggesting the importance of the interfacial resistance R_s. The R_s value can be evaluated from the value shown in Eq.(8) by assuming that δ = 7Å, and is shown in Fig.5. The extraction rate j calculated from Eqs.(9) and (10) with the R_o, R_f and R_s values is shown as the solid curves in Fig.5. The calculated values explain well the observed results.

6 CONCLUSION

1) The interfacial reaction rate can be directly measured by using microemul-system.
2) The rate constant for the reaction between the undissociated benzoylacetone and copper ion is nearly equal to that in the aqueous phase, if the concentration of benzoylacetone in the interfacial zone is assumed to be equal to that in the organic phase.
3) The rate of extraction of copper from the aqueous phase to the organic phase can be evaluated theoretically by using the interfacial reaction rate observed.

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ROLE OF INTERFACE IN THE KINETICS OF SYNERGIC EXTRACTION OF NICKEL(II)-DITHIZONE -1,10-PHENANTHROLINE COMPLEX

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ABSTRACT

The role of the interface in the kinetic mechanism of the synergistic extraction of nickel(II) with dithizone(HDz) and 1,10-phenanthroline(phen) or 4,7-diphenyl-1,10-phenanthroline(DPP) into chloroform was studied at 25℃ by means of a high-speed stirring apparatus installing a photodiode-array spectrophotometer. From the concentration dependence of HDz and phen or DPP on the initial extraction rates of $NiDz_2phen$ and $NiDz_2DPP$, the rate-controlling steps for the extraction under higher concentration of HDz were found to be the formation processes of $Niphen^{2+}$ and $NiDPP^{2+}$ in a bulk aqueous phase and at interface, respectively. Under higher concentration of phen or DPP than that of HDz, the formation of intermediate complexes at interface, probably $NiDzphen_2^+$ and $NiDzDPP_2^+$, were suggested.

1 INTRODUCTION

An importance of interfacial phenomena in extraction kinetics under the vigorously agitated conditions has been demonstrated by our previous studies for some representative chelate extraction and ion-association extraction systems. The most significant interfacial phenomena affecting the rate of chelate extraction were elucidated to be the interfacial adsorption of a ligand and the interfacial formation of a mono-complex (Watarai and Freiser, 1983; Watarai et al., 1986). As for ion-association systems, the interfacial adsorption of an ion-pair was the characteristic interfacial phenomena (Watarai and Shibuya, 1989; Watarai et al., 1990). In the present study, in order to assess the role of the interface in the synergistic extraction system, which is the third group of the representative solvent extraction systems, the kinetic mechanisms of the systems of Ni(II)-HDz-phen and Ni(II)-HDz-DPP were investigated by the use of the high-speed stirring cell.

2 EXPERIMENTAL

2.1 Chemicals

Dithizone was purified by a back extraction from its chloroform solution with ammonia water and by the following neutralization with sulfuric acid. Phen and DPP, both reagent grade, were used as purchased. The stock solution of nickel(II) was prepared by dissolving nickel(II) sulfate hexahydrate. The aqueous phases used in the extraction experiments were buffered by 0.006M acetate solution and the ionic strength was maintained at 0.1 by the addition

of sodium sulfate. Chloroform was purified by washing three times with equal volume of water prior to use.

2.2 Kinetic measurement

The extraction rate of the mixed ligand complex and the back extraction rate of phen with Ni(II) ion solution were measured by means of the high-speed stirring apparatus. In the present study, a photodiode-array uv-vis detector, Shimazu SPD-M6A, was also employed, taking the place of the single wavelength detector, Jacso UVIDEC 430A.

The procedure of the measurements of the extraction rate was as follows ; the extraction was initiated by an injection of nickel(II) solution into the agitated mixture of 45ml aqueous buffer solution and 50ml HDz in chloroform containing phen or DPP at the stirring rate of 4700rpm in almost all cases. From the dispersed mixture, the organic phase was contenuously separated by means of a Teflon phase separator and it was circulated through the flow cell installed in the detector. The data of the absorbance or spectra were recorded in a micro-computer with a constant acquisition rate.

The adduct formation rate in organic phase was measured by means of a stopped flow spectrophotometer, Photal RA-401, by mixing the two chloroform solutions of $NiDz_2$ and phen.

All the kinetic measurements were made at 25.0±0.1℃.

3 Results and discussion

3.1 Adduct formation rate

The reaction between $NiDz_2$ and phen in chloroform was rather fast and therefore the stopped-flow technique was required for the measurements. The rate constant for the reaction was determined as 1.74×10^5 $M^{-1}s^{-1}$.

3.2 Reaction of Ni^{2+} with phen

The consumption rate of phen in organic phase caused by the reaction with nickel(II) ion in aqueous phase was measured at the varing concentration of phen. The initial rates were proportional to the phen concentration. From the results, the rate constant for the formation of $Niphen^{2+}$ in aqueous phase was determined as 6.79×10^3 $M^{-1}s^{-1}$.

3.3 Extraction rate of $NiDz_2phen$

The kinetic runs of the extraction observed at 520nm which was the maximum absorption wavelength of $NiDz_2phen$ showed different profiles depending upon the relative concentration of phen to HDz as can be seen in Fig.1; when [phen]< [HDz], the extraction was slow but smooth with respect to time, wherease, when [phen]>[HDz], it showed a fast extraction step in the initial stage and the following slow extraction step from the middle of the extraction process. From the initial stage, the initial extraction rate r^0, defined by $(d[NiDz_2phen]_o/dt)_{t=0}$, was obtained after the correction of the overlapped absorbance of the

free HDz in the organic phase. The values of r^0 were increased with increase in both phen and HDz concentrations. However, the increase in HDz concentration higher than that of phen resulted in a saturation in the value of r^0.

3.4 Extraction rate of $NiDz_2DPP$

The extraction profiles in the DPP system also depended on the relative concentration of DPP to HDz as in the case of phen. The initial extraction rate was, however, much lower than that of the phen system. It increased almost linearly with increase in the DPP concentration. In higher concentration of HDz than that of DPP, it showed no dependence on the HDz concentration.

3.5 Formation of intermediate complex

The stopping of the stirring on the way of the extraction which was conducted under the condition of [phen]>[HDz] caused a significant increase in the absorbance at 520nm. However, the stopping after the equilibration did show only a little raise in the absorbance. These results suggested strongly the existance of an interfacial species which was formed as an intermediate. The concentration of HDz incorporated in the interfacial species was calculated as a function of time from the observed concentrations of $NiDz_2phen$ and the free

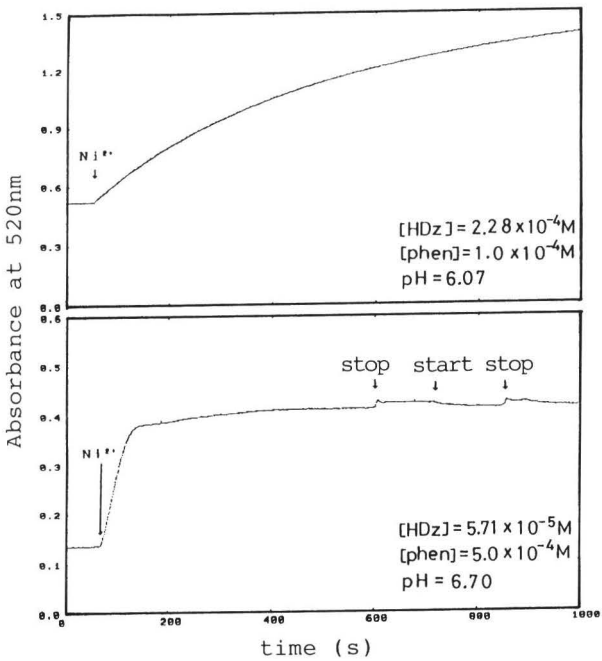


Fig. 1. The examples of the kinetic runs corresponding to the extraction of $NiDz_2phen$. The upper figure refers to the result in [phen]<[HDz], and the lower one to that in [phen]>[HDz].

HDz in organic phase and the total concentration of HDz added initially. The calculated results demonstrated clearly the formation of the interfacial complex. The maximum concentration of the interfacial complex increased with increase in the phen concentration and with increase in the stirring speed. In the systems of DPP also, an existence of interfacial comlex was suggested. The most probable species as the intermediates were considered to be $NiDzphen_2^+$ and $NiDzDPP_2^+$.

3.6 Extraction mechanism

The extraction rate of $NiDz_2$ which was controlled by the formation rate constant of $NiDz^+$, 5.97×10^3 $M^{-1}s^{-1}$, was much slower than the adduct formation rate in the organic phase and even slower than the formation rate of $Niphen^+$ in aqueous phase. Therefore, the synergistic effect on the initial extraction rate was assumed to be governed by the formation of $Niphen^+$ complex in aqueous phase, which rate constant was determined as 6.79×10^3 $M^{-1}s^{-1}$. This mechanism could satisfactorily explain the concentration effect of HDz and phen on the initial extraction rate. In the DPP system also, the rate-controlling step was suggested to be the formation rate of $NiDPP^+$. It has been shown, however, that this reaction occurs at interface with the rate constant of 6.4×10^3 $M^{-1}s^{-1}$, different from the case of phen.

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GALLIUM/ALUMINUM SEPARATION FROM SULFATE SOLUTIONS BY SOLVENT EXTRACTION USING D2EHPA

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ABSTRACT

Gallium(III) and aluminum(III) extraction from acidic sulfate solutions with D2EHPA in kerosene and stripping with H_2SO_4 from loaded D2EHPA have been studied and discussed in terms of potential Ga/Al separation, based on different extraction as well as stripping rates of the two metals. The results have shown that such separation is possible. The effect on separation of D2EHPA concentration, pH, and sulfate concentration during extraction and aqueous acidity during stripping is considered.

INTRODUCTION

The solvent extraction of Ga(III) and its separation from other metals has attracted significant attention in recent years due to the extensive use of gallium in electronics. Gallium separation is a challenging task since its concentration is usually quite low. For a given extraction system and conditions, separation can be achieved based upon different distribution coefficients of metals or upon their different extraction and/or stripping rates.

Di-2-ethyl-hexyl phosphoric acid (D2EHPA) is a well-known extractant for metals. Levin et al.(1968) have investigated the extraction behaviour of Ga(III) with several alkylphosphoric extractants from various acidic media, including D2EHPA and sulfuric acid solutions. Sato et al.(1978) have reported that Al(III) is extracted slowly with D2EHPA from such medium. Hence, it seems possible that these two, similar-in-properties, metals can be separated using their different rates with D2EHPA.

The subject of the present study is the potential for Ga/Al separation from acidic sulfate solutions using D2EHPA based on their different extraction and stripping rates.

2 EXPERIMENTAL

Extractant solutions of D2EHPA (BDH Chemicals, reagent grade) in kerosene (Fisher Scientific) were prepared. All

inorganic chemicals were of analytical grade. Gallium(III) and Al(III) solutions were prepared from their sulfate salts. The total sulfate concentration was varied with addition of Na_2SO_4. Acidity was adjusted using HNO_3, with appropriate $NaNO_3$ addition to maintain constant ionic strength for all experiments.

All extraction and stripping experiments were performed in separatory funnels agitated on a wrist-action shaker at O/A ratio = 1 and at room temperature. For the equilibrium tests funnels were left on the shaker for more than 24 hours in order to assure that equilibrium had been achieved.

Metal concentrations were determined by atomic absorption spectroscopy - in the aqueous phase - directly, and in the organic phase - after complete stripping with 15 wt.% H_2SO_4 and analyzing the strip solution. The results for both phases were consistent with the mass-balance requirements.

3 RESULTS AND DISCUSSION

3.1 Extraction equilibrium and Ga/Al separation

The relationship between the logarithm of the distribution coefficient (D) and pH for Ga(III) and Al(III) at the same concentration of D2EHPA is given on Fig. 1. As expected, the slope of both lines is n = 3, according to the overall reaction - eqn(1), and based on it - eqn(2), where K is the apparent equilibrium constant of the extraction reaction and $[(HR)_2]_{org}$ is the free extractant concentration (as dimer):

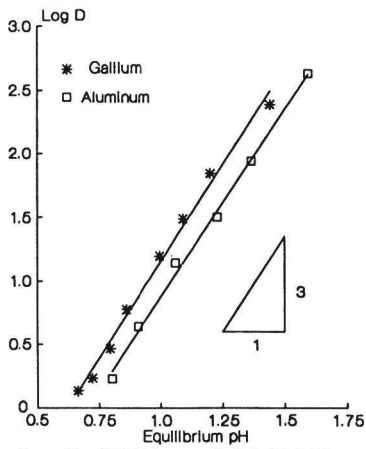


Fig. 1. Ga(III) and Al(III) extn., equilibrium. 10 vol % D2EHPA, $[Ga]_{init}$= 0.006 M; $[Al]_{init}$= 0.006 M

$$Me^{3+}_{aq} + (n+s)/2\ (HR)_{2,org} \rightleftharpoons MeR_n.sHR_{org} + nH^+_{aq} \qquad (1)$$

$$\lg D = \lg K + (n+s)/2 \lg [(HR)_2]_{org} + n\ pH \qquad (2)$$

For Al(III) Sato and Nakamura (1975) have found s = 3 and for Ga(III) Inoue et al.(1988) have reported s = 1, a value which has

been confirmed by our own studies on Ga(III) extraction from sulfate solutions. From the results on Fig. 1 it is possible to calculate what separation factor, $S = D_{Ga}/D_{Al}$, can be achieved for given experimental conditions. For our particular case S = 1.88. This value, which is rather small, indicates that no significant Ga/Al separation can be obtained when equilibrium for both metals is established. Based on eqn.(2) and the values of n and s for Ga(III) and Al(III) it follows that S will be expected to decrease as $[(HR)_2]_{org}$ increases.

3.2 Extraction kinetics and Ga/Al separation

Experiments were carried out with sulfate solutions of high Al and low Ga initial concentrations - $[Al]_{init}$ = 1850 ppm , $[Ga]_{init}$ = 210 ppm. The effects of D2EHPA , pH, and the total sulfate concentration on the rates of extraction are shown on Fig. 2 - 4. In order to estimate the degree of Ga/Al separation, a time-dependent parameter - separation ratio, $S_{R,t}$, is defined and the values calculated from the experimental data are given in Table 1. The results demonstrate that gallium is loaded in the organic phase much faster than aluminum. This is clearly the case at low extractant concentration (Fig. 2) and accordingly high values of $S_{R,t}$ are obtained (Table 1, a). When the extractant concentration is high, the separation ratios achieved (Table 1, d) are much lower due to the restrictions on further increase in the extraction rate of Ga following from its low initial concentration in the aqueous phase.

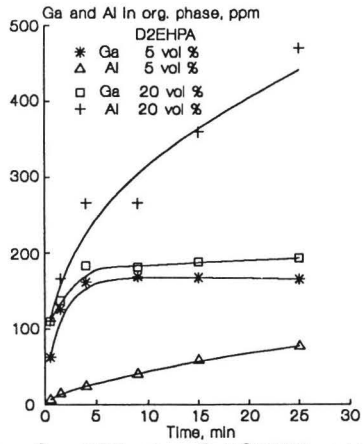


Fig. 2. Effect of D2EHPA concn. pH = 1.50 , $[SO_4]_T$ = 0.1 M

Lowering pH of the aqueous phase leads to marked decrease in the extraction rates of both metals (Fig. 3). The effect, however, is greater in case of gallium and, as a result, $S_{R,t}$ drops (Table 1, c).

It is known that Ga(III) and Al(III) form sulfate complexes, thus decreasing the concentration of free metal cations which are

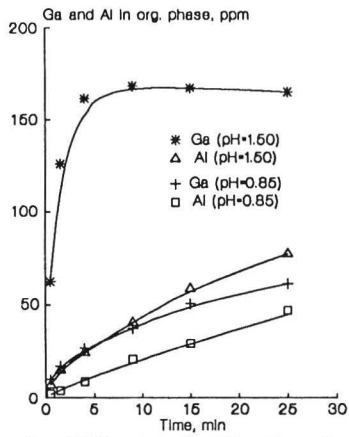


Fig. 3. Effect of pH. 5 vol % D2EHPA

the species taking place in the extraction reaction. Therefore, the amount of sulfate is an important factor for extraction equilibrium and kinetics of the two metals. Results for Ga(III) and Al(III) extraction from solution with increased total sulfate concentration ($[SO_4]_T$ = 0.6 M) are given on Fig. 4 and compared with those reported on Fig. 2 for otherwise the same conditions. The extraction rates for both metals decrease with increasing $[SO_4]_T$ for reasons indicated above, but more importantly, $S_{R,t}$ remains virtually the same (Table 1, b). This implies that both rates are equally affected by the sulfate complexation and therefore it should not be a major parameter with regard to the Ga/Al separation. The observed differences in the extraction kinetics of Ga(III) and Al(III) with D2EHPA can be explained with the different ligand exchange rates for the two metals. In aqueous solutions their small and highly charged cations are hydrated - $[Ga(H_2O)_6]^{3+}$, $[Al(H_2O)_6]^{3+}$, and during the extraction reaction water ligands are substituted with those of the extractant in a number of consecutive steps with one of them being rate-controlling. It is known that the rate of ligand exchange (homogeneous kinetics) depends mostly on the nature of the metal cation and to a lesser extent on the particular ligand. The water exchange rate constants for Ga(III) and Al(III) are - $k_{Ga} = 1.82 \times 10^3\ s^{-1}$, $k_{Al} = 1.7 \times 10^{-1}\ s^{-1}$ (Fiat and Connick, 1968). They differ significantly and therefore it can be

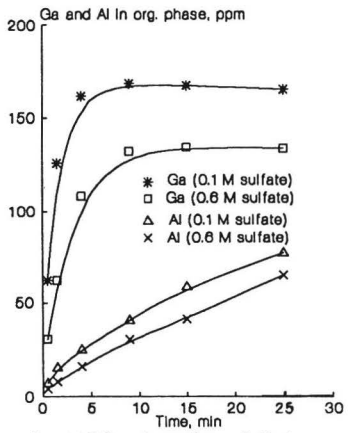


Fig. 4. Effect of sulfate concn. pH = 1.50, 5 vol% D2EHPA

expected the actual extractant ligand - inorganic ligand exchange rate for Ga(III) to be greater than the one for Al(III).

TABLE 1

Separation ratios, $S_{R,t}$, calculated from the exp.data on Fig.2-5, defined as $([Ga]/[Al])_{org,t}/([Ga]/[Al])_{aq,init}$ - for extraction, and $([Ga]/[Al])_{aq,t}/([Ga]/[Al])_{org,init}$ - for stripping.

Time	extraction				stripping	
(min)	a	b	c	d	e	f
0.5	80.0	72.9	42.3	9.8	33.8	15.0
1.5	73.3	67.7	39.8	7.5	17.9	8.5
4.0	58.7	58.7	27.0	5.9	10.1	5.1
9.0	36.7	28.3	15.7	4.8	6.3	3.4
15.0	25.1	28.4	15.1	4.2	4.7	2.6
25.0	18.7	18.0	11.4	3.7	-	-
conditions:	a	b	c	d	e	f
D2EHPA vol%	5	5	5	20	5	5
pH	1.50	1.50	0.85	1.50	-	-
$[SO_4]_T$ M	0.1	0.6	0.1	0.1	-	-
H_2SO_4 M	-	-	-	-	0.85	1.69

3.3 Stripping kinetics and Ga/Al separation

Separation of Ga and Al can also be achieved based on their different stripping rates - results for two H_2SO_4 concentrations (stripping reagent) are given on Fig. 5. They show that Ga is stripped considerably faster than Al and both rates increase with the acidity. For Ga, under the particular conditions, the effect cannot be clearly demonstrated since its stripping is already fast and complete at the lower acidity. Increasing the

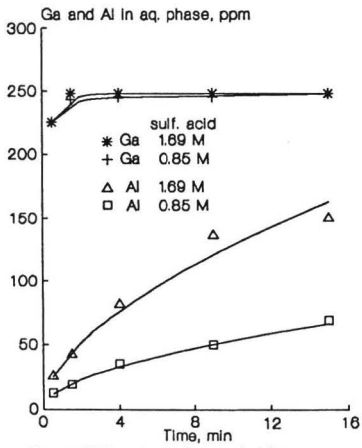


Fig. 5. Effect of acidity on stripping rate of Ga and Al. 5 vol % D2EHPA, $[Ga]_{init,org}$ = 248 ppm, $[Al]_{init,org}$ = 400 ppm

acid concentration, in this case, serves only to increase the stripping rate of aluminum and that results in lower separation ratios (Table 1, f). Therefore, better separation of gallium can be achieved at lower acidities where Ga is still stripped fast enough while the aluminum stripping remains slow.

4 CONCLUSIONS

It has been demonstrated that gallium can be separated from aluminum in their mixed acidic sulfate solutions by solvent extraction with D2EHPA based on the significantly different extraction rates of the two metals. This is explained qualitatively with the different water exchange rates for Ga(III) and Al(III). Better separation ratios can be obtained at lower D2EHPA concentration and higher pH but they appear not to be affected by the concentration of sulfates in the aqueous phase. Further Ga/Al separation can be achieved based on their different stripping rates with H_2SO_4 solutions from loaded D2EHPA.

Maximum separation ratio can be achieved when the concentrations of D2EHPA for extraction, and H_2SO_4 for stripping are sufficiently low that, transfer rates for gallium will still be fast, while those for aluminum remain slow.

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STUDIES ON MECHANISM OF EXTRACTION OF IRON(III) FROM SULFATE SOLUTION AND STRIPPING WITH SULFURIC ACID BY FT-IR AND LASER LIGHT SCATTERING SPECTROMETRY I.HDEHP OR RNH_2 AS EXTRACTANT WITH OCTANE AS DILUENT

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ABSTRACT:
Through the investigation of the two typical extractant systems by FT-IR and Laser Light Scattering Spectrometry and measurements of composition and water content in the extracted organic phase, it was found that iron(III) is extracted mainly in unhydrated form by HDEHP and in hydrated form by RNH_2. It also indicates that extraction of iron(III) with HDEHP is through the formation of reverse micelle in organic phase and with RNH_2 is through the microemulsion of water in oil type. The size of reverse vesicle was found larger than the size of microemulsion and it also indicated the importance of the role of water in the extraction process. The HDEHP in inert solvent is in dimer form H_2A_2 and it will partially convert to monomer form during extraction. The stripping of iron by sulfuric acid is through a process of destruction of the reverse micelle in HDEHP system and is not through the destruction of the w/o emulsion in RNH_2 system. The RNH_2 acts as RNH_3^+ cation surfactant in sulfuric acid and microemulsion is stable. The dependency of rate of extraction on hydration of iron(III) and extractant concentrations in both HDEHP and RNH_2 systems has been confirmed.

1 INTRODUCTION

Di(2-ethylhexyl) phosphoric acid (HDEHP) and primary amine (RNH_2) are extractant with wide applications(Alguacid and Amer, 1986; Blake, et al.,1958; Sato and Nakamura, 1971.). Although iron(III) in sulfuric acid can be extracted with HDEHP or RNH_2, the stripping of extracted Fe(III) with sulfuric acid in HDEHP system is different in a number of ways from the stripping of iron in RNH_2 system. The kinetic studies on extraction have also indicated that the rate of the extraction of Fe(III) with RNH_2 is higher than that with HDEHP(Catteral and Peverill, 1970; Coleman and Roddy,1971; Seeley and Crouse, 1971.). But there is very little information on the behaviour and characteristics of this nature. In order to understand the extraction mechanism of iron(III) from sulfuric acid by HDEHP and RNH_2 respectively, the extracted organic phase is studied in present work.

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2 EXPERIMENTAL:

A mechanical electric shaker was used to mix aqueous and organic phase. HDEHP used was purified by copper salt method. Primary amine (N1923) used in this sudy with formula $RR'CHNH_2$ and a total number of carbon atoms 19 to 23, was purified by distillation method. The octane of chemical purity grade was used as diluent. The other chemicals used were of analytical grade. Fe(III) was analysed by titration with potassium dichromate solution. The concentration of acid was determined by titration with NaOH solution or pH of a solution was measured by a pH meter. The water content was determined by Carl Fischer titration with a microcoulometric detector. FT-IR spectra of organic phase was recorded with Nicolet 7199B FT-IR spectrometer. KBr windows was used. The absolute scattered intensity was measured at scattering angle 90°. An Ar Laser was operated at 488 nm with an output power in the 200-400 mW range.

3 RESULTS AND DISCUSSION:

3.1 Determination of water content of organic phase and stripping of iron(III) from loaded organic phase with sulfuric acid solution:

In this work, octane was the only diluent used in organic phase. The results show that the water content of organic phase is strongly dependent on the initial acidity in the HDEHP system as shown in Table 1 and on the concentration of primary amine in the N1923 system as shown in Fig.1 respectively.

TABLE 1

The composition of organic phase of HDEHP(5%)-octane system in contact with aqueous phase with different acidity

aqueous acidity		equilibrium organic phase		
(pH)	(mol/dm^3)	Fe(mol/dm^3)	H_2O(mol/dm^3)	Fe/H_2O
	/	/	0.0044	
2		0.0568	0.0528	1.1
	0.28	0.0336	0.0124	2.7
	0.5	0.0236	0.0073	3.2
	5	0.0209	0.0027	7.7

Aqueous phase: Fe^{3+}=4-5 g/dm^3.

3.2 FT-IR spectra of organic phase:

Effect of addition of diluent and amine on the FT-IR spectra of extracted species in loaded organic phase in HDEHP system was shown in Table 2. It can be seen that the presence of P=O stretching band at 1229 cm^{-1} , the OH stretching band at 2337 cm^{-1} and [P-O]-C stretching band at 1036 cm^{-1} in the spectra of diluent solution of HDEHP. However, in the spectra of amine salt of HDEHP, the

absorption band of OH stretching disappears, and P=O stretching is shifted to low frequency of 1197 cm^{-1}, which is assigned to POO^- asymmetric stretching. A similar result was obtained with loaded organic phase from iron(III) sulfate solution as shown in Fig. 2. It is reasonable to consider that HDEHP exists predominantly as ion-associated species in this two cases.

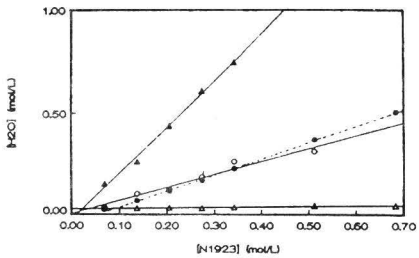


Fig.1. Comparison of H_2O content in organic phase of N1923-octane. Aqueous Phase:
▲: 1mol/dm^3 H_2SO_4, Fe^{3+}=0g/dm^3;
●: 1mol/dm^3 H_2SO_4, Fe^{3+}=5g/dm^3;
△: pH=2, no Fe^{3+};
○: pH=2, Fe^{3+}=5g/dm^3.

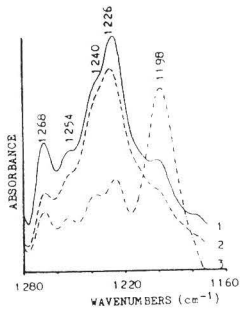


Fig.2. Effect of H_2SO_4 on deconvoluted bands of P=O and POO^- in HDEHP(5%)-octane system.
1. no reaction with water solution;
2. 1mol/dm^3 H_2SO_4, Fe^{3+}=0g/dm^3;
3. 1mol/dm^3 H_2SO_4, Fe^{3+}=4g/dm^3.

TABLE 2.

The effect of diluent and amine on FT-IR spectra of HDEHP(cm^{-1})

HDEHP pure	HDEHP(5%)	HDEHP amine salt	Assignment
1029.6(vs)	1035.7(vs)	1058.8(vs)	ν P-O-C, ν POO^-
1230.5(vs)	1228.6(vs)	1196.7(vs)	ν P=O
1687.6(s)	/	/	δ OH
2306.6(s)	2336.5(vw)	/	ν OH

Table 3 shows the FT-IR spectra of extracted species in organic phase loaded in N1923 system. The presence of a band in the region 3300--3500 cm^{-1} allows one to confirm the presence of water in the loaded organic phase. The infrared spectrum of RNH_2 in octane shows the NH_2 asymmetrical bending band at 1614 cm^{-1} and the NH_2 symmetrical bending band at 799 cm^{-1}, which are ascribed to the presence of monomer. In the FT-IR spectra of extracted species from aqueous ferric sulfate solution, the NH_2 bending bands disappear and 1610 cm^{-1} and 1510 cm^{-1} peaks of NH_3^+ in organic phase were observed. The position of peaks of NH_3^+ change slightly with the increasing of sulfuric acid concentration. It is reasonable to consider that N1923 exists predominantly as cation species RNH_3^+ in loaded organic phase and does not attach directly to iron(III). Simultaneously, comparison of the FT-IR spectra of extracted species

with aqueous solution of Na_2SO_4, the infrared spectra shows that the SO_4^{2-} stretching bands are at 620 cm^{-1} and 1107 cm^{-1}, which are ascribed to the presence of free SO_4^{2-} ions in aqueous solution. Similarily, the absorption at 617 cm^{-1} and 1110 cm^{-1} in the loaded organic phase from the extraction of aqueous ferric sulfate solution with pH=2 was investigated. The stretching bands at 601, 1134, 1192 cm^{-1} were found in the loaded organic phase from the extraction of extraction of Fe(III) solution with 1mol/dm^3 H_2SO_4. It seems that the HSO_4^- may be formed in the organic phase at high acid concentration.

TABLE 3

The effect of diluent and acid on FT-IR spectra of N1923(cm^{-1})

N1923 pure	N1923(10%)	N1923(15%) extracted Fe with pH=2	N1923(8%) extracted Fe with 1M H_2SO_4	Na_2SO_4 Solution	Assignment
			601.5		ν_4 SO_4^{2-}
		617.4		620.5	ν_4 SO_4^{2-}
799.4	794.3				δ NH_2
		1110.4		1106.5	ν_3 SO_4^{2-}
			1134.5		ν_3 SO_4^{2-}
			1192.1		ν_3 SO_4^{2-}
1582.1		1509.8	1510.1		δ_s NH_3^+
1614.2	1616.9				δ NH_2
		1609.3	1604.5	1648.8	$\delta_{as}NH_3^+$+δ H_2O
3299.5					ν NH_2
3368.7					ν NH_2
		3411.4	3426.1	3429.0	ν H_2O

3.3 Laser Light Scattering Spectroscopy:

The photoelectron count time correlation function was measurement at scattering angle 90 with 64-channel digital correlator. Based on the diffusion coefficient deduced from autocorrelation function using the cumulates method, the apparent mean hydrodynamic radius, Rh was calculated from Einstein-Stokes equation as shown in Table 4 and 5.

TABLE 4.

Particle size obtained from correlation spectroscopy in the organic phase of HDEHP(5%)-octane system

	Species of Fe(III) extracted from aqueous solution with different acidity				
	before reaction	pH=2	0.28(mol/dm^3)	0.5(mol/dm^3)	5(mol/dm^3)
Rh(A)	/	41	2099	1340	/

Aqueous phase: Fe =4 g/dm^3

TABLE 5

Particle size obtained from loaded organic phase in N1923-octane system

N1923(%)	0.5	2.0	4.0	5.0	7.5	10
Rh(Å)	/	28.8	38.3	51.8	56.8	40.1

Aqueous phase: Fe = 5 g/dm^3

According to the results shown in Tables 4 and 5, the proposed structures of reverse micelle or microemulsion are shown in Figs.3 and 4 respectively. The species extracted in organic phase loaded with HDEHP contain no water, as called reverse micelle solutions. The extracted species in organic phase loaded by N1923 contain solubilized water, as called water-in-oil microemulsions.

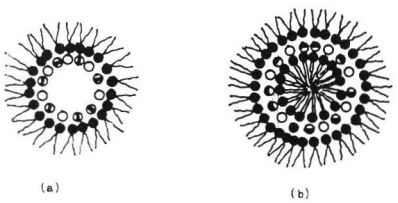


Fig.3. Model of reverse micelle in organic phase of the HDEHP-octane extracted system.
(a) pH>2, reverse micelle;
(b) pH<1, reverse vesicle.
:HDEHP
:Fe^{3+}
:H^+
:OH^-

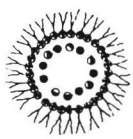


Fig.4. Model of microemulsion in organic phase of the N1923-octane extracted system.
:RNH_3^+
:OH^-, SO_4^{2-}
:H_2O, Fe^{3+}

3.4 Mechanism of extraction of iron(III) :

The quantitative treatment of liquid-liquid distribution has been studied widely. But the importance of the role of water in extraction process has not been much studied and many phenomena observed remain unexplained. In this work, a relatively simple model system consisting of a reverse micelle systems in equilibrium with an aqueous solution is considered.

Therefore, with low pH in aqueous phase, it can be assumed that the extraction reaction of Fe(III) by HDEHP may be expressed as follows:

$$Fe^{3+}_{(a)} + nHA_{(o)} = FeA_3HA_{(n-3)(o)} + 3H^+_{(a)} \qquad (1)$$

where n>3.

When pH of an aqueous phase is relatively high, the following extraction reaction is proposed:

$$Fe^{3+}_{(a)} + mHA_{(o)} + H_2O = Fe(OH)A_2HA_{(m-2)(o)} + 3H^+_{(a)} \quad (2)$$

where $m>2$.

The higher the initial acidity in aqueous phase, the larger the value of n and m are, which may lead to the different compositions of species extracted as reported in the literature(Yu and Chen, 1989).

In the meanwhile, the following extraction reactions are suggested for N1923-Octane system.

At low sulfuric acidity (pH>1):

$$Fe^{3+}_{(a)} + H_2O + SO_4^{2-}_{(a)} + n(RNH_3)_2SO_4 = [Fe(OH)SO_4][(RNH_3)_2SO_4]_{n(o)} + H^+_{(a)} \quad (3)$$

At high sulfuric acidity (pH<1):

$$Fe^{3+}_{(a)} + HSO_4^-_{(a)} + SO_4^{2-}_{(a)} + n(RNH_3)_2SO_4 = [Fe(HSO_4)(SO_4)][(RNH_3)_2SO_4]_{n(o)} \quad (4)$$

The spectra and water content of Fe(III) loaded organic phase suggest that the complex formed contains not only the Fe(OH) unit, but also the Fe-O-Fe unit, which the oxygen bridge comes from the water molecule.

The stripping reaction of Fe(III)-loaded HDEHP with high concentration sulfuric acid solution was studied. It was considered that the reverse micelle have to be disintegrated during stripping. The stripping reaction of Fe(III)-loaded N1923 with sulfuric acid solution was also studied. The w/o microemulsion in N1923 system has no change probably after stripping.

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ON DETERMINATION OF RATE PROCESSES IN EXTRACTION FROM CONCENTRATION MEASUREMENTS OF DIFFUSING SPECIES

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ABSTRACT

For extraction of Cu(II) with acidic organophosphorus extractant, local concentrations of metal ion and its complex near the interface were measured by means of scanning light beam absorptimetry and the rate processes were discussed on the basis of the changes with time in concentrations near the interface. With comparing the experimental data with the solutions to the diffusion equation, it was shown that the rate of reaction is extremely fast under usual conditions and the rate of extraction is controlled alone by the diffusional process, except in the very early stage of the extraction.

INTRODUCTION

In this and last decades, there have appeared many articles on kinetics and mechanism of metal extraction and some reliable extraction models have been proposed. In most of the work, however, verifications of them have been made on the basis of the overall extraction rates measured with a stirred transfer cell which includes complicated hydrodynamic effects. Here, on the extraction of divalent metal with acidic organophosphorus reagents, experiments were carried out with a static transfer cell and the spatial distributions of the diffusing species near the interface were measured in time course of extraction by a scanning light beam spectrophotometer. With the aid of exisiting reaction models, the problem of mass transport through the interface between aqueous and organic phases was formulated and the rate processes were discussed by comparing the mathematical solutions for spatial and temporal species concentrations with the experimental results, focussing on changes with time in concentrations of diffusing species near the interface.

1 THEORETICAL CONSIDERATIONS ON RATE PROCESSES

1.1 Background of kinetic model for interfacial reaction

The overall reaction equation at the interfacial zone for metal extraction with organophosphorus extractant (simply HR) is given by, for divalent metals,

$$M^{2+} + (2+n)(HR) \rightleftharpoons MR_2(HR)_n + 2H^+, \quad \text{with} \quad K_{ex} = [MR_2(HR)_n][H^+]^2/[M^{2+}][HR]^{2+n} \quad (1)$$

where n is 2 for Cu(II) and Co(II), and 4 for Ni(II). Komazawa et al (1983)

extended the reaction model in the aqueous homogeneous phase presented by Eigen and Tamm (1962) to the interfacial reaction and proposed that the reaction occurs in the two succeeding steps; 1) the hydrated M^{2+} reacts with a dimer species $(HR)_2$ to form $M(H_2O)_4^{2+}2R^-$ and 2) this reacts with another free dimer $(HR)_2$ and is dehydrated to form the stable complex $MR_2(HR)_2$ (in the organic phase, the extractant molecules exist as the dimer species; $K_{dm} \simeq 10^7$ [cm^3/mol]). They assumed that the latter dehydration reaction is the rate determining and derived the rate equation:

$$R = d[MR_2(HR)_2]/dt = \vec{k}_2 \cdot K_1 [M^{2+}]_i [(HR)_2]_i / [H^+]_i - \overleftarrow{k}_2 [MR_2(HR)_2]_i \qquad (2)$$

where K_1 $(=\vec{k}_1/\overleftarrow{k}_1)$ is the equilibrium constant for reaction of step 1 and $\vec{k}_2$, $\overleftarrow{k}_2$ are the rate constants for reaction of step 2, related to the equilibrium constant as $K_{ex,dm} (\equiv [MR_2(HR)_2][H^+]^2/[M^{2+}][(HR)_2]^2) = \vec{k}_2 K_1/\overleftarrow{k}_2$, with i denoting the interfacial zone. They concluded that the rate of extraction is controlled by the interfacial reaction and obtained the values of rate constants.

Later, Miyake et al. (1990) reported that the reaction proceeds in the following steps: 1a) the M^{2+} reacts with HR and 1b) reacts in parallel with dissociated R^- to form the intermediate 1:1 complex MR^{+1} and 2) this reacts with a free R^- and two HR species to form the final stable complex. They assumed that the former is the rate determining step and derived the rate equation in the form:

$$R = \vec{k}^*[HR]_i [M^{2+}]_i - \overleftarrow{k}^*[MR_2(HR)_2]_i [H^+]_i^2 / [HR]_i^3, \qquad (3)$$

where $\vec{k}^* = \vec{k}_{1a} + \vec{k}_{1b} K_a / P_{HR} [H^+]_i$, $\overleftarrow{k}^* = \vec{k}^*/K_{ex}$ $(= \overleftarrow{k}_{1a} K_{ex1a} K_{ex2} + \overleftarrow{k}_{1b} K_{ex1b} K_{ex2} / [H^+]_i)$. They concluded, in contrast to the above, that the interfacial reaction is very rapid compared with the rate of diffusion in the stagnant layer and the extraction is controlled by the diffusional process.

1.2 Diffusion with interfacial reaction

The solubility of HR in the aqueous phase is so small that the reaction proceeds mainly at the interface, and the concentrations c_J's of the species are governed by, neglecting the bulk transport,

$$\frac{\partial c_J}{\partial t} = D_J \frac{\partial^2 c_J}{\partial z^2}, \qquad j = M, HR, MR \qquad (4)$$

with M, HR, MR denoting the species M^{2+}, $(HR)_2$, and $MR_2(HR)_2$, respectively.

The initial and the infinite medium boundary conditions are

$$c_J(z,0) = c_J^0, \quad \infty > z > -\infty, \quad z \neq 0, \quad j = M, HR, MR \qquad (5\text{-a})$$

$$c_J(\infty, t) = c_J^0, \quad t > 0, \quad j = HR, MR \qquad (5\text{-b})$$

$$c_J(-\infty, t) = c_J^0, \quad t > 0, \quad j = M \qquad (5\text{-c})$$

If there accumulate no species at the interface, hold the relations:

$$D_{HR} \cdot \partial c_{HR}/\partial z - (2+n) D_{MR} \cdot \partial c_{MR}/\partial z = 0, \quad z = 0, \ t > 0 \qquad (5\text{-d})$$

$$D_M \cdot \partial c_M/\partial z - D_{MR} \cdot \partial c_{MR}/\partial z = 0, \quad z = 0, \ t > 0 \qquad (5\text{-e})$$

To close this set of equations, another boundary condition which is directly related to the scheme of reaction at the interface is required.

In either case of the existing models stated above, the rate equation can be expressed by the linear equation when $[(HR)_2] \gg [M^{2+}]$ and $[H^+]$ is kept constant, and the remaining boundary condition is given by

$$R = \vec{\kappa} c_M - \overleftarrow{\kappa} c_{MR}, \qquad z=0, \quad t>0 \tag{6}$$

The solutions for the concentration of species j are

$$c_j/c_M^0 = a\cdot(\vec{\kappa}/d\sqrt{D_j})\cdot[\mathrm{erfc}(|z|/2\sqrt{D_j t}) - \exp(d^2 t + d|z|/2\sqrt{D_j})\cdot\mathrm{erfc}(d\sqrt{t} + |z|/2\sqrt{D_j t})] + b \tag{7}$$

where $d=\vec{\kappa}/\sqrt{D_{MR}} + \overleftarrow{\kappa}/\sqrt{D_M}$, and a=-1, b=1 for $j=M^{2+}$, a=1, b=0 for $j=(HR)_2$, a=-2, $b=c_{HR}^0/c_M^0$ for $j=MR_2(HR)_2$.

When the rate of reaction is very rapid when compared with that of diffusion, the following equilibrium relation holds, in place of Eq.(6)

$$c_{MR} = K_d c_M, \qquad z=0, \quad t>0 \tag{8}$$

with the distribution coefficient $K_d (\equiv [MR_2(HR)_2]/[M^{2+}])$. In this case, the solution reduces to

$$c_j/c_M^0 = a\cdot\overline{K_d}\cdot\mathrm{erfc}(|z|/2\sqrt{D_j t}) + b \tag{9}$$

where $\overline{K_d} = K_d/(K_d + \sqrt{D_M/D_{MR}})$, a=1, b=1 for $j=M^{2+}$, $a=\sqrt{D_M/D_{HR}}$, $b=c_{HR}^0/c_M^0$ for $j=(HR)_2$, and $a=\sqrt{D_M/D_{RM}}$, b=0 for $j=MR_2(HR)_2$.

1-3 Determination of the rate controlling step

The concentrations of metal and its complex at the interface are, from Eq.(7)

$$c_j = c_M^0\cdot a\cdot(\vec{\kappa}/d\sqrt{D_j})[1-\exp(d^2 t)\cdot\mathrm{erfc}(d\sqrt{t})] \tag{10}$$

The concentration of each species at the interface changes with time in course of extraction depending on the rate constants. Therefore, if the rate of reaction is comparable to that of diffusion, it could be detected. With the experimental data for changes in concentration very near the interface, we can determine the values of rate constants from Eq.(7). And, if the concentrations in the phases are spatially uniform, the extraction rate is considered to be limited by the reaction. If no changes in concentrations at the interface are found, the extraction is considered to be controlled just by the diffusional process.

2 EXPERIMENTAL

2.1 Reagents and solutions

Organic solutions were prepared by diluting the di(2-ethylhexyl) phosphoric

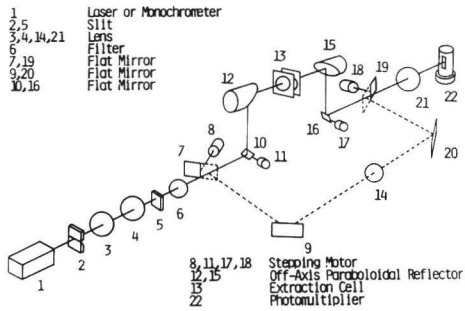


Fig.1 Optical system of scanning spectroscopy

acid, D2EHPA (DP-8R Daihachi Chemical Ind.Co.,Ltd.,with purity of more than 95%) or 2-ethylhexyl phophonic acid mono 2-ethylhexyl ester, EHPNA (PC-88A Daihachi Chemical Ind.Co.,Ltd., with purity of more than 90%) in a diluent n-heptane. The reagent concentration was arranged at 0.06 or 0.3mol/dm^3. The aqueous solutions were prepared by dissolving copper sulfate in distilled water. The pH value was kept at 3.8～4.2 by adding a buffer solution (CH_3COOH/CH_3COONa), the ion strength being set at 0.1mol/dm^3. The copper concentration was arranged in the range of $5\cdot10^{-3}$～$2\cdot10^{-2}$mol/dm^3. The thermodynamic equilibrium date for this extraction system are given in the published papers.

2.2 Measurments of local concentrations

A cylindrical cell made of stainless steel with a 46mm-diameter optical glass fixed at each end was used for the extraction cell, the optical length being 20mm. After pouring the 20mℓ organic solution into the cell and confirming it static, a desired amount of the aqueous solution was poured carefully so as not to disturb the interface. The local absorbances in the both phases near the interface were measured with our spectrophotometer with a light beam scanning device as shown in Fig.1. The light beam from 1mW He-Ne laser (or monochrometer (N25; Nihon Bunko Co.Ltd.)) is focussed to 200μm radius by the lens (f=200) and is splitted into the main and compensation beams by a chopper mirror (or a cube beam splitter). The main beam is reflected by a rotatable plane mirror and is turned into a horizontal beam by an off-axis paraboloidal reflector. The beam goes through the optical cell and is reflected by another paraboloidal reflector and plane mirror, and goes into the photomultiplier through a chopper. The local absorbances at 632.8nm of metal and complex were measured in the course of forward extraction at several minutes intervals. The light beam can scan a span of 8 mm at 530μm intervals at 1mm/sec. Measurements were made at 25°C.

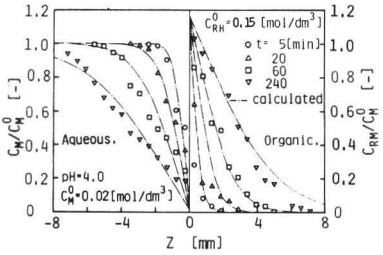


Fig.2 Concentration profiles of copper ion and its complex in course of extraction with D2EHPA in n-heptane.

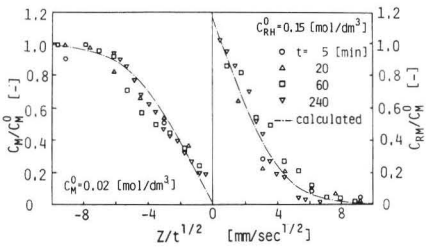


Fig.3 Concentration profiles of copper ion and its complex against $z/\sqrt{t}$.

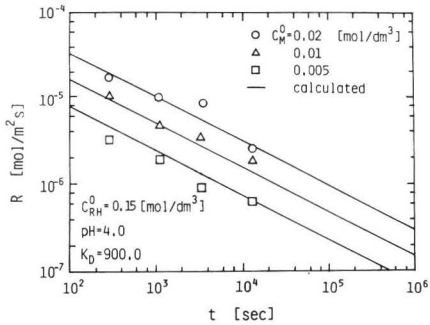


Fig.4 Rate of extraction at arbitrary time, effect of initial concentration of copper ion.

3 RESULTS AND DISCUSSION

The concentration profiles of copper ion and its complex measured for $C_M{}^0$ = 0.02mol/dm^3 at several definite times under the conditions of $C_{HR}{}^0$=0.15mol/dm^3 and pH=4 are shown in Fig.2. The chain lines in the figure show the concentration profiles calculated from Eq.(9), the solution to transport with instantaneous reaction. The diffusivity of ion was estimated from Nernst-Haskell equation and those of reagent and complex were from Wilke-Chang equation (D_M = $3.58\cdot10^{-10}$, D_{MR} = $6.24\cdot10^{-10}$, and D_{HR} = $9.46\cdot10^{-10}$ m^2/sec). The experimental plots are closely related to the calculated curves, the concentration of each species converging almost a constant value at the interface. To illustrate this more clearly, the concentrations are plotted against the variable $z/\sqrt{t}$ in Fig.3, which shows all the data lie on a single curve. This indicates that the

rate of interfacial reaction is very rapid and the extraction is controlled by the diffusional process. For extraction with EHPNA, the similar results were obtained, though not being presented here.

Figure 4 shows the extraction rates at arbitrary time in course of extraction. The experimental data are found to be closely related to the calculated curves. Thus the extraction rate at every moment is explained by considering only the diffusional transport with instantaneous interfacial reaction.

For extraction of Fe^{3+} in water (perchloric acid/sodium perchlorate) with D2EHPA in benzene, Matsuyama et al(1990), following the study of Roddy et al (1971), reported that the interfacial reaction can limit the rate of extraction. According to their results, the rate constant $\vec{\kappa}$ for forward reaction is in the order of 10^{-7}m/sec, and therefore the interfacial rate process might be detected from measurements of the local concentrations at several minutes intervals. Experiments on this system are now under investigation.

CONCLUSION

For extraction of Cu(II) with D2EHPA or with EHPNA, the concentration profiles in organic and aqueous phases near the interface were measured in course of forward extraction by a scanning light beam spectrophotometer. Mathematical solutions to the diffusion equation were obtained assuming the complex formation proceeds at the interface. It was found, from comparison of the experimental results with the solutions that the rate of extraction is limited by the diffusinal process not by the interfacial reaction.

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EXTRACTION KINETICS OF HOLMIUM(III) AND YTTRIUM(III) WITH D2EHPA IN MEMBRANE EXTRACTOR USING A HOLLOW FIBER

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ABSTRACT
KAZUHARU YOSHIZUKA, YOSHITSUGU SAKAMOTO, YOSHINARI BABA, KATSUTOSHI INOUE and FUMIYUKI NAKASHIO, 1990. Extraction kinetics of holmium(III) and yttrium(III) with D2EHPA in membrane extractor using a hollow fiber.

Kinetic study on the solvent extraction of holmium(III) and yttrium(III) with bis(2-ethylhexyl)phosphoric acid (D2EHPA) from nitrate media was conducted at 303 K using a membrane extractor consisting of a hollow fiber, together with the distribution equilibria of these metals and interfacial equilibria of D2EHPA and its metal complexes between the organic and aqueous phases. It was found that the metals (M) were extracted with D2EHPA (HR) as a type of $MR_3 3HR$ into the organic phase and the extraction equilibrium constants were evaluated. Furthermore, it was clarified that dimeric D2EHPA can be adsorbed at the interface between the organic and aqueous phases, while the interfacial activities of D2EHPA-metal complexes were negligibly small. The apparent reaction orders of extraction rate for both metals were -2, 1 and 2, with respect to hydrogen ion activity, concentrations of metal ion and dimeric D2EHPA, while the apparent reaction orders in stripping rate were 1, 1 and -1, with respect to hydrogen ion activity, concentrations of metal complex and dimeric D2EHPA, respectively. The diffusional effects were reasonably explained by the diffusion model accompanied by an interfacial reaction, taking account of the velocity distributions of the aqueous and organic phases through the inner and outer sides of a hollow fiber.

1. INTRODUCTION

The separation and refining processes of rare earth elements have been mainly carried out by the solvent extraction with dialkylphosphoric acids, especially bis(2-ethylhexyl)phosphoric acid (henceforce, abbreviated to D2EHPA), and many fundamental studies on the extraction of rare earth elements have been conducted(Coleman, 1971, Vandegrift, 1977, Sato, 1975, 1989). However, most of the previous investigations of the separation of rare earth elements were concerned with the extraction equilibrium, while the studies on the extraction kinetics are few(Danesi, 1982, Imai, 1987).

Recently, the application of hollow fiber modules to membrane extraction processes has been attempted for metal recovery(Kim, 1984), and protein extraction(Dahuron, 1988). In order to improve the membrane extraction processes, the kinetics and mechanism of extraction and stripping through the hollow fiber membrane must be elucidated because these processes are governed by kinetics rather than equilibrium.

In the present study, the extraction and stripping of holmium(III) and yttrium(III) classified to heavy rare earth element group with D2EHPA were carried out by a membrane extractor using a hollow fiber(Yoshizuka, 1986a), together with measurements of the distribution equilibria of these metals with D2EHPA and the interfacial adsorption equilibria of D2EHPA and its metal complexes, in order to obtain more detailed information on the kinetics and equilibria of rare earth elements with D2EHPA.

2. EXPERIMENTAL

2.1 Reagents

DP-8R(Lot No. K20801), a commercial metal extraction reagent, was used as D2EHPA (denoted by HR for monomeric species and as H_2R_2 for dimeric species hereafter). The purity of the reagent was found to be above 98% by means of neutralization titration.

The metal complexes, MR_3, were prepared by adding an aqueous solution of the nitrate salt of holmium or yttrium to a methanol solution of D2EHPA at about 333 K, adjusting pH = 4.0 by 100 mol/m^3 acetic acid - sodium acetate buffer solution. The resulted complexes were filtered, rinsed with methanol several times and dried in vacuo.

2.2 Distribution equilibria of holmium(III)and yttrium(III)

Organic solutions were prepared by dissolving D2EHPA and/or metal complex in toluene. The aqueous solutions were prepared by dissolving nitrate salt of holmium or yttrium in the aqueous mixtures of 100 mol/m^3 sodium nitrate and 100 mol/m^3 nitric acid solution. Nitric acid solutions were used as the stripping solutions.

Distribution equilibria were measured batchwise in a conventional method.

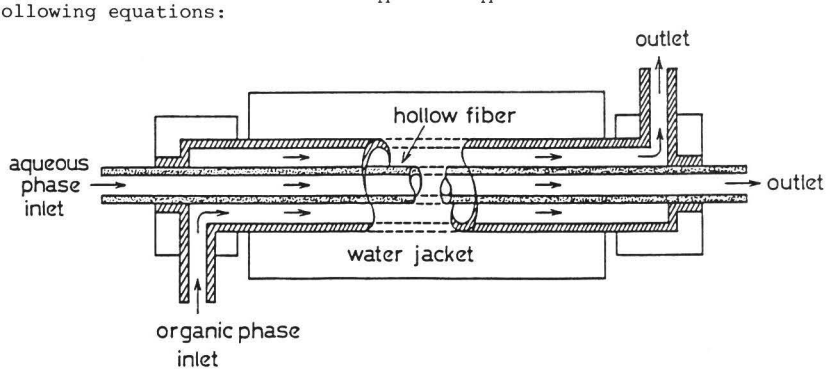
2.3 Interfacial tension

Interfacial tension between the organic and aqueous phases was measured at 303 K by the pendant drop method(Yoshizuka, 1986b). Since the solubilities of metal complexes in toluene are too low to measure the interfacial tension of metal complexes alone, D2EHPA was added in the organic phase together with the metal complexes.

2.4 Extraction and stripping rates

A membrane extractor using a hollow fiber shown in **Fig.1** was used for the measurements of extraction and stripping rates. The experimental procedure were the same as described in the previous paper(Yoshizuka, 1986a).

To evaluate the experimental results, the apparent permeabilities for the extraction and stripping of metal, P_M and P_M' respectively, were defined by the following equations:



Inner radius of hollow fiber $r_1 = 4.7 \times 10^{-4}$ m,
Length of membrane extractor $L = 0.25$ m,
Volumetric flow rate of aqueous solution $Q_{aq} = 1 \times 10^{-9} - 3 \times 10^{-9}$ m^3/s,
Volumetric flow rate of organic solution $Q_{org} = 2 \times 10^{-9} - 6 \times 10^{-9}$ m^3/s.

Fig.1. Membrane extractor using a hollow fiber.

$$P_M \ (= J_M/C_{M0}) = E\, Q_{aq}/(2\,\pi\, r_1 L) \qquad (1)$$

$$P_M'\ (= J_M'/C_{M0}) = E'Q_{aq}/(2\,\pi\, r_1 L) \qquad (2)$$

3. RESULTS AND DISCUSSION

3.1 Distribution equilibria of holmium(III) and yttrium(III)

Extraction equilibria of trivalent metal ion (M^{3+}) with D2EHPA in aromatic diluents can be expressed as follows(Sato, 1975, Imai, 1987).

$$M^{3+} + 3\overline{H_2R_2} \rightleftharpoons \overline{MR_3 3HR} + 3H^+ \quad : K_{ex} \qquad (3)$$

The extraction equilibrium constant, K_{ex}, is written as follows.

$$K_{ex} = \frac{a_H^{\,3}}{[\overline{H_2R_2}]} \qquad (4)$$

The experimental results are plotted in **Fig.2** according to Eq.(4). Straight lines with slope of 3 were obtained for both metals. The extraction equilibrium constants, K_{ex}, at 303 K were evaluated as K_{ex}(Ho) = 8.53 and K_{ex}(Y) = 17.3, respectively.

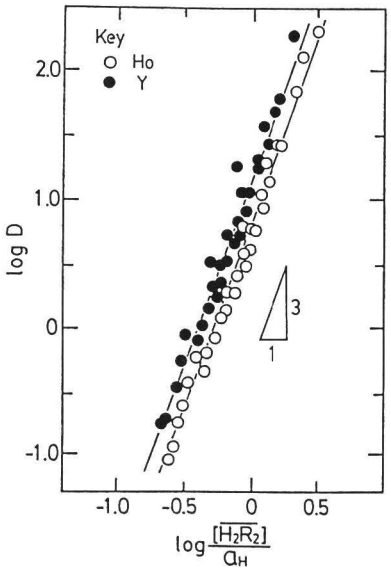


Fig.2. Equilibrium distribution of holmium(III) and yttrium(III).

3.2 Interfacial tension

Figures 3(a) and **3(b)** show the relation between interfacial tension and the analytical concentration of D2EHPA and the metal complexes, respectively. From these figures, it can be concluded that the adsorption of metal complex at the interface is negligibly small compared with D2EHPA.

The adsorption equilibrium of dimeric D2EHPA is expressed as follows:

$$\overline{H_2R_2} \rightleftharpoons H_2R_{2ad} \quad : K_{ad} \qquad (5)$$

The relation between interfacial tension, γ , and the concentration of H_2R_2 in the organic phases, $[\overline{H_2R_2}]$, is derived from the Gibbs equation for adsorption and the Langmuir adsorption isotherm, as follows:

$$\gamma = \gamma_0 - (RT/S_{ad}) \ln(1 + K_{ad}[\overline{H_2R_2}]) \qquad (6)$$

where γ_0 is the interfacial tension between toluene and the aqueous phases, S_{ad} is the interfacial area occupied by unit mole of dimeric species of D2EHPA.

From the experimental results shown in Fig.3(a) and Eq.(6), the values of K_{ad} and S_{ad} obtained by nonlinear regression are K_{ad} = 12.6 m^3/mol and S_{ad} = 6.7x10^5 m^2/mol, respectively.

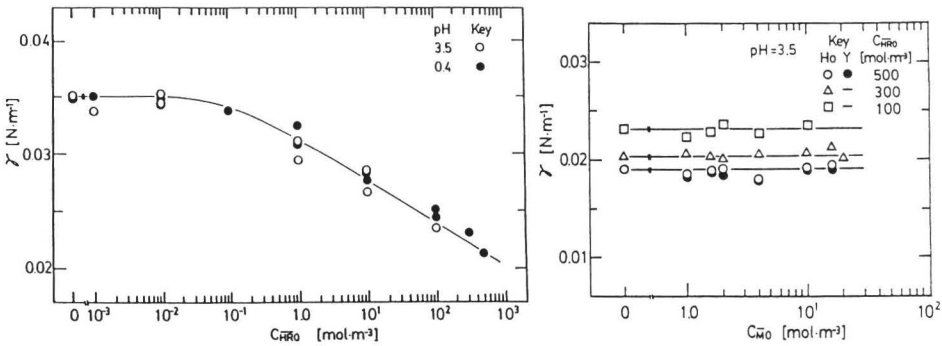


Fig.3. Interfacial tension of D2EHPA(a) and holmium and yttrium complexes with D2EHPA(b).

3.3 Extraction and stripping rates of holmium(III) and yttrium(III)

Figure 4 shows the relation between the apparent permeability for the extraction of metal, P_M, and pH of the feed aqueous solution. The plots are lying on the straight line with slope of 2.0 at low pH, while P_M is not affected by pH at high pH.

Figure 5 shows the relation between P_M and the feed concentration of D2EHPA, $C_{\overline{HRO}}$. At high pH, the plots are lying on the straight line with slope of 1.0 at low $C_{\overline{HRO}}$, while P_M is not affected by $C_{\overline{HRO}}$ at high $C_{\overline{HRO}}$. At low pH, the plots are lying on the straight line with slope of 2.0 at low $C_{\overline{HRO}}$, while P_M approach constant with increasing $C_{\overline{HRO}}$ in the same manner as at high pH.

Figure 6 shows the relation between the apparent permeability for the stripping of metal, P_M', and the hydrogen ion activity of feed aqueous solution, a_{HO}. The acid concentration used in this study was so high that the hydrogen ion activity was used in place of the concentration, C_{HO}. The plots are lying on the straight lines with the slope of 1.0 at low a_{HO}, while they approach constant at high a_{HO}.

Figure 7 shows the relation between P_M' and the feed concentration of D2EHPA, $C_{\overline{HRO}}$. At high C_{HO}, P_M' is independent of $C_{\overline{HRO}}$ at low $C_{\overline{HRO}}$, while at high $C_{\overline{HRO}}$, the slopes of this linear relation were about -1.0. At low C_{HO}, the slopes of this linear relation are also about -1.0. This suggests that the shielding effect caused by the adsorption of D2EHPA at the interface is remarkable.

From the experimental results in the ranges of low extraction and stripping rates where they are controlled by the interfacial reaction step, it was found that the apparent reaction orders of the extraction rate with respect to hydrogen ion activity, concentrations of metal ion and D2EHPA are -2, 1 and 2, respectively, while those of stripping rate with respect to hydrogen ion activity, concentrations of metal complex and D2EHPA are 1, 1 and -1, respectively. These apparent reaction orders are the same with the experimental results reported by Hirato et al.(1989) who measured the extraction and stripping rates of yttrium(III) with D2EHPA from the chloride media in a stirred transfer cell.

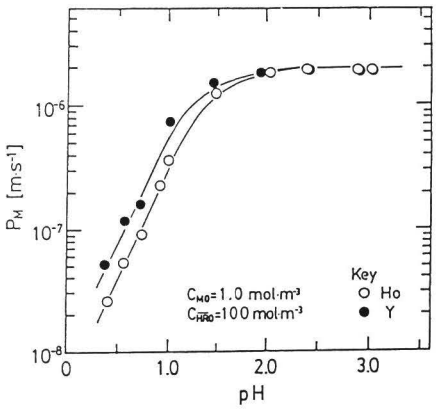


Fig.4. Relation between P_M and pH of feed aqueous solution.

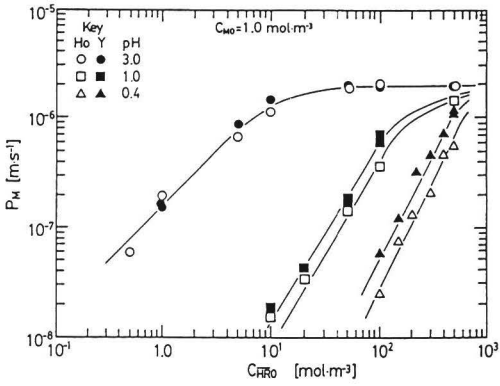


Fig.5. Relation between P_M and feed concentration of D2EHPA.

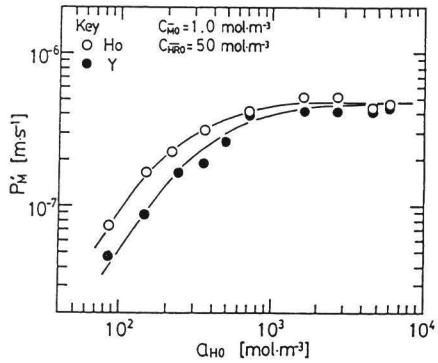


Fig.6. Relation between P_M' and hydrogen ion activity of feed aqueous solution.

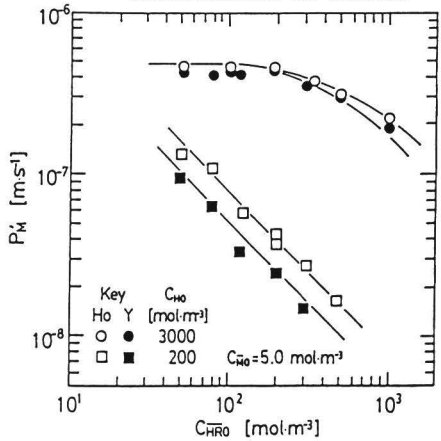


Fig.7. Relation between P_M' and feed concentration of D2EHPA.

Based on the experimental results mentioned above, the following interfacial reaction scheme between metal ions and D2EHPA was inferred:

$$M^{3+} + H_2R_{2ad} \rightleftharpoons MR^{2+}HR_{ad} + H^+ \quad (7)$$

$$MR^{2+}HR_{ad} + \overline{H_2R_2} \rightleftharpoons MR_2{}^{+}2HR_{ad} + H^+ \quad (8)$$

$$MR_2{}^{+}2HR_{ad} + \overline{H_2R_2} \rightleftharpoons \overline{MR_3 3HR} + H^+ \quad (9)$$

The interfacial reaction step described by Eq.(9) was considered to be the rate-controlling step among the interfacial reaction steps described by

Eqs.(5), (7)-(9).

Based on the Langmuir adsorption isotherm for the adsorbed D2EHPA and intermediate complexes, H_2R_{2ad}, $MR^{2+}HR_{ad}$ and $MR^2{}_2HR_{ad}$, and assuming that interfacial area occupied by unit mole of H_2R_2, S_{ad}, is equal to those of the intermediate complexes, the interfacial extraction and stripping rates are approximately as follows:

$$R = \frac{k_f C_M [\overline{H_2R_2}]^3/a_{HO}{}^2 - C_{\bar{M}} a_{HO}/K_{ex}}{1 + K_{ad}[\overline{H_2R_2}]} \tag{10}$$

$$R' = \frac{k_3' C_{\bar{M}} a_{HO} - K_{ex} C_M [\overline{H_2R_2}]^3/a_{HO}{}^2}{1 + K_{ad}[\overline{H_2R_2}]} \tag{11}$$

where k_f ($= k_3K_1K_2K_{ad}/S_{ad}$) is the overall forward reaction rate constant.

The data in the region of high extraction and stripping rates were analyzed on the basis of the diffusion model accompanied by an interfacial reaction, taking account of the velocity distributions of the laminar flow in aqueous and organic phases in the same manner to the previous paper(Yoshizuka, 1986a).

The overall forward and backward reaction rate constants, k_f and k_3' were evaluated by the trial-and-error method, as listed in **Table 1.** Solid lines in Figs.4-7 represent the results calculated by using these constants. The calculated results satisfactorily agree with the experimental results.

Table 1. Reaction rate constants obtained from analysis.

Metal	k_f[m^4/(mol·s)]	k_3'[m^4/(mol·s)]
holmium(III)	1.8×10^{-5}	3.2×10^{-7}
yttrium(III)	3.8×10^{-5}	2.2×10^{-7}

Acknowledgement

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A KINETIC STUDY ON THE EXTRACTION OF ERBIUM (III) FROM HYDROCHLORIC ACID SOLUTIONS WITH HEH/EHP*

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ABSTRACT

The kinetics of solvent extraction of erbium(III) in hydrochloric acid media with 2-ethylhexyl-phosphonic acid mono-2-ethylhexyl ester (HEH/EHP, HL) in n-heptane has been studied using growing drop technique at 30 ℃. The rate is found to be first order with respect to Er(III), a half order with respect to $H_2L_{2(O)}$ and inverse first order with respect to H^+ and the controlling reaction can be assumed to be reaction of Er(III) with L^- at the interface. The activation energy for the extraction is calculated to be 23.4KJ · mol^{-1}. The acceleration of perchlorate for the extraction system has been examined and it shows the enhancement of the rate of phase transfer by addition of ClO^-_4 ions in the aqueous phase.

INTRODUCTION

2-ethylhexylphosphonic acid mono-2-ethylhexyl ester is an excellent extractant for the extraction separation of rare earths (Li et al., 1980). Recently(Li et al., 1988a,b) we reported the extraction mechanism of rare earths(III) from aqueous solutions containing mineral (nitric, hydrochloric and sulphuric) acids by HEH/EHP. Previous work (Li et al., 1985) has also studied the extraction equilibria of rare earths(III), and it indicates that the equilibrium time of the extraction of rare earths (III) with HEH/EHP increases in the following order : $HClO_4 \sim HNO_3 < HCl < H_2SO_4$. However, the kinetic studies of the extraction of rare earths(III) with HEH/EHP have not been reported yet.

The present work reports study on the extraction kinetics of erbium(III) from hydrochloric acid solutions using HEH/EHP in n-heptane.

1 EXPERIMENTAL

HEH/EHP was supplied by Shanghai Institute of Organec Chemistry, Academia

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Sinica, and was purified with the conventional copper salt method, analytical grade n－heptane was employed for diluent. The stock solutions of erbium(Ⅲ) was prepared by dissolving its oxide (purity>99.9%) in concentrated hydrochloric acid. Other chemicals were of analytical reagent grade.

The concentration of erbium in aqueous phase or organic phase (stripping with a solution of 5 mol·dm_{-3} HCl) was determined by spectrophotometric method (Ren et al., 1987).

The experimental apparatus and procedures for the studies of extraction kinetics of erbium(Ⅲ) by growing drop method were described as Ref.(Hughes, et al., 1985). The extraction experiments (except temperature effect) were carried out at 30± 1 ℃ .

2 RESULTS AND DISCUSSIONS

The rate of mass transfer of Er(Ⅲ) from aqueous phase into organic phase exceeds significantly the rate of back reaction of Er(Ⅲ) because the kinetic study is made far from the conditions of extraction equilibrium using the growing drop method. Under the conditions of the present experiment the effect of the mass transfer of back reaction on the extraction rate has been neglected. The extraction rate R can be represented by the following equation:

$$R=k[Er^{3+}]^a[H_2L_2]^b_{(0)}[H^+]^c[Cl^-]^d \qquad (1)$$

where H_2L_2 refers to the dimeric reagent, and (0) indicates the organic phase.

2.1 Influence of the concentration of Er(Ⅲ) on the extraction rate

At constant aqueous acidities, ionic strength and concentration of the extractant Equation(1) can be written as

$$R=k'[Er^{3+}]^a \qquad (2)$$

Taking logarithms on both sides of (2),

$$\log R=\log k'+a\log[Er^{3+}] \qquad (3)$$

Figure 1 indicates that logR increases with incrcase in Er(Ⅲ) concentration, and the slope of straight line is 1.0 suggesting that the R is first order with respect to [Er (Ⅲ)], viz. a=1.

2.2 Influence of the aqueous acidity on the extraction rate

At constant concentrations of Er^{3+}, Cl^- and H_2L_2 Equation (1) can also be written as

$$\log R=\log k''+c\log[H^+]=\log k''-cpH \qquad (4)$$

A inverse first order dependence of the extraction rate on the H^+ concentration was observed (Fig. 2). It indicates that c is −1.

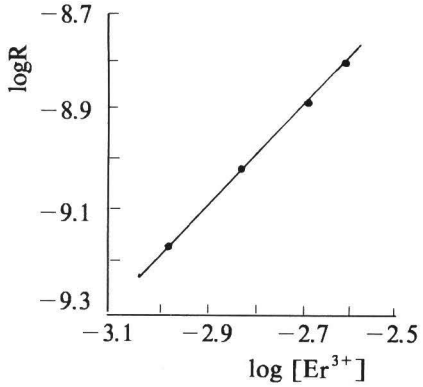


Fig. 1. logR vs log [Er(III)]
$[H_2L_2]=0.05mol \cdot dm^{-3}$;
$[Cl^-]=0.20mol \cdot dm^{-3}$;
pH=1.40.

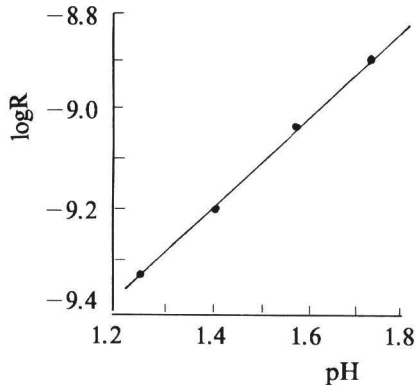


Fig. 2. logR vs pH
$[H_2L_2]=0.05mol \cdot dm^{-3}$;
$[Er^{3+}]=1.0\times10^{-3}mol \cdot dm^{-3}$;
$[Cl^-]=0.20mol \cdot dm^{-3}$.

2.3 Influence of hydrochloric concentration on the extraction rate

A similar way to Equation(2), varying hydrochloride concentration in the range of 0.30−1.50 mol • dm^{-3} Equation(1) may be represented as

$$\log R=\log k'''+d\ \log[Cl^-] \quad (5)$$

An apparent zero order dependence of the extraction rate on the Cl^- concentration was observed. It shows $d \simeq 0$.

2.4 Influence of the concentration of HEH/EHP on the extraction rate

Equation(1) may be represented as

$$\log R=\log k''' + b\ \log[H_2L_2]_{(0)} \quad (6)$$

A half order dependence on the H_2L_2 concentration was observed (Fig. 3). It indicates $b=1/2$.

Experiment of Ref. (Shen, et al., 1984) indicated that HEH/EHP is adsorbed at the interface in the form of single molecule. Thus, the following equilibrium must hold:

$$1/2(H_2L_2)_{(0)} \rightleftharpoons (HL)_{(0)} \rightleftharpoons (HL)_{(i)}$$

where (i) denotes at interface.

This suggests that erbium(III) in the aqueous phase first reacts with the monomer of HEH/EHP at interface because the monomer is in all probability more interfacially active than the dimer (Vandegrift, et al., 1980)

2.5 Influence of perchlorate ions on the extraction rate

Figure 4 indicates the R increases with increasing perchlorate ion concentration, which shows the enhancement of the rate of phase transfer by addition of ClO^-_4 ions in the aqueous phase.

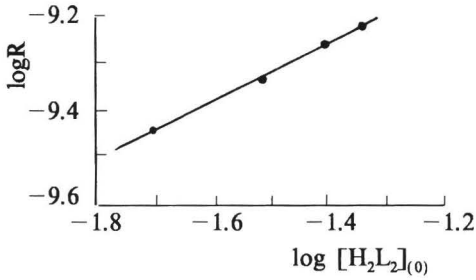


Fig. 3. logR vs log $[H_2L_2]_{(0)}$
$[Er^{3+}]=1.0\times10^{-3}$mol · dm^{-3};
$[Cl^-]=0.20$mol · dm^{-3};
pH=1.40.

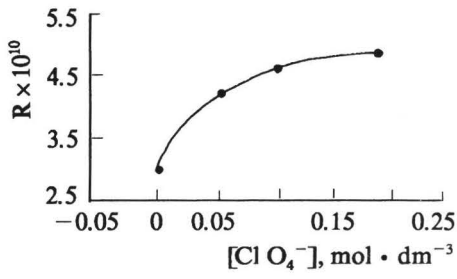


Fig. 4. R vs $[ClO_4^-]$
$[H_2L_2]=1.05\times10^{-2}$mol · dm^{-3};
$[Er^{3+}]=1.0\times10^{-3}$ mol · dm^{-3};
$[Cl^-]=0.20$mol · dm^{-3};
pH=1.80.

2.6 Influence of temperature on the extraction rate

In the range of 20−50 ℃, the effect of temperature on R is shown. According to the Arrehnius's formula:

$\log k' = -Ea/2.303RT + C$

where $k' = R/[Er^{3+}]$, Ea represents the activation energy, it was calculated to be 23.4KJ · mol^{-1} for chloride system and 13.2KJ · mol^{-1} for $Cl^- + ClO_4^-$ system their difference chiming in with the enhancement of the extraction rate by addition of ClO^-_4 ions in the aqueous phase.

2.7 Deduction of the extraction mechanism

As experimentized, the kinetic equation determined experimentally can be represented as follows:

$$R = k[Er(\text{III})][H_2L_2]^{1/2}_{(0)}/[H^+] \quad (7)$$

According to the results of kinetics and thermodynamics, the extraction mechanism for this system can be deduced as follows:

$$H_2L_{2(0)} \overset{K_1}{\rightleftharpoons} 2HL_{(i)} \quad (8)$$

$$HL_{(i)} \overset{K_2}{\rightleftharpoons} H^+ + L^-_{(i)} \quad (9)$$

$$Er^{3+} + L^-_{(i)} \xrightarrow{k_1} ErL^{2+}_{(i)} \quad (10)$$

$$ErL^{2+}_{(i)} + L^{-}_{(i)} \rightleftharpoons ErL^{+}_{2(i)} \quad (11)$$

$$ErL^{+}_{2(i)} + L^{-}_{(i)} \rightleftharpoons ErL_{3(0)} \quad (12)$$

$$ErL_{3(0)} + 1.5H_2L_{2(0)} \rightleftharpoons Er(HL_2)_{3(0)} \quad (13)$$

where Equation (10) is the rate-determining step. The rate equation can be represented as follows:

$$\begin{aligned} R &= k_1[Er^{3+}][L^{-}]_{(i)} \\ &= k_1 K^{1/2}_1 K_2 [Er^{3+}][H_2L_2]^{1/2}_{(0)} / [H^{+}] \\ &= k[Er^{3+}][H_2L_2]^{1/2}_{(0)} / [H^{+}] \end{aligned} \quad (14)$$

where $k = k_1 K^{1/2}_1 K_2$. According to eqns. (8) – (13) the rate equation deduced theoretically chimes in with eqn. (7).

3 CONCLUSIONS

A kinetic study of the erbium (III) from hydrochloric acid solutions into n-heptane of HEH/EHP using the growing drop technique is reported. The extraction mechanism has been discussed, and the controlling reaction can be assumed to be reaction of Er(III) with L^{-} at interface. The acceleration of perchlorate for the extraction system is observed.

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EQUILIBRIUM AND KINETICS OF COPPER EXTRACTION FROM ACIDIC SULPHATE SOLUTIONS WITH 1-(2'-HYDROXY-5'-NONYLPHENYL)-1-ETHANONE (E)-OXIME AND 1-(2'-HYDROXY-5-METHYLPHENYL)-1-DECANONE (E)-OXIME

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ABSTRACT

J.Szymanowski, Krzyżanowska, E., Cierpiszewski, R., and Prochaska, K. 1990. Equilibrium and kinetics of copper extraction from acidic sulphate solutions with 1-(2'-hydroxy-5'-nonylphenyl)--1-ethanone (E)-oxime and 1-(2'-hydroxy-5'-methylphenyl)-1--1-decanone (E)-oxime

1-(2'-Hydroxy-5'-nonylphenyl)-1-ethanone (E)-oxime extracts the same amount of copper and at the same pH range as 1-(2'-hydroxy-5'-methylphenyl)-1-decanone (E)-oxime. The extraction rate is much quicker for copper extraction with 1-(2'-hydroxy-5'-nonylphenyl)-1-ethanone (E)-oxime. It can by qualitatively explained by its higher solubility in aqueous solutions and/or by its higher adsorption and better orientation at the interface as the bulk volume process or the interfacial process are considered.

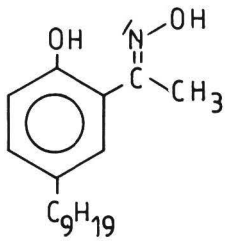
INTRODUCTION

Since Flett (1977) presented his ideas upon the interfacial mechanism of copper extraction by hydrophobic hydroxyoximes more than 150 papers were published upon the kinetics and mechanism of this process, and three different versions of mechanism, which are still under discussion, were proposed. They consider: i) the interfacial process with the adsorption of hydroxyoxime molecules at the interface (Flett, 1977, Danesi, 1980), ii) chelation in the bulk of the aqueous phase with the subsequent transfer of the complex from the aqueous phase to the organic one (Freiser 1984, 1988) and iii) the reaction in the aqueous film near the interface (Rod, 1980, Rod et al, 1981, Hughes and Rod, 1984).

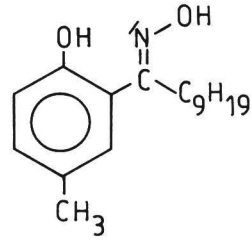
Results supporting each of these three versions of mechanism were presented by independent authors, and it seems that extraction can occur according to the each of these versions. Moreover, the mechanism can change depending upon the extraction conditions, i.e. concentrations, diluents, the method used for

measurements, e.t.c..

As continueing our studies of copper extraction with pure model compounds we decided to use pure individual 1-(2'-hydroxy-5'-nonyl phenyl)-1-ethanone (E)-oxime (I) and 1-(2'-hydroxy-5'-methyl-phenyl)-1-decanone (E)-oxime (II) having the same molecular mass.



I



II

It was expected that comparing the extraction properties of these isomeric oximes with their interfacial activities and solubilities in aqueous phases some new data could be obtained which would support one of the considered mechanism versions.

2 EXPERIMENTAL

Pure individual oximes I and II (Krzyżanowska et al, 1989)were used.

Equilibrium extraction studies were carried out in the standard way (Stępniak-Biniakiewicz and Szymanowski, 1981) using sodium sulphate and sulphuric acid to adjust pH and ionic strength. Initial copper concentration was $7.81 \cdot 10^{-4}$ M, the ionic strength was adjusted to $5.0 \cdot 10^{-2}$ M, while pH was changed from 1.5 to 3.5. Oxime concentration was equal to $3.6 \cdot 10^{-3}$, $7.20 \cdot 10^{-3}$ and $14,4 \cdot 10^{-3}$ M.

Extraction rate was determined at 20^{o}C by the ascending drop method using columns of the same inner diameter, 25mm, and various length, 85, 565, 980 and 1600 mm. Copper concentration in the continuous aqueous phase was 0.1 M, and its pH adjusted by sulphuric acid was 2 and 3. Oxime concentration in toluene was $3.6 \cdot 10^{-3}$ M.

Oxime solubilities at 0.1 M sodium sulphate solutions and partition coefficients at 0.1 M sodium sulphate aqueous solution/ toluene were determined spectrophotometrically.

The interfacial tension was measured by the drop method using 0.01 M sodium sulphate solution of pH 2.1 as the aqueous phase.

Toluene was used as the diluent. The interfacial tension data were interpreted as was described previously (Szymanowski and Prochaska, 1987, 1989)

3 RESULTS

Compounds considered exhibit quite the same hydrophobicity as characterized by their HLB value (HLB = 1.86) determined from gas chromatographic measurements (Szymanowski et al, 1987). Such a low HLB value is typical for very hydrophobic compounds. As a result, these hydroxyoximes must exibit very low solubilities in water and their partition coefficients must be relatively high. The same HLB values suggest similar solubilities and partition coefficients for both compounds in water and aqueous/organic phase, respectively.

TABLE 1
Oxime physicochemical data and pH(50) values for copper extraction.

Parameter	I	II
HLB	1.86	1.86
log P	3.63	4.27
Solubility (ppm)		
- by copper complex	1.62	1.11
- direct measurement	2.91	1.54
pH(50) for various copper concentrations:		
$3.6 \cdot 10^{-3}$	2.46	2.57
$7.2 \cdot 10^{-3}$	2.13	2.14
$14.4 \cdot 10^{-3}$	1.84	1.80

However, this is not a case and solubilities of the considered compounds in the aqueous phase are equal to 1.62 ppm and 2.91 ppm for compound I, and 1.11 ppm and 1.54 ppm for compound II as the both methods of determination are taken under consideration. Due to the low solubilities (low values of absorbance) the errors of determination are relatively high.

The partiton coefficients (lg P) are equal to 3.63 and 4.27 for compounds I and II, respectively.

Thus, the solubility and partition coefficient measurements show that compound I is better soluble in water than compound II. The ratio of hydroxyoxime solubilities in water can be estimated as 1.5-1.9. However, this estimation from the partition coefficients, is about 4.

The differences in equilibrium extraction data between oximes I and II are small and can be neglected. The values of pH(50) are quite similar (Table 1). The extracted complexes have the typical composition with the ratio of the ligand to metal equal to 2:1, which was discussed previously (Krzyżanowska, 1989).

The amount of copper transferred in the column increases significantly as the column length increases. At pH 2 approximately linear relations were obtained correlating the amount of copper transferred (E) with the contact time (τ). They are as follows: $E = 62.4\tau + 648$ for I and $E = 36.4\tau + 445$ for II, where E is given in $\mu g\ m^{-2}$. I extracts copper almost twice (1.7) quicker than II, but important copper amount is transferred during drop formation.

At pH 3 exponential relations were obtained. They are as follows: $E = 6586\tau^{0.280}$ for I and $E = 2422\tau^{0.345}$ for II. The extraction rates obtained by differentiating the exponential relations for contact time of 1s are $2.9 \cdot 10^{-8}$ mol/m^2s and $1.32 \cdot 10^{-8}$ mol/m^2s for I and II, respectively. Thus, for the contact time considered I extracts copper more than twice quicker (2.2) than II.

For both cases considered, the average extraction rate decreases as the contact time increases. This is caused by different contributions of various stages of copper transfer in extraction columns. The rate of copper transfer is the highest during the formation of drop. In this period, i.e. in the first second, the extraction rates is 4-8 times higher in comparison to the average extraction rate in the column. To eliminate this effect together with the end (top column) effects the shortest column was selected as the reference one and appropriate differences between the total amount of copper extracted in longer columns 2, 3 and 4 and the reference column were calculated. As the reduced amount of copper extracted in columns 2, 3 and 4 was correlated with the reduced contact time, linear relations were approximately obtained with their slopes of 333 and 55 $\mu g/m^2s$ for I and 117 and 28 $\mu g/m^2s$ for II at pH 3 and pH 2, respectively (Fig. 1). These corresponds to relative ratios of 2.8 and 2,0.

Thus, the observed relative extraction rates for copper extraction with oximes I and II can be explained by their various solubilities and partition coefficients.

However, I exhibits higher interfacial activity and decreases the interfacial tension more effectively than II (Fig. 2).

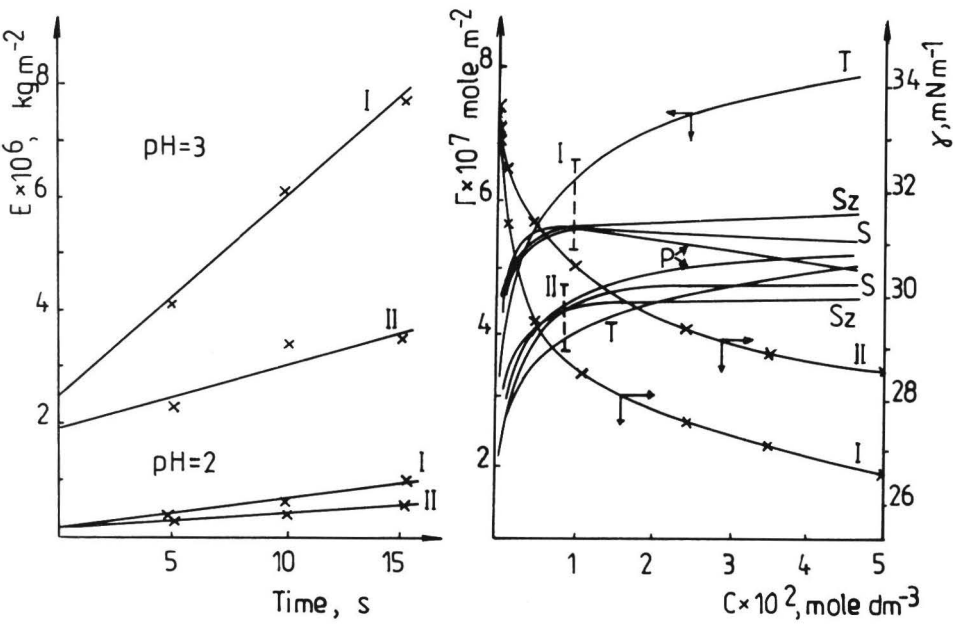


Fig. 1. Amount of copper transferred versus reduced contact time.
Fig. 2. Interfacial tension (γ) and surface excess (Γ) isotherms for oximes I and II (S, P, Sz and T denotes the Spline function, the polynomial, the Szyszkowski and Temkin isotherm, respectively).

I adsorbs better than II and, due to this, its concentration at the interface is higher in comparison to II. At the saturated interface the ratios of the surface excess computed for I and II according to the spline, polynomial, Szyszkowski, Frumkin and Temkin isotherms (Szymanowski and Prochaska, 1987) are equal to 1.12, 1.05, 1.24, 1.24 and 1.55, respectively. Thus, this ratio is lower than observed differences in extraction rate. The observed differences in the surface excess computed according to the various adsorption isotherms are typical.

The surface excess data does not explain the observed differences in the extraction rate. However, we cannot assume that reaction proceeds in the bulk of the aqueous phase because such small solubility data are determined with important errors which significantly effect their ratio. The observed differences in the extraction rate can be also explained by various orientation of

the extractant molecule at the interface.The molecule of I has the hydrophobic alkyl directly on the opposite site of the hydrophilic phenolic group. Due to this, for this oxime both the phenolic and oximino groups can easily penetrate the aqueous layers near the interface. Moreover, the solubility and partition data show that I is more hydrophilic than II. As a result, I can penetrate with its hydrophilic groups the aqueous layers near the interface more deeply than II. As a result, extraction of copper can proceed quicker with I in comparison to II.

Thus, the problem of reaction mechanism seems still open.

ACKNOWLEDGMENT

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SYNERGISTIC EXTRACTION OF METAL ION WITH LIX63 IN MICROEMULSION SYSTEM

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ABSTRACT

The synergistic extraction of cobalt(II) or copper(II) ions with LIX63 in AOT microemulsion system was discussed by focusing on the role of LIX63. When the concentration of LIX63 is higher than that of AOT, the neutral 1:2 complex of metal ion and AOT is produced and then the final extractable complex is formed by the addition of LIX63. With increasing the concentration of AOT, the microemulsion started to form and the metal ion was also extracted into the W/O microemulsion. The experimental results were quantitatively interpreted by assuming the occurrence of the complex $Co(AOT)_2(LIX63)_2$.

INTRODUCTION

The extraction mechanism of metal ions with aid of AOT microemulsion have been discussed by Harada et al(1990). Since the extraction process is governed by the electrostatic interaction between the metal ion and the sulfonate anion of AOT molecule, the selective separation of two metal ions with the same valence is performed less efficiently. For increasing the selectivity, we must introduce peculiar interactions with the metal ions in the microemulsion system. One of available methods is to add chelating agent into the extraction system. By adding the 5,8-diethyl-7-hydroxydodecane-6-one oxime, the active species of LIX63, strong synergism for the metal extraction have been observed in the both dialkyl naphthalene sulfonate and AOT microemulsion systems by Osseo-Asare et al(1980,1988). However, the mechanism of the synergism is not sufficiently interpreted.

We studied the extraction of cobalt(II) or copper(II) ions with the active species of LIX63 in AOT microemulsion system in order to elucidate the mechanism of the synergistic extraction.

2 EXPERIMENTAL

In this work we used the W/O microemulsion system of sodium di-(2-ethylhexyl)sulfosuccinate(AOT) in heptane. AOT(the purity 98.7%) and heptane supplied from Nacalai tesque Co., Ltd. were used without further purification. LIX63 supplied by Henkel Co.,Ltd. was purified according to the procedure of van der Zeeuw et al(1977). Cobalt(II) and copper(II) solutions were prepared by

dissolving their perchlorate salts in deionized water. The pH and ionic strength were adjusted to 2.0 and 1.0 moldm^{-3} with the perchloric acid and sodium perchlorate, respectively.

The heptane of 15 cm^3 dissolved AOT and LIX63 was contacted with the aqueous phase of 15 cm^3 adjusted pH, ionic strength and metal concentration in water bath controlled by 298 K. The small volume of the heptane(100-150 μl) at equilibrium was mixed with 10 cm^3 of 1N-HCl to analyze the concentration of metal ion in heptane with an atomic absorption spectrophotometer. The distribution coefficient of metal ion, D_M was calculated by

$$D_M = [\overline{M}]_T / [M]_T \qquad (1)$$

where $[\overline{M}]_T$ and $[M]_T$ are the total concentration of metal ion in the organic and aqueous phases, respectively. The amounts of water extracted into the heptane were analyzed by the Karl-Fisher method.

3 EXPERIMENTAL RESULTS

Figure 1 shows the effects of the concentration of LIX63-free AOT on the distribution coefficient of cobalt(II) ion and the water concentration in the heptane. When $[AOT]_F < 0.1$ mM, the $[H_2O]$ value was kept at a constant value, which corresponds to the value of the saturated concentration in pure heptane. When $[AOT]_F > 0.5$ mM, $[H_2O]$ was proportional to $[AOT]_F$. The cmc value of AOT was determined as 0.33mM.

Figures 2(a),(b) and (c) show the effects of AOT concentration in the heptane contained LIX63 on the distribution of cobalt(II) ion and the concentration of water in the heptane phase. The broken lines are the values for $[LIX63]_F = 0$. The water concentration in the heptane phase was lower than the broken line in the region of the intermediate concentration of AOT. This means that the

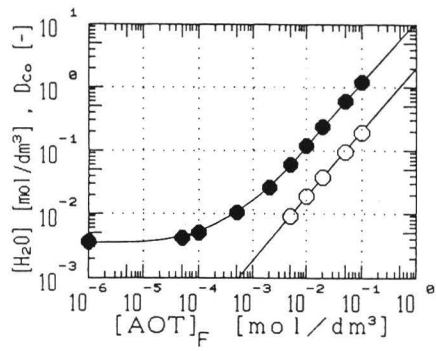


Fig.1 Effects of AOT on the distribution of cobalt(○) and water concentration(●) in the heptane phase. $[LIX63]_F = 0$.

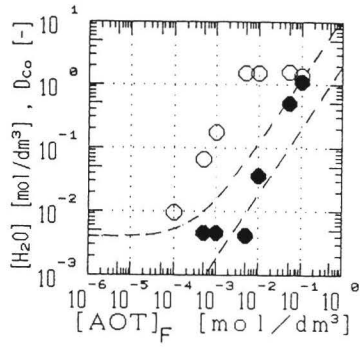


Fig.2(a)

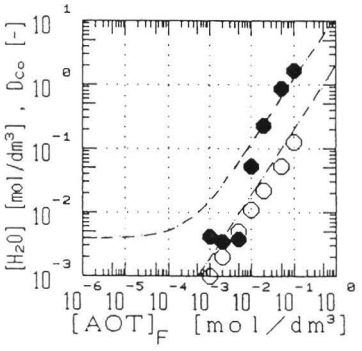


Fig.2(b)

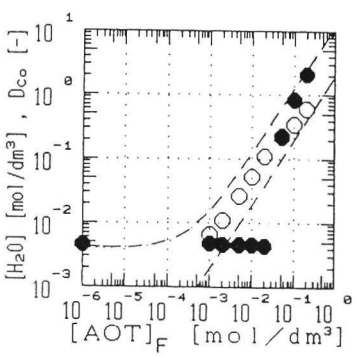


Fig.2(c)

Fig.2 Effects of AOT on the distribution of cobalt(○) and water concentration in the heptane phase(●).

	$[LIX63]_F$ (mM)	$[Co^{2+}]_F$ (mM)
(a)	10	4
(b)	10	500
(c)	50	100

apparent cmc value of AOT is reduced by the presence of LIX63. The higher concentration of LIX63, the higher apparent cmc of AOT. The distribution coefficient of cobalt(II) ion took a maximum for the low cobalt concentration, but for the high concentration it was proportional to [AOT]. At $[Co^{2+}]_F$=500 mM the value was smaller than that for [LIX63]=0.

The similar behaviors were also observed for the copper extraction as shown in Figures 3(a) and (b).

3. DISCUSSION

3.1 Qualitative interpretation

Figure 4 shows the effects of $[AOT]_F$ and $[LIX63]_F$ on the cobalt concentration in the heptane. When $[AOT]_F < 5$mM, $[\overline{Co^{2+}}]_T$ is proportional to $[AOT]_F$ and the value was equal to half $[AOT]_F$ irrespective of the cobalt concentration in the aqueous phase and the LIX63 concentration in the heptane phase. This relationship is represented by the broken line in Fig.4. When $[AOT]_F$ becomes high, $[\overline{Co^{2+}}]_T$ deviates from the broken line. The threshold concentration of AOT, at which deviated from the broken line, is almost constant under the constant concentration of LIX63. But the threshold concentration of AOT becomes high with the increasing LIX63 concentration. When the concentration of AOT is lower compared to LIX63 concentration, the cobalt(II) ion is extracted as the complex formed by the addition of AOT and LIX63. The composition of the complex is inferred as $Co(AOT)_2(LIX63)_n$ from the experimental results. The AOT microemul

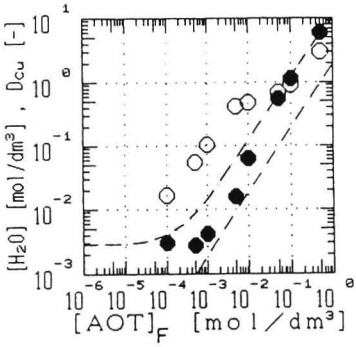


Fig.3(a)

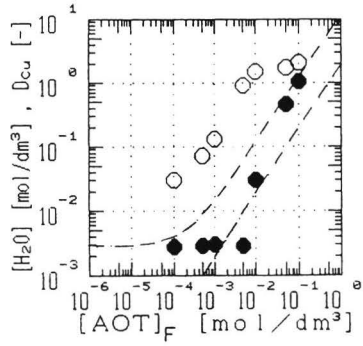


Fig.3(b)

Fig.3 Effects of AOT on the distribution of copper(○) and water concentration in the heptane phase(●).

	$[LIX63]_F$	$[Cu^{2+}]_F$
(a)	5 mM	5mM
(b)	10 mM	5mM

sion cannot be formed due to the formation of the stable complex. Since there are free AOT molecules in the heptane at high $[AOT]_F$, the microemulsion starts to form and the water concentration in heptane phase increases. Then, the cobalt(II) ion was solubilized into the microemulsion due to the electrostatic interaction.

The behavior of the copper extraction is similar to that of cobalt. Because the copper(II) ion was extracted by only the LIX63, at the low $[AOT]_F$ the copper concentration approaches to a constant value, which depends to the $[LIX63]_F$. At the higher $[AOT]_F$, the behavior is similar to that the extraction of cobalt(II) ion.

3.2 Mechanism of synergistic extraction

We assume that the complex of cobalt(II) ion is formed as follows.

$$Co^{2+} + 2AOT + nLIX63 \quad Co(AOT)_2(LIX63)_n \tag{2a}$$

$$K=[Co(AOT)_2(LIX63)_n]/([Co^{2+}][AOT]^2[LIX63]^n) \tag{2b}$$

Since the volume of the aqueous phase is equal to that of the organic phase, the material balance equations are expressed:

$$[Co^{2+}]_F=[Co^{2+}]_A+[Co^{2+}]_M+[Co(AOT)_2(LIX63)_n] \tag{3}$$

$$[LIX63]_F = [LIX63] + n[Co(AOT)_2(LIX63)_n] \quad (4)$$

$$[AOT]_F = [AOT] + 2[Co(AOT)_2(LIX63)_n] + n_{AOT}[ME] \quad (5)$$

where subscript "F" is the value of feed solution.

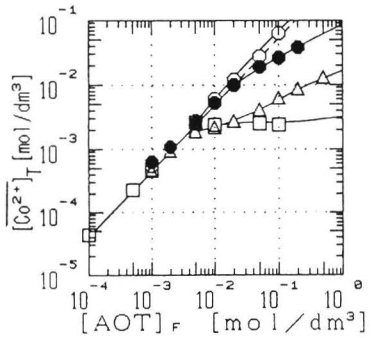


Fig.4 Effect of AOT concentration on the concentration of cobalt(II) in heptane phase. K=5x10^{11}, n=2

	$[Co^{2+}]_F$	$[LIX63]_F$	cmc* (unit is mM)
(○)	500	10	0.05
(●)	100	50	0.05
(△)	25	10	0.08
(□)	4	10	0.25

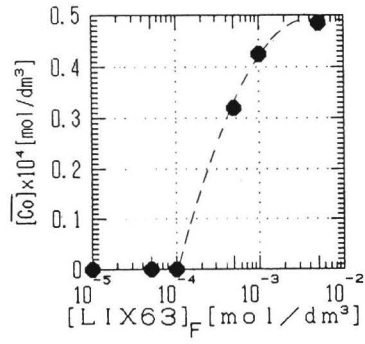


Fig.5 Effect of LIX63 concentration on the concentration of cobalt (II) ion in heptane phase.

$[AOT]_F$ = 0.1 mM
$[Co^{2+}]_F$ = 4 mM
pH = 2.0
I = 1.0 M

The concentration of microemulsion, [ME] can be estimated:

$$[ME] = ([AOT]_F - cmc^* - 2[Co(AOT)_2(LIX63)_n])/n_{AOT} \quad (6)$$

$$n_{AOT} = 4\pi R^2 / a_{AOT} \quad (7)$$

where R is radius of the microemulsion, it can be estimated as

$$R = 1.15 + 0.1525[H_2O]/[AOT] \text{ (unit nm)}, \quad (8)$$

a_{AOT} is the area occupied by an AOT molecule and is 0.6 nm^2. Under the experimental condition, $[H_2O]/[AOT] = 12$ from Fig.1.

If the concentration of cobalt solubilized into the microemulsion is independent of the presence of LIX63, it can be estimated by the empirical formula obtained from Fig.1.

$$[Co^{2+}]_M = 2.0\, n_{AOT}\, [ME]\, [Co^{2+}]_A \qquad (9)$$

The $[Co^{2+}]_M$ and $[Co^{2+}]_A$ are the concentrations of cobalt(II) ion extracted with the microemulsion and that in the aqueous phase at equilibrium, respectively.

When the microemulsion is formed, the concentration of AOT in eq.(2a) is equal to cmc*, which is corresponds to intrinsic cmc in the presence of complex. Since it is not equal to cmc for $[LIX63]_F=0$, the value is taken as an adjustable parameter in this study. The solid lines in Fig.4 were calculated using the parameter values shown in Fig.4. The cmc* is smaller than cmc=0.33 mM for $[LIX63]_F=0$.

Figure 5 shows the effect of $[LIX63]_F$ on the cobalt concentration in the heptane. The value steeply increases above $[LIX63]_F=0.1$ mM, which is equal to $[AOT]_F$. It appears that the value of $[Co^{2+}]$ approaches to 0.05 mM with increasing $[LIX63]_F$. It is estimated that from this result the n value of complex is equal to 2.

CONCLUSION

The synergistic extraction of cobalt(II) or copper(II) with LIX63 in AOT microemulsion system was studied. When $[AOT]_F$ is low, the metal was extracted as a complex, $Co(AOT)_2(LIX63)_2$. When concentration of AOT becomes high, the AOT microemulsion starts to form and the metal ion is also solubilized into the microemulsion.

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EXTRACTION OF PALLADIUM IN AQUEOUS HYDROCHLORIC ACID SOLUTION WITH TRI-n-OCTYLAMINE IN TOLUENE

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ABSTRACT
Extraction equilibria of palladium in aqueous hydrochloric acid with tri-n-octylamine in toluene was studied in various conditions. Water contents in an organic phase after the equilibrations were measured. The species of $(BH)_2PdCl_4$ was estimated to be formed by the following reaction between the ammonium chloride salt, (BHCl) and palladium chloride, $PdCl_4$.

$$2(BHCl)_{org} + PdCl^{2-}_{4,aq} = (BH)_2PdCl_{4,org} + 2Cl^-_{aq}$$

The formation constant for the reaction was evaluated as follows;

$$K_{12}=\{[(BH)_2PdCl_4^{2-}]a_{Cl}^2\}/\{[BHCl]^2 a_{PdCl_4}\}=9.4\times10^5[m^3/kmol]$$

The type of species formed was not affected by the water content in the organic phase. Furthermore, adsorption constants for the species were estimated by analysis of the variation of interfacial tension.

INTRODUCTION

Many studies for solvent extraction have been carried out to obtain basic informations for the design of recovery process on precious metal. Hydroxy oxime, organic phosphine or organic sulfide reagents have been used in these studies as the extractants. Many quantitative or qualitative analysis were made for the extractions(Bernard 1974, Cyu, Hoh et al., 1984, Cleare et al., 1971, Demopoulos 1986, Mojsky 1980). A little qantitative studies were, however made in the system of extraction by amines as the extractant. Imformations are important factors to optimum design of the extraction process. In the previous paper(Kawano et al. 1989), the formation constants of the species in the extraction of hydrochloric acid with tri-n-octyl amine in toluene were studied by the reaction models of ion paired formation and origomerization of ammonium chloride salt. In this paper, the kinds of chloro-complexes formed in the extraction of palladium with ammonium chloride salt and its formation constants were estimated. Furthermore, adsorption equilibrium for the species related were discussed.

1 EXPERIMENT

1.1 Reagent.

99.7% of tri-n-octylamine supplied by Koei Chemical Co. was used as an extractant without further purification. Palladium chloride, hydrochloric acid,

lithium chloride and toluene were guaranteed reagents. Distilled water was used as aqueous solvent.

1.2 Experimental method.

Known concentration of ammonium chloride salt of tri-n-octylamine (hereafter called TOA) of toluene solution and aqueous hydrochloric acid solution of palladium was shaken in a flask with stopper in water bath thermostated at 303K. After that, the concentrations of palladium in the aqueous solution were determined by an atomic absorption spectrophotometer. Water contents in the organic solutions were determined by the Karl Fischer titration. Further more, infrared absorption spctroscopies of the organic solutions were measured for various concentration. The interfacial tensions between the aqueous solutions and the organic solutions equilibrated each other for various concentrations were measured by the drop weight method to determine adsorption equilibrium constants on the interface for the species related.

2 EXPERIMENTAL RESULTS AND DISCUSSION

Effects of hydrogen ion on the distribution of palladium. The distribution ratio of palladium between the aqueous solution and the organic solution,D ($=C_{Pd,org}/C_{Pd,aq}$) were plotted against chloride ion concentration,[Cl^-] for various hydrogen ion concentrations in Fig.1. The concentration of chloride ion in the solution was adjused by the addition of lithium chloride into the solution. The solid circle shows the result of extraction of palladium from aqueous hydrochloric acid solution. The experimental values of D are clustered on a single line which are independent of hydrogen ion concentration. The distribution of palladium was then assumed to be independent of ion strength in this concentration.

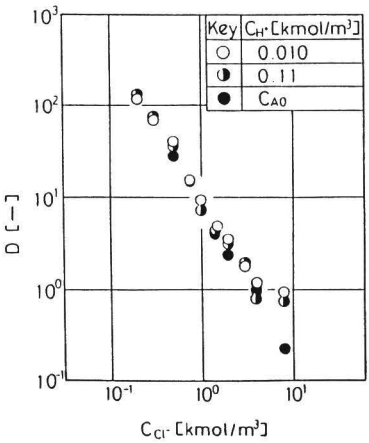


Fig.1 Effect of hydrogen ion concentration on distribution ratio of palladium

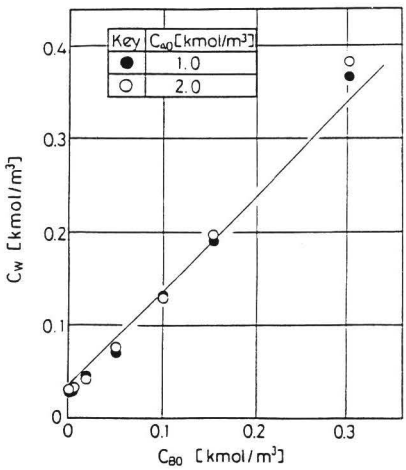


Fig.2 Water content in toluene solution of TOA for various concentration

Effect of water dissolved in the organic solution on the formation of the complexes. Water contents ,$C_{w,org}$ in the organic solution equilibrated with aqueous hydrochloric acid solution of palladium were plotted against initial concentration of the amine, C_{B0} in Fig.2. In the previous paper, equal moles of water with hydrochloric acid was reported to be distributed into toluene solution of TOA. A solid line in Fig.2 is the calculated result that palladium was not involved in the organic solution. The experimental values clustered on a single line which are independent of C_{HCl} and $C_{PdCl_4^{2-}}$. This result suggest that the amounts of water dissolved in the organic solution does not almost affect the formation of palladium-amine complexes.

Infrared spectra of the organic solution. Infrared spectra of the organic solution of TOA equilibrated with aqueous hydrochloric acid were measured. Absorption at 3700 and 3450 cm^{-1} due to water(Jedinakova et al., 1976, Keder 1965) and that at 2400 cm^{-1} due to N^+H species (Casei 1971) were observed. Absorbances of these bands were plotted against the concentration of hydrochloric acid in Fig.3. The adsorbances at 3700 and 3450 cm^{-1} increase, and approach a constant value and decrease again with $C_{A,aq}$.

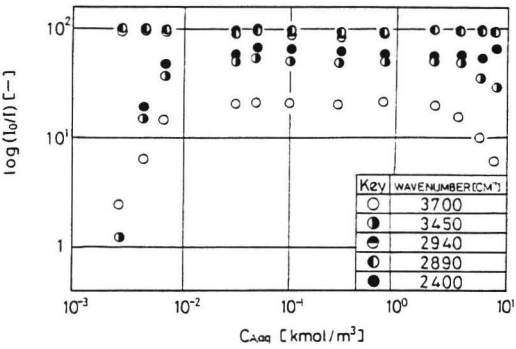


Fig.3 Effect of hydrochloric acid concentration on absorbances at some wavelength

Water content then increase with the concentration of the acid. That at 2400 cm^{-1} increase and approach constant values with $C_{A,aq}$, Then, the ammonium chloride salt, NH^+Cl^- gradually forms with increasing in $C_{A,aq}$ and is saturated at $C_{A,aq}$ greater than 0.01 kmol/m^3.

Effect of the initial concentrations of amine and palladium on the distribution ratio. The distribution ratio of palladiium, D were plotted against initial concentration of TOA in the organic solution, C_{B0} in Fig.4. The value of D increase with C_{B0}, but decrease with C_{HCl}. In the range where chloride ion larger than 0.2 kmol/m^3, palladium exist as the species of $PdCl_4^{2-}$ in the aqueous solution(Elding 1972). The ammonium chloride salts of the amine are equilibrated with three types origomers of ammonium chloride as $(BHCl)_i$ (i= 1,2 and 3) in the organic solution as follows(Kawano et al., 1989);

$$2(BHCl) = (BHCl)_2 \quad (1)$$

$$(BHCl) + (BHCl)_2 = (BHCl)_3 \quad (2)$$

The ammonium chloride salt was assumed to react with $PdCl_4^{2-}$ at the inter-

face to form two kinds of complexes by the following reactions;

$PdCl_4^{2-} + (BHCl)_2 = (BH)_2PdCl_4 + 2Cl^-$ (3)

$PdCl_4^{2-} + 2(BHCl)_2 = (BH)_2PdCl_4(BHCl)_2 + 2Cl^-$ (4)

The equilibrium constants for above reactions are written as follows;

$K_{12} = \{[(BH)_2PdCl_4].a_{Cl}^2\}/\{[BHCl]^2.a_{PdCl_4}\}$ (5)

$K_{14} = \{[(BH)_2PdCl_4(BHCl)_2].a_{Cl}^2\}/\{[BHCl]^2.a_{PdCl_4}\}$ (6)

Where a_{Cl} and a_{PdCl_4} are the activity of Cl^- and $PdCl_4^{2-}$ in the aqueous solutionn. The distribution ratio is written by the following equation using the average activity coefficients of hydrochloric acid*);

$D/[BHCl]^2 = K_{12}/\{\gamma_{HCl}^{0.6}C_{HCl}\}^2 + K_{14}\{[BHCl]^2/\{\gamma_{HCl}^{0.6}C_{HCl}\}^2$ (7)

After the equilibration, total concentration of the amine in the organic solution ,C_{BO} is given by the summation of the concentration of unreacted ammonium chloride salts and that of the complexes formed as,

$C_{BO} = [(BHCl)]+2[(BHCl)_2]+3[(BHCl)_3]+2[(BH)_2PdCl_4]+4[(BH)_4PdCl_6]$ (8)

In the region of $C_{BO}>>C_{Pd,aq}$, the concentrations of the complexes formed are negligiblly small compared with those of the ammonium chloride salts**). The following approximation was adopted,

$C_{BO} =[(BHCl)]+2[(BHCl)_2]+3[(BHCl)_3] = [BHCl]+2K_{20}[(BHCl)]^2+3K_{20}K_{30}[(BHCl)]^3$ (9)

The equilibrium constants K_{20} and K_{30} were estimated previously(Kawano et al., 1989). The concentration of (BHCl) for each C_{BO} was calculated by Eq.(9).

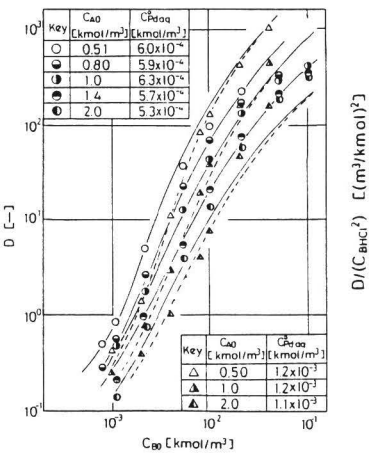


Fig.4 Effect of C_{BO} and C_{Cl} on the distribution of palladium

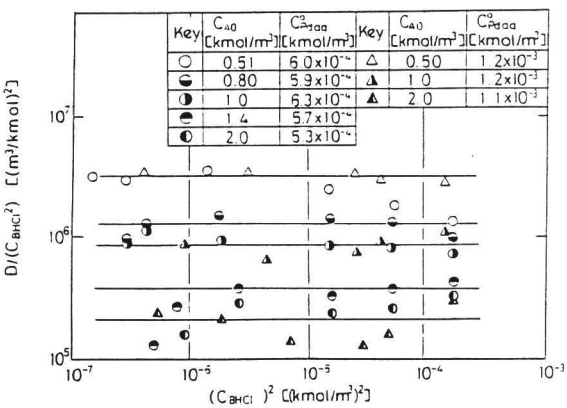


Fig.5 Relation between $D/[BHCl]^2$ and $[BHCl]^2$

*) In this region, the following assumptions for activity coefficients were made as; $\gamma_{PdCl_4}=1.0$ and $\gamma_H = \gamma_{Cl} = \gamma_{HCl}$.

**) The concentration of the complex calculated latter by using the formation constants was found to be negligibly small compared with those of ammonium chloride salts.

The values of $D/[BHCl]^2$ were plotted against $[BHCl]^2$ in Fig.5. These values were approximately held in a constant values depending on $[Cl^-]$. Consideration of the result with Eq.(7) suggest that the value of K_{14} is negligibly small compared with that of K_{12}. The constant value obtained in each $[Cl^-]$ in Fig.5 is plotted against $[\gamma_{HCl}{}^{0.6}.C_{HCl}]$ in log-log scale in Fig.6. The experimental value was plotted on the straight line having a slope of 2.0. Then, the value of K_{12} is estimated as $9.2\times10^5 m^3/kmol$. The value of [BHCl] was calculated again by using the values of equilibrium constants estimated as the functions of C_{B0} and $[PdCl_4{}^{2-}]$. The value of D calculated by Eq.(7) were shown by the solid lines in Fig.4. The experimental results agree well with the calculated results except for $[Cl^-]=8.0$ kmol/m^3. The extraction ratio of the acid with TOA,Z ($=C_{A,org}/$

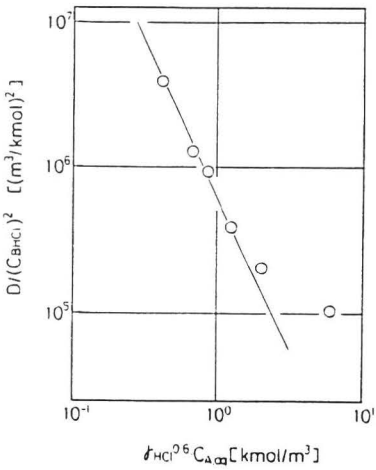


Fig.6 Effect of $\{\gamma_{HCl}{}^{0.6} C_{A,aq}\}$ on $D/[BHCl]^2$

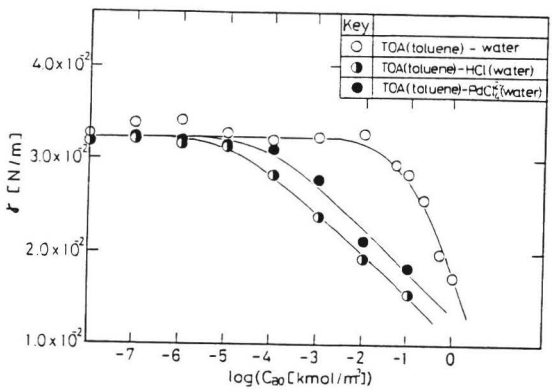


Fig7. Plots of the interfacial tension against C_{B0}

C_{B0}) was observed to increase to 1.5 at $C_{A,aq}= 8.0$kmol/m^3. Water content was also gradually decrease from $C_{A,aq}=4.0$ kmol/m^3 as shown in Fig.2. In this concentration range, the type of ammonium chloride salts in the organic solution is expected to differ from those in lower concentration of the acid. In the case which $(BH)_2PdCl_4)_2$ species was formed, the reaction models was impossible to interpret the experimental results by the similar analysis.

Adsorption equilibrium for the species. The interfacial tension of aqueous solution and toluene solution of the amine eqiulibrated each other were plotted against concentration of the amine in Fig.7. The interfacial tension decrease with increment of the amine concentration. As the solubility of an amine into the aqueous solution is very small, the results in Fig.7 suggest that the amine adsorb at the interface. Assuming that the species adsorb at the interface according to Langmuir type adsorption and also obey Gibb's adsorption isotherm,

an adsorption equilibrium constant and interfacial area occupied by adsorbed species were evaluated by plotts on a curve in Fig.7 as shown in Table 1. The interfacial tension for aqueous hydrochrolic acid or aqueous palladium chloride solution equilibrated with toluene solution of the amine were also plotted against the amine concentration in Fig.7. In these cases, all of the amine in toluene react with hydrochloric acid or palladium chloride in the aqueous solution to convert the ammonium chloride salt or the palladium-amine complex. Then, the ammonium chloride salt and its palladium complex are assumed to adsorb at the interface. Assuming the same isotherm equation for the adsorption of these species, adsorption constants and interfacial area occupied by these species were evaluated as shown in Table 1. The solid lines in Fig.7 are results calculated by using these constants.

Table 1 Adsorption constants and interfacial area for the species

	TOA	(BHCl)	$(BH)_2PdCl_4$
K_{ad} [m^3/mol]	1.39×10^{-2}	1.32×10^{2}	1.74×10
S_B [m^2/mol]	4.6×10^{5}	1.48×10^{6}	2.52×10^{6}

CONCLUSION

Extraction equilibrium of palladium with tri-n-octyl amine in toluene was measured for various concentrations. Water content and IR spectra of the organic acid after equilibration were measured . The following results were obtained;

(1) Palladium(II) chloride was extracted into toluene solution as the complex, $(BH)_2PdCl_4$.

(2) The equilibrium constant of the complex was estimated as following equation;
$K_{12}=\{[(BH)_2PdCl_4].a_{Cl}^2\}/\{[BHCl]^2.a_{PdCl_4}\}=9.2\times10^5$[$m^3$/kmol]

(3) Water distributed in the organic solution does not affect the formation of the complexes.

(4) In larger acid concentration than 6 kmol/m^3, the reaction between palladium(II) and ammonium chloride differes from this reaction model.

(5) The interfacial adsorption constants for the amine, ammonium chloride salt and its palladium(II) complex were estimated.

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INTERFACIAL MASS TRANSFER ON SMALL DROPS

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ABSTRACT

It was shown that mass transport at small drops (diameter 1 mm) is of complex nature. In a model not only constants describing reaction rates have to be taken into account, but also coupling effects of various kinds as well as various reaction mechanisms at the interface. An experimental setup including analytical methods was developed which is capable of measuring quantitatively the mass transport on such drops where influences of the measuring system are essentially avoided.

INTRODUCTION

The interest of our research concentrates on some reactive extraction systems relevant to the PUREX process, particulary on the mass transfer on small drops of constant diameter (1 mm). In this contribution we present results of the following systems:

1: $$H_3O^+ + NO_3^- + TBP \rightleftharpoons HNO_3 \cdot TBP + H_2O$$

2: $$H_3O^+ + UO_2^{++} + 3NO_3^- + 3TBP \rightleftharpoons HNO_3 \cdot TBP + UO_2(NO_3)_2 \cdot 2TBP + H_2O$$

It seemed extremely important to us to achieve a quantitative evaluation of the extraction process on the drops without interfering with it by the measurement. In our early investigations, we had collected a fairly large number of drops and removed them from the system for analysis. This procedure very likely renders incorrect results since the drops, before being analyzed, must coalesce; then the new interface, although reduced to a minimum, still was in contact with the stationary phase until a volume sufficiently large had collected and was removed.

APPARATUS

An apparatus was built with which the volume of only a few drops could be analyzed for the species mentioned above (volume of one drop: 0,5 μl).
This apparatus and the analytical method developed has been described in part before (Mas, 1988). The methods used included conductometry and laser-photometry. As described in (Mas, 1988), the total ion concentration was determined in the

analytical cell by conductometry and, simultaneously, the concentration of U(VI) ions was determined photometrically by means of a laser photometer equipped with optical fibres (Fig. 7). In the analytical cell two platinum electrodes are mounted and, vertically to them and a few millimeters apart, two quartz pins. One of them has a convex surface in order to focus the laser light at the opposite pin. The distance between them is 3.2 mm.

The platinum wire electrodes were coated with amorphous platinum. They had to be covered by water (volume: 130 μl), in order to obtain reproducible results. Finally the water layer was covered by cis-trans-decalin as "inert" liquid. In this study the drops (aqueous phase) were in the falling mode with the organic phase as stationary phase. Variable parameters were the concentraions of the aqueous and organic phases as well as the residence time of the drops in the stationary phase. The solvent for the organic phase was pure dodecane.

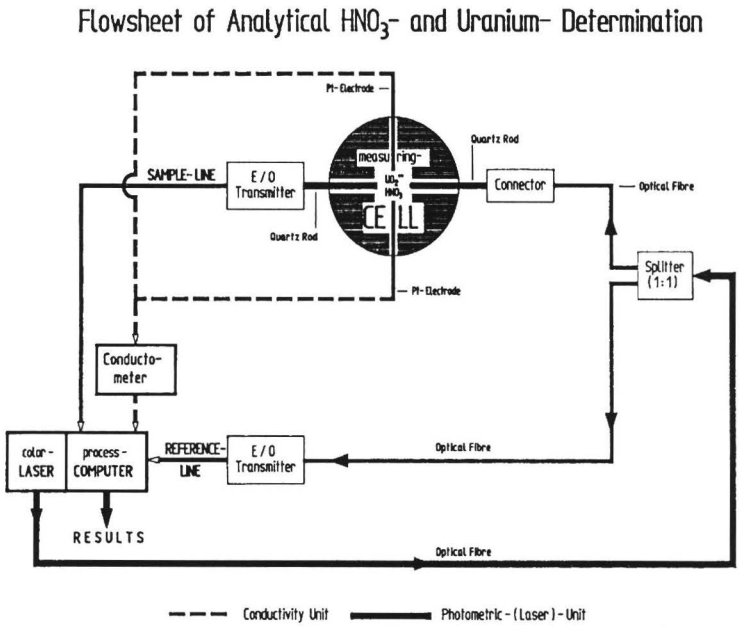


Fig. 7: Flowsheet

RESULTS AND DISCUSSION

The results of our experiments with the forward (extraction) and backward (re-extraction) reactions of system 1 are shown in Fig. 1 and 2. The yield of HNO_3 is plotted depending on the concentrations of TBP and the HNO_3·TPB complex,

respectively. In addition, the residence time of the drops was varied. Only in the case of re-extraction a definite influence of the residence time can be noticed. Different mass transfer rates of forward- and back-reactions at the interface must be assumed, therefore.

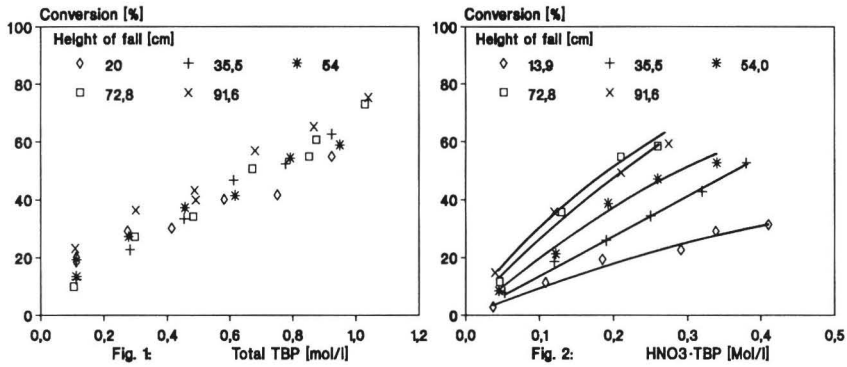


Fig.1: TBP-Conversion-Plots of HNO_3 extraction data obtained with different heights of fall. Drops: 0,4 M HNO_3.
Fig. 2: HNO_3-TBP-Conversions-Plots of HNO_3 re-extraction data obtained with different heights of fall. Drops: H_2O.

This is particularly obvious in Fig. 3 and 4 where the yield is plotted versus the residence time, and the total TBP-concentration was also varied. These curves show definitely a different behavior of the mass transfer.

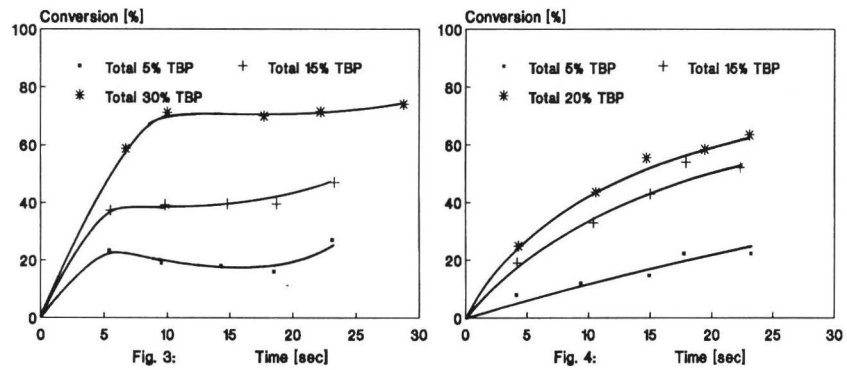


Fig. 3: Time-Conversion-Plots of HNO_3 extraction data obtained with three different TBP-Concentrations.
Fig. 4: Time-Conversion-Plots of HNO_3 re-extraction data obtained with three different TBP-Concentrations.

In all extraction runs the yield-vs-time curves tend to reach a plateau. The fast mechanism at the beginning of the process probably is replaced by a much slower mechanism, so that equilibrium could be attained only after very long times. In the re-extraction runs such a behavior is not as pronounced. The curves look as if equilibrium conditions could be reached with a constant rate. It is very likely that both diffusional and chemically reactive processes participate in the mass transfer (Nitsch et al., 1983; Mas, 1986).

The results of the simultaneous extraction of U(VI) and HNO_3 (System 2) are shown in Fig. 5 and 6.

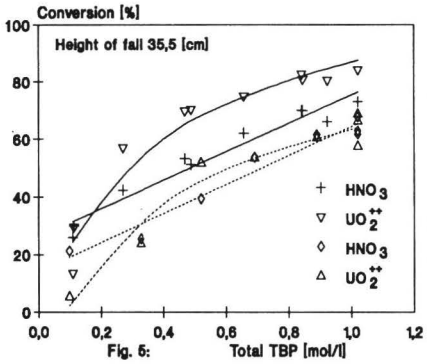


Fig. 5:

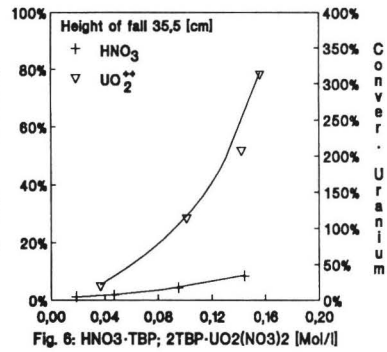


Fig. 6: HNO3·TBP; 2TBP·UO2(NO3)2 [Mol/l]

Fig. 5: TBP-Conversion-Plots of HNO_3 + $UO_2(NO_3)_2$ extraction data obtained with different heights of fall. Drops: 0,25 M HNO_3 + 0,2 M $UO_2(NO_3)_2$.
Fig. 6: Acid- and Uranium-Complex-Conversion-Plots of acid + uranyl nitrate re-extraction data obtained with a height of fall of 35,5 cm. Drops: H_2O.

For the extractive reaction mode the curves corresponding to different residence times are plotted. The curves for the extraction of both acid and uranyl nitrate are approximately parallel. From a comparison of these results with those of Fig. 1 can be deduced that the extraction of HNO_3 is slightly increased. In the re-extraction experiments, however acid re-extraction is strongly suppressed (as compared to Fig. 2) whereas uranyl nitrate is re-extracted so fast, that equilibrium conditions are even exceeded. This "overshooting" can in principle be explained by the following set of reactions:

$$[2\,TBP \cdot UO_2(NO_3)_2]_{org} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [UO_2(NO_3)_2]_{aq} + 2\,[TBP]_{aq} \tag{1}$$

$$[UO_2(NO_3)_2]_{aq} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} UO_2^{2+} + 2NO_3^- \tag{2}$$

$$[HNO_3 \cdot TBP]_{org} \underset{k_6}{\overset{k_5}{\rightleftharpoons}} H^+ + NO_3^- + [TBP]_{aq} \tag{3}$$

It is assumed that equilibrium of reaction (2) is established very quickly (k3>> k4). Also, electroneutrality is postulated to persist at the aqueous side of the interface, i. e. 2 $[UO_2^{++}]$ + $[H^+]$ = $[NO_3^-]$. Finally, the concentrations of uranium and HNO_3 in the organic phase are taken to be constant, as well as the TBP concentration of TBP in the aqueos phase.

This leads to the following two coupled differential equations representing the course of the concentrations of the various species:

$$\frac{d}{dt}[UO_2^{2+}] = k_1 \cdot [2\,TBP \cdot UO_2(NO_3)_2]_{org} - \frac{k_2 \cdot k_4}{k_3} \cdot [UO_2^{2+}] \cdot [NO_3^-]^2 \cdot [TBP]_{aq}^2$$

$$\frac{d}{dt}[NO_3^-] = 2 \cdot \frac{d}{dt}[UO_2^{2+}] + k_5 \cdot [HNO_3 \cdot TBP]_{org} - k_6 \cdot ([NO_3^-] - 2 \cdot [UO_2^{2+}]) \cdot [NO_3^-] \cdot [TBP]_{aq}$$

From the postulated electroneutrality follows for the acid concentration:

$$[H^+] = [NO_3^-] - 2\,[UO_2^{++}]$$

The time dependence of the relative concentrations of the various species is presented in Fig. 8.

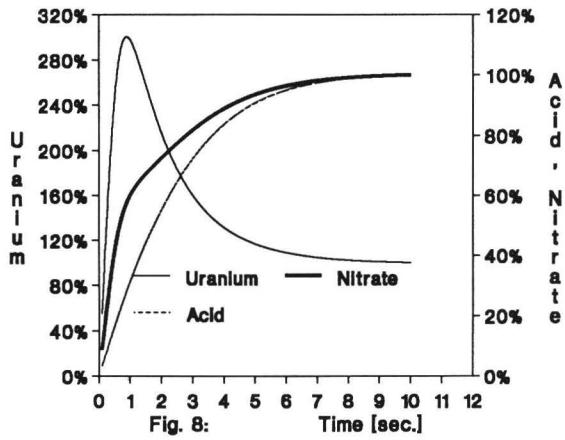


Fig. 8: Time-Conversion-Plot-Simulation of Acid, Nitrate and Uranium Re-extraction.

One finds an "overshooting" of the uranyl ions within the first seconds, whereas acid and nitrate approach equilibrium monotonously. The computer program for the solution of coupled differential equations was taken from (Ebert, 1989).

We are presently developing a model which takes into account the various processes taking place at the interface.

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EFFECT OF INTERFACIAL TENSION GRADIENT ON MOMENTUM AND MASS TRANSFER THROUGH A MOVING INTERFACE OF SINGLE DROPS

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ABSTRACT

The effect of interfacial tension gradient on interphase momentum and mass transfer through a moving interface of single drops was studied theoretically. Apporoximate equations for interfacial velocity, drag coefficient and Sherwood number were proposed with taking account of the interfacial tension gradient. The results of this theoretical study showed good agreement with previous experimental results.

INTRODUCTION

Momentum, heat and mass transfer phenomena through an interface of single drops are fundamental to thermal and/or diffusional operations such as liquid-liquid extraction, gas absorption, vaporization and condensation. The interphase transport phenomena are affected in a complex manner by interfacial variables such as velocity, turbulence, contamination, resistance, etc. From this point of view, much work has been carried out relating the transfer phenomena through an interface of single drops (a review by the authors was shown in Hirata, et al., 1985).

When an interfacial tension gradient caused by a temperature and/or a concentration difference exists at an interface, this gradient significantly affects the interfacial velocity. Consequently it also affects the rates of interphase momentum, heat and mass transfer. When an interfacial tension gradient is positive ($\partial\sigma/\partial x>0$), the mobility of the interface is enhanced. This enhancement of interfacial motion is often called the Marangoni effect. A negative interfacial tension gradient ($\partial\sigma/\partial x<0$), however, decreases the mobility of the interface. This suppression of motion is also well known as the interfacial contamination phenomenon.

This paper concentrates on the effect of interfacial tension gradient on interfacial velocity, interphase momentum and mass transfer through a moving interface of single drops in a wide range of Reynolds number.

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1. Theoretical analysis

1.1 Drag Coefficient and Sherwood Number

The approximate equations have been proposed for two semi-infinite phases in co-current-flow-contact along a moving plane interface from the solutions of two-dimensional laminar boundary layer equations with suitable boundary conditions (Hirata, et al., 1980). These equations being applied to single drops, in the range of $0<U_S/U_T<1$, the following equations are obtained.

$$C_D/C_{DS}=|1-(U_S/U_T)|[1+(2.88-a)(U_S/U_T)]^{1/2} \quad (1)$$

$$Sh/Sh_S=[1+(2.88-aSc^{-b})Sc^{1/3}(U_S/U_T)]^{1/2} \quad (2)$$

where,

$$a=[0.09+(U_S/U_T)^2]/[0.10+(U_S/U_T)^2] \quad (3)$$

$$b=3(U_S/U_T)/[2+12(U_S/U_T)]$$

U_S is the interfacial velocity and U_T is the terminal velocity of single drops. C_{DS} and Sh_S are, respectively, the drag coefficient and the Sherwood number of the rigid spheres, and these values can be described as follows.

Odar's equation; $C_{DS}=(24/Re)(1+0.125Re^{0.72})$ (4)

Ranz & Marshall's equation; $Sh_S=2+0.6Re^{1/2}Sc^{1/3}$ (5)

From Eqs.(1)-(3), followings can be deduced;

(a) The effect of the Schmidt number on the Sherwood number depends on the interfacial velocity. When the interface is rigid, the Sherwood number is proportional to the cube root of the Schmidt number. On the other hand, in the region of high Schmidt numbers and high interfacial velocities, the Sherwood number is proportional to the square root of the Schmidt number.

(b) The interfacial velocity which flows the same direction to a continuous phase enhances the rates of momentum and mass transfer.

(c) When Sc=1, the following equation is obtained.

$$C_D/[C_{DS}|1-(U_S/U_T)|]=Sh/Sh_S \quad (6)$$

1.2 Interfacial Velocity

The Navier-Stokes equations for steady, incompressible, axisymmetric flow in spherical coordinates were theoretically analyzed with suitable boundary conditions. The effect of the interfacial tension gradient was considered with the following stress balance equation at the interface.

$$\mu_d\left[r\frac{\partial}{\partial r}\left(\frac{U\theta}{r}\right)+\frac{1}{r}\frac{\partial Ur}{\partial\theta}\right]_d-\mu_c\left[r\frac{\partial}{\partial r}\left(\frac{U\theta}{r}\right)+\frac{1}{r}\frac{\partial Ur}{\partial\theta}\right]_c=\frac{1}{R}\frac{\partial\sigma}{\partial\theta} \quad (7)$$

When Re<<1, the creeping flow analysis by Hadamard-Rybczynski(1911) and when Re>>1, the perturbation method by Chao(1962) were respectively applied to this analysis, and the following equations were obtained.

$$\text{Re}<<1: \quad U_S(\theta)/U_T=[1/2(1+\kappa)](1-m)\sin\theta \tag{8}$$

$$\text{Re}>>1: \quad U_S(\theta)/U_T=(3/2)\sin\theta-(2/\sqrt{\pi\,\text{Re}})[(2+3\kappa+m)/(1+\sqrt{\gamma\,\kappa})] \times (2-3\cos\theta+\cos^3\theta)^{1/2}/\sin\theta \tag{9}$$

Eqs.(8) and (9) describe the local interfacial velocity on the drops. The average interfacial velocity are obtained as follows:

$$\text{Re}<<1: \quad U_S/U_T=\pi(1-m)/[8(1+\kappa)] \tag{10}$$

$$\text{Re}>>1: \quad U_S/U_T=(3\pi/8)[1-(8/3\pi)B\text{Re}^{-1/2}] \tag{11}$$

From Eqs.(10) and (11), the following equation can be approximated for a wide range of Reynolds numbers (see appendix).

$$U_S/U_T=(3\pi/8)-[(3\pi/8)-A(1-m)]\exp(-D\text{Re})I_0(D\text{Re}) \tag{12}$$

where,

$$A=\pi/[8(1+\kappa)], \quad B=2.197\sqrt{3/\pi}\,(2+3\kappa+m)/(1+\sqrt{\gamma\,\kappa}),$$
$$D=[(3\pi/8)-A(1-m)]^2/(2\pi B^2) \tag{13}$$

I_0 means the modified bessele function. γ and κ are, respectively, the ratio of the densities and the viscosities of the dispersed phase and continuous phase. The dimensionless numbers are defined as follows.

$$\text{Re}=2U_TR/\nu, \quad \text{Ma}=(\partial\sigma/\partial\theta)R/(\mu\nu) \tag{14}$$

$$\frac{\text{Ma}}{\text{Re}}=\frac{(\partial\sigma/\partial\theta)}{2U_T\mu}=\frac{\text{interfacial tension driven force}}{\text{viscous force}} \tag{15}$$

m means the degree of interfacial contamination, defined as $m=|4(\text{Ma}/\sin\theta)/(3\text{Re})|$. When the interface is clean, and no interfacial tension gradient, m should be zero (m=0). When m>0, the interfacial tension gradient suppresses the interfacial velocity, known well as the interfacial contamination phenomena.

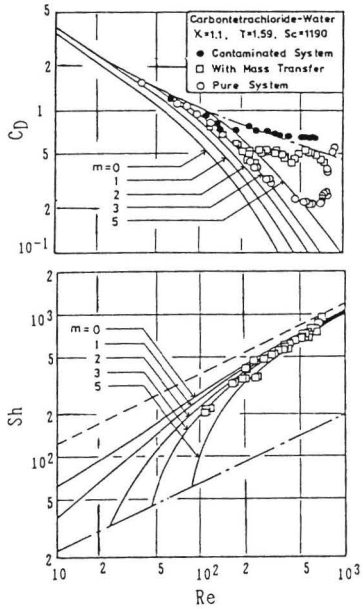
2. RESULTS AND DISCUSSION

2-1. Comparison with Previous Experimental Results

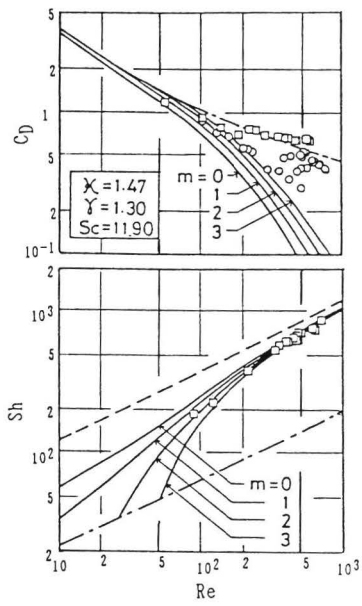
Fig.1 (a) and (b) show the comparison of this theoretical results with previous experimental results (Thorsen, et al., 1962,1968). It is shown that the theoretical results agree well with the experimental results.

2-2. Effect of Interfacial Tension Gradient on Momentum and Mass Transfer

Fig.2 shows the effects of the interfacial tension gradient on



a) Carbontetrachlorade-water system



b) o-dichlorobenzene-Water system

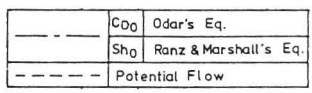


Fig. 1 Comparison of theoretical results with previous experimental results by Thorsen, et al. (1962, 1968)

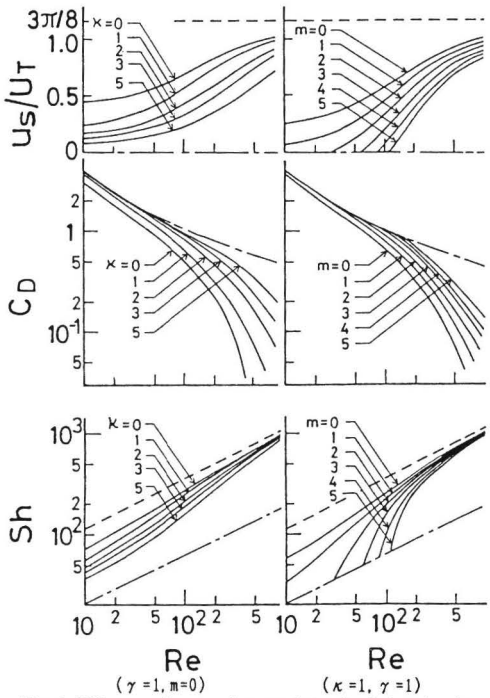


Fig. 2 Effects of κ and m on interfacial velocity, drag coefficient and Sherwood number (Sc=1000)

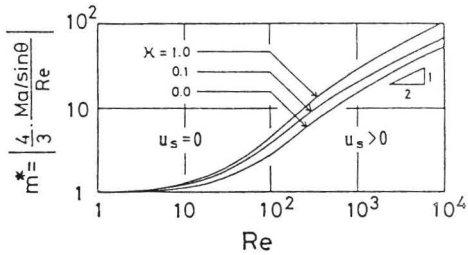


Fig. 3 Relationship between Reynolds number and m*, the critical value of m when interface becomes rigid ($\gamma=1$)

the interfacial velocity, the rates of momentum and mass transfer. From Fig.2, followings can be deduced;

(1)With an increase in the values of κ and m, the interfacial velocity decreases. It is suggested that the interfacial contamination phenomena is similar to the phenomena when the viscosity of the dispersed phase increases.

(2)The effect of m on the interfacial velocity at low Reynolds numbers is much larger than that at large Reynolds numbers. It means that small drops are more sensitive to the interfacial contamination than large drops.

(3)The effect of m on the drag coefficient can be considered as same as the effect of κ on the drag coefficient. On the other hand, the effect of m on the interfacial velocity and the Sherwood number is larger than the effect of κ .

(4)The effect of m on the drag coefficient is much larger at high Reynolds numbers than that at low Reynolds numbers. On the other hand, the effect of m on the Sherwood number is much larger at low Reynolds numbers than that at high Reynolds numbers.

(5)The exponent of Reynolds number for Sherwood number is larger than 1/2 at intermediate Reynolds numbers with interfacial contamination. With an increase in the value of m, the value of exponent increases.

(6)At low Reynolds numbers, a liquid drop with an interfacial contamination behaves like a rigid drop. With an increase in the Reynolds number, the inner circulation flow in a drop occurs rapidly. The value of Reynolds number at this point increases with increase in the value of m.

Fig.3 shows the relationship between Reynolds number and m^* which is the critical value of m when the interface becomes rigid. From Fig.3, the followings can be deduced;

(1)When $Re \leqq 1$, the interface becomes rigid at m=1. At this point, the following equation is obtained.

$$\partial \sigma / \partial \theta = -(gR^2 \rho_C |1-\gamma|/3)\sin\theta \qquad (16)$$

Eq.(16) is in agreement with previous theoretical results (Levan, et al., 1976).

(2)When $Re \gg 1$, the following relationships are obtained.

$$m^* \propto Re^{1/2} \qquad (17)$$

$$Ma_{C-}/\sin\theta \propto Re^{3/2} \qquad (18)$$

Ma_{C-} is the negative critical Marangoni number, at which the interface becomes rigid, and this value is proportional to the

three second power of the Reynolds number as same as the case of semi-infinite plane interface (Hirata, et al., 1989).

(3)With an decrease in the value of κ , the negative critical Marangoni number decreases.

CONCLUSION

The effect of the interfacial tension gradient on the interfacial velocity, the interphase momentum and mass transfer of single drops were studied theoretically. The theoretical results obtained showed a good agreement with previous experimental results for the drag coefficient and for the Sherwood number.

APPENDIX

Eq. (12) is obtained as follows from Eqs. (10) and (11).

$$Re<<1: \quad U_S/U_T=A(1-m) \tag{A-1}$$

$$Re>>1: \quad U_S/U_T=(3\pi/8)(1-B'Re^{-1/2}) \tag{A-2}$$

Following equations are defined.

$$U_S/U_T=\phi(Re) \tag{A-3}$$

$$\Phi(s)\equiv s\mathcal{L}[\phi(Re)]=s\int_0^{\infty}\phi(Re)e^{-sRe}dRe \tag{A-4}$$

From Eqs. (A-1)-(A-4), the following equations are obtained by Laplace transformation.

$$Re<<1: \quad \Phi(s)=s\mathcal{L}[\phi(Re)]=A(1-m) \tag{A-5}$$

$$Re>>1: \quad \Phi(s)=s\mathcal{L}[\phi(Re)]=(3\pi/8)[1-B'\sqrt{\pi s}] \tag{A-6}$$

where,

$$B'=(8/3)\pi\times B=2.197(8/3\pi)\sqrt{3/\pi}\,(2+3\kappa+m)/(1+\sqrt{\gamma\kappa}) \tag{A-7}$$

$\Phi(s)$ is assumed as follows to be applied to a wide range of Reynolds number.

$$\Phi(s)=a_1-[a_2 s/(a_3+s)]^{1/2} \tag{A-8}$$

Eqs. (A-9) and (A-10) are obtained by Taylor expansion for each range of Reynolds number.

$$Re<<1\ (s>>1): \quad \Phi(s)=a_1-(a_2/a_3)^{1/2}s^{1/2}+(a_2/a_3)^{1/2}(1/2a_3)s^{3/2}-\cdots\cdots \tag{A-9}$$

$$Re>>1\ (s<<1): \quad \Phi(s)=a_1-a_2^{1/2}+(a_2a_3)/2(1/s)-\cdots\cdots \tag{A-10}$$

Eqs. (A-5) and (A-6) are compared with Eqs. (A-9) and (A-10) respectively, and then constants a_1-a_3 are determined as follows.

$$a_1=3\pi/8, \quad a_2=[3\pi/8-A(1-m)]^2, \quad a_3=[3\pi/8-A(1-m)]^2/[\pi(3\pi/8)^2B'^2] \tag{A-11}$$

From Eqs. (A-3), (A-4), (A-8), (A-11), Eq. (12) is obtained.

$$U_S/U_T=\phi(Re)=\mathcal{L}^{-1}[\Phi(s)/s]=a_1-\sqrt{a_2}\exp(-a_3Re/2)I_0(a_3Re/2)$$
$$=(3\pi/8)-[(3\pi/8)-A(1-m)]\exp(-DRe)I_0(DRe) \tag{A-12}$$

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Two Phase Kinetics of the Solubilization in Reversed Micelles

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ABSTRACT

The rate of the solubilization of different polar substances in reversed AOT micelles was measured using a two-phase stirred cell. It was found that solubilization of metal ions and phenylalanine was very slow and determined by an interfacial process. The solubilization of methylene blue was governed by convective transport in the aqueous phase. Low interfacial tension promoted the solubilization rate in the both cases. It was found that thermal fluctuations of the surfactant layer influenced the micellar size.

INTRODUCTION

The tendency of reversed micelles (RM) to solubilize polar substances in the organic phase has initiated works about the application of such systems in liquid-liquid extraction of proteins, amino acids and metal ions [1].

Hitherto existing works on solubilization in water-in-oil microemulsions have focussed on the equilibrium studies. The kinetics of encapsulation of solubilized compounds in reversed micelles, however, has not been understood until recently. In our previous works we investigated the kinetics of solubilization of methylene blue (MB), lysozyme (L) and metal ions [2, 3] using a two-phase stirred cell. The stirred cell proved to be a very useful tool to investigate the kinetics of a "reactional" extraction [4]. Our preliminary results revealed that the solubilization of MB and L was controlled by convection and the mass transfer resistance was situated in the aqueous phase [2, 3]. The solubilization of metal ions (Ca^{2+}, K^{+}) was independent of the convection and dependent on the interfacial area which supported the interfacial mechanism of creation of reversed micelles [2].

Based on the results described above, a mechanism of the interfacial solubilization in reversed micelles similar to cytosis or spontaneous vesiculation has been proposed [2].

In this work more detailed studies of the solubilization of MB and metal cations have been performed. Additionally, the kinetics of the solubilization of amino acids have been studied. Special attention has been paid to the influence of the interfacial tension on the solubilization rate and to the question of the thermodynamical state of newly created reversed micelles (equilibrium size or not?).

EXPERIMENTAL

Kinetic experiments have been performed in the same stirred cell as in our previous works (Fig. 1) (for explanation see [2]). The details of the experimental and analytical methods are described elsewhere [2, 3]. The anionic surfactant, sodium di-2-ethylhexyl-sulfosuccinate (AOT), was obtained from Fluka and used without further purification. Isooctane (ACS grade, Merck) was purified by distillation. All salts and acids used were reagent grade or better.

RESULTS AND DISCUSSION

Size of reversed micelles:

The system oil-AOT-water is characterized by a low interfacial tension [5], thus the interfacial energy is also low. Therefore the total free energy of the system will mainly result from the entropy of mixing and the interfacial film curvature energy [5]. The latter depends on two parameters: the film rigidity K and the spontaneous curvature C_0 - both introduced by Helfrich [6]. If the bending energy and the thermal energy kT are of comparable value, the surfactant film fluctuates. Thus, the thermal undulation of the interface could be regarded as a prior step to the interfacial creation of reversed micelles (Fig. 2). If this mechanism is a suitable model, the size of the water core of reversed micelles should correspond to the fluctuation parameters double amplitude and a half wavelength.

Fig. 3 shows a comparison of literature data of aqueous core diameters of RMs [7] and calculated values based on capillary wave amplitudes and wavelengths. Details about the calculations and experimental data are given in [7]. There is very good agreement in the range 20 - 75 Å, fairly good agreement for bigger micelles. This deviation might be caused by the rigidity constant K = 1,1 kT [5] that has been used for all investigated systems, but which has only been determined for the sodium salt of AOT. Based on this comparison one can describe the influence of thermal fluctuation on the size of RM in the state of equilibrium with aqueous phase.

Kinetics of reversed micelle formation

The initial flux was calculated by dividing the slope of the measured course of concentration of solubilized species in the organic phase by the specific interfacial area of the stirred cell. The results for different divalent cations are presented in Fig. 4. The independence of flux on the stirring rate (convection) indicates the interfacial process as rate limiting. This independence of the stirring rate was also observed for different organic solvent as n-heptane, toluene or cyclohexane. Conspicuous is that metal ions of the transition group are transported one order of magnitude faster than representatives of the main group. The size of the micelles (connected with $w_0 = [H_2O]/[AOT]$) and the interfacial tension of both groups also vary strongly. One possible explanation is the formation of chelate structures

which is supported by the IR measurements [8]. The adsorption of such aggregates (superstructures) can differ from the adsorption of "normal", i. e. Ca, Sr sulfosuccinates, and one can expect that the values of interfacial tension and micelle size are also different for both groups of metal ions. Generally, in systems with low interfacial tension the solubilization is faster. Based on our "cytosis" model, this can be explained by a lower interfacial energy of formation of a new interface.

In a further series of experiments the kinetics of co-solubilization of two metal cations was studied. In contradiction to the solubilization of single cations, the cations of the main groups of the periodic system were solubilized faster than those of the transition group, and faster than single cations. The ratio of the concentration of both cations was constant during the kinetic experiments and corresponded to the ratio of the equilibrium state, but not to the ratio of metal concentration in the bulk phase (Table 1). This indicates that the micelles were created at an interface with equilibrium concentration of counter ions. The synergistic effect of added cations on the kinetic of calcium solubilization in RMs can be expressed by the following series:

$$K < Sr < Mg < Ni < Zn$$

which corresponds to Hoffmeister's one [9]. Once more the creation of a chelate and its adsorption can change the configuration of the interface and promote the solubilization of the metal ions from the main group. The solubilization of phenylalanine was independent of the stirring rate, which also in this case supports the interfacial process being dominant. However, the influence of the counter ion type is not so pronounced as in the case of L and MB solubilization [2, 3].

As previously proved [2], the solubilization of MB is governed by convection in the aqueous phase. Remarkable is the dependence of the mass transfer coefficient on the interfacial tension (Fig. 5). For lower interfacial tension the slope of the relationship $\beta = f(n)$ was much higher than for higher γ . Probably the contemplation of the interfacial tension and the gradient of interfacial tension at the interface induced by convection provides an explanation of this behaviour. Systems with small interfacial tension may yield negative or zero interfacial tension in the middle of the stirred cell. Spontaneous creation of RMs can destroy the gradient of γ over the interface. This gradient is responsible for the solidity of the liquid-liquid interface and for a lower mass transfer coefficient [4]. A similar phenomenon was observed in the case of lysozyme solubilization [3].

CONCLUSIONS

The kinetic results presented above show the suitability of the stirred cell to investigate the kinetics of the interfacial solubilization in RMs.

Thermally induced capillary waves can be regarded as a step prior to the interfacial creation of RMs. This assumption has been proved comparing the size of RM and wavelength and amplitude of undulation.

The solubilization of metal ions and phenylalanine is determined by an interfacial process. The solubilization of MB and L, however, is governed by convective transport in the aqueous phase. Low interfacial tension promotes the solubilization in both cases discussed above.

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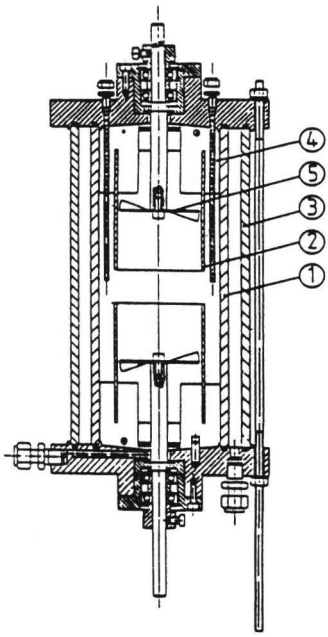


Fig. 1:

Schematic view of the stirred cell.

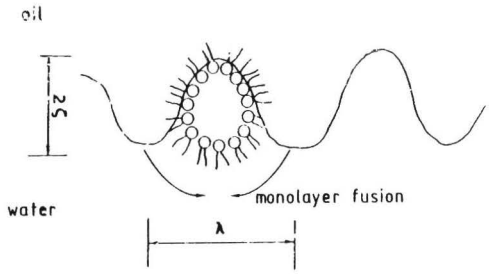


Fig. 2: The interfacial creation of reversed micelles.

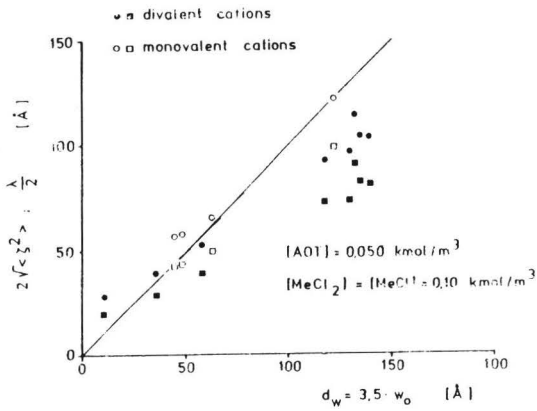


Fig. 3: The comparison of reversed micelle size with the parameters of the thermal fluctuations.

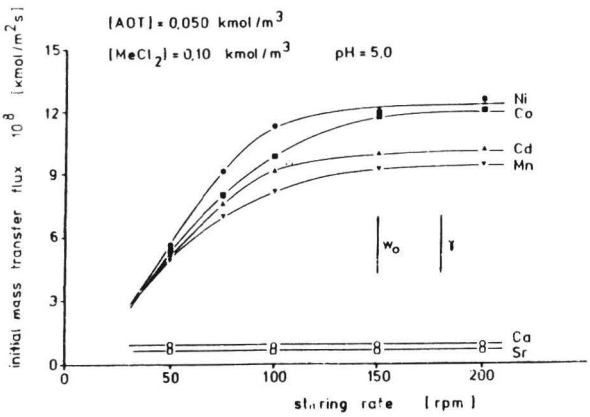


Fig. 4:

The dependence of the initial fluxes of metal ions on stirring speed.

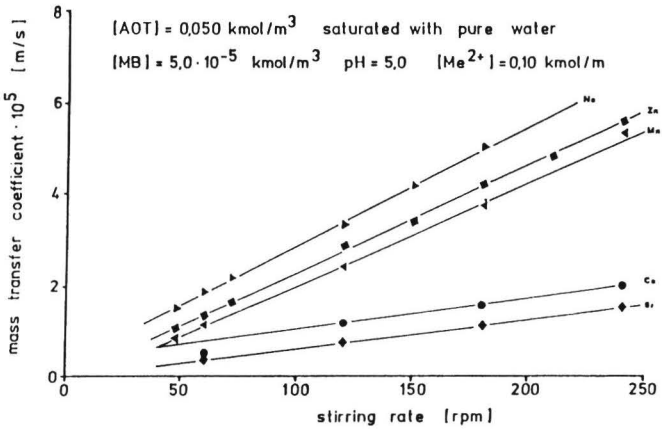


Fig. 5: The influence of stirring speed and interfacial tension on the individual mass transport coefficient.

No	Mixture components 1	2	$\left(\frac{[Me_1]}{[Me_2]}\right)_{eq}$	$\left(\frac{[Me_1]}{[Me_2]}\right)_{1-10}$	$\frac{j_{0\ Me_1}}{j_{0\ Me_2}}$
	Equilibrium mixtures				
1	Ca	Zn	3,21	3,37	3,60
2	Ca	Ni	2,25	2,61	3,25
3	Cs	K	0,92	0,96 a)	1,15
4	Sr	Ca	1,93	1,36	1,36
5	Ni	Zn	1,13	1,25	1,42
6	Ca	Mg	1,45	1,58	1,75
	Nonequilibrium mixtures				
7	Cs	Ni	1,78	3,30 - 2,60	3,85
8	K	Zn	1,72	3,60 - 2,86	3,26
9	K	Li	3,37	6,11 - 4,32	5,69
10	K	Ca	0,46	1,12	1,17
11	K	Sr	0,80	1,81	1,82

$[A\ O\ T]$ = 0,050 kmol/m^3
$[Me_1]_o = [Me_2]_o$ = 0,25 kmol/m^3 , pH = 5,0 , n = 150 rpm
a) between 2,5 - 10 h.

TABLE 1: The results of the solubilization of metal ions mixtures.

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STUDIES ON MECHANISM OF EXTRACTION OF IRON(III) FROM SULFATE SOLUTIONS AND STRIPPING WITH SULFURIC ACID BY FT-IR AND LASER LIGHT SCATTERING SPECTROMETRY II. HDEHP AND RNH_2 AS EXTRACTANT WITH OCTANE AS DILUENT

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ABSTRACT:

In this work, the composition and water content in extracted organic phase of mixture of HDEHP and RNH_2 as solvent were measured. The extracted organic phase has been studied as a function of RNH_2 concentration at different pH and also at different metal ion concentration with FT-IR and Laser Light Scattering Spectrometry. Results indicate that the extraction iron(III) from sulfate solution is through the formation of reverse micelle of water in oil type, and the stripping with dilute sulfuric acid is not through a process of destruction of the w/o emulsion. Thus, it is proposed that the mechanism of extraction and stripping involves the exchange of H_3O^+ with $Fe(H_2O)^{3+}$ at water/oil interface of the reverse micelle. Results also indicate the importance of the role of water in the extraction process. The sulfuric acid extracted into the organic phase is in free SO_4^{2-} form. It is confirmed that the Stokes'radius of the reverse micelle depends on the concentration of RNH_2 used in the organic phase.

1 INTRODUCTION:

Acid, especially sulfuric acid, is often used as leaching agent for non-ferrous metal ores. When the metals in leaching solution are extracted with organic solvent, iron is usually extracted ahead of the other metals and is the difficult impurity to strip from the loaded organic phase. Various techniques have been proposed in the past to overcome this diffculty. They include: (a)hydrolytic stripping(Doyle-Garner and Monhemius, 1985); (b)reduction stripping(Demopoulas and Gefrest 1984), which are associated with the problems such as expensive cost, high temperature operation and slow reaction rate.

In recent years, the development of solvent extraction system as an alternative for iron removal from sulfuric acid leaching solution has been widely studied(Demopoulas and Pouskouleli, 1989, Yu and Chen, 1989). Some new extraction system have been developed(Yu and Chen,1988a, 1988b). For example,

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the extraction of iron(III) in sulfate solution with a mixture of organic phosphorus acid and primary amine as solvent has been carried out and the stripping of iron extracted into this mixed solvent can be accomplished with dilution sulfuric acid. However, the importance of the role of water during extraction of iron(III) with mixed solvent has not been studied, and many phenomena observed remain unexplained. In order to understand the mechanism of extraction of iron(III) from sulfate solution with the mixed solvent and the stripping of Fe(III) extracted with sulfuric acid, the extracted species in loaded organic phase was characterized by FT-IR and laser light scattering spectroscopy and its composition as well as water content in organic phase were determined respectively.

2 EXPERIMENTAL PART:

The extraction was carried out with a mechanical electric shaker. Iron was analysed by titration with potassium dichromate. pH value of solution was measured with a pH meter.

FT-IR spectra of organic phase was recorded with Nicolett 7199B FT-IR spectrometer. KBr windows was used. The absolute scattered intensity was measured at scattering angle 90°. An Ar laser was operated at 488 nm with an output power in the 200-400 mW range. Water content of organic phase was determined by Carl Fischer titration with microcoulometric detector.

Primary amine (N1923) used in this study has formula RR'CHNH$_2$ and with a total number of carbon atoms 19 to 23. Further purification was carried out by distillation prior to the investigation, the fraction of 185-195 ℃/133 Pas was selected as the extractant and with molecular weight of 293.0. HDEHP (P204) used was purified by copper salt method and its content was higher than 99.5%. The octane of chemical pure grade was used as the diluent. The other chemicals were analytical pure grade.

3 RESULTS AND DISCUSSION:

3.1 Extraction of Fe(III) under different conditions:

TABLE 1

Saturated capacity of Fe(III) with HDEHP and N1923 as solvent

H_2SO_4 (mol/dm^3)	<0.05	~0.25	~1.0
Fe (mol/dm^3)	0.0869	0.0560	0.0385
[P204+N1923]/Fe	3.96	6.14	8.94

Organic phase: HDEHP(0.183mol/dm^3), N1923(0.161mol/dm^3);

Aqueous phase: Fe^{3+}= 9-10 g/dm^3

Table 1 shows the results of studies on saturation capacity. The saturated

capacity is a function of the initial pH values of the solution. At rather high pH, the aqueous phase contains a high concentration of hydroxy-ferric irons and P204-N1923 has rather high extraction capacity of 1 mole Fe for four moles of total concentration of P204 and N1923. At lower pH, such as 0.25 M H_2SO_4, the saturated capacity is ~1/6 moles Fe per mole of (P204 + N1923). In highly acidic solution, the saturated capacity of iron per mole of (P204 + N1923) is even lower, and the capacity seems to have no definite value.

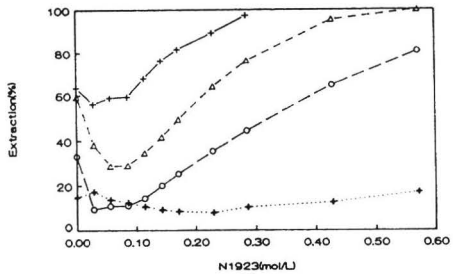


Fig. 1. Effect of N1923 on Fe(III) Extraction in P204(0.18mol/dm^3)-N1923 system.
Aqueous phase: Fe^{3+}=3-5g/dm^3.
H_2SO_4 concentration: + :pH=2; △:0.27mol/dm^3; ○:1mol/dm^3; ✦:5mol/dm^3.

Figure 1 indicates the effects of initial aqueous phase acid content and primary amine (N1923) concentraction on the percentage of iron extraction. At low aqueous acidity (pH=2), the percentage of extraction increases with increase in N1923 concentration; while at high aqueous acidity (0.55 M H_2SO_4), the extraction decreases with increasing N1923 up to 0.1M to reach a minimum and increases above this concentration. At rather high aqueous acidity (5M H_2SO_4), the extractability is practically constant with increase in N1923 concentration. Accordingly it is considered that the extraction of iron(III) from sulfuric acid solutions proceeds at least through two types of extraction process.

3.2 Determination of water content of organic phase:

The presence of linear relationships between the water content and primary amine (N1923) concentration can be seen in Fig.2. The results of water content versus iron(III) concentration in organic phase at constant H_2SO_4 concentration of 0.27 mol/dm^3 are plotted in Fig.3. The percentage of water content decreases with increase in iron(III) concentraction in organic phase. It can be considered that one Fe atom exchange with one H_2O molecule.

3.3 FT-IR spectra of organic phase:

The organic phases from the extraction of aqueous solutions cantaining same concentration of ferric sulfate with HDEHP, N1923 and HDEHP-N1923, respectively, were studied by FT-IR. The results are given in Table 2.

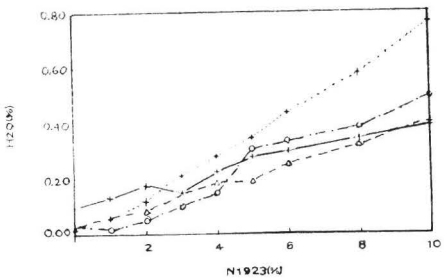


Fig. 2. Effect of H_2SO_4 on H_2O content in organic phase on Fe(III) extraction.
Organic phase:
HDEHP(5%)-N1923-octane
Aqueous phase:
H_2SO_4 concentration:
+ :pH=2; △:pH=1;
○:1mol/dm³; ✦:5mol/dm³.

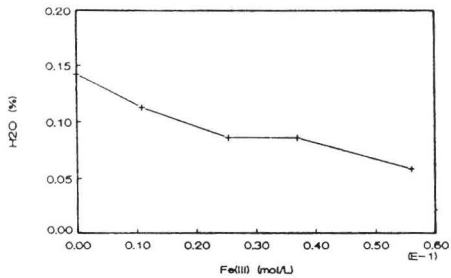


Fig. 3. Relation between iron(III) concentration and water content on Fe(III) loaded organic phase.
Organic phase:
HDEHP(5%)-N1923(5%)-octane
Aqueous phase:
0.27mol/dm³ H_2SO_4.

TABLE 2

Comparison of FT-IR spectra of different organic phase on Fe extraction

HDEHP(5%)	N1923(5%)	HDEHP(5%)-N1923(5%)	Assignment
/	606.2	/	$\nu_4\ SO_4^{2-}$
/	/	617.0	$\nu_4\ SO_4^{2-}$
/	966.7	/	$\nu_1\ SO_4^{2-}$
/	1025.0	/	$\nu_3\ SO_4^{2-}$
1033.7	/	1034.2	ν P-O-C
/	1108.8	1108.5	$\nu_3\ SO_4^{2-}$
/	1133.7	/	$\nu_3\ SO_4^{2-}$
/	1171.8	/	$\nu_3\ SO_4^{2-}$
1197.1	/	1198.4	$\nu_{as}\ PO_2^-$
/	1535.0	1512.3	$\delta_s\ NH_3^+$
/	1621.3	1606.9	$\delta_{as}\ NH_3^+ + \delta\ H_2O$

Aqueous phase: 0.23mol/dm³ H_2SO_4, 4g/dm³ Fe.

The absorption bands at 1034 and 1198 cm^{-1} are assigned to P-O-C stretching frequency and POO^- asymmetric frequency respectively in the extracted species of HDEHP-N1923. A similar result is also observed in HDEHP as solvent. Thus, the results of infrared study confirm that iron in the organic phase is bonded to the phosphoryl oxygen atom of HDEHP in both extractant systems. Simultaneously, the absorption bands at 617 and 1109 cm^{-1} are observed in extracted organic phase of HDEHP-N1923 as solvent, which are consistent with those expected for the sulfate group acting as a free ligand in water solution. Also, absorption bands at 606, 967, 1025, 1109, 1134 and 1172 cm^{-1} in extracted species were observed with N1923 as solvent, which are consistent with those

expected for the sulfate group acting as a bidentate ligand.

In the deconvoluted spectra of the organic phase after extracting the ferric sulfate solution(Fig.4), by increasing the primary amine(N1923) concentration, the intensity of the $PO\bar{O}$ asymmetric vibration at 1199 cm^{-1} decrease, to reach a minimum and then increase again. A similar result is also observed in Figure 1. From the results shown in Figure 5, it can be suggested the HDEHP linked directly to iron(III).

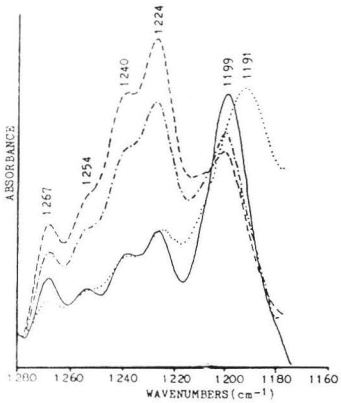


Fig. 4. Effect of N1923 on deconvolved P=O bands of FT-IR on Fe^{3+} loaded organic phase of HDEHP(10%)-N1923-octane. Concentration of N1923 in organic phase: —— 0%; --- 4%; —·— 8%; ····· 15%. Aqueous phase: 1mol/dm^3 H_2SO_4,Fe^{3+}=4g/dm^3.

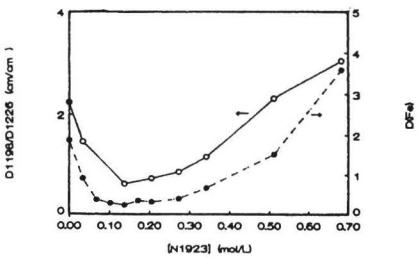


Fig. 5. Comparison of the relationships of D_{1198}/D_{1226} and Fe extraction with N1923 concentration in organic phase. Organic phase: HDEHP(10%)-N1923-octane; Aqueous phase: 1mol/dm^3 H_2SO_4; Fe^{3+}=4g/dm^3.

3.4 Laser Light Scattering Spectroscopy:

The photoelectron count time correlation function was measured at scattering angle 90 with 64-channel digital correlator. Based on the diffusion coefficient deduced from autocorrelation function using the cumulates method, the apparent mean hydrodynamic radius, Rh was calculated with Einstein-Stokes equation and the results are shown in Table 3.

TABLE 3

Particle size in the loaded organic phase of HDEHP-N1923-octane

initial acidity(mol/dm^3)	/	0.22	1.03	0.27	0.5	5
extracted species	/	acid	acid	iron(III)	stripping	stripping
Rh(Å)	47.6	26.6	29.3	32.1	28.6	36.0

It was found that the value of Rh remains constant about 30 Å under different conditions. According to the results, the proposed structure of reverse micelle is shown in Fig.6.

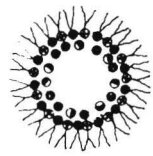


Fig. 6. Model of reverse micelle in organic phase of the HDEHP-N1923 system.
●≪ :HDEHP(P204); ◑ :OH^-, SO_4^{2-};
⊕≪ :RNH_3^+(N1923); ◐ :H_2O, Fe^{3+}.

3.5 Mechanism of extraction process:

According to the above experimental data, the following extraction reaction can be suggested:

$$Fe^{3+}_{(A)} + SO_4^{2-}_{(A)} + mHA_{(O)} + n(RNH_3)_2SO_4{}_{(O)} = [Fe(SO_4)A][(RNH_3)_2SO_4]_n[HA]_{(m-1)}{}_{(O)} + H^+_{(A)} \quad (1)$$

or

$$Fe^{3+}_{(A)} + SO_4^{2-}_{(A)} + H_2O + mHA_{(O)} + n(RNH_3)_2SO_4{}_{(O)} = [Fe(SO_4)(OH)][(RNH_3)_2SO_4]_n[HA]_m{}_{(O)} + H^+_{(A)} \quad (2)$$

The higher the initial acidity of an aqueous phase, the larger the value of n and m are, which may lead to explain that the capacity have no definite value. In fact, the extraction mechanism is very complicated, and it may involve an hydrated ion exchange at water/oil interface of proposed reverse micelle with $Fe(H_2O)_x^{3+}$ to replace H_3O^+

By taking these facts into consideration, it is assumed that the mechanism of exchange of hydrous species is more reasonable for the extraction or stripping of iron(III), and that the primary amine cation RNH_3^+ play a role in exchange between the hydrous iron(III) and Hydronium ion. According to the variation of Fe/H_2O molar ratio in loaded organic phase determined by Carl-Fischer titration, it was considered that $Fe(H_2O)_2^{3+}$ was extracted into the organic phase, and the three molar H_3O^+ were back into the aqueous phase during extraction.

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A MODEL FOR THE RATE OF TWO PHASE NITRATION OF SOME HIGHLY REACTIVE AROMATIC HYDROCARBONS

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ABSTRACT

The two phase nitration of m-xylene and mesitylene at 25°C has been conducted in a continuous stirred tank reactor 1.06 dm^3 in capacity. It has been shown that the rate data predicted, using a model, assuming an instantaneous reaction at a plane in the acid phase close to the interface and those actually measured in the reactor, agreed to within 10-20%. The relative rates of nitration of m-xylene and mesitylene determined under two phase conditions were found to be almost identical with those obtained in homogeneous system. This may indicate that the overall rates of nitration of such substrates in both reaction systems are controlled by a physical phenomenon which could be the speed of diffusion of reactants within the reaction media.

INTRODUCTION

The mononitration of aromatic hydrocarbons by aqueous mixtures of nitric and sulphuric acids (mixed acid) is a process of considerable industrial importance. In such systems two slightly miscible phases are involved and hence, the transfer of reactants between the phases plays a key role in the determination of the overall rate of reaction. (Sohrabi, 1983a,b, 1986, 1988a, 1981, 1977)

Some aspects of homogeneous and two phase aromatic nitration have been reported by Hanson et al (1975, 1976a) and Sohrabi (1988b, 1976).

It has been shown that in case of nitration of highly reactive aromatic hydrocarbons, a limit has been reached beyond which, the introduction of further activated substrates had no effect on the rate of nitration (Coombes et al 1968, Hoggett et al, 1971, Sohrabi, 1976). This limit has been called the rate of encounter of aromatic hydrocarbons and nitronium ions.

Olah (1970) postulated that in such systems, the normal mechanism of substitution was replaced by one in which the rate determining step was the formation of a π -complex. Recently, it was shown (Sohrabi, 1990) that the occurrence of encounter rate could be the consequence of microdiffusional phenomena or reaction during mixing.

In the present study, the rate data obtained from the two phase nitration of highly reactive aromatic hydrocarbons has been correlated by a model assuming an instantaneous reaction between the two reactants. Also, a comparison has been made between the results obtained from two phase systems and those available for homogeneous reactions. In this way the relative importance of diffusional limitations in case of fast reactions in homogeneous systems may be

established.

2 EXPERIMENTAL

2.1 Reactor

The reactor was 1.06 dm^3 in capacity (13 cm long and 10.2 cm internal diameter) and was constructed of stainless steel type EN58J. Four vertical baffles, each one tenth the diameter of the tank, mounted against the tank wall at right angles to it, were spaced at 90° intervals around the reactor. Cooling was provided by means of a coil supported in the tank baffles.

The temperature was measured by means of an iron-constantan thermocouple housed in a sheath. The reactants were fed to the reactor from two glass reservoirs by means of metering pumps. Further details of this reactor may be found elsewhere (Sohrabi, 1983a).

2.2 Laminar-Jet

The apparatus used in this study was basically similar to that employed by Hanson and Ismail (1976b). It was so designed to produce a jet of mixed acid passing through the aromatic phase. The equipment consisted of a cylindrical jet chamber made of "Pyrex" glass 11.5 cm long and 7.5 cm internal diameter.

The whole unit was housed in a constant temperature room.

2.3 Analytical techniques

The heterogeneous nitration of aromatic hydrocarbons occurs in the acid phase and the extent of reaction in the organic phase is insignificant (Sohrabi 1988b).

To start the nitration in CSTR, the reactor was initially filled with distilled water. The agitator motor was switched on and the reactants were introduced at the appropriate rates. The cooling water was adjusted to keep the temperature constant at 25 $\pm$ 0.2°C.

When steady state conditions were established, samples were drawn through a sampling tube connected to the effluent pipe.

Two sets of samples were taken during each run: (i), the organic phase, washed with excess distilled water, and (ii), the aqueous phase.

The organic phase samples were analysed for aromatic hydrocarbons and various nitro aromatic isomers. The overall concentration of nitro aromatic compounds was also measured by a u.v. visible spectrophotometer.

Isomer distribution and hydrocarbon content of the samples were determined by gas-liquid chromatography. The flame ionization detector was used. A 2.7 m stainless steel column, packed with 14 g Apiezon L on Chromosorb P of 80-100 mesh was employed and gave a good separation of isomers working at 210°C. Nitrogen was used as the carrier gas. Analytical accuracy was within 1-2%.

Nitric acid in the aqueous phase was determined by the method of Barduhn and Kobe (1956). Nitrous acid was analysed using colorimetric method (Hanson et al, 1976c).

3 RESULTS AND DISCUSSION

It has been shown that the two phase nitration of less reactive aromatic hydrocarbons such as benzene and toluene followed a fast reaction regime (Hanson et al, 1976a, Giles et al, 1976).

By considering that the estimated rates of nitration of m-xylene and mesitylene relative to that of toluene are 20 and 800 respectively, it seems reasonable to assume an instantaneous reaction regime for these substrates. In such a regime, the reaction takes place in the acid phase at a plane close to the interface and the overall rate is governed by the speed of diffusion of the two reactants in the reaction media.

The differential equations describing such a situation are as follows:

$$D_1 \frac{\partial^2 C_1}{\partial x^2} = \frac{\partial C_1}{\partial t} \qquad x > \lambda \qquad (1)$$

$$D_2 \frac{\partial^2 C_2}{\partial x^2} = \frac{\partial C_2}{\partial t} \qquad x < \lambda \qquad (2)$$

where subscripts 1 and 2 are refered to nitric acid and aromatic hydrocarbon respectively and λ is the distance of the reaction plane from the interface

The following boundary conditions are applicable (Astarita, 1967, Danckwerts, 1970):

At the interface: $x = 0 \qquad C_2 = [ArH]^*_a$

At $t = 0$: $\qquad C_1 = [HNO_3]_a$

In the bulk acid phase: $x \to \infty \qquad C_1 = [HNO_3]_a$

At the reaction plane: $x = \lambda \quad , D_1 \frac{\partial C_1}{\partial x} = -D_2 \frac{\partial C_2}{\partial x} \quad , C_1 = 0, C_2 = 0$

Solutions of the above equations, involving a moving boundary, may be obtained by a standard technique and is:

$$R = A \sqrt{(D_{ArH})/\pi t}\ [ArH]^*_a \ / \ (\text{erf} \sqrt{(\alpha / D_{ArH})}) \qquad (3)$$

where, R is the rate of reaction per unit volume of the acid phase, α is a constant and t is the absorption time, and D is the diffusion coefficient.

Equation (3) may be simplified provided that the interfacial concentration of aromatic hydrocarbon be much smaller than the bulk concentration of nitric

acid (Brian et al, 1961), i.e. $[ArH]^*_a \ll [HNO_3]_a$

Assuming that such a condition exists within the reactor, then the enhancement factor (I), may be written as:

$$\frac{1}{\text{erf}\left(\sqrt{\alpha/D_{ArH}}\right)} = I = \frac{1 + (D_{HNO_3}/D_{ArH})([HNO_3]_a / [ArH]^*_a)}{\sqrt{(D_{HNO_3}/D_{ArH})}} \qquad (4)$$

Substitution gives:

$$R = A([HNO_3]_a + [ArH]^*_a D_{ArH}/D_{HNO_3}) \sqrt{(D_{HNO_3}/\pi t)} \qquad (5)$$

Testing of the model demanded a knowledge of the values for the system parameters. Diffusivities were obtained using the laminar-jet technique. Values for saturation concentrations of aromatic hydrocarbons in mixed acid were determined by solubility measurement (Sohrabi, 1988b) and interfacial area was known from the previous studies (Sohrabi, 1983a, 1986).

The rate data obtained for the two phase nitration of mesitylene and m-xylene and those predicted using equation(5), are presented in table 1.

TABLE 1

Two phase nitration of aromatic hydrocarbons by mixed acid at 25°C.

Hydrocarbon nitrated	Residence time(min)	Conversion (%)	Rates of nitration ($mol.l^{-1}.s^{-1}$) observed (*)	calculated
	1.2	16	3.55×10^{-2}	4.18×10^{-2}
	1.8	23	3.21×10^{-2}	3.82×10^{-2}
	2.7	35	3.06×10^{-2}	3.29×10^{-2}
m-Xylene	3.9	48	2.81×10^{-2}	3.10×10^{-2}
	7.4	60	2.23×10^{-2}	1.96×10^{-2}
	10.1	71	1.78×10^{-2}	1.48×10^{-2}
	21.9	83	1.02×10^{-2}	0.91×10^{-2}
	1.1	15	3.57×10^{-2}	4.17×10^{-2}
	2.3	24	3.12×10^{-2}	3.42×10^{-2}
	4.5	47	2.76×10^{-2}	3.08×10^{-2}
Mesitylene	8.1	63	2.12×10^{-2}	2.21×10^{-2}
	11.0	75	1.60×10^{-2}	1.48×10^{-2}
	21.8	81	1.19×10^{-2}	1.04×10^{-2}

(*) Speed of agitation: 2000 $\pm$ 200 rev/min

It may be observed that the degree of agreement between the experimental and calculated rate values is within 15-20%.

Such a discrepancy may be attributed to the errors involved in the determination of diffusivities and measurement of solubilities.

In table 2, the relative rates of nitration of m-xylene and mesitylene determined in both homogeneous and two phase systems are compared with the

estimated values.

TABLE 2

Rates of nitration of aromatic hydrocarbons relative to that of benzene at 25°C.

Aromatic hydrocarbon	observed relative rates(*) (homogeneous)	observed relative rates (two phase)	estimated relative rates (#)
m-Xylene	38	29	2080
Mesitylene	36	28	46400

(*) Combes et al, 1968
(#) Calculated from the toluene:benzene ratio combined with isomer distribution in mixed acid (see Appendix).

It can be seen that the actual relative rates in single and two phase nitration are almost identical whereas, the predicted data are several orders of magnitude greater than the experimental results. This may indicate that the overall rates of nitration in both homogeneous and two phase systems are affected or controlled by a similar phenomenon which could be the speed of diffusion of reactants within the reaction media.

If this is accepted, then the partial or complete disappearance of intermolecular selectivities may be interpreted as the effect of a physical phenomenon and hence, the change in mechanism of nitration as postulated by some previous investigators may not be justified.

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APPENDIX

Estimation of theoretical relative rates.

The theoretical rate of nitration of an aromatic hydrocarbon relative to that of benzene (k_S/k_B) may be calculated from the following equation (Hoggett et al, 1971):

$$100nf_i = 6(k_S/k_B)(\%\text{i-isomer}) \qquad \text{(A.1)}$$

where, f_i, is the partial rate factor related to ith position in substrate S, and n, is the number of i positions.

Values for f_i can be estimated from the partial rate factors for toluene.

Example: Calculation of theoretical relative rate of nitration of mesitylene by mixed acid.

Step 1, calculation of partial rate factors for nitration of toluene (T).

data for toluene:

relative reactivity, $k_T/k_B = 24$ (experimental and theoretical values are assumed to be identical)

isomer distribution, o- : 58.15%; p-: 36.78%; m-: 5.07%

Applying equation (A.1):

$(100)(2)f_{o-} = (6)(24)(58.15)$; $f_{o-} = 41.86$

$(100)(1)f_{p-} = (6)(24)(36.78)$; $f_{p-} = 52.96$

$(100)(2)f_{m-} = (6)(24)(5.07)$; $f_{m-} = 3.65$

Step 2, Calculation of partial rate factors for nitration of mesitylene (M).

$$(f_i)_M = (f_{o-})_T^2 (f_{p-})_T$$

$$= (41.86)^2(52.96) \cong 92800$$

Step 3, Calculation of relative rate.

Using equation (A.1),

$$(100)(3)(92800) = (6)(k_M/k_B)(100)$$

$$k_M/k_B \cong 46400$$

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A MODEL FOR THE MONONITRATION OF CHLOROBENZENE IN A LIQUID-LIQUID CONTACTOR

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ABSTRACT

Mononitration of chlorobenzene by aqueous mixtures of nitric and sulphuric acids at 25°C has been studied in a continuous, co-current tubular reactor, 148 cm high, 3.8 cm internal diameter and packed with 8 mm Raschig rings. A model for the overall conversion of chlorobenzene, based on the assumption of plug flow for both phases, coupled with a slow reaction within the aqueous phase has been presented. It has been shown that the data predicted using the model and those actually measured in the effluent agreed to within 20%. The discrepancy between the observed and calculated values, apart from the experimental errors, may be attributed to the assumption of plug flow of fluids and the mutual solubility of the two liquid phases.

INTRODUCTION

Liquid-liquid reactions, performed in packed beds are widely encountered in various chemical industries. The preliminary requirement for the determination of general models for such reactions, is the knowledge of their kinetic regimes.

In this study, a model for the overall conversion of slow reactions, conducted in isothermal co-current liquid-liquid contactors is presented.

As an example for such reactions, the two phase mononitration of chlorobenzene under certain conditions may be mentioned (Chapman, 1976, Sohrabi,1972). Industrial mononitration of chlorobenzene is usually carried out in a two liquid phase system using aqueous mixtures of nitric and sulphuric acids as the nitrating agent.

2 EXPERIMENTAL

2.1 Chemicals

The chemicals used in the present study were all analytical grade.

2.2 Packed column

The reactor was a column made of "Pyrex" glass, 148 cm high, 3.8 cm internal diameter and packed with 8 mm Raschig rings. The two reactants (mixed acid and chlorobenzene) were stored in glass aspirators and were fed to the top of the reactor via appropriate flow meters and controllers. Cooling was provided by circulating water at the correct temperature through a jacket constructed

around the column. The reactor was fitted with three iron-constantan thermocouples placed at three different locations. The thermocouples were wired to temperature compensated recorders and provided measurement to $\pm$0.2°C. Further details of the equipment may be found elsewhere (Sohrabi et al, 1990).

2.3 Analytical technique

When steady state conditions were established, samples were drawn through a sampling tube connected to the effluent pipe near exit from the reactor. The samples were thoroughly washed by excess distilled water and allowed to separate into two distinct layers. The organic phase was analysed for chlorobenzene and various mononitrochlorobenzene isomers. The overall concentration of isomers was also measured by a u.v. visible spectrophotometer at 350nm.

Isomer distribution and chlorobenzene content of the samples were determined by gas-liquid chromatography . The instrument was linked to a recorder and an integrator. The flame ionization detector was used. A 2.7 m stainless steel column, packed with 14 g Apiezon L on Chromosorb P of 80-100 mesh was employed and gave a good separation of isomers working at 180°C. Nitrogen was used as the carrier gas with a constant flow rate of 45 cm^3/min. Analytical accuracy was within 1-2%. Further details of the analytical technique are available elsewhere (Hanson et al, 1976).

3 RESULTS AND DISCUSSION

Reaction between chlorobenzene and nitric acid is irreversible, second order and may assume to occur only in the acid phase. Although some reaction may take place in the organic phase, nevertheless, its contribution to the overall rate is extremely small (less than 0.1%, Sohrabi, 1988) and hence, may be justifiably neglected. It is also clear that the total molar flow rates of aqueous and organic phases are constant throughout the reactor. The following assumptions were also made:

1: Solubility of nitrochlorobenzene in the acid phase is negligible.

2: Solubility of mineral acids in the organic phase is extremely small.

3: The reaction of nitric acid with mononitrochlorobenzene can be neglected

4: Both phases are in plug flow.

Based on the above assumptions and the fact that the two phase nitration of chlorobenzene under experimental conditions employed in this study, is a slow reaction within the aqueous phase, a model for such a reaction was derived and tested.

A differential mass balance for co-current flow in the column is:

$$d\left(\frac{LC_{co}}{C_o}\right) = d\left(\frac{L'C_{na}}{C'_o}\right) \qquad (1)$$

where, L and L', are the molar flow rates of organic and aqueous phases respectively, C_{co}, is the concentration of chlorobenzene in the organic phase, C_{na}, is the concentration of nitric acid in the acid phase, C_o and C'_o, are the molar densities of organic and aqeous phases respectively.

Equation (1) may be written as follows:

$$\frac{L}{C_o} dC_{co} = \frac{L'}{C'_o} dC_{na} \tag{2}$$

and:

$$C_{na} = C^o_{na} - \frac{LC'_o}{L'C_o} (C_o - C_{co}) \tag{3}$$

where, C^o_{na}, is the concentration of nitric acid in the aqueous feed.

The rate equation based on the unit volume of reaction or acid phase can be written as follows:

$$\text{Rate} = kC_{ca}C_{na} \tag{4}$$

where, k, is the second order rate constant and C_{ca}, is the concentration of chlorobenzene in the aqueous phase.

By combining equations (2) and (4), the following expression is obtained:

$$- \frac{L}{C_o} dC_{co} = - \frac{L'}{C'_o} = kC_{ca}C_{na}fdV \tag{5}$$

where, f, is the volume fraction of aqueous phase within the column, and V, is the void volume.

Defining a distribution coefficient for chlorobenzene as:

$$\frac{C_{co}}{C_{ca}} = \emptyset \tag{6}$$

Then:

$$- \frac{L}{C_o} dC_{co} = \frac{k}{\emptyset} C_{co}C_{na}fdV \tag{7}$$

Eliminating C_{na} between (3) and (7), rearranging and integrating will lead to the following equation:

$$C_{co} = C_o \frac{(C^o_{na}/L - C'_o/L')\exp[-(kfC_oV/\emptyset)(C^o_{na}/L - C'_o/L')]}{C^o_{na}/L - (C'_o/L')\exp[-(kfC_oV/\emptyset)(C^o_{na}/L - C'_o/L')]} \tag{8}$$

or in dimensionless form:

$$X_C = \frac{1 - \exp[-(kfC_o V/\emptyset)(C^o_{na}/L - C'_o/L')]}{1 - (C'_o L/C^o_{na} L')\exp[-(kfC_o V/\emptyset)(C^o_{na}/L - C'_o/L')]} \quad (9)$$

where, X_C, is the conversion of chlorobenzene.

Testing the applicability of the above model clearly demands a knowledge of the system parameters. Values for the second order rate constant were taken from the literature (Hoggett et al, 1971), f, was calculated according to the method described by Horak and Pasek (1981), and $\emptyset$ was determined by solubility measurements (Sohrabi, 1972 and Hanson et al, 1975).

In table 1, a comparison has been made between the conversion of chlorobenzene in exit from the reactor and those predicted from equation (9).

TABLE 1

Two phase nitration of chlorobenzene by mixed acid in the fixed bed reactor at 25°C.

Flow rates (cm^3/s)		Composition of acid phase (mole%)			Conversion of chlorobenzene (%)	
acid	organic	HNO_3	H_2SO_4	H_2O	observed	calculated
2.12	1.02	15	30	55	15.1	17.9
3.16	1.14	15	30	55	20.8	18.5
2.30	1.25	15	30	55	19.7	22.1
1.34	2.09	15	30	55	11.3	10.9
1.34	4.10	15	30	55	5.2	7.1
4.26	1.14	15	30	55	31.2	36.6
4.35	2.17	15	30	55	17.8	16.3
4.71	1.26	15	30	55	29.3	33.4
2.23	1.11	15	25	60	1.1	1.8
3.27	1.32	15	25	60	2.6	2.1
2.66	1.29	15	25	60	3.2	4.7
4.12	1.26	15	25	60	4.1	5.3
4.54	2.05	15	25	60	2.8	3.3
1.25	2.84	15	25	60	1.1	1.8

It may be observed from the above table that the degree of agreement is within 20%. The discrepancy between the experimental and predicted values may be attributed to the assumption of plug flow of both phases and to the determination of distribution coefficient for chlorobenzene. Also, the mutual solubility of the two liquid phases could be another source of discrepancy.

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EMULSION AND ACCUMULATION AT AQUEOUS/ORGANIC INTERFACE OF MIXER-SETTLERS

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ABSTRACT

The emulsion which results from Di-n-butylphosphoric acid (HDBP) and zirconium (HDBP-Zr emulsion) was studied on the formation ratio to the emulsion of nonsoluble fission product residues (nonsoluble residues emulsion) in the codecontamination cycle without solvent washing. HDBP-Zr emulsion was found three times of nonsoluble residues emulsion by one week's operation of the codecontamination cycle with the spent nuclear fuel burnt to 28,000 MWd/MTU and cooled 1,000 days. In this codecontamination cycle, 1% HDBP was salted out at the aqueous/organic interface as HDBP-Zr emulsion, and 10% HDBP dissolved in the recycling solvent stream as HDBP-U complex. It was found that HDBP-Zr emulsion accelerates the volume growth of nonsoluble residues emulsion by the emulsifying effect.

1. INTRODUCTION

In the previous study, Gonda (1982) examined the origin of emulsion formation at the aqueous/organic interface of mixer-settlers by a short time solvent extraction using the irradiated fuel with the burnup of 28,000 MWd/MTU and the cooling time of 1,000 days. The main element in the emulsion was ruthenium, most of which remain undissolved in the dissolver solution of spent nuclear fuel as the nonsoluble fission product residues. At that time, zirconium was not detected in the emulsion. From those results, it was concluded that the emulsion did not result from HDBP-Zr complex, but from the nonsoluble fission product residues under a short time solvent extraction. However, HDBP-Zr emulsion is produced together with the nonsoluble residues emulsion when carrying on the solvent extraction process with the high burnup of spent nuclear fuel, or when encountering some troubles unavoidable to stop the process for a long time, as it is. In some cases, HDBP-Zr emulsion gives rise to hydrodynamic failures in the extraction steps (Boudary et al, 1974, Huppert et al, 1974 and Ochsenfeld et al 1979).

The present study was carried out to determine the formation ratio of HDBP-Zr emulsion to the nonsoluble residues emulsion in a long time operation of the codecontamination cycle without solvent washing.

2. EXPERIMENTAL

Figure 1 is the flowsheet operated for the present emulsion formation and measurement. The feed solution was prepared with the dissolver solution of the spent nuclear fuel with the burnup of 28,000 MWd/MTU and the cooling time of 1,000 days. The dissolver solution was used to prepare the feed solution without clarification. The residence time of organic stream in the mixing chamber was 1 min, and that of aqueous stream was 0.7 min. These residence times are much the same as those operated usually in full-scale reprocessing plant. The uranium and plutonium loading factor of the recycling solvent was 1 ~ 70% in the extraction section and 70% in the scrubbing section at the end of the operation. The operation of mixer-settlers were two. One was one week's operation (RUN A). The other was two weeks operation (RUN B). The bank of the mixer-settlers used for this experiment was made of plexiglass and completely transparent. The volume of mixing chamber is 27 ml, and that of settling chamber is 110 ml. The aqueous/organic interfacial space of settling is 28 cm^2. The mixing was done with the four wings turbine type stirrer. The stirring rate was 1,500 rpm. All of the emulsion was recovered at every stage for the measurement of volume and gamma emitting nuclides.

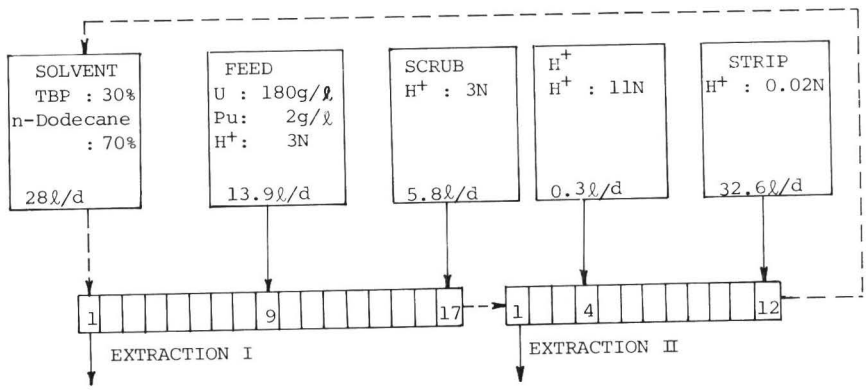


Fig. 1 Experimental flow sheet

3. RESULT AND DISCUSSION

The obtained results of RUN A and RUN B are shown in Figure 2. A noticeable amount of ^{95}Zr was determined together with ^{106}Ru in the emulsion.

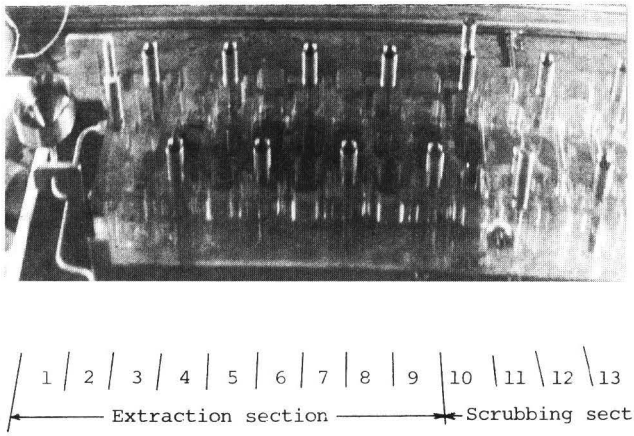


Fig. 2. Emulsion formed at extraction section of EXTRACTION I

Figure 3 shows the ^{95}Zr and ^{106}Ru concentration profiles of RUN A and RUN B. In each extraction stage of RUN A and RUN B, the emulsion was almost equal in the concentration of ^{106}Ru and ^{95}Zr, respectively. In the scrubbing stage, the emulsion decreased with stage.

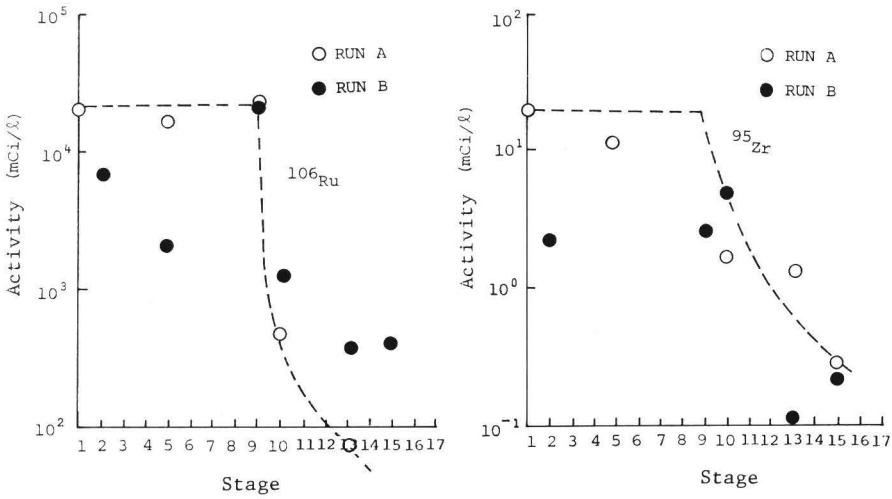


Fig. 3 Concentration profiles in EXTRACTION I bank

From $^{106}Ru/^{95}Zr$ of the emulsion, the total Ru/Zr ratio 1/3 was obtained roughly that agreed with the total Ru/Zr ratio of the dissolver solution employed as the feed solution. While the total Ru/Zr ratio of the spent nuclear fuel with the burnup of 28,000 MWd/MTU and the cooling time of 1,000 days is

1/1.5, the nonsoluble ruthenium is nearly 50% in the dissolution of such a high burnup fuel (Campbell, 1978, Johnson, 1978, Plodinec, 1978, Stacy et al, 1978 and Kley Kamp, 1978), and the real total Ru/Zr in the feed solution is also 1/3 as equivalent as the total Ru/Zr in the emulsion. Namely, it seems that a nearly equivalent emulsifying effect is expected between ruthenium and zirconium in the finishing point of RUN A.

For the present emulsion measurements, 10ℓ of 30% TBP/n-dodecane was used recycling without solvent washing. About 2,000 ppm HDBP was determined in the recycling solvent of RUN A. If all the HDBP made the complex with zirconium and salted out zirconium in the emulsion, the amount of zirconium in the emulsion should reach about 4 g. But the amount of zirconium in the emulsion was calculated as 3×10^{-2} g from the volume of emulsion and the zirconium concentration in each stage of the mixer-settlers. 3×10^{-2} g zirconium is equivalent to about 1% of 4 g zirconium calculated on the assumption that all the HDBP in RUN A makes the complex with zirconium, Zr-2HDBP. Namely, only 1% HDBP makes the complex with zirconium in RUN A. At the finishing period of operation, 0.1 g/ℓ of uranium was found in the aqueous raffinate coming out from the mixer-settlers. HDBP still binds uranium and plutonium in the organic stream of the back extraction section. The back extraction with diluent nitric acid strips only 10% HDBP (Gonda et at). The rest remains in the organic stream and circulates in the extraction process. The uranium bound with HDBP shows the distribution coefficient of nearly 1 at the first stage under the process condition employed for the present condecontamination cycle (Stoller et al, 1961). Therefore, the recycling solvent holds 0.1 g/ℓ of uranium. The amount of uranium bound with HDBP is expected to be 1 g from the total volume of recycling solvent. 1 g uranium corresponds to 10% of the 10 g uranium which all the HDBP, 20 g in the recycling solvent is assumed to associate with. From these results obtained, it was understood that the recycling solvent held about 90% free HDBP.

Figure 4 shows the volume of mixed emulsions and the mean thickness calculated from the interfacial space of settler. These was found an exponential increase of the mixed emulsions in volume in RUN B. This result differs from the expectation that HDBP-Zr emulsion increases in proportion to radiated exposure of the solvent. Gamma spectrometry measured almost same ^{106}Ru concentration to that of RUN A, but lower ^{95}Zr concentration as shown in Fig. 3. It means that the nonsoluble residues emulsion is formed with a same residues concentration in both RUN A and RUN B. On the other hand, HDBP-Zr emulsion of RUN B decreased in concentration till one-tenth of the concentration obtained in RUN A. The decrease in HDBP-Zr emulsion was caused by the tenfold volume increase of the nonsoluble residues emulsion. From these results, it appeares that HDBP-Zr emulsion remains in almost same formation rate in one to two weeks operation of the codecontamination cycle.

The exponential increase of nonsoluble residues emulsion can be explained on the basis of the following expectation.

(1) HDBP-Zr emulsion has an emulsifying effect to collect a certain amount of nonsoluble residues emulsion and forms the mixed emulsion.

(2) The formed mixed emulsion furthermore collects the nonsoluble fission product residues to increase the volume.

The result of RUN A agreed with the result of Ochsenfeld et al that the emulsion, they call crud, is mainly composed of HDBP-Zr complexes accompanied with the fine particles of nonsoluble residues. The result of RUN B showed that the main part of emulsion changed from HDBP-Zr complex to the nonsoluble fission product residues by the emulsifying effect of the mixed emulsions of HDBP-Zr complex and the nonsoluble product residues.

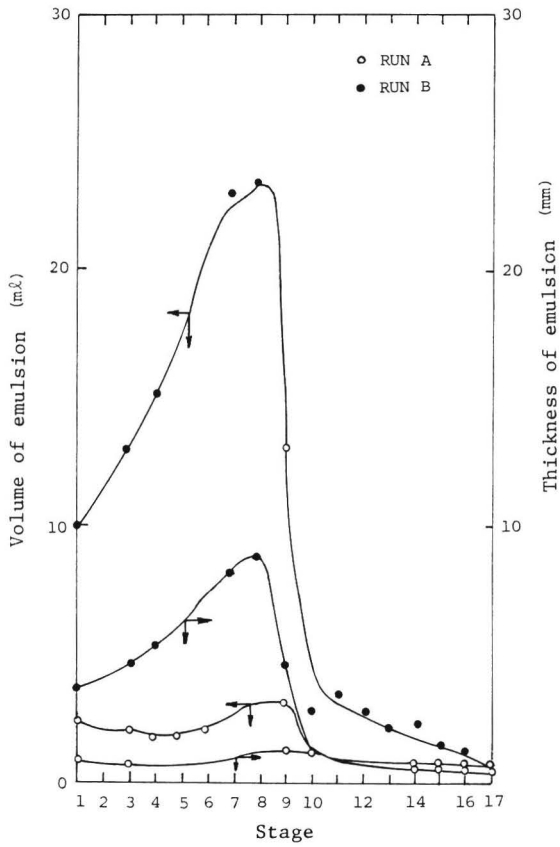


Fig. 4 Volume and thickness of emulsion in mixer-settlers

4. CONCLUSION

HDBP-Zr emulsion was studied on the formation yield in the codecontamination cycle. About 1% of HDBP produced at one week's operation of the codecontamination cycle without solvent washing formed HDBP-Zr emulsion. It was found that HDBP-Zr emulsion accelerates the formation of nonsoluble residues emulsion and accumulates at the aqueous/organic interface of mixer-settlers. Ordinary codecontamination cycle has the solvent washing process and prevents HDBP from accumulating in process. Therefore, the most of emulsion formed and accumulated in ordinary condecontamination cycle is concluded to originate from the nonsoluble fission product residues that are transfered from the dissolution process and remaines suspended in the feed solution to solvent extraction process.

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COALESCENCE OF AN EMULSION IN A PACKED BED (I) SELECTING THE PACKED FIBRE

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ABSTRACT
The separation of dispersions in emulsion by passing through a coalescing fibrous bed has many advantages over other types of separation methods in simplicity and efficiency. As a new conception, the difference of wetting work which characterizes the fibre wettability difference between continuous and dispersed phases has been presented in this paper .It may be used as an important criterion when correctly selecting fibre media to obtain a high degree of coalescence for treating oil in water emulsion. It is found that polypropylene fibre has an excellent coalescence efficiency.

1 INTRODUCTION

The separation of dispersions in emulsion by passing through a packed coalescing fibrous bed has many advantages over other types of separation methods in simplicity and efficiency. In order to separate the dispersion, the droplets must coalesce first. This can be achieved by passing the liquid mixture through the packed bed where the droplets are intercepted and adhered to the packing fibres. The coalescence of the adhered droplets with the droplets of the bulk can then take place. This means that the diameter of the droplets adhering to the fibre increases until such time as the drag force transmitted from the flow fluid causes re-entrainment into the stream. A sequence of collision, adhesion, coalescence and re-entrainment takes place throughout the bed until the size of the droplets leaving the outlet have increased to such a size that they can be separated from the continuous phase fluid by gravity settling.

In the early time, the coalescence method was used mostly to remove water from aviation jet fuel. Recently, envoirnmental concerns have involved much interest in the removal of oil from water. They emphasize on the treatment of bulky oily wastewater which is produced from chemical, mechanical and hydrometallurgical processes (Langdon, et al, 1972, 1979). The literature has been reviewed extensively by Sherony et al (1978).

This paper presents a new conception, the difference of wetting work, which characterizes the wettability difference between continuous phase and dispersed phase at the packing fibre surface. It may be used as an important criterion for correctly selecting the packing fibre to obtain a high degree of coalescence.

2 DIFFERENCE OF WETTING WORK

The necessary condition of coalescence, of which dispersed droplets of emulsion take place in packing medium, is that the dispersed phase is easier to wet the surface of the

packing medium than the continuous phase. So that, a part of dispersed droplets can keep adhering on the surface of the packing medium firmly, and then a sequence of collsion, adhersion and coalescence can evolve.

Solid surface wetted by a kind of liquid is a process where the gas-solid interface is changed into the liquid-solid interface, and the surface of the liquid is not changed.

From the viewpoint of thermodynamics, the free energy drop or external work of this process per unit area under constant pressure and constant temperature condition is expressed as

$$-\triangle G = W = \sigma_{g-s} - \sigma_{l-s} \tag{1}$$

where, W is defined as the wetting work, σ_{g-s} and σ_{l-s} are interfacial tension between gas-solid and between liquid-solid respectively.

According to above analysis, the free energy change of the wetting process substituting dispersed phase (subscript d) for continuous phase (subscript c) of emulsion discribed in Fig. 1 can be shown by the following equation:

$$\begin{aligned} -\triangle G &= -\triangle G_d + \triangle G_c = W_d - W_c \\ &= (\sigma_{g-s} - \sigma_{d-s}) - (\sigma_{g-s} - \sigma_{c-s}) \end{aligned} \tag{2}$$

where, $W_d - W_c$ be written as $\triangle W$ is the difference of wetting work.

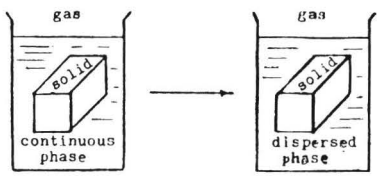


Fig. 1 Wetting process substituting dispersed phase for continuous phase of emulsion

Gas-solid interfacial tension σ_{g-s} and liquid-solid interfacial tension σ_{l-s} can not be directly determined under present experimental conditions. However by experiment, we can directly determine the contact angle θ and gas-liquid interfacial tension σ_{g-l}, and by means of the dependent relation between these variables, we can calculate the difference of wetting work $\triangle W$.

From Equation (2) and Young's wetting equation, we can obtain another equation to calculate the difference of wetting work $\triangle W$

$$\triangle W = W_d - W_c = \sigma_{g-d} \cos\theta_d - \sigma_{g-c} \cos\theta_c \tag{3}$$

where, σ_{g-d} and σ_{g-c} are the dispersed phase surface tension and continuous

phase surface tension respectively, θ_d and θ_c are the contact angles of dispersed phase on solid surface and continuous phase on the solid surface respectively. ΔW can be calculated from these four variables by means of equation (3).

Since in practice it is not easy to obtain an absolutely pure solid surface, and this surface is always rough and heterogeneous, hysteresis effect exists in the determination of the contact angle, which evolves receding contact angle θ_r and advancing-contact angle θ_a independently. Worlfram (1978) presented the conception of Young's equilibrium contact angle θ_E,

$$\cos\theta_E = 1/2\ (\cos\theta_a + \cos\theta_r) \qquad (4)$$

Consequently, Young's equilibium contact angle can be substituted for the relevant θ_a and θ_r in Equation (4) in practical calculation.

From the viewpoint of thermodynamics, when $-\Delta G \geqslant 0$, this process discribed in Fig. 1 is a spontaneous process. $\Delta W \geqslant 0$ is the necessery condition of the dispersed phase to wet the solid surface in priority. It can be used to measure the capability to substitute the continuous phase for dispersed phase on the solid surface. Thus, $\Delta W \geqslant 0$ is an important criterion in correctly selecting the packing medium fibre to obtain a better degree of coalescence in different systems.

3 EXPERIMENT

3.1 Preparation of emulsion

Emulsion used in this experiment was O/W type emulsion in which continuous phase was deionized water and dispersed phase was organic oil composed of 50% of p-xylene,45% of n-decane and 5% of paraffin oil. The effect of paraffin oil was regulating the viscosity of oil dispersed phase. P-xylene was used in oil phase because it had a characteristic absorption peak in ultroviolent region.

0.500 g oil was exactly weighed, and was mixed in 100 ml deionized water. After vigorously shaking 2 minutes, the mixture was emulsified 5 minutes by means of CPS-1A type Supersonic Disperser (produced by Shanghai Supersonic Instrument Co. China), then, diluted with deionized water to 1000 ml. This kind of emulsion formed by above process was utilized in this experiment where the oil content was 500 ppm.

The diameters of the dispersion droplet were determined with BI-90 type Particle Size Analyser(produced by Brookhaven Instrument Co. USA). The droplet size distribution was in comformance with normal distribution function,its average diameter being about 0.4×10^{-6}m.

3.2 Measurement of interfacial properties

The interfacial tension of liquid phase was measured by adopting JZHY-180 Interfacial Tension Measuring Apparatus on the basis of hang-ring method, and then, compared with the values measured by using drop-volume method.

The contact angles between liquids and the surface of the fibres were measured by using WDS-I type contact angle measuring apparatus, whose measuring principle and method were

discribed in literature (X Wu,1983). In order to avoid the measurement error caused by the fibre surface pollution, we pretreated these fibres by the following method:

After immersed in 0.5 N HCl for 10 hr and another 10 hr in 0.5 N NaOH, then rinsed to neutrality with deionized water, fibres were baked in oven at 70°C for 24 hr to remove water adhered on their surface.

3.3 Experimental apparatus

Fig. 2 illustrates the schematic diagram of experimental apparatus.

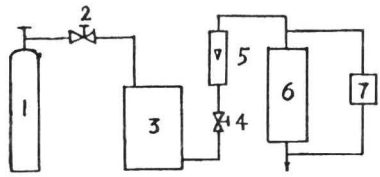


Fig. 2 Schemetic diagram of experimental apparatus
1. gas cylinder 2. pressure control valve 3. storage vat 4. flow control valve
5. flowrater 6. packed bed 7. pressure drop manometer

A number of chemical fibres and a glass fibre were selected as packing media. The diameter of these fibres were about $3.0\text{-}3.5\times10^{-6}$m. Before packed, all the surface of these fibres was pretreated with the procedure as discribed in above section.

3.4 Microanalysis of oil content in water phase

The oil content in effluent water was extracted by organic solvent and then was microanalysised by means of UV-3000 type Ultroviolent Absorption Spectrophotometer (SHMADZU Co. Japan). The extractant was n-Hexane (analysis reagent) pretreated by the absorption of Aluminium oxide and Silica-gel in order to remove micro content aromatics from it. Xylene contained in oil phase exhibited a ultroviolent characteristic peak, it could be used for accurate quantitative analysis.

4 RESULT AND DISCUSSION

In the process of dispersed droplets coalescence in the packed fibrous bed, many smaller droplets of dispersed phase coagulated into a number of bigger droplets. Not only did the number of droplets gradually decrease , but also the droplet size distribution gradually changed. The droplet size distribution curve moved from big to small droplet size. It is obvious that the bigger size droplets were easier to coagulate than the smaller size droplets in the coalescence process. In the tiny vessels of packing fibre (the effective equivalent diameter of the vessel was much greater than the size of the dispersed droplet), bigger size droplets were very easier to be caught by the wall of tiny vessels. But the probability that smaller size droplets collided with the wall of tiny vessels was very small, so that, these droplets could flow through the tiny vessels keeping far apart from the wall.

TABLE 1

Results of the interfacial tension (J/m^2)

interface	hang-ring method	drop-volume method	average value
gas-water	72.02	72.32	72.17
gas-oil	30.40	30.22	30.31
oil-water	40.63	40.83	40.73

TABLE 2

Results of the contact angle and the difference of wetting work

packing medium	water-solid contact angle			oil-solid contact angle			difference of wetting work
	θ_a	θ_r	θ_E	θ_a	θ_r	θ_E	$\triangle W$ (J/m^2)
polypropylene fibre	115	105	109.9	50	41	45.5	45.81
polyvinyl chloride fibre	85	74	79.5	55	50	52.5	5.30
polyacrylonitrile fibre	87	75	81.0	58	52	55.1	6.10
polyester fibre	89	74	81.6	62	45	54.0	7.27
polyamide fibre	69	61	65.1	60	51	55.6	-13.26
viscose staple fibre	46	36	41.3	75	70	72.5	-45.10
glass fibre	52	41	46.8	85	75	80.0	-44.14

Table 1 and table 2 illustrated the results of determination of the interfacial properties.

The fibres investigated in this paper fall roughly into two categories on the basis of the values of the difference of the wetting work enumerated in Table 2. First category is $\triangle W \geqslant 0$, second, $\triangle W < 0$. According to the theoretical analysis above, the former could be used as the packing medium for treating O/W type emulsion because the dispersed oil phase of this type emulsion takes preferential wetting of these fibres surface over the continuous water phase.

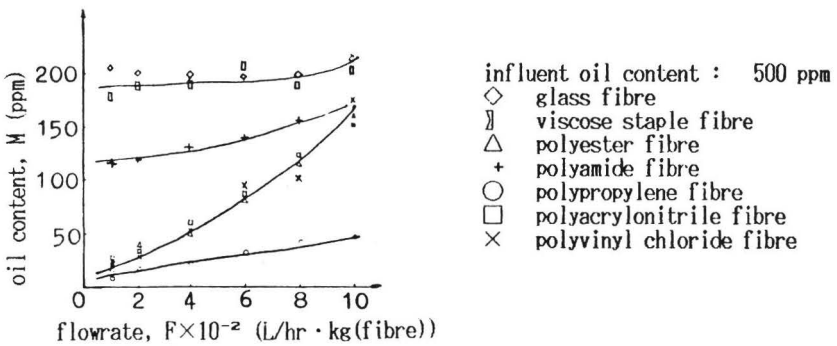


Fig. 3 Coalescence efficiency of fibres at different flow rate

When experimental conditions are all the same, polypropylene fibre which has a bigger difference of wetting work processes an excellent coalescence efficiency. Polyvinyl chloride (PVC) fibre, polyacrylonitrile fibre and polyester fibre are quite similar in the difference of wetting work, therefore, they are also quite similar in coalescence efficiency, which smaller than polypropylene fibre and display a same curve in Fig. 3.

Generally speaking, the oil content in the effluent oily wastewater must be below 10 ppm in accordance with the requirement of environmental protection. Therefore, we had better select polypropylene as packing medium to treat oily effluents from industries. When handing capacity of oily wastewater is small, the latter three fibres could also be selected.

From the point of view of molecular structure, polypropylene fibre on which monomeric molecule (-CH_2 -$CH(CH_3)$-) does not have a polar radical is easy to act with the non-polar molecule of dispersed oil phase and a better coalescence efficiency can usually been seen in treating O/W type emulsion.

It could be regarded as that polyvinyl chloride fibre(-CH_2 -CHCl-)$_n$ and polyacrylonitrile fibre (-CH_2 -CHCN-)$_n$ are respectively produced by substituting polar-radical -Cl and -CN for non-polar radical $-CH_3$, of monomeric molecule of polypropylene (-CH_2 -$CH(CH_3)$-)$_n$. These two kinds of fibres are easy to act with polar molecule of water because there are polarity on their monomeric molecules. Therefore, they have worse coalescence efficiency to treat O/W type emulsion than polypropylene fibre. And also there is a polar-radical on the monomeric molecule of polyester fibre. From this point of view, we could correctly choose the packing medium fibre for coalescence bed according to the molecule of dispersed phase existing polarity or not.

Another category fibres including polyamide fibre, viscose staple fibre and glass fibre which are $\triangle W < 0$ could not be used as the packing medium to treat O/W type emulsion.

The reason for decreasing oil content from 500 ppm in influent to 150-200 ppm in effluent illustrated in Fig. 3 might be that the tiny vessels in packing medium promote the collision among dispersed droplets themselves. The probability of coagulation caused by this kind of collision is much smaller than the collision between the droplets in the whole stream and the droplets attached to the fibre.

Conversely, if fibre of this category was used for treating W/O type emulsion, it would exist a higher coalescence efficiency.

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6. METAL EXTRACTION (PRECIOUS AND RARE METALS)

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SOLVENT-EXTRACTION PROCESSES FOR THE SEPARATION OF THE RARE-EARTH METALS

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ABSTRACT

In this paper the application of different classes of solvent-extraction reagents to the recovery and separation of the rare-earth metals is reviewed, and some aspects of the chemistry of these systems are discussed.

Solvating extractants such as tri-n-butyl phosphate (TBP) are useful both in the recovery of mixed rare-earth products from nitrate liquors (complexes of the type $Ln(NO_3)_3(TBP)_3$ being formed in the organic phase) and in the highly selective separation of cerium(IV) from the trivalent lanthanides (when complexes of stoichiometry $Ce(NO_3)_4(TBP)_2$ or $H_2Ce(NO_3)_6(TBP)_2$ are extracted).

Cation-exchange extractants, especially organophosphorus acids such as D2EHPA, are invaluable in the preliminary division of the rare earths into light, middle and heavy fractions, as well as for the subsequent separation of individual metals within these fractions. In some cases, as for the lanthanum-cerium pair, improved separations can be obtained with extractants of the phosphonic and phosphinic acid types. The characteristics of the extraction of the trivalent lanthanides and yttrium by different carboxylic acids can be related to the steric parameter of the substituent alkyl group. For sterically hindered acids such as Versatic 10, complexes of stoichiometry $LnA_3(HA)_3$ are extracted, and the $pH_{0.5}$ values decrease steadily from lanthanum to lutetium. For non-hindered acids such as 3-cyclohexylpropanoic acid, dimeric complexes such as $(LnA_3(HA)_3)_2$ are formed, and the $pH_{0.5}$ values decrease to a minimum near the middle of the lanthanide series and thereafter increase again.

Anion-exchange extractants, particularly quaternary ammonium salts, offer distinct advantages over other reagent types in certain instances, such as the separation of yttrium from the heavy rare-earth fraction in thiocyanate media, and the separation of neodymium from praseodymium in nitrate media. In these systems, complexes of the types $(R_4N)LnX_4$ and $(R_4N)_2LnX_5$ are extracted, where X represents the thiocyanate or nitrate anion. The order of extraction of the individual rare earths is reversed in the nitrate system (La > Ce . . .> Lu) compared with the thiocyanate system (La < Ce . . .<Lu), probably owing to steric factors. With the extractant Aliquat 336 nitrate (tricaprylmethylammonium nitrate) the separation factors for some pairs of adjacent metals, such as praseodymium-neodymium (β 2,1) and europium-gadolinium (1,8) exceed those obtained with organophosphorus acids such as EHEHPA (1,3 and 1,4, respectively).

INTRODUCTION

The refining of mixtures of rare earths into their individual components in a high state of purity can be accomplished using a relatively small range of solvent extractants. Interestingly, however, the use of the three principal groups of reagents defined in the conventional classification of extractants (i.e. solvating, cation-exchange and anion-exchange types) appears to be essential in a comprehensive separation process.

In this paper, the applications of the different classes of extractant to rare-earth refining are illustrated, and relevant aspects of the chemistry of these systems are discussed. Although it is not possible to give comprehensive rationalizations of the differences in selectivities between extractants, some definite trends in extraction behaviour can be identified, particularly with regard to the relative importance of electrostatic and steric effects in the extracted complexes.

2. SOLVATING EXTRACTANTS

Extraction by solvation involves the replacement by the extractant of some or all of the coordinated water molecules from an aquated metal cation (or an aquated hydrogen ion) to form a species that is soluble in the organic phase. The presence of a suitable anion is also necessary in order to balance the charge in the extracted complex. The most useful solvating extractants in rare-earth refining are neutral organophosphorus compounds containing a phosphoryl group as the metal-coordinating site. These compounds form the well-known series of trialkyl phosphates, dialkyl alkylphosphonates, alkyl dialkylphosphinates, and trialkylphosphine oxides, in which C-O-P bonds are progressively replaced by direct C-P bonds.

The extraction of the trivalent rare-earth metals (Ln^{3+}) from nitrate media by neutral organophosphorus compounds (L) almost always involves a reaction of stoichiometry,

$$Ln^{3+} + 3\ NO_3^- + 3\ \overline{L} = \overline{Ln(NO_3)_3L_3},$$

where bars denote the presence of the species in the organic phase. In the case of the small scandium ion, complexes of the type $Sc(NO_3)_3L_2$ appear to form when the extractant is highly sterically hindered (Du Preez and Preston, 1986). When the nitrate anion is replaced by thiocyanate, complexes of the type $Ln(NCS)_3L_x$ are extracted, where x can be 3, 4 or 5, depending upon the steric complexity of the neutral organophosphorus compound and the size of the rare-earth cation (Preston *et al.*, 1988).

In our experience, we have found that neutral organophosphorus compounds are useful in the bulk recovery of a mixed rare-earth product from nitrate liquors, but that they are less useful in separations amongst the trivalent lanthanides. Such separations are hindered by the presence of characteristic extraction maxima towards the middle of the lanthanide series (Figure 1). The stabilities and hence, under a given set of conditions, the extractabilities of the lanthanide complexes might be expected to increase through the series from La^{3+} to Lu^{3+} (i.e. with decreasing cationic radius), since the electrostatic interaction between cation and ligand should be proportional to the reciprocal of the cationic radius. The existence of maxima in the extractions by neutral organophosphorus compounds seems to indicate that, once the cationic radius decreases beyond a certain size, steric considerations become more important than electrostatic effects (Du Preez and Preston, 1986). In these systems the extraction of yttrium usually lies between that of erbium and that of thulium, this location (rather than on the ascending part of the curve corresponding to the lighter lanthanides) being justified by inspection of the dependence of the appropriate separation factors upon aqueous nitrate concentration. The separation of yttrium from the lighter lanthanides (typified by lanthanum in Fig. 2) increases markedly with increase in nitrate concentration, whereas there is no such effect on its separation from the heavier metals (e.g. thulium).

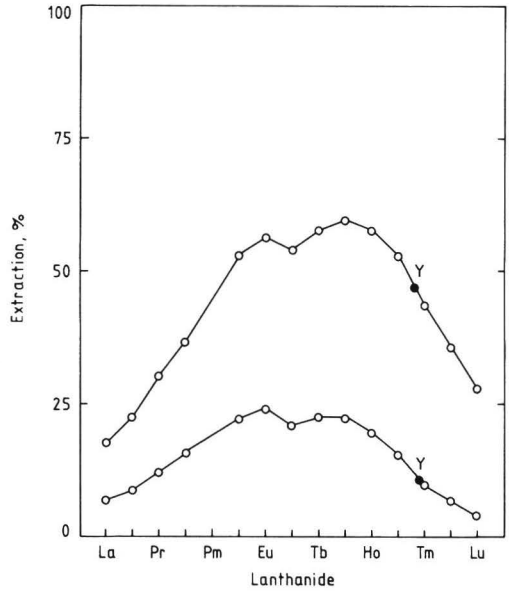


Fig. 1. Extraction of the trivalent lanthanides and yttrium from nitrate media by 2,0M TBP in toluene at 20°C. Aqueous phases 0,01M metal nitrates in 1M HNO_3/2M NH_4NO_3 (lower curve) and in 1M HNO_3/5M NH_4NO_3 (upper curve).

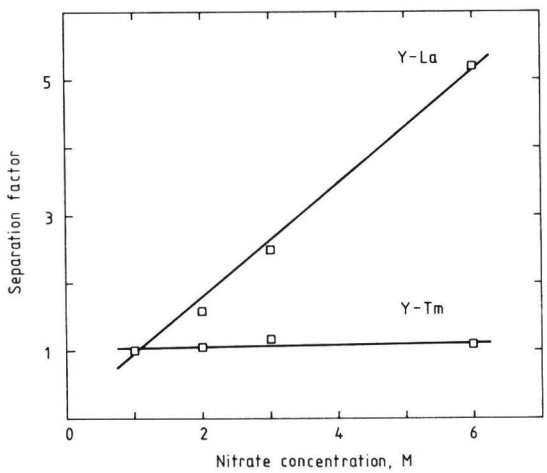


Fig. 2. Separation factors between yttrium and lanthanum, and between yttrium and thulium in extractions of 0,05M metal nitrates from mixtures of 1M HNO_3 and NH_4NO_3 by 1,0M di-n-pentyl n-hexylphosphonate in toluene at 20°C.

The efficient separation of cerium(IV) from the trivalent lanthanides is possible using neutral organophosphorus compounds. Thus, the extraction of cerium(IV) from nitrate solutions by TBP was reported in early studies by Warf (1949), and developed into a practical process by Korpusov *et al.* (1962). The data in Table 1 show that very high separation factors can be obtained for cerium(IV) over the trivalent lanthanides, particularly the more weakly extracted light and heavy elements (exemplified by lanthanum and ytterbium, respectively).

TABLE 1

Separation factors for the extraction of Ce^{4+} and Ln^{3+} as 0,05M metal nitrates from 2M NH_4NO_3/1M HNO_3 by TBP in iso-octane at 20°C

Ln^{3+}	Separation factor, β_{Ln}^{Ce}	
	15 vol. % TBP	30 vol. % TBP
La	4600	2400
Gd	1900	1200
Yb	5900	3600

The extracted complex of cerium(IV) has been formulated as $Ce(NO_3)_4(TBP)_2$ (Healy and McKay, 1956) or as $H_2Ce(NO_3)_6(TBP)_2$ (Korpusov *et al.*, 1962). The second-order dependence of the distribution of cerium(IV) on extractant concentration compared with the third-order dependence observed for the $Ln(NO_3)_3(TBP)_3$ complexes of the trivalent lanthanides results in a decrease in the separation factors at higher TBP concentrations.

The high potential of the Ce^{4+}/Ce^{3+} couple causes the relatively rapid oxidation of diluents containing aromatic or unsaturated aliphatic components, with consequent losses of cerium as the weakly extractable cerium(III). However, saturated aliphatic diluents such as n-heptane and iso-octane (i.e. 2,2,4-trimethylpentane) are resistant to the oxidizing action of cerium(IV). For practical purposes, aliphatic diluents of low volatility, such as Escaid 110 and Shellsol K, are suitable.

Stripping of cerium(IV) from the organic phase is best effected by its reduction to cerium(III) using, for example, solutions of hydrogen peroxide (Warf, 1949; Korpusov *et al.*, 1962),

$$2\ \overline{Ce(NO_3)_4(TBP)_2} + H_2O_2 = 2\ Ce^{3+} + 8\ NO_3^- + 2\ H^+ + O_2 + 4\ \overline{TBP}$$

Cerium dioxide products of high purity (> 99,99 per cent) can be recovered from the strip liquors in such processes.

3. CATION-EXCHANGE EXTRACTANTS

3.1 *Organophosphorus acids*

Extraction by cation exchange involves the displacement of, most commonly, a hydrogen ion from the extractant by the extracted metal, with the resultant formation of an electrically neutral, organic-soluble complex. Thus, for example, in the extraction of the

rare-earth metals by organophosphorus acids (which exist in the dimeric H_2A_2 form in organic solvents of low polarity) it is well known that the extraction follows the stoichiometry,

$$Ln^{3+} + \overline{3H_2A_2} = \overline{Ln(HA_2)_3} + 3H^+$$

As a result, the distribution of the lanthanides is pH-dependent, and separation between adjacent metals can be achieved by careful control of equilibrium pH values in a multistage extraction assembly. Separations can be enhanced by the use of scrubbing circuits in which pH-independent exchange reactions such as the following occur:

$$Sm^{3+} + \overline{Nd(HA_2)_3} = \overline{Sm(HA_2)_3} + Nd^{3+},$$

Monobasic organophosphorus acids comprise the well-known series of phosphoric, phosphonic, and phosphinic acids. With a given organophosphorus acid, the extraction of the lanthanides increases with atomic number, presumably as a result of the increase in strength of the electrostatic interaction between the extractant anion (HA_2^-) and the lanthanide cation as the size of the latter decreases. The extraction of yttrium lies between that of holmium and erbium, as would be expected on the basis of its cationic radius. These characteristics are evident in Fig. 3, which shows the extraction of the rare-earths by di(2-ethylhexyl)phosphinic acid.

The usefulness of organophosphorus acids in separating a rare-earth mixture into light, middle, and heavy (yttrium) fractions is also apparent from Fig. 3. It is convenient to split the light and middle fractions between neodymium and samarium, since the separation of these two elements is enhanced by the absence of promethium, which does not occur in nature. The separation of the middle and heavy fractions can advantageously be made between gadolinium and terbium.

With regard to the effect of the structure of organophosphorus acids on the separation of adjacent rare-earth metals, the early studies of Kolarik and Pankova (1966) indicated that the structure and size of the substituent alkyl group in phosphoric acids did not markedly affect their separation efficiency. In later work by Yuan *et al.* (1982), it was found that more sterically hindered substituents generally gave rise to higher selectivity for one lanthanide over another. A recent study of some phosphinic acids by Cecconie and Freiser (1989) appears to contradict this finding, however.

In our own studies, we examined the separation of lanthanum and cerium by organophosphorus acids with alkyl groups of differing steric complexity (Table 2). The separation of the metals follows the trends phosphoric < phosphonic < phosphinic acids, and n-octyl < 2-ethylhexyl < 3-octyl (i.e., the order of increasing steric hindrance), with a limiting value of 0,4 pH units being reached for the separation between the extraction curves of these metals.

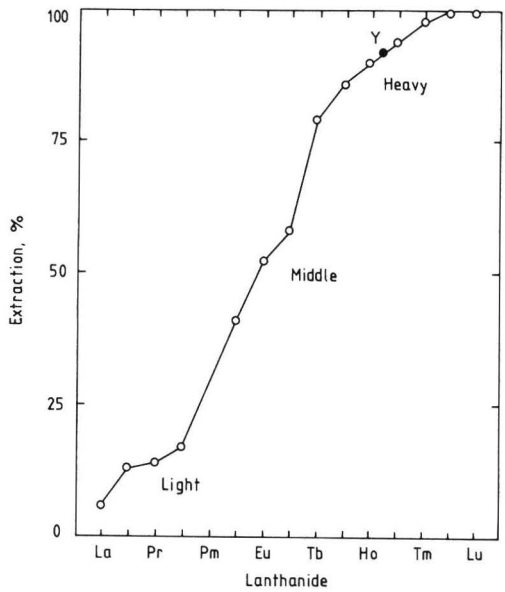


Fig. 3. Extraction of the trivalent lanthanides and yttrium (0,02 M as nitrates) from 0,40 $NaNO_3$ at pH 3,0 by 0,20 M solutions of di(2-ethylhexyl)phosphinic acid in toluene at 20°C.

TABLE 2

Separations between trivalent lanthanum and cerium (0,02 M as nitrates in 0,40 M $NaNO_3$) with 0,20 M organophosphorus acids in toluene at 20°C.

Extractant type	La-Ce separation at $pH_{0,5}$ (pH units)		
	n-Octyl	2-Ethylhexyl	3-Octyl
Phosphoric	0,13	0,24	0,25
Phosphonic	0,26	0,38	-
Phosphinic	0,41	0,41	0,39

The separations across the first (La-Gd) and second halves (Gd-Lu) of the lanthanide series for the organophosphorus acids with 2-ethylhexyl substituents, and for the highly sterically hindered di(3-octyl)phosphinic acid are shown in Table 3. Here, the separations do not follow the trends observed for lanthanum and cerium, the values for the lanthanum-gadolinium and gadolinium-lutetium separations amounting to 0,9 to 1,2 pH units in all cases. This behaviour contrasts sharply with the marked changes observed in the nickel-cobalt and magnesium-calcium separations through this series of acids (Preston and Du Preez, 1988).

TABLE 3

Separations between trivalent lanthanides and between divalent base metals (0,02 M as nitrates in 0,40 M $NaNO_3$) with 0,20 M organophosphorus acids in toluene at 20°C.

Extractant	Separation at $pH_{0,5}$ (pH units)			
	La-Gd	Gd-Lu	Ni-Co	Mg-Ca
D2EHPA	0,91	1,03	0,53	0,88
EHEHPA	1,22	1,12	1,43	0,35
D2EHPinA	1,07	1,01	1,93	-0,56
D3OPinA	0,89	0,93	2,41	-1,41

3.2 *Carboxylic acids*

The extraction of the rare-earth metals by carboxylic acids has not been well studied, with the notable exceptions of the early works of Alekperov and Geibatova (1968) and Korpusov *et al.* (1974). In a general study of the extraction of metal cations by carboxylic acids (Preston, 1985), we observed a contrast in the behaviour of Versatic 10 and naphthenic acids towards the metals lanthanum, cerium, neodymium, gadolinium, holmium, and ytterbium. Thus, the $pH_{0,5}$ values for extraction of the above metals by Versatic acid were found to decrease more or less linearly with decreasing cationic radius, whereas for naphthenic acid a minimum $pH_{0,5}$ value was reached in the middle of the series, with a slight increase in the $pH_{0,5}$ occurring thereafter. This behaviour has now been investigated in more detail for the full series of lanthanides and yttrium using carboxylic acids of different molecular structures (Fig. 4).

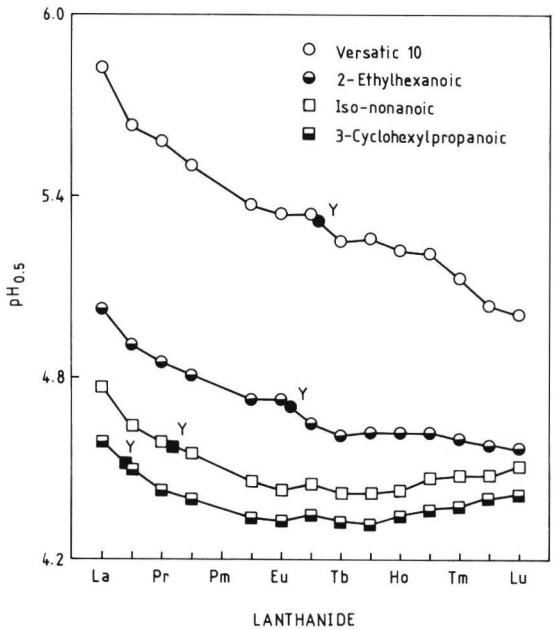


Fig. 4. Extraction of the trivalent lanthanides and yttrium (0,05 M as nitrates) from 1,0 M $NaNO_3$ by 0,50 M solutions of carboxylic acids in xylene at 20°C.

It became apparent in this study that the contrasting behaviour of, for example, Versatic 10 and iso-nonanoic acids is a result of their different steric complexities, which can be quantified by means of the steric parameters (- E_S) of the substituent alkyl groups (MacPhee *et al.*, 1978; Panaye *et al.*, 1980). The overall difference in $pH_{0,5}$ values between lanthanum and lutetium increases linearly with increasing steric parameter (Fig. 5). Further, the extraction of yttrium resembles that of the middle rare earths for sterically hindered acids, but moves towards that of the light rare earths with progressive decrease in the steric complexity of the extractant. As a result of this behaviour, the difference between the $pH_{0,5}$ values of lanthanum and yttrium is also a linear function of the steric parameter (Fig. 5).

Slope analysis studies with Versatic 10 acid ($-E_S$ = 3,63) showed that the extracted complexes of lanthanum, gadolinium, and lutetium have the stoichiometry $LnA_3(HA)_3$, where HA represents the carboxylic acid. With 3-cyclohexylpropanoic acid, an extractant of low steric hindrance ($-E_S$ = 0,34, cf. 0,31 for n-hexanoic acid), the extracted complexes were found to be dimeric, with stoichiometries of $(LnA_3(HA)_3)_2$, where Ln = La or Gd, and $(LuA_3(HA)_2)_2$. It appears that dimerization is energetically favourable only for carboxylic

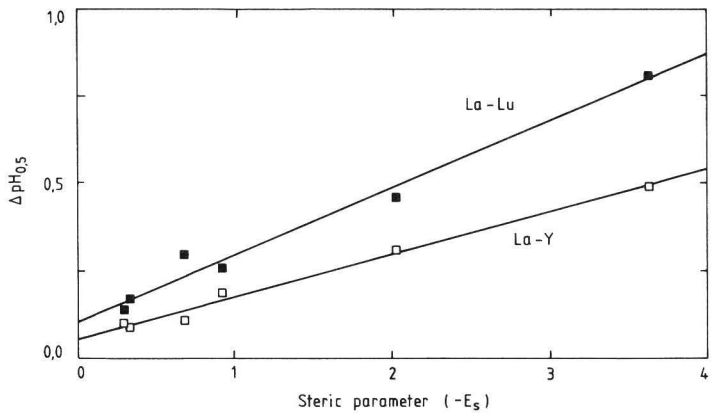


Fig. 5. Difference between $pH_{0,5}$ values of lanthanum and lutetium and of lanthanum and yttrium as a function of the steric parameter of the substituent alkyl group in carboxylic acids.

acids of low steric hindrance and, for the larger cations, two monomer $LnA_3(HA)_3$ units can combine via bridging carboxylate groups without loss of HA ligands. The lanthanide cations in the dimeric complex then show a coordination number of seven, neglecting any aquo ligands that may be present. For the smaller lanthanide cations, dimerization appears less favourable and for steric reasons, the combination of two monomer units requires the elimination of one HA ligand from each, forming six-coordinate species.

4. ANION-EXCHANGE EXTRACTANTS

Extraction by anion exchange usually involves the replacement of a simple inorganic anion from an ion-pair type extractant, such as a quaternary ammonium salt, by a complex metallic anion in reactions such as,

$$\overline{R_4N.NCS} + Ln^{3+} + 3\ NCS^- = \overline{R_4N.Ln(NCS)_4} \text{ and}$$

$$\overline{R_4N.NO_3} + Ln^{3+} + 3\ NO_3^- = \overline{R_4N.Ln(NO_3)_4}.$$

The above two examples are interesting in that the dependence of extraction upon atomic number of the metal increases steadily through the lanthanide series in the thiocyanate system, but decreases throughout in the nitrate system (Fig. 6).

The extraction of the different lanthanides in the thiocyanate system appears to indicate the absence of any steric constraints in the coordination of the requisite number (four or five) of the monodentate, linear NCS^- entities, the extractions showing the expected increase with increasing electrostatic interaction between cation and ligand. In nitrate media, the steady decrease in extraction with increasing atomic number (and hence decreasing cationic radius) suggests that steric factors predominate, presumably due to the high coordination number required for the binding of four or five bidentate nitrate ligands.

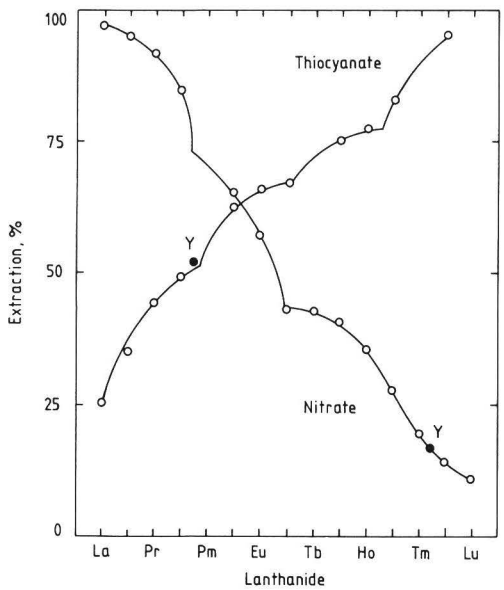


Fig. 6. Extraction of the trivalent lanthanides and yttrium (0,02 M as nitrates) from 4,0 M $NaNO_3$ by 0,50 M solutions of Aliquat 336 nitrate in xylene at 20°C and from 2,0 M KNCS by 0,25 M solutions of Aliquat 336 thiocyanate in toluene at 30°C.

In the thiocyanate system, yttrium behaves as a light lanthanide lying between neodymium and samarium, whereas in the nitrate system it behaves as a heavy lanthanide lying between thulium and ytterbium. This gives rise to the possibility of the separation of yttrium in thiocyanate media from the fraction containing dysprosium, holmium, and erbium to which it reports in extractions with organophosphorus acids. It is unnecessary to add thiocyanate to the aqueous phase, since extraction can take place from nitrate media according to the reaction,

$$\overline{4\ R_4N.NCS} + Ln^{3+} + 3\ NO_3^- = \overline{R_4N.Ln(NCS)_4} + \overline{3\ R_4N.NO_3},$$

thereby minimizing the troublesome decomposition of thiocyanate in acidic aqueous phases. Separation factors for the Aliquat 336 thiocyanate system are compared with those for Aliquat 336 nitrate and 2-ethylhexyl 2-ethylhexylphosphonate in Table 4.

TABLE 4

Separation factors for the extraction of heavy lanthanides and yttrium (0,02 M as nitrates) by Aliquat 336 thiocyanate and nitrate, and 2-ethylhexyl 2-ethylhexylphosphonate

Metal pair	Separation factor		
	$R_4N.NCS$[a]	$R_4N.NO_3$[b]	EHEHPA[c]
Dy-Y	4,3	2,6	2,0[d]
Ho-Y	5,0	2,4	1,3[d]
Er-Y	5,5	1,9	1,4

[a] 1,0 M in toluene at 30°C (aqueous phase 2,0 M NH_4NO_3)
[b] 1,0 M in toluene at 30°C (aqueous phase 6,0 M NH_4NO_3)
[c] 0,2 M in toluene at 20°C (aqueous phase 0,4 M $NaNO_3$)
[d] Expressed as β^Y_{Ln}, all others as β^{Ln}_Y

In most instances, separation factors between adjacent lanthanides in the quaternary ammonium nitrate systems do not compare favourably with those in organophosphorus acid systems. However, notable exceptions occur in the separations of praseodymium from neodymium and europium from gadolinium (Table 5).

TABLE 5

Separation factors for the extraction of adjacent lanthanides (0,02 M as nitrates) by Aliquat 336 nitrate and organophosphorus acids at 20°C.

Metal pair	Separation factor[a]		
A-B	$R_4N.NO_3$[b]	D2EHPA[c]	EHEHPA[c]
La-Ce	1,7	2,7	4,5
Ce-Pr	1,7	1,5	2,1
Pr-Nd	2,1	1,2	1,3
Sm-Eu	1,4	1,8	1,8
Eu-Gd	1,8	1,5	1,4

[a] Separation factors expressed as β_B^A for $R_4N.NO_3$, and as β_A^B for organophosphorus acids.
[b] 0,50 M in xylene (aqueous phase 3,9 M $NaNO_3$/0,02 M HNO_3).
[c] 0,20 M in toluene (aqueous phase 0,4 M $NaNO_3$)

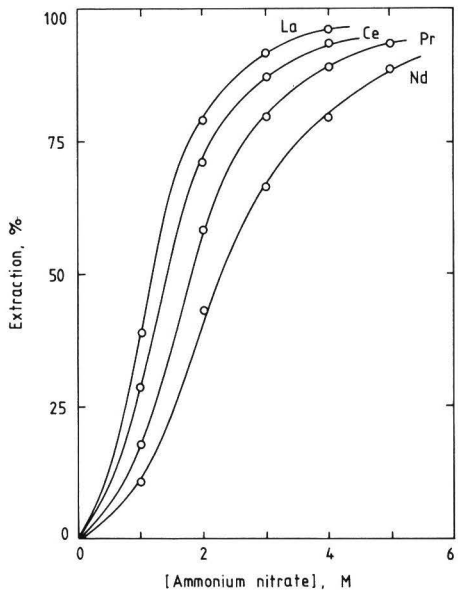


Fig. 7. Extraction of trivalent light rare earths (0,02 M as nitrates) from solutions of ammonium nitrate containing 0,01 M nitric acid by 1,0 M Aliquat 336 nitrate in toluene at 25°C.

The extraction of the light rare earths (0,02 M as nitrates) from solutions of ammonium nitrate containing 0,01 M nitric acid by 1,0 M Aliquat 336 nitrate in toluene at

25°C is shown in Fig. 7. Provided that sufficient extraction and scrubbing stages are employed, such a system can be used to remove lanthanum, cerium, and praseodymium from a light rare-earth fraction to leave a raffinate from which magnet-grade (95 to 96 per cent) neodymium oxide can be precipitated.

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SOLVENT EXTRACTION OF LANTHANOID(III) WITH A MACROCYCLIC CROWN ETHER AND HALOGENATED CARBOXYLIC ACIDS

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ABSTRACT

Extraction of lanthanoid (Ln) from aqueous solutions of halogenated carboxylates such as trichloroacetate (TCA) has been investigated with 18-crown-6 (18C6) in 1,2-dichloroethane. From the equilibrium study in the 18C6-TCA system, the complexes extracted were found to be Ln(18C6)·3TCA for La, Ce, Pr, Nd, Sm, and Eu and a mixture of Ln(18C6)·3TCA and $Ln(18C6)_2$·3TCA for Tb, Tm, and Lu. The extraction constants steeply decreased with increase in the atomic number. The stronger acids such as trichloroacetic acid and tribromoacetic acid gave the higher separation factors for Ln. The separation factors could be further increased by adding EDTA as a masking agent for heavier Ln in the aqueous phase. The very high separation factors especially among light Ln were achieved.

INTRODUCTION

Solvent extraction of metal ions with macrocyclic crown ethers has been extensively studied in recent years. The complexation of metal ions with crown ethers is primarily dominated by the fitness of the metal ions into the cavity of crown ethers. The effective separation of lanthanoid(III) (Ln) ions based on the difference in their size may be expected with crown ethers.

Several studies on the extraction of Ln have been reported with 15-crown-5, 18-crown-6, and their derivatives in the presence of organic or inorganic acids, e.g., picric acid (Wang et al., 1983; Hasegawa et al., 1987; Nakagawa et al., 1988), didodecylnaphthalenesulfonic acid (Ensor et al., 1986), perchloric acid (Khalifa et al., 1988), and 2-thenoyltrifluoroacetone (Aly et al., 1985; Ensor et al., 1988). In those reports, however, the separation efficiency among Ln was not so high. In our previous report (Samy et al., 1988), it has been found that the extractability of Ln steeply decreases with the atomic number when trichloroacetic acid is used in the combination with 18-crown-6.

In this paper, the extraction equilibrium of Ln with 18-crown-6 (18C6) and trichloroacetate (TCA) is studied in detail. The effect of counter anions on the extraction and separation efficiency is discussed with a series of halogenated carboxylates. Furthermore, a new method for enhancement of the separation efficiency of Ln is demonstrated using an aqueous complexing agent such as EDTA.

EXPERIMENTAL

Materials

18-Crown-6 (GR) was purified by the recrystallization. Trichloroacetic acid

(GR), tribromoacetic acid (GR), 2,2-dichloropropionic acid, 2,3-dibromopropionic acid, and heptafluorobutyric acid (GR) were used as obtained. Lithium carboxylate solutions were prepared from the carboxylic acid and LiOH solutions.

Radioisotopes of Ln were prepared in the same manner (Samy et al., 1988).

Extraction procedure of lanthanoid(III)

An aqueous solution of lithium carboxylate (0.05 - 2 M) containing 10^{-5} M Ln labeled with its radioisotope was shaken for 30 min with 1,2-dichloroethane containing 0.003 - 0.1 M 18C6 at 25 °C. The distribution ratio (D) of Ln was calculated from the γ-activities of both phases. The equilibrium pH was measured with a glass electrode immediately after shaking.

Determination of partition coefficient of 18-crown-6

A 1,2-dichloroethane solution of 10^{-3} - 10^{-1} M 18C6 was shaken with a 1.0 M lithium trichloroacetate (LiTCA) solution at pH 3.5. Then the organic phase was shaken with a solution containing an excess of potassium picrate. On the other hand, the aqueous phase was shaken with 1,2-dichloroethane in the presence of potassium picrate. The partition coefficient was calculated to be 0.66 ± 0.06 from the absorbance of picrate extracted into the organic phase at 375 nm.

RESULTS AND DISCUSSION

Extraction equilibrium

In our previous work (Samy et al., 1988), the extraction behavior of several Ln with 0.010 M 18C6 in 1,2-dichloroethane from 1.0 M LiTCA solutions has been clarified. The distribution ratios of Ln increased with increase in pH and reached certain values independent on pH at the pH range from 3 to 5. This pH range was chosen as optimum conditions in the following studies.

The effect of the Ln concentration on the distribution ratio of Ln is shown in Fig. 1. The distribution ratios of La(III), Pr(III), and Tb(III) do not depend on their concentration at the range as wide as 1 x 10^{-6} - 1 x 10^{-3} M. This result means that no polymerization or dissociation of the extractable species occurs in the organic phase.

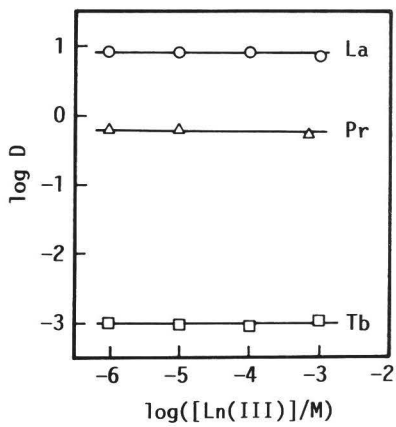


Fig.1. Effect of the Ln(III) concentration on the distribution ratio of Ln(III). 0.010 M 18C6, 1.0 M LiTCA, pH 3-4, 1,2-dichloroethane.

The extraction equilibrium of Ln^{3+} with 18C6 and the TCA anion is given as,

$$Ln^{3+} + n\ 18C6_{org} + 3\ TCA^- \rightleftharpoons Ln(18C6)_n \cdot 3TCA_{org} \quad (1)$$

$$K_{ex} = [Ln(18C6)_n \cdot 3TCA]_{org} / [Ln^{3+}][18C6]^n_{org}[TCA^-]^3 , \quad (2)$$

where K_{ex} denotes the extraction constant and the subscript org, the organic phase. When the complexation of Ln with 18C6 and TCA in the aqueous phase is negligible, the distribution ratio of Ln can be simply expressed as $D = [Ln(18C6)_n \cdot 3TCA]_{org}/[Ln^{3+}]$. Therefore, the following equation is given;

$$\log D = 3 \log[TCA^-] + n \log[18C6]_{org} + \log K_{ex} . \quad (3)$$

The effect of TCA concentration in the aqueous phase on the distribution ratio of Ln was investigated. The ionic strength was maintained to 1.0 M with LiCl. The plots of log D vs. log[TCA^-] are shown in Fig. 2. They give straight lines with the slope of 2.8 for La(III), 2.8 for Ce(III) and 2.9 for Pr(III), which are closed to the theoretical value, 3, shown in Eq. 3.

Figure 3 shows the plots of log D against $\log[18C6]_{org}$ which was calculated with the partition coefficient of 18C6. The plots for La(III), Ce(III), Pr(III), Nd(III), Sm(III), and Eu(III) give straight lines with a slope of unity. These results indicate that 18C6 forms only the 1 : 1 complex with the lighter Ln. The plots for Tb(III), Tm(III) and Lu(III) appear to be straight lines with the slope of about 1.5. Then in the wider concentration region of 18C6 as 0.001 - 0.1 M, the distribution ratio of Tb(III) and Lu(III) was measured

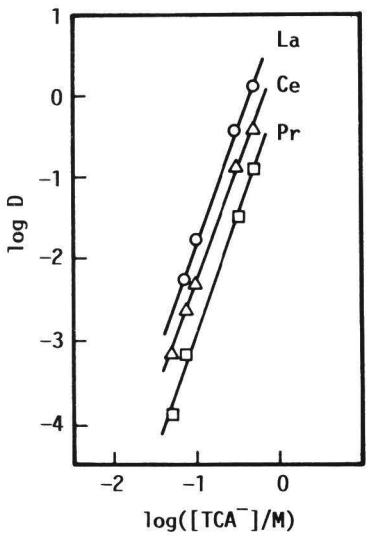


Fig.2. Effect of the TCA^- concentration on the distribution ratio of Ln(III) at a constant ionic strength (1.0 M LiCl). 0.010 M 18C6, pH 2.8-5.0, 1,2-dichloroethane.

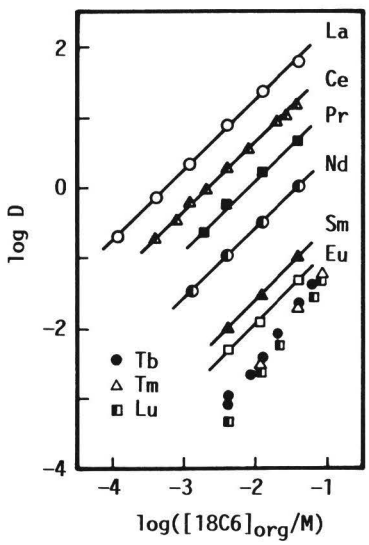


Fig.3. Effect of the 18C6 concentration on the distribution ratio of Ln(III). 1.0 M LiTCA, pH 3.0-4.8, 1,2-dichloroethane.

using 2.0 M TCA solutions at pH 3.4 - 3.9. The slope of the plots of log D vs. $\log[18C6]_{org}$ was close to unity in the low concentration region of 18C6 as less than 10^{-2} M and became higher than unity in the higher concentration region. These suggest that 18C6 forms the 1:1 and the 1:2 complex with the heavy Ln.

The log K_{ex} values of the extractable species, Ln(18C6)·3TCA, were calculated to be 3.25 ± 0.04 for La(III), 2.64 ± 0.04 for Ce(III), 2.11 ± 0.07 for Pr(III), 1.39 ± 0.05 for Nd(III), 0.40 ± 0.04 for Sm(III), and 0.03 ± 0.05 for Eu(III). The values steeply fell with the atomic number of Ln. This sequence is opposite to that observed in the many other extraction systems and agrees with that of decrease in the size of Ln ions. The cavity radius of 18C6 has been reported to be 1.34 - 1.43 Å(Izatt et al., 1985). The crystal radii of Ln regularly decrease from 1.36 Å for La(III) to 1.17 Å for Lu(III) if the coordination number of Ln is assumed to be nine (Shannon, 1976). Consequently, the selectivity in the present extraction system is due to the fitness of Ln ions into the cavity of 18C6.

Effect of counter anions on the extractability and the selectivity

To elucidate the role of counter anions a series of halogenated carboxylic acids such as heptafluorobutyric acid (HHFB), tribromoacetic acid (HTBA), 2,2-dichloropropionic acid (HDCP), and 2,3-dibromopropionic acid (HDBP) were examined in the extraction of Ln with 18C6. The results for Ce(III) and Tb(III) are shown in Table 1. The distribution ratio of Ce(III) with HTBA and HDBP having larger molar volume is fairly higher than that with HTCA and HDCP. The extraction ability of counter anions is principally related to their size although HHFB is exceptional. The separation factor for Ce(III) and Tb(III) increases in the following order; HDBP < HDCP < HHFB < HTCA ∿HTBA. This order agrees with the decreasing order of the pK_a of carboxylic acids except for HHFB. The complexation ability of carboxylates for metal ions can be considered to increase with increase in the pK_a. The carboxylates with higher basicity more strongly bond with medium or heavy Ln rather than with lighter Ln (Ensor et al., 1980).

TABLE 1
Effect of halogenated carboxylic acids on the extraction of lanthanoid(III) with 18-crown-6 at 25 °C.

Acid	V_m[a]/cm^3mol^{-1}	pK_a[b]	pH	log D(Ce)	log(D(Ce)/D(Tb))
HHFB	139.8	-1.03	3.3	0.194	2.873
HTCA	99.0	-0.96	3.4	0.250	3.310
HTBA	114.3	-0.75	2.2	1.155	3.306
HDCP	102.5	0.96	3.3	-0.138	2.716
HDBP	111.4	2.26	3.7	0.966	2.400

Organic phase: 0.010 M 18C6 in 1,2-dichloroethane; aqueous phase:1.0 M lithium carboxylate except for 0.91 M LiDBP.
[a]Molar volume calculated using the additivity of molar volume(Barton, 1983).
[b]Calculated using substituent constants(Perrin et al., 1981).

On the other hand, 18C6 forms more stable complexes with lighter Ln. Therefore, since the extractability of Ln is affected by the complexation of both 18C6 and carboxylates, the difference in the extractability among Ln decreases. However, weak bases such as TCA are difficult to form stable mixed ligand complexes with Ln-18C6 but may rather form ion pairs or outer sphere complexes. Hence, the selectivity of Ln is affected by only the complexation with 18C6.

Enhancement of the selectivity

A skillful method for the enhancement of selectivity among Ln is proposed. The distribution ratio of Ln can be written in the presence of a complexing agent, EDTA(H_4Y); $D = [Ln(18C6)_n \cdot 3TCA]_{org}/([Ln^{3+}] + [LnHY] + [LnY^-])$. Therefore, the following equation is derived from Eq. 2 using the formation constant of the EDTA complexes, K_{MHY} and K_{MY},

$$\log D = 3 \log[TCA^-] + n \log[18C6]_{org} + \log K_{ex} - \log(1 + K_{MHY}[HY^{3-}] + K_{MY}[Y^{4-}]). \quad (4)$$

Since the stability constants of Ln-EDTA complexes increase with the atomic number of Ln, the last term on the right hand side in Eq. 4 should become larger negative values as the atomic number increases. Therefore, the separation of Ln would be promoted by both the selectivity of the extraction with 18C6 and that of the complexation with EDTA in the aqueous phase.

Figure 4 shows the effect of EDTA on the distribution ratio of Ln at various pH. The distribution ratio decreases with increase in pH by the complexa-

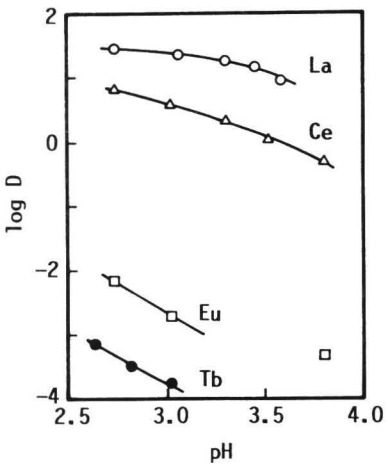


Fig.4. Effect of pH on the extraction of Ln(III) with 0.010 M 18C6 from 2.0 M LiTCA solutions in the presence of 2×10^{-5} M EDTA. 1,2-Dichloroethane.

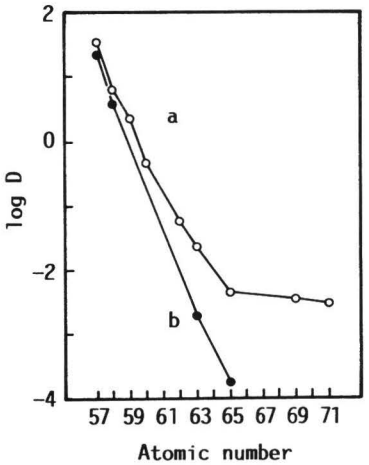


Fig.5. Effect of EDTA on the distribution ratio of Ln(III) in the 0.010 M 18C6-2.0 M LiTCA system. a, Without EDTA at pH 3.2-3.5; b, 2×10^{-5} M EDTA at pH 3.0-3.1.

tion of Ln with EDTA as expected from Eq. 4. The larger lowering of the distribution ratio with pH is found for heavier Ln, so that the difference of the distribution ratios among Ln increases. Figure 5 shows the relationship between the distribution ratio of Ln and the atomic number in the presence or absence of EDTA. The distribution ratio steeply decreases with the atomic number. The separation factors among Ln are raised by the addition of EDTA.

The separation factors for Ln are summarized in Table 2. The distribution ratios of seven Ln in the presence of EDTA were simultaneously determined using a Ge detector connected with a multichannel analyzer. The separation factors especially for the light Ln in the present 18C6-TCA-EDTA system are surprisingly higher than those previously reported, e.g., the HDEHP system (Ceccaroli, 1981).

The high separation efficiency for Ln with crown ethers can be achieved using 18C6, a strong carboxylic acid, HTCA, and a complexing agent, EDTA.

TABLE 2
Separation factors in the extraction of lanthanoid(III) with 18-crown-6 and trichloroacetate into 1,2-dichloroethane at 25 °C.

Ln	D(La)/D(Ln) 18C6-TCA-EDTA[a]	D(La)/D(Ln) 18C6-TCA[b]	D(Ln)/D(La) HDEHP-NH_4SCN[c]
Ce	3.93	4.07	6.10
Nd	2.37×10^2	7.24×10	1.51×10
Sm	6.69×10^3	7.08×10^2	1.40×10^2
Eu	3.35×10^4	1.66×10^3	3.20×10^2
Tb	7.08×10^5		2.80×10^3
Lu	$> 10^6$		1.24×10^6

[a]Multielement extraction in 0.010 M 18C6-1.0 M LiTCA-2.0 M LiCl-5.0×10^{-5} M EDTA at pH 3.44; log D(La) = 1.815.
[b]Calculated from $K_{ex}(La)/K_{ex}(Ln)$(see the text).
[c]Ceccaroli et al., 1981.

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STRIPPING RARE EARTH FROM ITS LOADED DI(2-ETHYLHEXYL)-PHOSPHATE COMPLEX BY OXALIC ACID

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ABSTRACT

Rare earth oxalate precipitated by directly contacting rare earth-loaded di(2-ethylhexyl)phosphoric acid (HDEHP) with oxalic acid solution was studied. The optimal conditions of A/O ratio, concentration of oxalic acid and three-phase separation were determinated and analyzed. Single stage of self-designed mixer-settler was used to carry out the three-phase extraction system, which satisfies the rare earth stripping, organic recirculating, and solid oxalate discharging from the mixer-settler. The application of direct precipitation method to rare earth stripping is of benefit to both chemicals and energy saving.

INTRODUCTION

Up to date, the technique of solvent extraction is primarily adapted in the rare earth industry (Ritcey and Ashbrook, 1979; Kaczmarek, 1981). The extractants widely used in rare earth extraction include di(2-ethylhexyl)phosphoric acid (HDEHP) (Peppard, et al., 1957; Hung, et al., 1982), tri-n-butyl phosphate (TBP)(Bauer and Shaw, 1964) and quaternary amine (e.g., Aliquat 336)(Moor,1964). Among these extractants, the HDEHP is usually employed in the rare earth-chloride media system. For a RE-HCl-HDEHP-kerosene system, the extraction reaction between HDEHP and rare earth (RE) could be expressed as

$$RE^{3+} + 3\,\overline{(HDEHP)_2} \rightleftharpoons \overline{RE(DEHP)_3(HDEHP)_3} + 3\,H^+ \qquad (1)$$

where the bar indicates organic species. HDEHP generally exists as dimeric form to incorporate in reaction. From eqn. (1), it is obvious that low acidity is favourable to the forward extraction and high acidity to reverse stripping. The most of final product of rare earth are of oxide form in commercial plant. Owing to the low solubility product of rare earth oxalate and ready to calcine to oxides, the oxalic acid is used in commercial process to precipitate rare earth oxalate from RE chloride solution after accomplishing separation and purification. From rare earth loaded in organic to the formation of rare earth

oxalate, tedious procedures are involved, usually including high acidic stripping, acid elimination and pH adjustment.

In the present study, the precipitation of rare earth oxalate by directly contacting RE-loaded HDEHP-kerosene organic solution with aqueous oxalic acid solution was investigated. The goal was to simplify the operation of RE stripping and RE oxalate precipitation.

2 EXPERIMENTAL

2.1 Reagents and procedures

HDEHP (Union Carbide Co., USA) with a purity of 95% was used without further purification. High grade kerosene (Union Chemical Works Ltd., Taiwan) was used as diluent. RE-HDEHP-kerosene solution was prepared by extracting RE into organic phase (HDEHP diluted in kerosene) from rare earth chloride solution. The rare earth chloride solution was prepared by dissolving the mixed rare earth oxides in hydrochloric acid. In the mixed rare earth oxides, Pr and Nd were the major constituents. The oxalic acid (MERCK) used was analytical grade.

2.2 Procedures

All tests were carried out by a shake-out method (Hoh et al., 1982). The RE-loaded organic solution mixed a given volume ratio of oxalic acid was poured into a separator funnel and then shaken mechanically for 60 minutes. After sufficient mixing, the whole volume was poured into a graduated cylinder for settling. The phase separation was observed and the height of the precipitate was recorded.

The continuous flow experiment was carried out with single stage of self-designed mixer-settler.

3 RESULTS AND DISCUSSION

3.1 Precipitation of rare earth oxalate

The solubility product of rare earth oxalate is very small (e.g., 2.5×10^{-27} for La, 3.2×10^{-26} for Ce, and 5.3×10^{-29} for Y), therefore, rare earth may be precipitated completely as oxalate salt in the presence of excess oxalic acid. The rare earth oxalate usually consists of crystalline water which can be expressed as $(RE)_2(C_2O_4)_2.xH_2O$. In the present study, the RE-loaded HDEHP organic was directly contacted with oxalic acid, and then the precipitate was formed. The heterogeneous phases reaction may be theoretically formulated as

$$2\ \overline{RE(DEHP)_3(HDEHP)_3} + 3\ H_2C_2O_4 + x\ H_2O \longrightarrow 6\ \overline{(HDEHP)_2} + (RE)_2(C_2O_4)_3.xH_2O\downarrow \qquad (2)$$

The effect of precipitation of RE oxalate was carried out by shake-out method. Phase volume ratio, concentration of oxalic acid, and RE in organic solution were selected as the study parameters. The concentration of HDEHP in kerosene was 1M for all cases. At the preliminary tests, the organic with 0.05M RE were shaken-out with 0.04M, 0.08M, 0.1M, 0.2M, 0.4M, 0.6M, 0.8M, and 1.0M of oxalic acid solution, respectively, by 1:1 volume ratio. The results showed that three phases were clearly separated after settling for the cases in which the concentration of oxalic acid were greater than 0.2M. The top lucid layers were organic and aqueous phases, and the bottom layer was oxalate precipitate. In the case of 0.2M oxalic acid, the colloidal was existed in the organic phase. Additionally, the phase separation became worse when the concentration of oxalic acid was less than 0.2M. A viscous colloidal was formed in such cases, and only a little amount of water appeared at the bottom of cylinder. Based on the above observation, it was anticipated that the oxalate crystalline may be very fine under the presence of insufficient excess of oxalic acid, so that the precipitates were dispersed in both of aqueous and organic and resulted in the formation of colloid.

As shown by further tests in Table 1, it was plausible that only a few ppm of rare earth was left in organic phase for all cases. It was thus evidenced that the aqueous oxalic acid can strip the rare earth from RE-loaded HDEHP almost completely. It seemed no restriction to achieve complete stripping, however oxalic acid must be excessive and aqueous volume must be enough to accommodate the oxalate precipitates.

The volume of precipitate (ppt) in Table 1 was recorded at the 90th day for settling via gravity force. In the first three cases with same TRE concentration, the same amount of RE precipitated was expected for the cases of same phase ratio. In fact different volumes of ppt were observed. Also the apparent stoichiometric number of oxalic acid with respect to RE, which calculated directly with concentration and initial volume, did not coincide with each other. The theoretical stoichiometric number is 1.5 as shown in eqn. (2). For the cases of 0.056 M TRE, all were less than 1.5. All were greater than 1.5 for other cases of 0.028 M TRE. It reveals that the growth rate and the orientation of ppt aggregate may be quite different in the different solutions.

From the operating viewpoint, fast phase separation was crucial. As noted in Table 1, fast phase separation was occurred in phase volume ratio of around 1:1. The colloidal was formed when the phase ratio of O/A was large (e.g., O/A=5 in Case 1). The solution became viscous and could not be separated. It was attributed to the interfacial condition and an insufficient aqueous room for precipitates.

TABLE 1

Stripping rare earth from organic by aqueous oxalic acid

Phase Volume Ratio (O/A)	Case 1: $[TRE]_i$ =0.056M $[H_2C_2O_4]_i$=1.0M				Case 2: $[TRE]_i$ =0.056M $[H_2C_2O_4]_i$=0.5M			
	$[TRE]_f$ (ppm)	$[H_2C_2O_4]_f$ (M)	ppt/Aq. (v/v)	S	$[TRE]_f$ (ppm)	$[H_2C_2O_4]_f$ (M)	ppt/Aq. (v/v)	S
100/20	1	-	-					
50/20	<0.5	-	0.641	c				
50/30	<0.5	0.873	0.467	c	<0.5	0.371	0.417	a
25/20	<0.5	0.903	0.383	a	<0.5	0.405	0.253	a
25/25	<0.5	0.917	0.302	a	<1	0.425	0.196	a
20/25					<0.5	0.442	0.160	a
30/50	<0.5	0.952	0.160	a	<0.5	0.459	0.120	ab
30/75	<0.5	0.973	0.108	ab	<0.5	0.470	0.067	ab
25/125	<0.5	0.979	0.096	ab	<0.5	0.477	0.032	ab
Phase Volume Ratio (O/A)	Case 3: $[TRE]_i$ =0.056M $[H_2C_2O_4]_i$=0.34M				Case 4: $[TRE]_i$ =0.028M $[H_2C_2O_4]_i$=0.54M			
	$[TRE]_f$ (ppm)	$[H_2C_2O_4]_f$ (M)	ppt/Aq. (v/v)	S	$[TRE]_f$ (ppm)	$[H_2C_2O_4]_f$ (M)	ppt/Aq. (v/v)	S
50/30	<1	0.210	0.403	c	<0.5	0.461	0.233	ac
25/20	<0.5	0.240	0.350	c	<0.5	0.481	0.150	a
25/25	<0.5	0.263	0.296	c	<0.5	0.491	0.108	a
20/25	<1	0.276	0.244	c	<1	0.495	0.104	a
30/50	<0.5	0.294	0.158	ac	<0.5	0.508	0.061	ab
30/75	<0.5	0.312	0.128	ac	<0.5	0.516	0.036	ab
25/125	<0.5	0.326	0.080	ab	<0.5	0.522	0.020	ab

Note: " S " represents the situation of three phases separation.
a --- clear three phases and interface.
b --- a few precipitate dispersing in organic phase.
c --- some water-in-oil bubbles suspensing in aqueous phase and some embedded in precipitate.

3.2 Organic solution recycle

Recycling of organic solution was one of the features in solvent extraction system. Each cycle of organic includes extraction, scrubbing, stripping and washing, in which the organic contacts with different aqueous solution in sequence. No matter what solution contacted and how long it took, the extractability of extractant solution should be maintained.

The extractability was expressed by extraction percentage, and determined by shake-out test. The results were listed in Table 2. The data indicated that no any change on extraction percentage between the freshed (the 1st) and the reused organics (the 2nd and the 3rd) was found. The concentration of total extractant (including HDEHP and mono-2-ethylhexyl phosphoric acid, H2MEHP) was slightly increased. It could be explained that the entraintment of oxalic acid in organic

TABLE 2

Extractability test of recycled organic solution

Test No.	Organic Solution			Feed		Raffinate		Extraction Percentage
	HDEHP, M	H2MEHP, M	Total, M	TRE, M	pH	TRE, M	pH	
1st	0.877	0.166	1.043	0.15	3.15	0.08	1.15	46.7
2nd	0.899	0.177	1.076	0.15	3.15	0.08	1.14	46.7
3rd	0.900	0.180	1.080	0.15	3.15	0.08	1.08	46.7

Note: The RE-HDEHP-kerosene organic was stripped by 1M $H_2C_2O_4$ with O:A=1:1.

phase results in the deviation of potentiometrical titration. Also the lose of diluent kerosene is another possible. Anyway, the test results elucidated that the HDEHP-kerosene organic can be recycled in an extraction system, because the organic phase was still lucid and its extraction activity was unchanged after contacting with oxalic acid solution.

3.3 Mixer-settler for continuous flow

Based on the shake-out experimental data, a mixer-settler suitable for continuous flow operation was designed. The mixer-settler consists of three chambers, as shown in Fig.1.

Chamber "A" provides sufficient room for mixing. The total flow rate of both organic and aqueous streams should be controlled to be having proper resident time. Chamber "B", with large spatial volume and inclined bottom, enhances the three phases taking longer time for settling and the solid phase slipping down automatically. Chamber "C" assembled a stirrer makes the precipitate to fly about. The precipitate can be discharged continuously from upper exit of chamber "C". The position of exit is also used to control the level of interface between organic and aqueous phases. During the continuous flow operation, both streams of RE-loaded organic and oxalic acid solution were pumped into

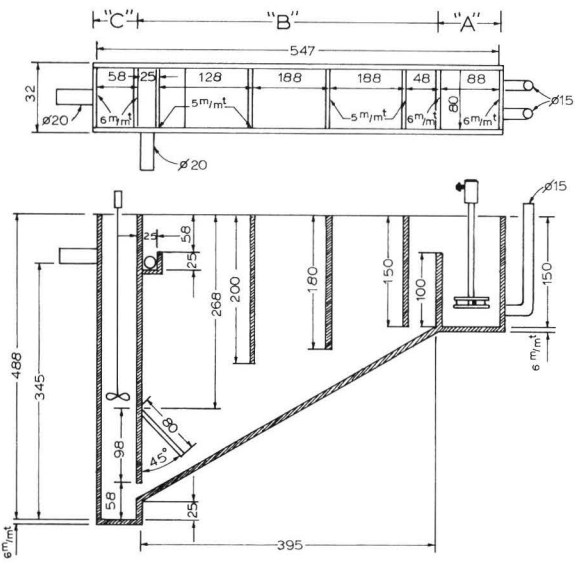


Fig. 1. Mixer-settler for continuous flow

TABLE 3

Experimental results of continuous operation by single stage mixer-settler

Run No.	Flow Rate ml/min	La	Ce	Pr	Nd	Sm	$[H_2C_2O_4]_f$ M	Notes:
				ppm				Initial condition
								Org.: 1M HDEHP; 0.05M TRE
1*	O/A=30/30	.2	<.1	.4	2.7	<.1	0.432	Aq. : 0.5M oxalic acid
2	O/A=40/40	.1	<.1	.3	2.5	<.1	0.438	Mixing & dia. of stirrer head
3	O/A=50/50	.4	<.1	1.1	5.9	<.1	0.432	1400 min^{-1}, 4 cm
4	O/A=60/60	.3	<.1	.8	4.3	<.1	0.433	* 1800 min^{-1}, 3cm

chamber "A" simultaneously by metering pumps. Samples were taken from chamber "A" and were analyzed for the residual RE in organic and the oxalic acid in aqueous phase, separately. The results were satisfactory as shown in Table 3. The rare earth left in the organic phase was less than 10 ppm, and lucid phases were obtained in chamber "B".

4 CONCLUSION

It was feasible, from the results of shake-out tests, that the rare earth can be stripped out from RE-loaded HDEHP-kerosene by directly contacting with aqueous oxalic acid. The heterogeneous stripping meets the requirements of (1) complete stripping, (2) well organic-aqueous-solid phase separation, (3) reusable organic HDEHP-kerosene solution, and (4) recovery of the excess oxalic acid. A single stage of mixer-settler was designed conceptually. It is suitable for continuous operation with complete stripping, organic recycling and continuous discharging the precipitates.

The heterogeneous stripping can be applied in traditional rare earth extraction process, and can be in place of stripping with high acid, acid removal and oxalate precipitaton. From economic point of view, it is of benefit to both chemicals and energy saving. Further studies have to be done to ensure the reliability of the recycled organic.

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STUDIES ON THE EXTRACTION OF ReO_4^- BY USE OF CROWN ETHERS

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The distribution of ReO_4^- between aqueous solutions of alkali metal hydroxides and organic solutions of 12C4, 15C5, 18C6, DB18C6, DCH18C6 and DB24C8 dissolved in 1,2-dichloeroethane follows the model of size matching of the cation to crown cavity. The highest power of extraction was obtained for the ion pair K^+DCH18C6ReO_4^- and Na^+12C4ReO_4^- which is reflected on the relation of logD_{Re} vs the cationic diameters. Preliminary results of the slope analysis reveal the exraction of 1:1:1 complexes for M^+ crown ReO_4^- and 1:2:1 complexes for $K^+(15C5)_2ReO_4^-$ and $Rb^+(15C5)_2$-ReO_4^-. On the other hand, the extraction of Re increases steadily with the polarity of the organic solvent where the relation of logD_{Re} vs the log of dielectric constant is almost linear. The order of extraction follows the sequence: benzene < chloroform < chlorobenzene < 1,2-dichloroethane < nitrobenzene. The stability of the extracted complexes is clearly manifested by the enthalpy of extraction, ΔH_{ex} (KJ/mole), which was determined for K^+12C4ReO_4^- (22.8), K^+18C6ReO_4^- (-16.3), $K^+(15C5)_2ReO_4^-$ (-36.3), Li^+18C6ReO_4^- (23.4), and Na^+18C6ReO_4^- (-5.9).

INTRODUCTION

The selectivity of crown ehters and cryptands towards the extraction of hydronium ion, alkali- and alkaline earth metal ions could be utilized for the extraction separation of cations capable of forming anionic species. These anions combine with the solvated cations to form thermodynamically stable ion-pairs (solvent separated or contact ion pairs). In general the value of the distribution coefficient of the anionic species D_X is affected by the charge dencity-size of the cation, size and substitutions of the crown cavity, nature of the organic solvent, consequently the degree of association in the organic phase, and the constituents of the aqueous phase (especially the presence of simple aliphatic alcohols) [Hiraoka, 1978].

With a high selectivety, TeO_4^- was separated from various elements in acidic as well as basic solutions using crown ethers [Jalhoom 1986 a,b, 1988]. A potential extraction for Re was accessible from neutral (chlorides of alkali and alkaline earth metal ions) and acidic (HCl and H_2SO_4) solutions [Jewad, Al-Murab, Jalhoom, 1989]

In this work data are given on the distribution of ReO_4^- be-

tween aqueous solutions of alkali metal hydroxides and crown ethers dissolved in 1,2-dichloroethane (DCE).

The extraction of ReO_4^- from solutions of alkali metal hydroxides may be simply represented by:

$$M_{aq}^+ + lL_{org} + ReO_4^- \xrightleftharpoons{K_{ex}} (M^+L_lReO_4^-)_{org} \qquad (1)$$

and

$$\log D_{Re} = \log K_{ex} + \log [M^+] + l\log[L]_{org} \qquad (2)$$

where $M^+ = Li^+$, Na^+, K^+, Rb^+, and Cs^+; L= 12C4, 15C5, 18C6, DB18C6, DCH18C6, and DB24C8.

EXPERIMENTAL

Crown ethers were supplied by Fluka and Merck. Fresh solutions of the hydroxides (analar BDH products or prepared from passing chlorides on a strong anion exchange resin) were standardized before use. Fresh stock solutions of rhenium were prepared by dissolving the exact weight of Re_2O_7 (99.9% Riedel Dehean) in distilled water to prepare 0.00011 mole/litre Re. Organic solvents of analar grade (BDH) were used without further purification.

Distribution experiments were performed in a jacketed Lewis cell so as to maintain the temperature within ±0.1°C. The concentration of Re in the aqueous phase was determined by the thiocyanate method [Marczenko 1986]. The concentration in the organic phase was determined by stripping or by the difference of the concentrations in the aqueous phase before and after the extraction.

RESULTS AND DISCUSSION

In general the extraction of rehnium increases with the increase of the cations concentration in the aqueious phase and the concentration of the crown ether in the organic phase.

Variation of $\log D_{Re}$ with the cationic diameter of the extracted ion pair $M^+ReO_4^-$ is shown in Fig. 1. Except with DB18C6 and DB24C8, the model of size holds. Peak maxima are achieved at Na^+ 12C4ReO_4^- and K^+-other crowns. The anomalous behaviour of the dibenzo compounds has also been observed with TcO_4^- extraction

[Jalhoom 1988] which might be ascribed to the lower solubility of the extracted complex in the organic phase. Due to its enhanced basicity and flexibility, DCH18C6 gives the best Re extraction.

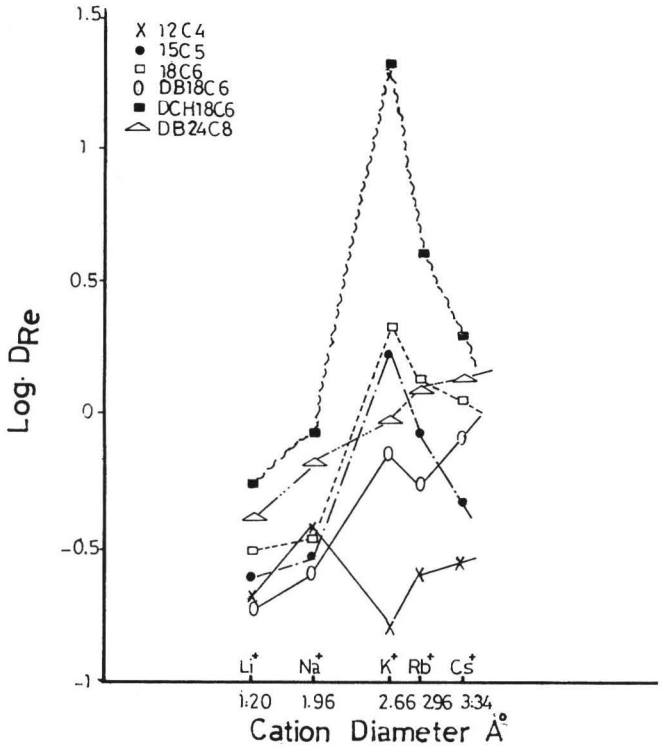


Fig.(1). Relation of Log·D_{Re} vs. Cation Diameter
0.01M Crown-DCE-0.1M MOH, [Re] =0.00011M

Slope analysis data for the relation of logD_{Re} vs log[L] in the organic phase reveal, in general, the extraction of the 1:1:1, complex $M^+:L:ReO_4^-$ where the value of the slope approaches unity. However, a slope of around 2 was obtained for K^+-15C5 and Rb^+-15C5 which indicates the extraction of the sandwitched structure $K^+(15C5)_2ReO_4^-$ and $Rb^+(15C5)_2ReO_4^-$. Values lower than or equal to 0.5 may, on the other hand, indicate either the presence of an error coming from the large solubility of 12C4 and its complexes in the aqueous phase or the formation of 2:1:2 or club sandwitch structure of the type 2:3:2.

Table 1
Data of the slope analysis for the relations $\log D_{Re}$ vs log[L]

		12C4 1.2-1.5Å	15C5 1.7-2.2Å	18C6 2.6-3.2Å	DB24C8 4.5-5.6Å
Li^+	1.20Å	0.40	0.45	0.50	1.20
Na^+	1.96Å	1.0	1.0	0.50	0.50
K^+	2.66Å	0.51	1.50	0.68	0.63
Rb^+	2.96Å	0.35	1.8	0.80	1.0
Cs^+	3.34Å	0.56	0.90	1.3	0.92

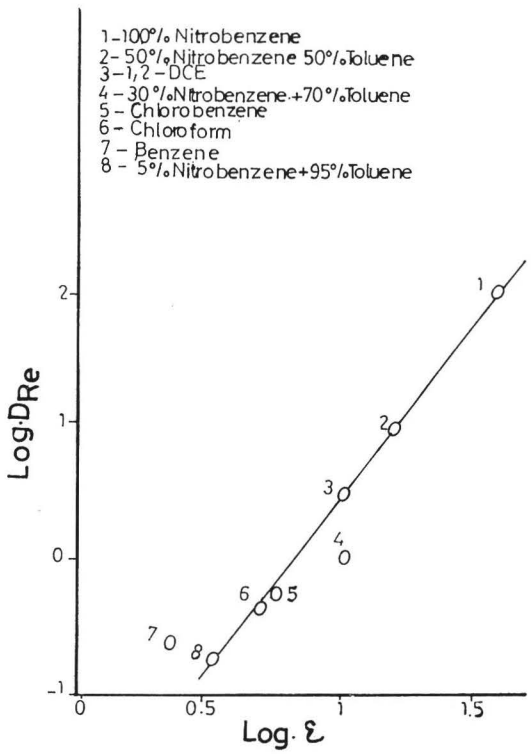


Fig.(2) Relation of Log.D vs Log. dielectric constant
0.01M DB18C6 - 3MKOH, [Re] =0.00011M

The relation of $\log D_{Re}$ vs the log of dielectric constant of some organic solvents is linear (Fig. 2). The order of extraction is toluene < 5% nitobenzene + 95% toluene < benzene < chloroform < 30% nitrobenzene + 70% toluene < 1,2-dichloroethane < 50% nitrobenzene + 50% toluene < nitrobenzene. This linearity reflects the

electrostatic contribution to the free energy of solvation predicted by Born equation. Methanol on the other hand gives perceptible enhancement for the extraction of Re. The presence of 60% methanol in the aqueous phase causes an increase around one order of magnitude in the value of D_{Re} when K^+-DB18C6 was used.

On the other hand the enthalpy of extraction (ΔH_{ex}) determined by the temperature coefficient method can also reflects on the structure of the extacted complelx. The mutual size contribution of cation-crown cavity to the electrostatic interactions between the solvated counter ions of the ion pairs is clearly manifested by ΔH_{ex} for $Li^+18C6ReO_4^-$ (23.4 KJ/mol), $Na^+18C6ReO_4^-$ (-5.9 KJ/mole), $K^+18C6ReO_4^-$ (-16.3 KJ/mole), $K^+(15C5)_2ReO_4^-$ (-36.3 KJ/mole), and $K^+12C4ReO_4^-$ (+23.8 KJ/mole).

The separation of ReO_4^- ions from MoO_4^{2-}, WO_4^{2-}, CrO_4^{2-}, and MnO_4^- ions is accessible at the basic and acidic solutions.

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SOLVENT EXTRACTION OF MERCURY(II) FROM HYDROCHLORIC ACID SOLUTIONS

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ABSTRACT
The extraction of mercury(II) from hydrochloric acid solutions by sulphur containing compounds (dihexyl sulphide, DHS and dihexyl sulphoxide, DHSO), high-molecular weight amines (trioctylamine, TOA and trioctylmethylammonium chloride, TOMAC), and neutral organophosphorus compounds (tributyl phosphate, TBP and trioctyl phosphine oxide, TOPO) has been investigated under different conditions. As a result, it is found that the extraction efficiency for mercury-(II) of DHS, DHSO, TOA, TOMAC, TBP and TOPO is in the order TOMAC>TOA>TOPO>DHSO> DHS>TBP. With increasing aqueous hydrochloric acid concentrations, the distribution coefficient for DHS decreases below 1 mol dm^{-3} acid and its decrease becomes gently above this acidity; the distribution coefficient for DHSO decreases up to a minimum at 2 mol dm^{-3} acid and then rises above this acidity; the distribution coefficient for TOA increases gradually up to a maximum at 1 mol dm^{-3} acid and falls over this acidity, but becomes gently at 4 mol dm^{-3} acid and again falls sharply above 6 mol dm^{-3}; the distribution coefficient for TOMAC increases gradually up to a maximum at 1-2 mol dm^{-3} acid and falls at higher acidities; the distribution coefficient for TBP decreases with aqueous acidity up to a minimum at ~1 mol dm^{-3} acid and then rises at higher acidities.

1 INTRODUCTION

We have used sulphur containing compounds such as dihexyl sulphide (DHS, R_2S) and dihexyl sulphoxide (DHSO, R_2SO) for solvent extraction of mercury(II) from aqueous acid solutions (Sato et al., 1983, 1986 a,b). In contrast, we have investigated the extraction of some metals from aqueous acid solutions by high-molecular weight amines such as trioctylamine (TOA, R_3N) and triocthyl-methylammonium chloride (TOMAC, $R_3R'NCl$) and by neutral organophosphorus compound such as tributyl phosphate (TBP) and trioctyl phosphine oxide (TOPO). In this paper, therefore, we extend the work to obtain further information on the extraction of mercury(II) from hydrochloric acid solutions by DHS, DHSO, TOA, TOMAC, TBP and TOPO.

2 EXPERIMENTAL

Reagents

High purity DHS (Daihachi Chemical Industry Co., Ltd., Osaka) was used without further purification. The DHSO was synehesized by means of oxidation from

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DHS as follows (Ogura et al., 1972) : 1) 35 cm^3 each of acetic acid and acetic anhydride and 20 cm^3 of aqueous solution of hydrogen peroxide in 30 % were added to 50 cm^3 of DHS dropwisely for during 1 hr.; the mixture was cooled with ice, and then the resulting mixture was stripped for 3 hr. at 0°C. 2) After end of the reaction was confirmed by TLC, DHSO extracted into chloroform was washed at first with water and then with 10 % sodium carbonate, and finally with water again. 3) White crystal obtained from the removal of chloroform by evaporator was refined by recrystallization method. The DHS and DHSO were dissolved in benzene.

High purity TOA and TOMAC (Koei Chemical Industry Co., Ltd., Osaka) were used without further purification and diluted with benzene.

TBP (Daihachi Chemical Industry Co., Ltd.) was purified by the usual method (Alcock et al., 1956), and TOPO (Hokko Chemical Industry Co., Ltd.) was used without further purification. TBP and TOPO were diluted and dissolved, respectively, in benzene.

Aqueous solutions of mercury(II) were prepared by dissolving its chloride in hydrochloric acid of the selected concentration, and in general the mercury concentration was 1 g dm^{-3} mercuric chloride (0.00368 mol dm^{-3} $HgCl_2$). The used chemicals were of analytical reagent grade.

Extraction and analytical procedures

Equal volumes (15 cm^3 each) of organic and aqueous phases were placed in 50 cm^3 stoppered conical flasks and shaken for a selected in a water bath thermostatted at 20°C, except the experiment on temperature effect. Preliminary experiments showed that equilibrium was complete in 10 min for all extractants.

The mixture was quickly separated by centrifuge, and metal in organic phase was stripped with hydrochloric acid of 1 mol dm^{-3} for DHS and DHSO, and with nitric acid of 0.5 mol dm^{-3} for TBP. The concentration of mercury in aqueous solution was determined by EDTA titration at pH 10 in the presence of excess Mg-EDTA using Eriochrome Black T (BT) as indicator (Flaschka, 1972). But the concentration of mercury in the organic phase for TOA, TOMAC and TOPO was determined by the subtraction of the initial aqueous total concentration of mercury from the organic concentration of mercury. The distribution coefficient, E_a°, was obtained as the ratio of the equilibrium concentration of mercury(II) in the organic phase to that in aqueous phase. The concentration of chloride and the water content in the organic phase were examined by Volhard's method with nitrobenzene and Karl Fischer titration.

IR, Raman and NMR spectral measurements

The infrared (IR) spectra of the organic extracts were measured on a JASCO infrared recording spectrophotometer Model IRA-1 (4000-650 cm^{-1}) and IR-F (700-200 cm^{-1}) using a capillary film between tallium halide plates or polyethylene films. The Raman spectra of the organic extracts were measured on a JASCO

Laser Raman Spectrophotometer Model R-300. Nuclear magnetic resonance (NMR) spectra were obtained for the organic extracts dissolved in carbon tetrachloride using JEOL Model JNM-PMX60SO NMR spectrometer in the use of tetramethylsilane as an internal reference.

Measurement of apparent molecular weight

The apparent molecular weight of the complexes prepared by evaporation of the organic diluent in the organic extracts saturated by metal was determined in benzene on a Hitachi Model 115 isothermal molecular weight apparatus.

3 RESULTS AND DISCUSSION

3.1 Extraction isotherms by DHS and DHSO

The extraction of mercury(II) from hydrochloric acid solutions containing 1 g dm^{-3} mercuric chloride was carried out with DHS and DHSO in benzene. The distribution coefficient for DHS decreases with aqueous acidity below 1 mol dm^{-3} acid and its decrease becomes gently above this acidity, while the distribution coefficient for DHSO decreases with increasing aqueous acidity and approaches a minimum at 2 mol dm^{-3} acid, and then rises above this acidity, although the extraction efficiency for mercury(II) of DHSO is higher than that of DHS. The log-log plots of E_a° vs. the equilibrated concentration of DHS and DHSO at constant hydrochloric acid concentrations give straight lines with the slope of nearly two. These results suggest that the distribution coefficient has the second power dependence on the concentrations of DHS and DHSO, indicating the formation of di-solvate in the extraction at low aqueous acidity by DHS and DHSO.

In the extraction of mercury(II) at low aqueous acidity ($[HCl]_{init\ aq} \leq 2$ mol dm^{-3}) by DHS or DHSO in benzene, the continuous variation of $[Hg]_{org}$ as a function of molar fraction of $[Hg]_{init\ aq}/([Hg]_{init\ aq} + [R_2S]_{init}$ or $[R_2SO]_{init}$) at a fixed total $[Hg]_{init\ aq} + [R_2S]_{init}$ or $[R_2SO]_{init}$ shows the maxima at the molar fractions of 0.5 and 0.33 at initial aqueous hydrochloric acid concentrations in 0.1 and 1 mol dm^{-3}, respectively. This implies that the combination molar ratio of DHS or DHSO with mercury is in the molar ratios of 1 : 1 and 2 : 1 in the extraction from hydrochloric acid solutions at 0.1 and 1 mol dm^{-3} respectively. Besides the repeated extractions of mercury(II) from fresh aqueous solution containing 0.1 mol dm^{-3} mercuric chloride with 0.2 mol dm^{-3} DHS and DHSO in benzene at constant hydrochloric acid concentration of 0.02 mol dm^{-3} give the result that the molar ratio $[R_2S]$ or $[R_2SO]/[Hg]$ in the organic phase approaches a limiting value of unity, suggesting that the stoichiometrical species $HgCl_2 \cdot R_2S$ or $HgCl_2 \cdot R_2SO$ is formed in the increase of mercury(II) loading.

On the one hand the extraction of mercury(II) from hydrochloric acid solutions at higher acidity by DHSO was surveyed by the similar manners to its ex-

traction at low acidity. As a result it was found that the stoichiometric species of $HgCl_2 \cdot 2R_2SO$, $HgCl_2 \cdot HCl \cdot 3R_2SO$ and $HgCl_2 \cdot 2HCl \cdot 2R_2SO$ are formed gradually in the organic phase with increasing aqueous acidity.

The organic extracts of mercury(II) from fresh aqueous solutions containing 0.1 mol dm^{-3} of mercuric chloride in 0.02 mol dm^{-3} hydrochloric acid with 0.2 mol dm^{-3} DHS and DHSO in benzene at 20°C were examined by IR spectrophotometry. The organic extracts exhibit the following absorptions in addition to the absorption bands of the alkyl groups due to DHS and DHSO : for the extracts by DHS, the C-S stretching vibration at 720 cm^{-1}, shifted from the bands which appear at 760 and 720 cm^{-1} in a free DHS, and the Hg-Cl stretching frequency at 290 cm^{-1}; for the extraction by DHSO, the spectra of the organic extracts exhibit absorptions due to the S=O stretching vibrations at 990 cm^{-1}, shifted from the band which appears at 1050 cm^{-1} in a free DHSO, and the Hg-O and Hg-Cl stretching frequencies at 365 and 300 cm^{-1}, respectively. Accordingly the IR result indicates the formation of species in which chloride is coordinated to mercury, supported by the result of the determination of chloride concentration in the organic phase, and simultaneously it confirms that the DHSO coodinates to mercury through the oxygen atom. This result is also supported by NMR spectral one.

Furthermore the Raman spectra of the organic extracts from 0.02 mol dm^{-3} hydrochloric acid solutions by DHS and DHSO in benzene reveal the absorptions due to $HgCl_2$ at 280 and 310 cm^{-1} respectively, suggesting the formation of the species $HgCl_2 \cdot 2R_2S$ and $HgCl_2 \cdot 2R_2SO$. With increasing the concentration of mercury in the organic phase, however, the absorptions at 310 and 320 cm^{-1} appear as shoulder in addition to the bands due to the species with DHS and DHSO, respectively, suggesting the formation of polymeric species. This is supported by the result for the measurement of the apparent molecular weight of the complex which exists as a dimer. In addition, the organic extracts of mercury(II) from aqueous solutions containing mercuric chloride in 1, 3 and 7 mol dm^{-3} hydrochloric acid give the absorption bands at 310, 285 and 270 cm^{-1} assigned to $HgCl_2$, $HgCl_3^-$ and $HgCl_4^{2-}$, respectively.

Hence it is considered that the extractions of mercury(II) by DHS and DHSO are expressed as the following equilibrium equations : for the extraction by DHS,

$$HgCl_2(a) + 2R_2S(o) \rightleftharpoons HgCl_2 \cdot 2R_2S(o) \qquad (1)$$

and with increasing the concentration of mercury in the organic phase

$$2HgCl_2(a) + 2R_2S(o) \rightleftharpoons Hg_2Cl_4 \cdot 2R_2S(o) \ ; \qquad (2)$$

for the extraction by DHSO, at low aqueous acidity

$$HgCl_2(a) + 2R_2SO(o) \rightleftharpoons HgCl_2 \cdot 2R_2SO(o) \qquad (3)$$

and with increasing mercury in the organic phase

$$2HgCl_2(a) + 2R_2SO(o) \rightleftharpoons Hg_2Cl_4 \cdot 2R_2SO(o), \quad (4)$$

and then at higher acidity, depending on the aqueous acidity

$$HgCl_3^-(a) + H^+(a) + 3R_2SO(o) \rightleftharpoons HHgCl_3 \cdot 3R_2SO(o) \quad (5)$$

and

$$HgCl_4^{2-}(a) + 2H^+(a) + 2R_2SO(o) \rightleftharpoons H_2HgCl_4 \cdot 2R_2SO(o) \quad (6)$$

where (a) and (o) represent aqueous and organic phases respectively.

3.2 Extraction isothrms by TOA and TOMAC

The extraction of mercury(II) from aqueous solutions containing mercuric chloride in hydrochloric acid by TOA and TOMAC in benzene was carried out by varying aqueous acidity. With increasing aqueous hydrochloric acid concentrations, the distribution coefficient for TOA increases gradually up to a maximum at 1 mol dm^{-3} acid and falls over this acidity, but becomes gently at 4 mol dm^{-3} acid and again falls sharply above 6 mol dm^{-3}, while the distribution coefficient for TOMAC increases gradually up to a maximum at 1-2 mol dm^{-3} acid and falls at higher acidities, although the extraction efficiency for mercury-(II) of TOMAC is higher than that of TOA.

From the results for the dependency of distribution coefficient on TOA concentration and the continuous variation of $[Hg]_{org}$ as a function of $[Hg]_{init\ aq}$ at fixed total concentration of $[Hg]_{init\ aq}$ and $[TOA]_{init}$, it is found that the organic species is in the molar ratios of [TOA]/[Hg] = 1 and 2 at low and higher aqueous acidities, respectively. For the extraction by TOMAC, the continuous variation examination and the loading test of $[Hg]_{org}$ indicated that the composition of the organic species has the molar ratio of [TOMAC]/[Hg] = 1. Further the IR spectrophotometry and the measurement of the apparent molecular weight were carried out for the organic extracts of mercury(II) from hydrochloric acid solutions by TOA and TOMAC in benzene. Furthermore the Raman spectra of the organic extracts from aqueous solutions containing mercury in hydrochloric acid revealed the absorptions due to $HgCl_2$, $HgCl_3^-$ and $HgCl_4^{2-}$ with increasing the aqueous acidity.

Therefore it is thought that the extractions of mercury(II) by TOA and TOMAC are expressed as the following equilibrium equations : for the extraction by TOA, at low aqueous acidity

$$2HgCl_2(a) + 2R_3NHCl(o) \rightleftharpoons (R_3NH)_2Hg_2Cl_6(o) \quad (7)$$

and at higher aqueous acidity

$$HgCl_2(a) + 2R_3NHCl(o) \rightleftharpoons (R_3NH)_2HgCl_4(o) \ ; \quad (8)$$

for the extraction by TOMAC,

$$2HgCl_3^-(a) + 2R_3R'NCl(o) \rightleftharpoons (R_3R'N)_2Hg_2Cl_6(o) + 2Cl^-(a). \quad (9)$$

This is also supported by IR and NMR spectral results.

3.3 Extraction isotherms by TBP and TOPO

The extraction of mercury(II) from aqueous solutions containing mercuric

chloride in hydrochloric acid by TBP and TOPO in benzene was carried out at different aqueous acidities. With increasing aqueous acidity, the distribution coefficient for TBP decreases below 1 mol dm^{-3} acid and rises above this acidity, while the distribution coefficient for TOPO decreases below 1 mol dm^{-3} acid and rises to maximum at 4 mol dm^{-3} acid and then falls at higher acidity. The extraction efficiency for mercury(II) of TOPO is higher than that of TBP. For these extraction systems, the solvent-dependency and the continuous variation of mercury concentration in the organic phase were examined under various conditions. Further the organic extracts were surveyed by IR, NMR and Raman spectral results.

Thus it is inferred that the extraction of mercury(II) from hydrochloric acid solutions by TBP and TOPO is expressed by the following equilibrium equations : with increasing aqueous acidity, for TBP

$$HgCl_2(a) + 2TBP(o) \rightleftharpoons HgCl_2 \cdot 2TBP(o), \quad (10)$$

$$HgCl_3^-(a) + H^+(a) + 3TBP(o) \rightleftharpoons HHgCl_3 \cdot 3TBP(o) \quad (11)$$

and

$$HgCl_4^{2-}(a) + 2H^+(a) + 4TBP(o) \rightleftharpoons H_2HgCl_4 \cdot 4TBP(o), \quad (12)$$

and for TOPO

$$HgCl_2(a) + 2TOPO(o) \rightleftharpoons HgCl \cdot 2TOPO(o), \quad (13)$$

$$HgCl_3(a) + H^+(a) + 2TOPO(o) \rightleftharpoons HHgCl_3 \cdot 2TOPO(o) \quad (14)$$

and

$$HgCl_4^{2-}(a) + 2H^+(a) + 2TOPO(o) \rightleftharpoons H_2HgCl_4 \cdot 2TOPO(o). \quad (15)$$

3.4 Temperature effect

In the extraction of mercury(II) from hydrochloric acid solutions at 10-50°C, with rising temperature the distribution coefficients for DHS, DHSO, TBP and TOPO decrease, while the distribution coefficients for TOA and TOMAC increase, although the extraction efficiency for mercury(II) is in the order TOMAC>TOA> TOPO>DHSO>DHS>TBP.

ACKNOWLEDGEMENTS

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THE PECULARITIES OF MOLYBDENUM(VI) AND VANADIUM(V) EXTRACTION BY LIPOPHILIC QUATERNARY AMMONIUM SALTS

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ABSTRACT

The solvent extraction of molybdenum(VI) and vanadium(V) by a lipophilic quaternary ammonium salts (Aliquat 336®) has been investigated in a large domain of acidity (pH = 0 to 14). The extraction of Mo(VI) is the most efficient between about pH = 1 and pH = 7, whereas the extraction of V(V) can be efficiently achieved from pH = 1 up to about pH = 10. In both cases, the extraction is rapid in agreement with a mere anion exchange mechanism involving the polyanionic species of Mo(VI) and V(V). The stripping of Mo(VI) and V(V) can be performed by mixing the organic phases with aqueous alkaline solutions. The stripping is the result of the transformation of the polyanionic species of Mo(VI) and V(V) into MoO_4^{2-} and VO_4^{3-}, respectively. Such a transformationis rapid for molybdenum(VI) (equilibrium reached within a few minutes), but slow for vanadium(V) (more than 1 hour is required). During the extraction or stripping steps, unexpected side-reactions have been observed. One of them is the slow precipitation of $(R_3R'N)_2Mo_6O_{19}$ from the organic phase when an aliphatic diluent such as kerosene is used. Other side-reactions are redox in nature. In particular, during extraction of V(V) from acidic solutions both a blue color develops in the aqueous phase likely as a result of the appearence of VO^{2+}, and green isopolyanionic species such as $[V_3(V)V_7(IV)O_{24}H]^{4-}$ or $[V_7(V)V_3(IV)O_{26}H]^{4-}$ slowly appear in the organic phase. In the same way, a blue color associated with the appearence of isopolyanionic species such as $[Mo_4(VI)Mo_2(V)O_{18}]^{2-}$ develops in the organic phase during the stripping of Mo(VI). Such phenomena have however a limited extent under the usual conditions of solvent extraction.

INTRODUCTION

This paper deals with the recovery and separation of molybdenum(VI) and vanadium(V) from aqueous leaching solutions of spent catalysts used in the mineral-oil industry. Besides alumina, the composition of such catalysts is as follows : molybdenum 5 to 10 %, vanadium 5 to 15 %, nickel or cobalt 2 to 5 % and phosphorus (variable). It should be pointed out that vanadium is not present in the fresh catalysts. In fact, vanadium is a poison of the catalysts and comes from crude-oil. It is shown here that recovery and separation of molybdenum (VI) and vanadium (V) can be achieved by liquid-liquid extraction with a lipophilic quaternary ammonium salt (namely, Aliquat 336®). The solvent extraction of molybdenum (VI) and vanadium (V) by lipophilic quaternary ammonium salts or high-molecular weight amines has been extensively investigated (Karagiozov et Vasilev, 1981 and 1984; Lee et al., 1984; Ritcey and Lucas, 1979; Sato et al., 1986; Wang et al., 1988), but the best conditions of their separation were not reported. Moreover, we report the existence of a series of side-reactions occurring either during extraction or stripping of these two metal species.

EXPERIMENTAL

Reagents

Aliquat 336®, kerosene and mesitylene were from Janssen Chimica, Fluka AG. and Merck, respectively. The other reagents from various suppliers were all analytical grade.

Analytical

The determinations of Mo, V and P in aqueous phases were carried out either by atomic absorption spectrophotometry with a Video 11 Instrument Laboratory spectrophotometer or by ICP with an ICP 1500 Plasma-Therm instrument. The other spectroscopic instruments used were a HP 8451A UV-visible spectrophotometer, a Perkin-Elmer 580B infrared spectrometer and T 800 Coderg Raman spectrometer. Chloride ions determinations were performed in a classical way by titrimetry with silver nitrate (Charlot, 1974). Finally, pH measurements were carried out with a TB/HA glass electrode and a PHN 75 pH-meter (Tacussel, France).

RESULTS AND DISCUSSION

1 Solvent extraction of Mo(VI), V(V) and P(V) by Aliquat 336®. Optimum conditions of separation

1.1 Extraction of Mo(VI), V(V) and P(V) taken separately

(a) Molybdenum (VI)

In figure 1, the percentage of extraction of Mo(VI) has been plotted as a function of pH for various concentrations of Aliquat 336®.

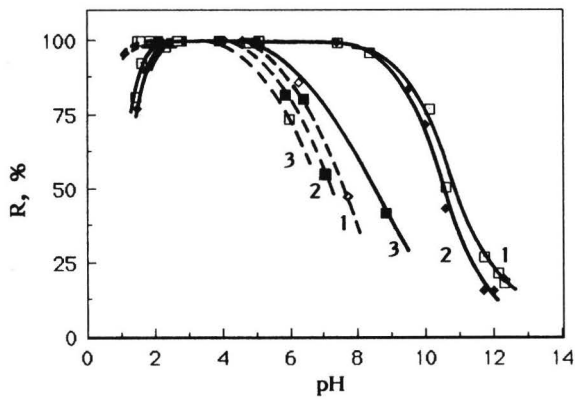


Fig. 1. Percentage of extraction of Mo(VI) and V(V) (taken separately and initially 0.10 mol/L) at equilibrium by Aliquat 336® as a function of pH, at 25°C. Diluent = kerosene + 10% (weight) n-decanol. [Aliquat 336®] (mol/L) = (1) 0.20; (2) 0.10 and (3) 0.05. Phase ratio = 1. Mo(VI) : - - - - - - - - - - - - -; V(V) : ————————

Examination of this figure shows that the yield of extraction reaches its highest values between pH = 1.5 and 5.5 where Mo(VI) exists as anionic condensated species, but decreases below pH = 1.5 and above pH = 5.5 as a result of the appearence of cationic species and MoO_4^{2-} in the aqueous phase, respectively. It should be pointed out that the extraction of Mo(VI) by Aliquat 336® is rapid

(equilibrium reached within a few minutes) in agreement with a mere anion exchange mechanism involving the polyanionic species of Mo(VI). IR spectra of the extracted species have been recorded after elimination of the diluent and are represented in figure 2. Examination of these spectra suggests that the extracted species is originially a tetra or an octamolybdate [e.g. $(R_3R'N)_4Mo_8O_{26}$] but has a tendency to become slowly a hexamolybdate [e.g. $(R_3R'N)_2Mo_6O_{19}$] (Fucks, 1973).

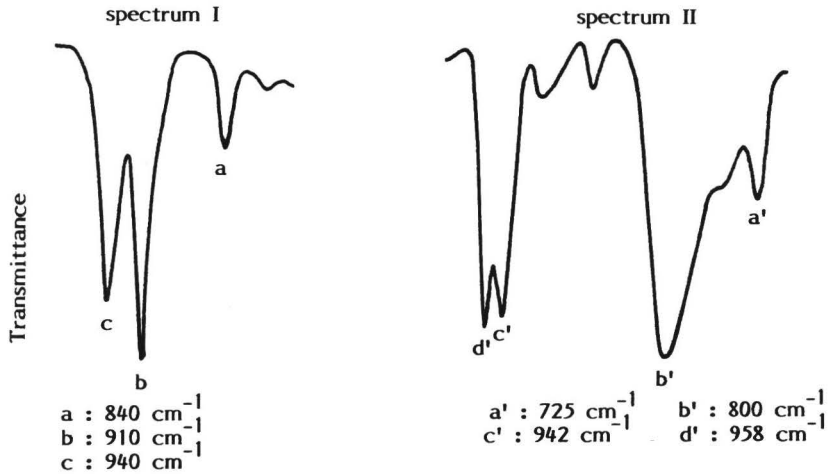


Fig. 2. IR spectra of the organic phase after extraction of molybdenum(VI) by Aliquat 336® at pH = 3. Contact time : (spectrum I) 10 min; (spectrum II) 3 days. [Toluene (spectrum I) and $CHCl_3$ (spectrum II) used as diluents were eliminated just before the IR spectra were recorded].

(b) Vanadium(V)

In figure 1, the percentage of extraction of V(V) has also been plotted as a function of pH for various concentration of Aliquat 336®. Examination of this figure shows that the yield of extraction of V(V) reaches its highest values between pH= 2 and 8 which corresponds to the existence of condensated anionic species of V(V) (compounds such as $(R_3R'N)_4H_2V_{10}O_{28}$ or $(R_3R'N)_5HV_{10}O_{28}$ are likely extracted). On the other hand the yield of extraction decreases below pH 2 and above pH 8 as V(V) exists in the aqueous phase under cationic forms and as HVO_4^{2-} or VO_4^{3-}, respectively.

(c) Phosphorus (V)

P(V) is poorly extracted by Aliquat 336® (for instance a 0.2 mol/L solution of Aliquat 336® in kerosene + 10% (weight) n-decanol extracts 1.2×10^{-2}, 4×10^{-3} and less than 10^{-4} mol/L of P(V) from an aqueous phase containing initially 0.2 mol/L of P(V), at pH = 2, 5 and > 8, respectively) . As in the case of Mo(VI) and V(V), the extraction of P(V) is a result of an anion exchange which may correspond to the two following reactions :

$$R_3R'N^+Cl^-(org) + H_2PO_4^-(aq) \quad <===> \quad R_3R'N^+H_2PO_4^-(org) + Cl^-(aq)$$

$$R_3R'N^+Cl^-(org) + H_3PO_4(aq) \quad <===> \quad R_3R'N^+H_2PO_4^-(org) + H^+(aq) + Cl^-(aq)$$

1.2 Extraction of Mo(VI), V(V) and P(V) from an aqueous phase containing them simultaneously

In figure 3, the yield of extraction of Mo(VI), V(V) and P(V) from an aqueous phase containing the mixture of the three species has been plotted as a function of pH. Examination of this figure shows that vanadium (V) can be selectively extracted at about pH 9. On the other hand the extraction of Mo(VI) is not totally selective in respect of P(V), probably as a result of the formation of phosphomolybdates (or phosphovanadomolybdates before extraction of vanadium).

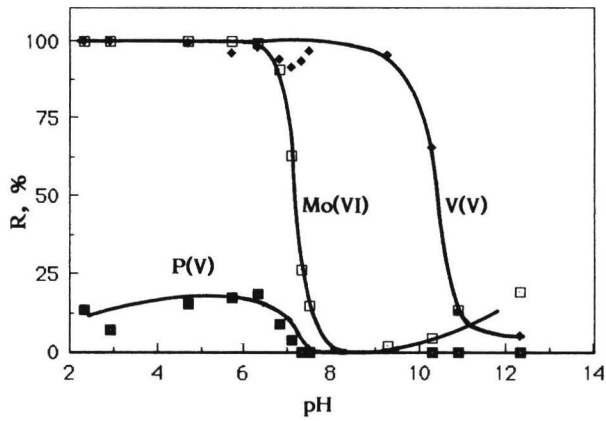


Fig. 3. Percentage of extraction of Mo(VI), V(V) and P(V) at equilibrium by Aliquat 336® (initially 0.20 mol/L) as a function of pH, at 25°C. Diluent = mesitylene. The aqueous phases initially contained 0.20 mol/L Mo(VI) + 0.20 mol/L V(V) + 0.30 mol/L P(V). Phase ratio = 1.

Examination of figure 4 shows that the stripping of Mo(VI) by NaOH is rapid whereas the stripping of V(V) is relatively slow.

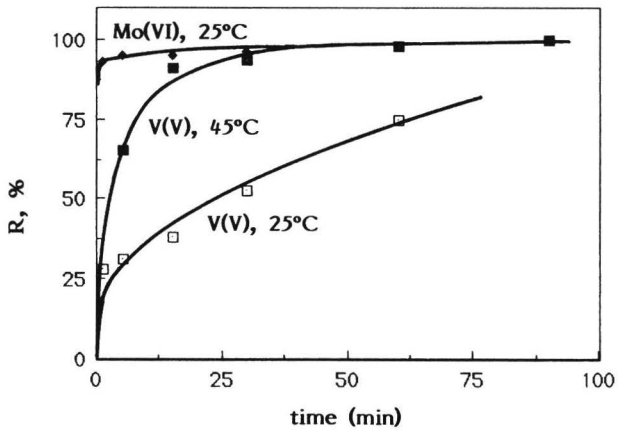


Fig. 4. Stripping rate of Mo(VI) and V(V) (taken separately and previously extracted by 0.20 mol/L Aliquat 336®, at pH = 2.6 [Mo] or 2.1 [V]) by 1 mol/L NaOH. Phase ratio = 1.

2 Side-reactions occurring during extraction or stripping of Mo(VI) and V(V)

Various side-reactions have been observed during extraction or stripping of Mo(VI) and V(V). They are reported and discussed in this section.

2.1 Precipitation phenomena occurring during extraction of Mo(VI)

When molybdenum (VI) is extracted by Aliquat 336® in solution in kerosene + 10% (weight) n-decanol, a solid phase slowly precipitates from the organic phase (especially between pH = 2 and pH = 4, and when the concentration of Aliquat 336® is low, i.e. $< 5 \times 10^{-2}$ mol/L). This precipitate has been isolated and identified by elemental analysis and IR and Raman spectroscopies mainly as an hexamolybdate, namely $(R_3R'N)_2Mo_6O_{19}$. Up to 40% of the molybdenum present in the system can be found in this precipitate. Such a precipitation which is very slow (several hours) compared to the kinetics of extraction (a few minutes) can be avoided by using an aromatic diluent as for instance toluene or mesitylene. However, as already pointed out in section 1, the use of aromatic diluent does not inhibit the appearence of hexamolybdate, but merely allows its solubilization in the organic phase, conversely to what happens with an aliphatic diluent such as kerosene.

2.2 Redox phenomena

The polyoxometalates behave as rather strong oxidizing agents and therefore easily undergo reductions which are accompanied by only minor structural changes (Pope, 1983).

(a) Redox phenomena occurring during extraction of vanadium(V) by Aliquat 336®

During extraction of V(V) from acidic solutions both a blue color develops within a few minutes in the aqueous phase likely as a result of the appearence of VO^{2+}, and a green color slowly appears (within a few days at room temperature, but within a few hours at 50°C) in the organic phase probably as a result of the formation of isopolyanionic species such as $[V_3(V)V_7(IV)O_{24}H]^{4-}$ or $[V_7(V)V_3(IV)O_{26}H]^{4-}$ (Ostrowetsky, 1964 b and c). It should be pointed out that such phenomena occur only in a narrow range of acidity, namely between about pH = 1 and pH = 2.5. The reducing agent is either n-decanol when this compound is used as additive or the impurities of Aliquat 336® in the other cases. Although such phenomena are spectacular, they involve a very small amount of vanadium (about 1%).

(b) Redox phenomena occurring during stripping of molybdenum(VI) by sodium hydroxide

In the case of molybdenum no redox phenomenon has been observed during the extraction stage. On the other hand, a blue color likely associated with the appearence of isopolyanionic species such as $[Mo_4(VI)Mo_2(V)O_{18}]^{2-}$ develops instantaneously in the organic phase during the stripping of Mo(VI) (previously extracted by Aliquat 336®) by sodium hydroxide (Ostrowetsky, 1964 a). Examination of figure 5 shows that the acidity of the aqueous phase from which molybdenum(VI) is extracted has almost no influence on the occurrence of such redox phenomena, at least as long as $2.5 < pH < 6.7$. The reducing agent(s) are likely impurities present in Aliquat 336®. Here again, it should be noticed that such phenomena are spectacular but involve a very small quantity of molydenum (at the most 0.3 %).

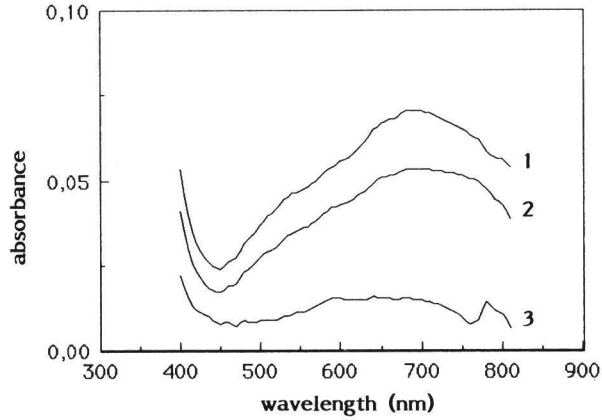


Fig. 5. Electronic absorption spectra of the organic phase after stripping of Mo(VI) by 1 mol/L NaOH. The pH of the aqueous phase from which Mo(VI) was extracted was : (1) 2.5; (2) 6.7 and (3) 6.9.

CONCLUSION

This study shows that Aliquat 336® can be used to recover and separate Mo(VI) and V(V) present in the aqueous leaching solutions of spent catalysts used in the mineral-oil industry. Various side-reactions occurring during the extraction and stripping steps are also reported, but it is shown that they have only a limited extent under the usual conditions of solvent extraction.

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SYNERGISTIC EXTRACTION OF RHODIUM WITH 2-MERCAPTO-BENZOTHIAZOLE AND TRI-N-OCTYLAMINE

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ABSTRACT

The synergistic enhancements were observed when rhodium(III) was extracted with 1,2-dichloroethane containing two extractants, 2-mercaptobenzothiazole(MBT) and tri-n-octylamine(TOA). In order to determine the composition of the synergistic species, equilibrium distribution ratios were investigated by studying the effects of extraction variables, i.e., acidity of solution, concentration of extractants and different combinations of two extractants. From the results obtained by NMR, slope analysis and thermogravimetric analysis, the composition of the extracted complexes was postulated to be $Rh{\cdot}(MBT)_2{\cdot}TOA{\cdot}Cl$. On the basis of these results, the mechanism was proposed for the synergistic extraction of Rh by use of these mixed ligand systems.

1. INTRODUCTION

During the last several years the present authors have been working on the synergistic extraction of platinum group metals(PGM) with a view to developing methods for their separation[1,2].

The present work deals with the synergistic effects that were observed in the extraction of rhodium(III) with various organic solvents containing MBT and TOA. The details of the present work are described in this paper.

2. EXPERIMENTAL

2.1. Extraction system

All organic solvents were purified by washing it with distilled water. 2-Mercaptobenzothiazole(MBT), tri-n-octylamine(TOA), tri-n-hexylamine(THA) and tri-n-butylamine(TBA) of G.R. grade were used without further purification. A $5X10^{-5}$ M rhodium solution was prepared by dissolving aliquots of rhodium chloride hydrate in concentrated HCl. The solution obtained was evaporated to dryness and the residue was dissolved in 0.01M HCl. The rhodium solution was extracted with 1,2-dichloroethane containing MBT and TOA. A shaking time of about 4 hours was found to be adequate for the attainment of equilibrium. The mixtures were then allowed to stand for about 1 hour for phase separation. After phase separation, the two

phases were separated and rhodium(III) concentration in the aqueous phase was determined by atomic absorption spectrometry. Rhodium(III) concentration in the organic phase was calculated from the mass balance of rhodium(III) in the aqueous phase before and after equilibration.

2.2. Composition of the synergistic species

In order to study the nature of the Rh complex formed in the extraction, the organic phase was allowed to evaporate at room temperature. The adducts thus obtained were dissolved in $CDCl_3$ and the NMR spectrum was recorded. The adducts were analysed by thermogravimetry.

The NMR data were obtained with a Bruker FT-100 AM NMR spectrometer. The thermogravimetric analysis(TGA) data were obtained with a Du Pont 9900 thermal analysis system. The rate of heating was 1°C min^{-1}.

3. RESULTS

3.1. Extraction system

When rhodium(III) was extracted with MBT and TOA a synergistic effect was observed. Of the various organic solvents tested, a synergistic effect was obtained with the dichloromethane, 1,2-dichloroethane, chloroform and benzene(TABLE 1). A similar enhancement in the extraction of rhodium(III) was observed when various amines were used as the extractant as shown in TABLE 2.

TABLE 1

Extraction of Rh with MBT and TOA using various organic solvents.

Organic solvent	**D(1)**	**D(2)**	**D(1,2)**	**ΔD**
Dichloromethane	0.78	1.63	9.24	6.83
1,2-Dichloroethane	0.21	1.13	5.75	4.41
Chloroform	0.19	0.47	3.11	2.45
Benzene	0.08	0.38	1.83	1.37

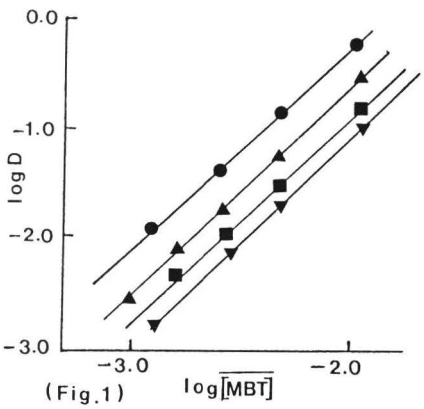
Aqueous phase : 0.01 M HCl.
D(1): Distribution coefficient of Rh obtained with the 0.01 M MBT alone. D(2): Distribution coefficient of Rh obtained with the 0.01 M TOA alone. D(1,2): Distribution coefficient of Rh obtained with the 0.01 M MBT plus 0.01 M TOA.

TABLE 2

Extraction of Rh with MBT and various amines.

Extractant	D(2)	D(1,2)	ΔD
TOA	1.13	5.75	4.41
THA	0.55	2.06	1.30
TBA	0.20	0.80	0.39

Aqueous phase : 0.01 M HCl containing $5X10^{-5}$ M of Rh(III). Organic phase : 1,2-dichloroethane containing 10^{-2} M TOA of the amines.
TOA = tri-n-octylamine ; THA = tri-n-hexylamine and TBA = tri-n-butylamine. D(2): Distribution coefficient of Rh(III) obtained with the amines alone. [the distribution coefficient of Rh(III) obtained with MBT alone, D(1)=0.21]. D(1,2): Distribution coefficient of Rh(III) obtained with MBT plus an amines.



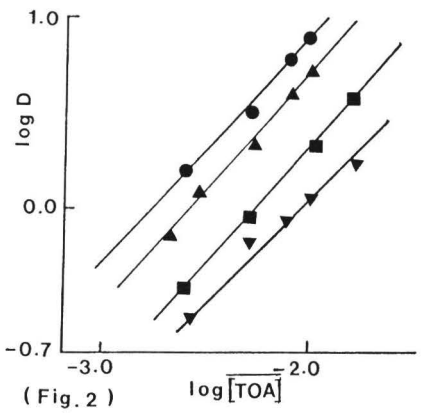


Fig.1 Effect of MBT concentration on rhodium(III) extraction in various organic solvents.

Fig.2 Effect of the concentration of TOA in various organic solvents on the synergistic extraction of rhodium(III) using 0.01 M of MBT: (●) dichloromethane, (▲) 1,2-dichloroethane, (■) chloroform and (▼) benzene.

Fig. 1 gives log D vs. log [MBT] plots of the extraction of Rh(III) with MBT when the organic phase is dichloromethane, 1,2-dichloroethane, chloroform and benzene. The distribution ratios increase with the increase in MBT concentration and the plotted points appear to lie on a straight line of slope 2. Fig. 2 shows the relation between the distribution

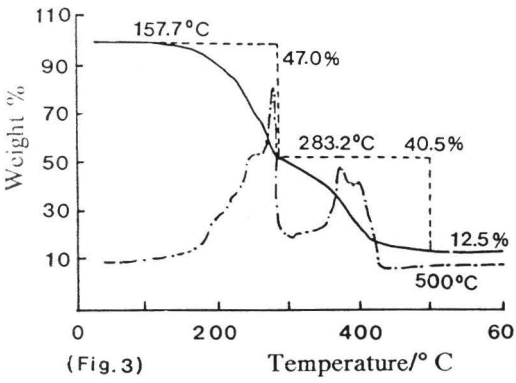
ratio and the concentration of TOA in the presence of MBT. The plotted points in Fig. 2 lie on a straight line of slope 1. From the analysis data(Fig. 1, 2), it appears that the synergistic species of Rh has the following composition; Rh : MBT : TOA = 1 : 2 : 1.

3.2. Thermogravimetry and NMR spectra

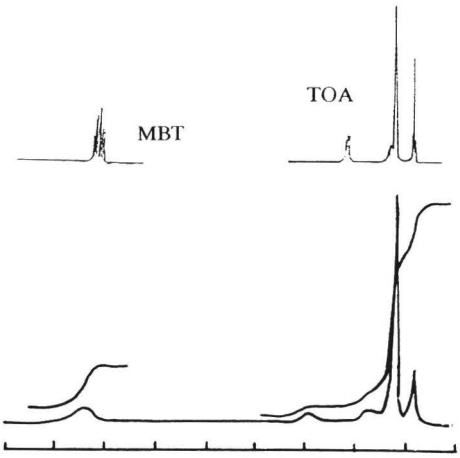
In order to determine the composition of the synergistic species of rhodium, the 1,2-dichloroethane solution was evaporated to dryness and the adduct was analysed thermogravimetrically; the thermal decomposition curves are shown in Fig. 3. The weight of the adduct began to decrease at 158°C; a final, constant weight, corresponding to 12.5% of the original weight, was obtained at 500°C. If the final weight corresponds to Rh, the relative molecular weight of the original adduct can be calculated to be 823.2(102.9 /0.125=823.2). The weight loss of 47% that occurs between 158 and 283.2°C corresponds to a relative molecular weight of 389.6(823.2 X 0.47 = 389.6). If the relative atomic weight of Cl(35.45) is substracted from 389.6, a value of 354.15 is obtained, which corresponds approximately to the relative molecular weight of TOA(353.68). Accordingly it was concluded that 1 atom Cl and 1 molecule of TOA were lost over this temperature range. The weight loss of 40.5% between 283.2 and 500°C corresponds to 333.4(823.2 X 0.405 = 333.4). This value corresponds approximately to the relative molecular weight of 2 MBT(166.25 X 2 = 332.5).

In order to complement the TGA finding, the NMR of $CDCl_3$ solution containing the synergistic extract of Rh, prepared as described above, was recored. As shown in Fig. 4, the integral of the peak areas of MBT in the 7.1-7.9 p.p.m. range was 24, while that of TOA in the 0.9-3.2 p.p.m. range was 151. Accordingly, the total areas of each of the multiplets are in the ratio of 24 : 151 = 1 : 6.3, which agrees well with the ratio of the number of protons of these two extractants, 8 for 2 MBT and 51 for TOA(8 : 51 = 1 :6.4). Both of these chemical shifts can be ascribed to the formation of a synergistic species of Rh in which these two extractants were present in a ratio of 2 : 1 = MBT : TOA.

From the slope analysis(Fig. 1, 2), the TGA(Fig. 3) and the NMR spectrum(Fig. 4), it appeared that the Rh species had the following composition; Rh : MBT : TOA : Cl = 1 : 2 : 1 : 1.



(Fig.3)



(Fig.4)

Fig.3 Thermogram of the Rh-MBT-TOA system. Sample size 10.44mg. Heating rate. 1°C min^{-1}

Fig.4 Proton NMR spectrum of the Rh-MBT-TOA system.

4. DISCUSSIONS

4.1. Selection of mixed ligand system

In the present work MBT was used as extractant, which is one of the efficient precipitants for Rh[3]. Amines and quaternary ammonium salts are widely used among the nitrogen containing extractants for PGM . A large number of studies have been published on the extraction of PGM with this class of extractants[4]. For this reason, the mixture of MBT and TOA was selected as the extractant for the present work.

Of the various solvents tested, i.e., dichloromethane, 1,2-dichloroethane, chloroform and benzene, the distribution ratios increase in the order: benzene < chloroform < 1.2-dichloroethane < dichloromethane (TABLE 1). Of the various amines tested, the larger the carbon number of the extractant, the higher the enhancement of the synergistic extraction of Rh (TABLE 2).

4.2. Mechanism of the synergistic extraction

From the results mentioned above, the following mechanism is proposed for the synergistic phenomena observed in the present study.

$$RhCl_6^{3-} + MBT^- \rightleftharpoons (RhCl_2 \cdot MBT_2)^- + 4Cl^- \quad (1)$$

$$(RhCl_2 \cdot MBT_2)^- + \overline{HCl \cdot TOA} \rightleftharpoons \overline{(HTOA) \cdot (RhCl_2 \cdot MBT_2)} + Cl^- \quad (2)$$

$$\overline{(HTOA) \cdot (RhCl_2 \cdot MBT_2)} \rightleftharpoons \overline{(Rh \cdot MBT_2 \cdot TOA \cdot Cl)} + HCl \quad (3)$$

A bar above the chemical formula denotes the organic phase. From these data, a possible explanation for the proposed mechanism is as follows. The extraction process proceeds via the exchange reaction (2) following by the penetration reaction (3), as discussed by Gindin et al[5], to form the synergistic species finally as $Rh \cdot (MBT)_2 \cdot TOA \cdot Cl$.

5. CONCLUSION

An extraction method has been developed for the Rh(III) with 1,2-dichloroethane containing MBT and TOA. In an attempt to explain the extraction mechanism involved, the composition of the extracted species was determined by NMR spectroscopy, slope analysis and TGA. From these studies, the species appears to have the composition Rh : MBT : TOA : Cl = 1 : 2 : 1 : 1.

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SOLVENT EXTRACTION OF PALLADIUM(II) AND PLATINUM(IV) WITH AMINO- AND AMIDO-CARBOXYLIC ACIDS

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ABSTRACT
Kazuharu Yoshizuka, Yoshinari Baba, Katsutoshi Inoue, Fumio Wada and Tsutomu Matsuda, 1990 Solvent extraction of palladium(II) and platinum(IV) with amino- and amide-carboxylic acids

N,N-dioctylglycine and N,N-dioctylsuccinamic acids were synthesized to investigate their extraction behaviors for platinum(IV) and palladium(II) from acidic aqueous chloride media. Toluene was used as a diluent. These reagents were found to exist as dimeric species in toluene from the measurement of their apparent molecular weights. From the concentration dependencies of the reactant species, i.e. hydrogen and chloride ions as well as the extracting reagents on the distribution coefficients of these metals, it was concluded that palladium(II) and platinum(IV) are extracted with both reagents as 1:2 metal:reagent chelates and 1:4:2 metal:chloride ion:reagent solvated complexes respectively according to the reactions as follows:

$$PdCl_4^{2-} + H_2R_2 = PdR_2 + 2H^+ + 4Cl^-$$
$$PtCl_6^{2-} + H_2R_2 = Pt\cdot 2HR\cdot Cl_4 + 2Cl^-$$

The equilibrium constants for these extraction reactions were evaluated for both of these reagents. Infrared spectra of the free reagents as well as the palladium(II) and platinum(IV) complexes with these reagents were also studied for the purpose of obtaining some information on the interaction between metal ions and the reagent molecules to confirm the above-mentioned conclusion on the extraction equilibrium.

1. INTRODUCTION

In early 1970s, the National Institute for Metallurgy of South Africa (NIM, now MINTEK) developed the acetic acid derivative of Amberlite LA-2, a long-chain secondary alkylamine, as an effective extractant for palladium(II) and platinum (IV), which has been successfully utilized on a commercial scale by Lonrho Refinery Ltd. (Edwards, 1979). With this extractant, both metals can be effectively extracted from dilute hydrochloric acid solutions and easily stripped with concentrated hydrochloric acid solutions from the solvent. Contrarily, primary, secondary, and tertiary amines, which are the conventional metal extractants, so strongly extract these metals that stripping is very difficult even with very concentrated hydrochloric acid solutions. The difference of the extraction mechanism with these two types of reagents is responsible for that of the extraction behaviors.

Although many works have been conducted on the complex formation between metals including palladium(II) and amino-acids, peptides and their related ligands in aqueous solutions (Pettit, 1985), there have been only few works on the fundumental chemistry of solvent extraction with amino-acid types of extracting reagents (Zhang, 1985, 1987, Uhlig, 1986, Sevdic, 1974). In the present paper, the authors synthesized N,N-dioctylglycine

(DOG), one of the amino-acid derivatives, and N,N-dioctylsuccinamide (DOSA), one of amide-acid derivatives, as model compounds of the acetic acid derivative of Amberlite LA-2 to make fundamental investigation on their extraction behaviors for palladium(II) and platinum(IV) from acidic chloride media.

2. EXPERIMENTAL

2.1 Reagents

DOG and DOSA were synthesized from dioctylamine and monochloroacetic acid and succinic anhydride, respectively, in benzene under nitrogen atmosphere by conventional methods according to the reactions:

$$(C_8H_{19})_2NH + ClCH_2COOH = (C_8H_{19})_2NCH_2COOH + HCl$$

$$(C_8H_{19})_2NH + (CH_2CO)_2O = (C_8H_{19})_2NC(=O)CH_2CH_2COOH$$

The yield and purity of the purified product of DOG were 56% and 93%, respectively, while those of DOSA were 88% and 96%, respectively. These reagents were used by diluting to a required concentration with analytical grade of toluene. The apparent molecular weights of these reagents were measured by means of vapor-phase osmometry using a Hitachi model 117 osmometer to examine the degree of aggregation of these reagents in toluene. As the result, it was found that the great majority of DOG exists as dimeric species whilst DOSA only partly exists as the dimeric species. The dimerization constant of DOSA was evaluated as Kd = 200±36 dm^3 /mol; the number-averaged aggregation number was 1.54±0.08 in the region of analytical concentration from 0.002 to 0.03 mol/dm^3

2.2 Procedure

Palladium(II) was extracted from aqueous mixtures of hydrochloric acid and sodium chloride whilst platinum(IV) was from those of hydrochloric acid and lithium chloride. Equal volumes of aqueous and organic phases were shaken in a flask immersed in a thermostated water bath maintained at 30±0.1 ℃ for 2 and 24 h for palladium and platinum respectively in the extraction with DOG while they were vigorously shaken for over 24 h using an mechanical shaker in an air bath maintained at the same temperature in the extraction with DOS to attain equilibrium. Initial and equilibrium metal concentrations in the aqueous phase were determined by using a Nippon Jarrell-Ash model AA-782 atomic absorption spectrophotometer. The metal concentrations in the organic phase were calculated from the mass balance of the metal contents in the aqueous phase before and after the equilibria.

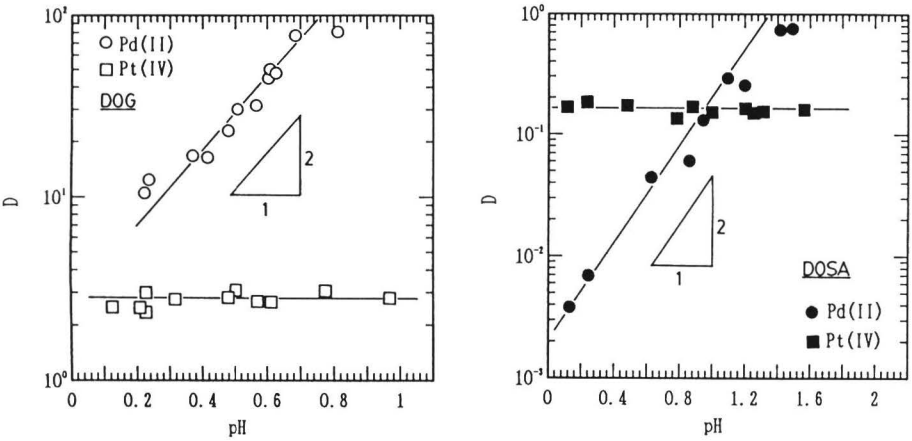
2.3 Infrared spectra

Infrared spectra of the free reagents and their complexes of palladium(II) and platinum (IV) in dichloromethane ($CDCl_3$) were taken in the region 4000 - 650cm^{-1} on a JASCO model A-100 infrared spectrophotometer, using 0.05 mm CaF_2 IR cells at 30 ℃.

3 RESULTS AND DISCUSSION

3.1 Distribution equilibria

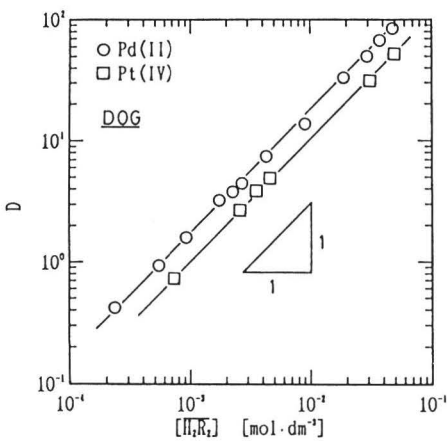
Figures 1 and 2 show the effect of pH on the distribution coefficients of palladium (II) and platinum(IV) in the extraction with DOG and DOSA, respectively from aqueous mixtures of hydrochloric acid and sodium chloride (Pd) or lithium chloride (Pt) in which total chloride ion concentration was maintained at 1.0 mol/dm ^{3} . Here, pH was calculated from the hydrogen ion concentration determined by means of titration and the activity coefficient of hydrogen ion in these aqueous chloride mixtures (Ohtaki, 1969, Harned, 1959) at pH ≦ 1 while it was measured using a TOA model HM-20E pH meter at pH > 1.

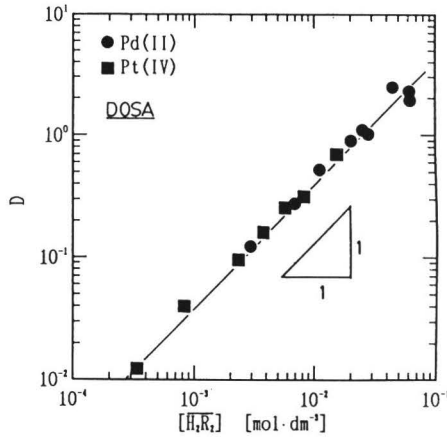


Figs. 1 and 2 Effect of pH on the distribution coefficients of palladium(II) and platinum(IV) in the extraction with 10 mmol dm^{-3} DOG (Fig. 1) and DOSA (Fig. 2) in toluene (total chloride ion concentration = 1.0 mol dm^{-3})

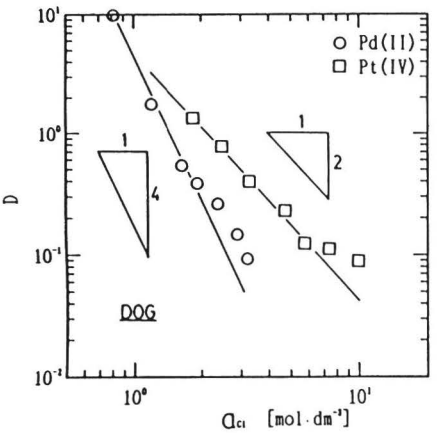
The plots for the extraction of palladium(II) are lying on straight lines with the slope of 2 in both figures, which suggests that two hydrogen ions are released by substitution with one metal ion during extraction.

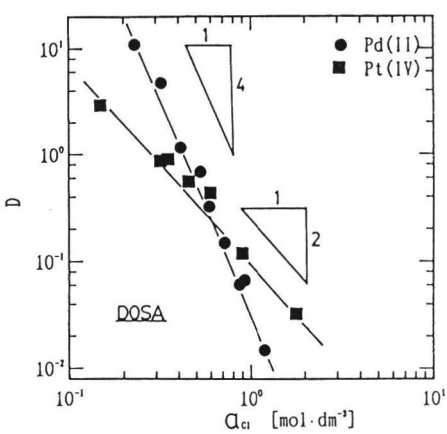
Figures 3 and 4 show the effect of the concentration of the dimeric species of the reagents on the distribution coefficients in the extraction with DOG and DOSA respectively, where the concentrations of the dimeric species were calculated as the half of the analytical reagent concentration in the case of DOG and calculated using the dimerization constant evaluated earlier in the case of DOSA. The plots are lying on straight lines with the slope of unity for both metals in both figures. This fact suggests that both of these metals are extracted as 1:2 metal:reagent complexes with both of these reagents.





Figures 3 and 4 Effect of the concentration of dimeric extractant on the distribution coefficients of palladium(II) and platinum(IV) in the extraction with DOG (Fig. 3) and with DOSA (Fig. 4) in toluene; aqueous phase = 1.0 mol dm^{-3} hydrochloric acid (Fig. 3), = aqueous chloride mixture where total chloride ion concentration = 1.0 mol dm^{-3}, pH = 1 (Fig. 4)





Figures 5 and 6 Effect of chloride ion activity on the distribution coefficients of palladium(II) and platinum(IV) in the extraction with 10 mmol dm^{-3} DOG (Fig. 5, hydrogen ion concentration = 1.0 mol dm^{-3}) and DOSA (Fig. 4, hydrogen ion concentration = 0.1 mol dm^{-3})

Figures 5 and 6 shows the effect of activity of chloride ion on the distribution coefficients in the extraction with DOG and DOSA respectively from the aqueous chloride media in which hydrogen ion concentration is maintained constant. Here, the activity of chloride ion was calculated from the chloride ion concentration and the activity coefficient of chloride ion (Harned, 1959). In Fig. 6, the plots are lying on straight lines with the slopes of -4 and -2 for the extraction of palladium(II) and platinum(IV), respectively, suggesting that four and two chloride ions are released per unit metal ion during extraction of palladium(II) and platinum(IV) respectively. Also in Fig. 5, plots are lying on the straight lines with the slopes of -4 and -2 for the extraction of palladium (II) and platinum(IV) respectively in the low concentration region of chloride ion though they deviates upward from the straight lines in the high concentration region, which may be attributed to the salting out effect by chloride ion.

From the above-mentioned concentration dependences of the reactant species on the distribution coefficients and by taking into consideration that majorities of palladium (II) and platinum(IV) exist as the tetrachloro and hexachloro complexes in the aqueous solutions with high concentration of chloride ion under the present experimental conditions, the followings can be concluded for both reagents: palladium(II) is extracted as a metal-chelates according to the extraction reaction expressed by Eq. (1) whilst platinum (IV) is as a solvated complex according to that expressed by Eq. (2).

$$PdCl_4^{2-} + H_2R_2 \rightleftarrows PdR_2 + 2H^+ + 4Cl^- ; \quad Ke_{Pd} \qquad (1)$$

$$PtCl_6^{2-} + H_2R_2 \rightleftarrows Pt\cdot 2HR\cdot Cl_4 + 2Cl^- ; \quad Ke_{Pt} \qquad (2)$$

Based on the above-described extraction reaction, the distribution coefficients are approximately expressed by Eqs. (3) and (4) for palladium(II) and platinum(IV) respectively in such a high concentration region of chloride ion as under the present experimental conditions.

$$D(Pd) \simeq Ke_{Pd}[H_2R_2]/a_H^2 a_{Cl}^4 \qquad (3)$$

$$D(Pt) \simeq Ke_{Pt}[H_2R_2]/a_{Cl}^2 \qquad (4)$$

These equations can interpret all the concentration dependencies of the reactant species on the distribution coefficients of each metal either in the extraction by DOG or by DOSA obtained experimentally.

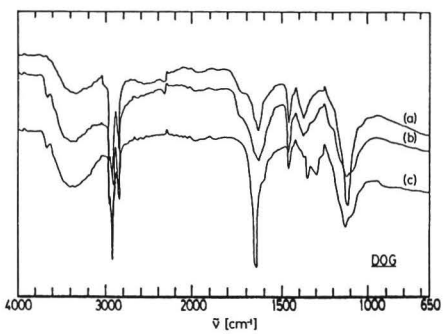
The equilibrium constants for the extraction reactions, Ke_{Pd} and Ke_{Pt}, were evaluated for each reagent using all the data shown in Figs. 1-6 based on Eqs. (3) and (4) as listed in Table 1.

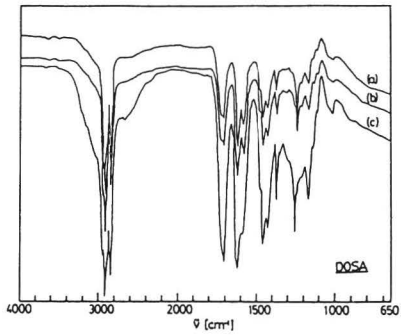
TABLE 1 Extraction equilibrium constants of the extraction reactions of palladium(II) and platinum(IV) with DOG and DOSA

	Ke_{Pd} [(mol/dm3)^5]	Ke_{Pt} [mol/dm^3]
DOG	2.2×10^2	6.3×10^2
DOSA	1.1×10^{-1}	2.8×10^1

3.2 Infrared spectra

Figures 7 and 8 show the infrared spectra of the palladium(II) and platinum(IV) complexes as well as the free reagents of DOG and DOSA, respectively. In both figures, the





Figs. 7 and 8 Infrared spectra of free reagent(a) and the platinum(IV)(b) and palladium (II)(c) complexes of DOG (Fig. 7) and DOSA (Fig. 8)

spectra of the platinum(IV) complexes(b) resemble those of the free reagents(a). On the other hand, the spectra of palladium(II) complexes(c) are significantly different from those of the platinum(IV) complexes and free reagents. That is, in Fig. 7, the C=O stretching band of the free reagent at 1630 cm^{-1} is shifted to 1650 cm^{-1} on the complexation with palladium(II), suggesting that the Pd-O bond in the glycino palladium(II) complex is covalent (Sawyer, 1960). Similarly, in Fig. 8, the spectrum of palladium(II) complex is significantly different from those of free reagent and platinum(IV) complex in the region of the C=O stretching bands at 1710 cm^{-1} (carbonyl group of amide) and 1630 cm^{-1} (carboxyl group); these absorption bands are assigned to the bidentate (chelated) succinamic acid group (Nakamoto, 1986). These facts suggest that palladium(II) is extracted as chelates of the type, PdR_2 , while platinum(IV) is extracted as solvated complexes of the type, $Pt{\cdot}2HR{\cdot}Cl_4$; these results are in accordance with those obtained in the experiments of the distribution equilibria.

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THE SEPARATION OF RARE EARTH ELEMENTS BY THE POROUS RESIN IMPREGNATED WITH 2-ETHYLHEXYL HYDROGEN 2-ETHYLHEXYLPHOSPHONATE

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ABSTRACT

A reagent impregnated resin has been prepared from 2-ethylhexyl hydrogen 2-ethylhexylphosphonate (PC-88A) and Amberlite XAD-7 beads. The distribution ratio of the rare earth metal ions (3+) between the resin and acid aqueous solution has been measured as a function of pH and the concentration of the reagent. The chromatographic separation of the rare earth metals has been carried out by using PC-88A (50w/w%) impregnated resin as a stationary phase and hydrochloric acid as a mobile phase. A favorable separation can be achieved for some rare earth metals by adjusting the acidity of the mobile phase.

INTRODUCTION

The solvent extraction technology has been extensively applied to the practical separation of rare earth metals. Among the extractants commonly employed at present, di(2-ethylhexyl) hydrogen phosphate (D2EHPA) and 2-ethylhexyl hydrogen 2-ethylhexylphosphonate (PC-88A) are known to have advantages of high separation efficiency for rare earth metals and of low solubility in water (Peppard, 1961, Ying, et al., 1985, Mori, et al., 1986, Wakui, et al., 1989). However, separation via solvent extraction requires multistage cycles of extraction and back-extraction in order to attain favorable separation. On the other hand, chromatographic separation is a convenient procedure to obtain highly purified metals. The column separation process is typically carried out with the combination of a cation exchanger as a stationary phase and a solution of a chelating reagent as a selective mobile phase. When we use highly selective resin as a stationary phase in the chromatographic system, diluted mineral acids can be used as eluents in place of expensive chelating reagents.

In this report, we used an ion-selective resin as a stationary phase which can readily be prepared by impregnation of extractant (PC-88A) into porous polymer beads. We measured the distribution behavior of rare earth metals toward the PC-88A impregnated resin in order to elucidate the separation efficiency of this system. The effectiveness of the impregnated resin column for the chromatographic separation of some rare earths was examined.

2 EXPERIMENTAL

2.1 Reagents.

The PC-88A (95% or higher purity) was kindly donated from Daihachi Chemical Co. and was used as received. A lanthanide chloride solution was prepared by dissolving the corresponding oxide (99.9%, Wako Pure Chemical Industry Ltd.) into hydrochloric acid of an analytical grade. Other chemicals were of reagent grade and were used with no further purification.

2.2 Resin bed.

Amberlite XAD-7 beads (20-60 mesh) were used as the polymer support for the preparation of the impregnated resin. Resin beads were washed successively with 2 M (M = mol dm^{-3}) nitric acid and acetone, and then dried *in vacuo* prior to use.

A 5.25 cm^3 of PC-88A was diluted with 30 cm^3 of acetone. To this solution was added a 5 g portion of the XAD-7 beads and the mixture was stirred under the reduced pressure. After 30 min, the acetone was evaporated off. The obtained resin contains 50 w/w% of PC-88A which corresponds to 1.6 mmol of PC-88A per one gram of the resin. The content of PC-88A can be adjusted by dilution with dodecane prior to impregnation.

Leaking of PC-88A from the resin is practically negligible, *i.e.*, the loss of PC-88A is less than 3% upon shaking the impregnated resin (150 mg) with 10^{-2} M hydrochloric acid (600 cm^3) for several days.

2.3 Distribution ratio.

The batch extraction of the metal ions was typically carried out under the following procedures. The PC-88A impregnated resin (0.05-0.5 g) was immersed in 10-30 cm^3 of metal ion solution ([metal] = 10^{-5}-10^{-4} M, I = 0.2 M (HCl-NaCl)) at various acidity and the mixture was shaken for more than 5 h at room temperature. After filtration, the amount of metal ion in the aqueous solution was determined by a SEIKO ICP-atomic emission spectrometer, model SPS-1200A, and the pH value of this solution was measured with a glass electrode (TOA GS-5011C).

The distribution ratio D was defined as the ratio of the total equilibrium concentration of metal in the impregnated organic phase to those in the aqueous phase.

2.4 Chromatography

The PC-88A-impregnated resin (PC-88A: 50w/w%) was immersed in a diluted hydrochloric acid overnight and then packed in a jacketed glass column (ϕ 1

cm - i.d.). Thermostated water (45-47 °C) was circulated around the column by using a thermoregulator (HS-1, Tokyo Rikakikai Co. Ltd.) during the column operation. The column was conditioned for several hours with an eluting solution *e.g.* hydrochloric acid of the suitable acidity. Then 1 cm^3 of a sample solution ([M] = 0.1 M for each metal ion) was loaded on the top of the column and eluted with hydrochloric acid at a constant flow rate. The effluent was fractionated into portions of 10-14 cm^3 and the metal ions in each fraction were determined with ICP-AES method.

3 RESULTS AND DISCUSSION

For the analysis of distribution behavior in the present system, we assumed the impregnated resin to be an organic phase, in analogy with a solvent extraction system. It has been proposed that D2EHPA, which is structurally close to PC-88A, behaves as a dimer in the extraction systems (Peppard, et al., 1957, Kosinski, et al., 1969). In addition, neutral PC-88A in a higher concentration range tends to form adducts with the lanthanide complexes (Mori, et al., 1986). Thus the reaction of PC-88A with lanthanide ions can be expressed as follows :

$$M^{3+} + n\,((HR)_2)_r \overset{K}{\rightleftharpoons} (M(HR_2)_3((HR)_2)_{n-3})_r + 3\,H^+ \qquad (1)$$

where HR denotes PC-88A in the neutral form. The subscript r represents the species in the resin phase. The equilibrium constant of the above reaction should be given by Eq. 2:

$$K = ([M(HR_2)_3((HR)_2)_{n-3}]_r[H^+]^3) \,/\, ([M^{3+}][(HR)_2]_r^n) \qquad (2)$$

The distribution ratio (D) of the metal ion between the resin phase and the aqueous phase is defined by

$$D = [M(HR_2)_3((HR)_2)_{n-3}]_r \,/\, [M^{3+}] \qquad (3)$$

From Eqs. 2 and 3, the following relationship can be obtained:

$$\log D = \log K + n \log [(HR)_2]_r + 3\,pH \qquad (4)$$

Equation 4 predicts that the plots of log D against log $[(HR)_2]_r$ and pH give straight lines of slopes n and 3, respectively.

Figure 1 shows the log D vs. pH profiles for the extraction of Y(III) and twelve kinds of lanthanide(III) ions. For the extraction of rare earth metals other than La, linear plots with slopes ranging from 2.7 to 3.1 were observed, which is in good agreement with the estimation derived from Eq. 4. Thus, the extraction of the metal ion is accompanied by the release of three protons. On the contrary, the slope for La, 2.2, is exceptionally smaller than those for other lanthanides. In this case, some extraction mechanism other

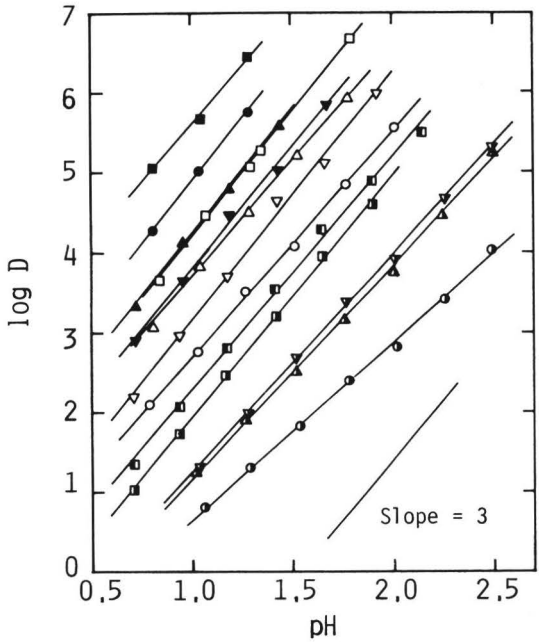


Fig. 1 Distribution ratio of rare earth elements between the aqueous phase and PC-88A-impregnated resin (PC-88A: 50 w/w%). I = 0.2 M (HCl-NaCl).
Symbols; ◑: La ▲: Pr ▽: Nd ◨: Sm ◧: Eu ○: Gd ▽: Tb △: Dy
▼: Ho ▲: Er ●: Tm ■: Lu □: Y.

than those expressed in Eq. 1 might be involved. The distribution ratio (D) at the given pH increases with the decrease in ionic radii of lanthanides, in analogy with the trends observed for the solvent extraction system with D2EHPA (Peppard, 1961). The difference of the distribution ratio between La and Lu is fairly large (about 5 log units), showing the potential usefulness of the resin as a stationary phase in the chromatographic system.

Plots of log D against the concentration of PC-88A for the extraction of La and Lu gave straight lines with the slopes of 3.9 and 3.6, respectively (Fig.2). From Eq. 4, this observation can be interpreted by a mechanism in which four dimerized PC-88A are involved in the extracted species. Since three protons are released upon the extraction of Lu ion, one of the four $(PC\text{-}88A)_2$ should be neutral to form an adduct with the complex.

A chromatographic separation of Gd and Y pair was carried out by using a column of the PC-88A impregnated resin (ϕ 1.0 x 93.5 cm). Compared with the conventional process using EDTA as an eluent, the ratio of D values, *i.e.*

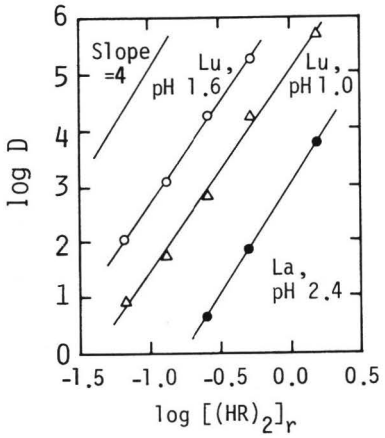


Fig. 2. Distribution ratio of La and Lu as a function of concentration of PC-88A (HR) in the impregnated resin. I = 0.2 M (HCl-NaCl).

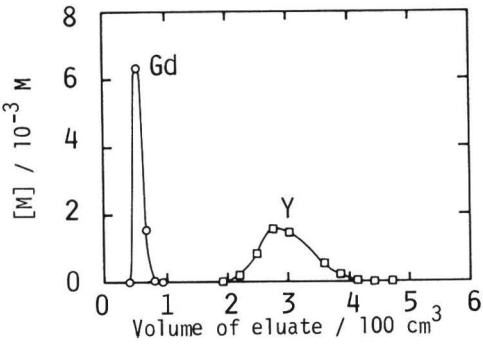


Fig. 3. Separation of Gd and Y with PC-88A-impregnated resin column (ϕ 1.0 x 93.5 cm) at 45 °C.
Stationary phase: PC-88A-impregnated XAD-7 (50 w/w%).
Mobile phase: 0.9 M HCl.
Flow rate: 26 cm^3/h.
Amount of each metal: 0.1 mmol.

separation factor, of the present system for Y/Gd pair is remarkably large; about 30. In practice, these metal ions were successfully separated into the components by elution with 0.9 M hydrochloric acid, as shown in Fig. 3.

A similar column system was applied to mutual separation of the following rare earth mixtures: La-Pr-Nd and Ho-Er-Tm. The chromatograms are given in Figs. 4 and 5 along with the chromatographic conditions. A good separation can be attained for the pair whose separation factor is sufficiently large. In fact, lanthanum was favorably separated from Pr and Nd, while the resolution of Pr and Nd pairs remained insufficient due to the small separation factor. The degree of overlap of two peaks is not serious for the separation of Ho-Er-Tm whose separation factors are mutually rather large. In this case, the acidity of the mobile phase is much higher than that used in the La-Pr-Nd system. Since the distribution ratio is a function of acidity as shown in Fig. 1, the concentration of acid in the mobile phase is one of the most important parameters which affect the chromatographic separation. Usually, solution of higher acidity is required for the elution of the metal ions having higher distribution ratio.

One of the major advantages of the present system over the traditional ion-exchange column is that a favorable separation can be achieved without

using an expensive reagent as an eluent. In addition, elution with acid solution may simplify the isolation procedure of dissolved substances, *i.e.*, the recovery of a reagent from the eluate is not necessary after the isolation of metals.

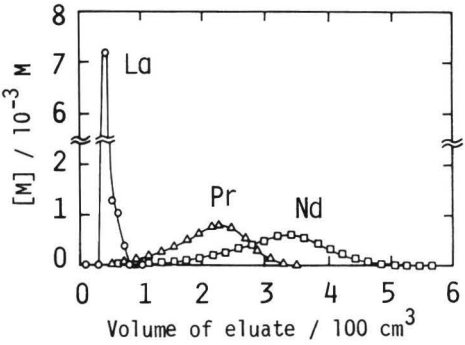


Fig. 4. Separation of La, Pr and Nd with PC-88A-impregnated resin column (ϕ 1.0 x 94.5 cm) at 47 °C.
Stationary phase: PC-88A-impregnated XAD-7 (50 w/w%).
Mobile phase: 0.1 M HCl.
Flow rate: 20 cm^3 /h.

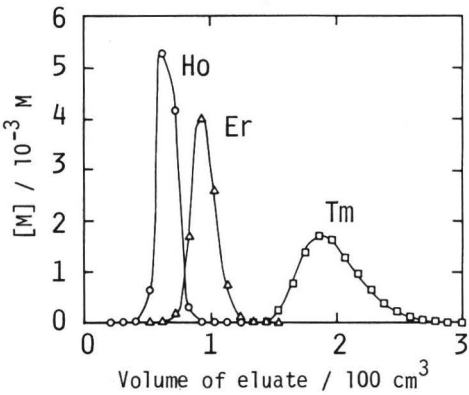


Fig. 5. Separation of Ho, Er and Tm with PC-88A-impregnated resin column (ϕ 1.0 x 94.5 cm) at 47 °C.
Stationary phase: PC-88A-impregnated XAD-7 (50 w/w%).
Mobile phase: 1.4 M HCl.
Flow rate: 15 cm^3 /h.

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SILVER EXTRACTION FROM PHOTOGRAPHIC FIXING SOLUTIONS

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ABSTRACT
Stenström, S., 1990. Silver extraction from photographic fixing solutions.
Silver recovery from photographic thiosulphate solutions can be performed by solvent extraction with amines or quaternary ammonium chlorides. With Aliquat 336 the distribution coefficient for silver was measured as 9.0 from a 0.5 molar thiosulphate solution. Stripping can be performed by using potassium nitrate, ammonium chloride or by changing the thiosulphate concentration. The results for analytical solutions were further shown to be applicable to industrial solutions. One stage silver extraction with Aliquat 336 ranged from 68.5 to 98.9 % for graphical, bleach and photographic fixing solutions.

1. INTRODUCTION

Silver is used extensively in photographic and X-ray films as well as in various photographic papers. The excess of non-reacted silver halide salts is normally dissolved in a sodium or ammonium thiosulphate fixing solution from which silver is recovered. In order to allow emission of this solution in Sweden to effluents or municipal wastewater treatment works the silver content must be reduced below 1mg/l.

So far, no work has been performed on evaluating solvent extraction techniques, either together with the initial high silver content solution or with the electrolyzed low silver content solution. The aim of this work is to investigate such methods in order to allow either recycle or emission of the photographic fixing solution.

2. PROCESSES USED FOR SILVER RECOVERY

Electrolysis is traditionally used for silver recovery from thiosulphate fixing solutions (Gmelin, 1973). This method is highly efficient at high silver concentrations and is capable of reducing the silver concentration down to about 100 mg/l. At lower silver concentrations decomposition of the thiosulphate and other metal impurities such as cadmium and chromium complicate the recovery process.

From an environmental point of view the best way of reducing emissions would be to reuse the major part of the fixing solution after silver recovery and appropriate chemical adjustment. The silver concentration in the part which is not recycled must be

reduced to the environmental emission level of 1 mg/l. Some process alternatives are shown in Fig. 1.

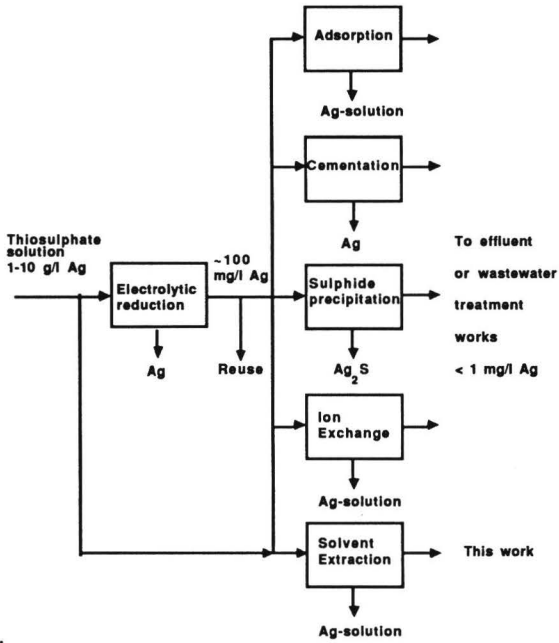


Fig. 1. Processes used for silver recovery.

Sulphide precipitation as well as reduction with less noble metals such as iron are two common operations used for this purpose. Zeolites effectively adsorb silver from solutions and this can be used as a tool to remove low concentrations of silver from the solution. However all of these processes possesses drawbacks either from environmental or technical point of view.

3. SOLVENT EXTRACTION

A comparatively large number of silver extraction data in various media have been collected for different amine extractants. The primary amine Primene JM-T is a poor silver extractant from 2 M HCl as shown by Seeley et al. (1966), but extracts silver with distribution coefficients of 100 from 0.005 M H_2SO_4 as reported by Marcus et al. (1969). Several tertiary amines are excellent extractants for silver. Selmer-Olsen (1966) reported quantitative extraction from 2 M HCl with 20 % (v/v) tri-iso-octylamine in carbon tetrachloride. Quaternary ammonium salts are good silver extractants from hydrochloric acid. Seeley et al. (1966) have reported distribution coefficients of 30 for silver extraction from 2 M HCl with 0.1 M Aliquat 336 in 97 % diethylbenzene and 3 % tridecanol.

Literature data for thiosulphate solutions are limited to amine extractants. Shevchuk et al. (1988) used octadecyl ammoniumnitrate to extract silver for analytical purposes at a pH of 6.5 and Le et al. (1987, 1988) performed experiments in nitrate and thiosulphate media with the primary amine N 1923. From nitrate media extraction was quantitative at pH 3.

No literature data for photographic solutions is available which necessitates measurement of distribution data for a number of different commercial extractants.

4. MATERIALS

The distribution coefficients were determined by equilibrating equal volumes (25 ml) of the aqueous and organic phases in separatory funnels at room temperature. Analyses of the silver content in the aqueous phase were performed with standard AAS equipment. The extractants were used as supplied by the manufacturer; HDEHP from Hoechst, TOPO from Cyanamid, Primene JM-T and Amberlite LA-2 from Rohm & Haas, LIX 70, LIX 984, Alamine 336 and Aliquat 336 from Henkel Corp. All other chemicals were of analytical grade. The extractants were dissolved in Shellsol-A which is a 99 %(v/v) aromatic kerosene. Initially the behaviour in pure thiosulphate solutions was evaluated by adding silver nitrate to an ammonium or sodium thiosulphate solution.

5. EXTRACTANT SELECTION

The different extractants were tested as 0.1 molar solutions with an aqueous phase consisting of 1 g/l Ag in 0.5 molar ammonium thiosulphate. The results of the equilibrations are shown in Table 1.

TABLE 1

Silver distribution coefficients with 0.1 M extractants from 0.5 M $(NH_4)_2S_2O_3$ containing 1 g/l Ag.

Extractant	Equilibration	D_{Ag}	pH_{eq}
Primene JM-T	-	0.08	7.5
	HCl[a]	4.6	5.3
	H_2SO_4[a]	6.0	3.5
Amberlite LA-2	-	0.05	6.5
	HCl[a]	3.7	4.2
	H_2SO_4[a]	4.1[b]	3.8
Alamine 336	-	0.05	5.8
	HCl[a]	0.37[b]	3.8
	H_2SO_4[a]	0.62[b]	3.3
Aliquat 336	Cl^-	9.0	6.0
	Cl^-	11.8[d]	7.8
	SO_4^{2-} [c]	1.4	-
	NO_3^- [c]	1.2	-
TOMAC[e]	Cl^-	13.7	5.8
	Cl^-	12.8[d]	6.5

[a] Pre-equilibrated with 0.5 M HCl or 0.5 M H_2SO_4

[b] Precipitate in the aqueous phase after phase separation

[c] Pre-equilibrated three times with 0.5 M H_2SO_4 or 0.5 M HNO_3

[d] From 0.5 M $Na_2S_2O_3$ with 1 g/l Ag

[e] Tri-octylmethyl ammoniumchloride

Low distribution coefficients ranging from 0.01 up to 0.07 were obtained with the chelating and the solvating extractants and substantial silver extraction was only observed with the various amines. Amines require the formation of amine salts in order to be effective extractants and this is not possible from an ammonium thiosulphate solution, thus without pre-equilibration the primary, secondary and tertiary amines were found to be poor extractants. The distribution coefficients were <0.08 and the equilibrium pH-values ranged from 7.5 with Primene JM-T to 5.8 with Alamine 336.

Pre-equilibration with the sulphuric acid salt of Primene JM-T increases the distribution coefficient to 6.0. Lower equilibrium pH values resulted in the formation of a precipitate from thiosulphate degradation products.

The quaternary ammonium compounds are effective extractants also at high pH values and a distribution coefficient of 9.0 was measured for Aliquat 336 in the normal chloride form. Conversion to the sulphate or the nitrate form resulted in distribution coefficients of only 1.4 and 1.2, respectively. Comparable results were obtained with the analytical extractant TOMAC.

Amines were shown to be the most effective silver extractants from thiosulphate solutions. The quaternary ammonium compounds were selected for further studies because of their high distribution coefficients and low pH sensitivity.

6. STRIPPING

The silver in the organic phase must be stripped to a suitable salt solution from which silver is easily recovered by electrolysis. A number of salts were tested as 0.5 molar solutions for silver stripping from an organic phase containing 0.88 g/l Ag. The experiments were performed with equal volumes of the aqueous and organic phases. The results are shown in Table 2.

Nitrates are very effective silver stripping agents, chlorides less effective and no stripping is obtained with ammonium sulphate and ammonium acetate. Potassium nitrate and ammonium chloride were further tested for silver stripping at various concentrations, the results are shown in Fig. 2.

A 0.25 molar potassium nitrate solution stripps 84.7 % silver while a 4 molar ammonium chloride solution is needed in order to strip 83.7 %. However, nitrates bind very effectively to the alkylammonium ion, thus the solvent must be reconditioned before being returned to the extraction stages. In this respect ammonium chloride is a better choice enabling conditioning of the solvent to in the stripping stages.

Silver extraction from thiosulphate solutions is dependant on the thiosulphate concentration, an increase in thiosulphate concentration results in a decrease of silver extraction. One further stripping possibility would thus be to use different thiosulphate concentrations in the extraction and stripping stages. For a successful operation the thiosulphate concentration in the stripping stages need to be 2-3 molar which could be a drawback for the electrolytical silver recovery.

TABLE 2

Stripping 0.1 M Aliquat 336 with different salt solutions.

Stripping solution 0.5 M	Percentage Ag stripped
NaCl	7.5
KNO_3	94.1
HNO_3	73.9
H_2SO_4	1.2
NH_3	10.1
$(NH_4)_2SO_4$	<1
NH_4Cl	8.5
CH_3COONH_4	<1

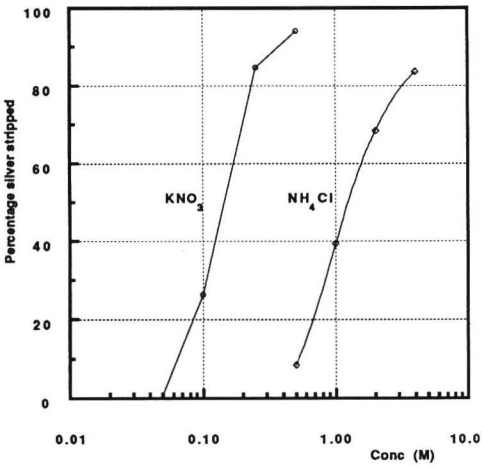


Fig. 2. Silver stripping with potassium nitrate and ammonium chloride.

7. DILUENT AND MODIFIER SELECTION

From environmental as well as working environment point of view aromatic kerosenes possess several drawbacks. The aqueous solubility is higher as compared with aliphatic kerosenes resulting in diluent losses and emissions to effluents. For these reasons Exxsol D 100 containing 0.9 % (w/w) aromatics was selected together with n-decanol as modifier. In order to prevent third-phase formation with 0.1 molar Aliquat 336 addition of 2 % of n-decanol is needed resulting in a distribution coefficient of 6.4 as is shown in Fig. 3.

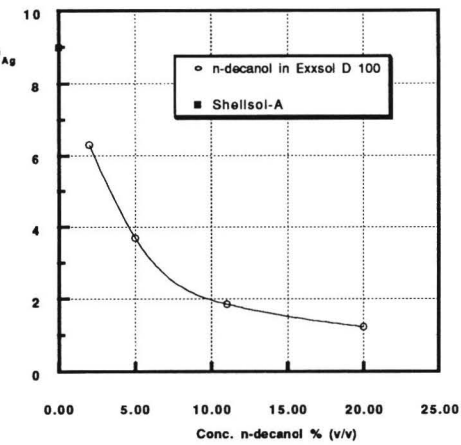


Fig. 3. D_{Ag} for different modifier conc.

8. CONCLUSION

Silver recovery from photographic thiosulphate solutions can be performed by solvent extraction with amines or quaternary ammonium chlorides. With Aliquat 336 no pH-adjustment is necessary and the distribution coefficient for silver was measured as 9.0 from a 0.5 molar thiosulphate solution. The distribution of silver decreases with increasing thiosulphate concentrations. Stripping can be performed by using potassium nitrate, ammonium chloride or by changing the thiosulphate concentration .

The results for analytical solutions were further shown to be applicable to industrial solutions which in excess of thiosulphate also contain sodium acetate, acetic acid, boric acid, sodium sulphite as well as low concentrations of aluminium chloride. One stage silver extraction with Aliquat 336 ranged from 68.5 to 98.9 % for graphical, bleach and photographic fixing solutions.

In aqueous thiosulphate solution silver complexes are formed according to:

$$mAg^{+} + nS_2O_3^{2-} \rightleftharpoons Ag_m(S_2O_3)_n^{m-2n} \quad (1)$$

Results with quaternary ammonium chlorides indicate that these complexes are extracted by exchange with chlorides:

$$p(m-2n)R_3NCH_3Cl + pAg_m(S_2O_3)_n^{m-2n} \rightleftharpoons (R_3NCH_3)_{p(m-2n)}[Ag_m(S_2O_3)_n]_p + p(m-2n)Cl^{-} \quad (2)$$

Lee et al. (1987, 1988) showed that from thiosulphate media species with m=1 and n=1 and 3 were extracted with the primary amine N 1923. This is in agreement with our preliminary results for Aliquat 336.

In industrial solutions the behaviour is further complicated by complexation with other anions as well as coextraction of thiosulphate, thiosulphate degradation products, halides and heavy metals such as cadmium and chromium.

Solvent extraction techniques have shown promising results for silver recovery, however in order to present a closed loop process where the environmental limits will be satisfied further knowledge must be gathered about different complexation and extraction equilibria in photographic fixing solutions.

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MECHANISM OF GALLIUM EXTRACTION BY TRI-N-OCTYLAMINE

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ABSTRACT

Gallium extraction by tri-n-octylamine (TOA) from hydrochloride solutions has been studied. Conducted spectrophotometric study of produced extracts has allowed to find changes resulting in cationic and anionic parts of components forming extraction system. For instance, Raman-spectra has indicated the presence of extractable complex with tetrahedral non-solvated anion $[GaCl_4]^-$ in the molecule. ^1H nuclear magnetic resonance spectra points to the fact of formation of protonated amine form. It is specified, that gallium extraction by TOA is going according to anion-exchanging mechanism with the formation of complex with the composition $[R_3NH]^+[GaCl_4]^-$ and effective extraction constant 13,4 ± 2,9.

INTRODUCTION

Analysis of the state of gallium in aqueous hydrochloride solutions allows to consider neutral and anion-exchanging extragents as the most effective from the point of view of selective extraction and concentration of valuable metal (Reznik, 1985).

Laws and mechanism of gallium extraction by tributylphosphate from before-mentioned media are in detail given in our earlier works (Kunaev et al., 1986; Ponomareva et al., 1988), which are supplementing a large quantity of publications, concerning this problem. Considerably less attention was given to gallium extraction from hydrochloride solutions by tertiary amines, the available data are limited only by laws of mutual influence of elements (Bagreev et al., 1978; 1982). The results of the studies of surface processes and of gallium extraction kinetics by TOA are given in other publications (Blaida et al., 1988; Abisheva et al., 1989). This paper is a logical continuation of those studies and is dedicated to the study of structure and composition of forming extractable complex and also to the determination of the effective constant of the process.

EXPERIMENTAL

Tri-n-octylamine of the firm "Hoechst", decylic alcohol, CCl_4 and other reagents with high degree of purity were used in this

work. Gallium solutions were prepared by dissolving of gallium with quality 99,999 in hydrochloric acid of the type "analytically pure" with the utilization of bi-distillated water. Analysis of the aqueous solutions for the gallium content has been made on the atomic absorption spectrophotometer of the firm "Hitachi". Gallium concentration in organic phase has been defined according to the difference among initial and equilibrium concentrations in aqueous phase. Raman spectra were recorded on the equipment "Pamanor-R" with the utilization of argon laser, ^1H nuclear magnetic resonance spectra - on the equipment "BS-467".

RESULTS AND DISCUSSION

Study of the kinetics of gallium extraction from hydrochloride solutions by TOA, of surface processes and also of stratification kinetics of dispersion's formation has shown that extraction system studied, belongs to structural-mechanical systems, i.e. to the systems, where particles of dispersive phase have the tendency of formation of floccules and aggregates (Shmidt et al.,1966). Formation of extractable complex in the case of macroconcentrations of Ga is going on the interface according to the reactions:

$$(R_3NHCl)_{2\ o} + GaCl_4^-{}_{aq} \overset{\text{slowly}}{\rightleftharpoons} (R_3NH)_2ClGaCl_{4\ o} + Cl^-_{aq} \qquad (1)$$

$$(R_3NH)_2ClGaCl_{4\ o} + GaCl_4^-{}_{aq} \overset{\text{quickly}}{\rightleftharpoons} 2R_3NHGaCl_{4\ o} + Cl^-_{aq} \qquad (2)$$

In case of gallium microconcentrations the process of complex formation is going according to the reaction:

$$1/2(R_3NHCl)_{2\ o} + GaCl_4^-{}_{aq} \rightleftharpoons R_3NHGaCl_{4\ o} + Cl^-_{aq} \qquad (3)$$

Thus, general equation of gallium extraction by TOA from hydrochloride solutions can be given as follows:

$$1/p(R_3NHCl)_{p\ o} + GaCl_4^-{}_{aq} \overset{K_{ex}}{\rightleftharpoons} R_3NHGaCl_{4\ o} + Cl^-_{aq} \qquad (4)$$

$$K_{ex} = \frac{[R_3NHGaCl_4]_o \cdot [Cl^-]_{aq}}{[(R_3NHCl)_p]_o^{1/p} \cdot [GaCl_4^-]_{aq}} \cdot \frac{\gamma_{compl.} \cdot \gamma_{Cl^-}}{\gamma_s^{1/p} \cdot \gamma_{GaCl_4^-}} \qquad (5)$$

and independently from the process conditions, the molar ratio of amine to metal in extractable complex is unity.

Raman-spectroscopic study of hydrochloride system: gallium - TOA

The Raman spectra of original gallium-containing solutions with the concentration 1,52 mol/dm^3, pure tri-n-octylamine and TOA extract, containing 0,43 mol/dm^3 of gallium (Fig. 1) were made for the study of the anionic part of extractable complex forming during gallium extraction by TOA. In this case the spectra of amine salt R_3NHCl coincides with the spectra of original tri-n-octylamine.

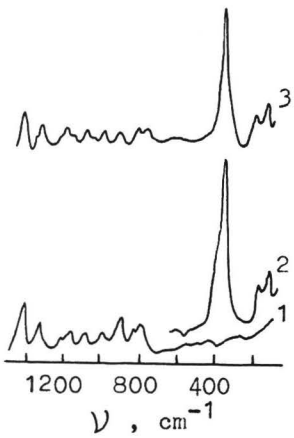


Fig. 1. Raman spectra of the compounds: 1 - TOA; 2 - solution, containing 1,52 mol/dm^3 of gallium and 6 mol/dm^3 HCl; 3 - TOA extract, containing 0,43 mol/dm^3 of gallium.

Raman spectra produced correspond to undistorted (unsolvated) tetrahedral anion $[GaCl_4]^-$ with the following characteristic bands (Schug and Katsin, 1962):

$\Delta\nu_2(E)$ = 117 cm^{-1} - strong depolarized peak;
$\Delta\nu_4(F_2)$ = 148 cm^{-1} - strong depolarized peak;
$\Delta\nu_1(A_1)$ = 346 cm^{-1} - very strong highly-polarized peak;
$\Delta\nu_3(F_2)$ = 386 cm^{-1} - depolarized peak (is not fixed on our spectra).

Spectra of ^1H nuclear magnetic resonance

^1H NMR spectra of 25% solution of TOA in CCl_4 (utilization of this inert diluent was necessary for the production of clearly expressed lines of chemical shifts), 25 % solution of amine salt TOA·HCl in CCl_4, and of extract produced as the result of interaction of extragent with solution, containing 0,43 mol/dm^3 of

gallium and 4 mol/dm^3 of HCl , are given on the Fig. 2.

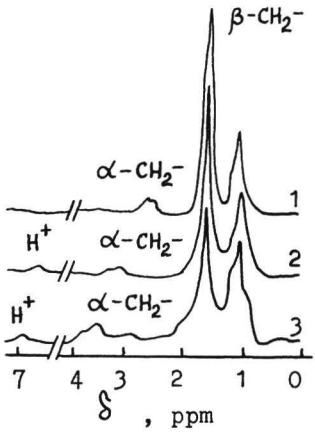


Fig. 2. ^{1}H NMR spectra of the compounds: 1 - TOA (25% solution in CCl_4); 2 - TOA-HCl (25% solution in CCl_4); 3 - TOA-$GaCl_4^-$ (25 % solution in CCl_4).

Thus it is seen from Fig.2, that in protonic part of amine molecule expressed changes are taking place as the result of interactions: on the undivided electronic pair of nitrogen atom the proton appears from hydrochloric acid ($\delta_{obs.}$ = 6,75 ppm) and from complex chlorogallic acid ($\delta_{obs.}$ =7,03 ppm) with the formation of $(R_3NH)^+$. During this α -CH_2-groups are displaced to the more acidic region. The change of chemical shift is larger during interaction of amine with the proton of chlorogallic acid, which confirms the known fact that $HGaCl_4$ is more strong acid than HCl. Less marked changes are taking place with β -CH_2-groups of amine, which are more remote from reaction centre.

Calculation of effective constant of gallium extraction by TOA

Thus the process studied is going according to the reaction (4) with the extraction constant (5). Yagodin (1981, p.102) assumes that if the association degree of amine salt is small and every molecule in associate can react independently from others, then changes of association degree of amine salts do not influence onto extraction constants and onto distribution coefficients, i.e. it is accepted that activity coefficients relation in organic phase is equal to 1 and their change can not be taken

into account. Besides this, if it is considered the region of concentrations of reactive components, where it is possible not to take into consideration the formation of intermediate products in aqueous phase, hydrolysis products and presence of soluted extractable complex, then the relation $[R_3NHGaCl_4]:[GaCl_4^-]$ can be considered as equal to distribution coefficient D.

On the basis of the assumption made, the expression (5) can be written as follows:

$$K_{ex} = D \cdot \frac{[Cl^-]_{aq}}{[R_3NHCl]_o} \cdot \frac{\gamma_{Cl^-}}{\gamma_{GaCl_4^-}} \qquad (6)$$

Anion activity $[GaCl_4]^-$ in aqueous phase is defined from the following expression:

$$a_{GaCl_4^-} = \frac{\beta_4 \cdot a_{Cl^-}^4}{1 + \sum_{i=1}^{4} \beta_i \cdot a_{Cl^-}^i} \cdot C_{Ga}, \qquad (7)$$

where β_4 and β_i - constant of stability of complex $[GaCl_4]^-$ and i-complex in aqueous phase, respectively; C_{Ga} - equilibrium concentration of gallium in aqueous phase. Taking into consideration small values of constants of stability of gallium chloride complexes $\beta_i < 10^{-2}$, $\beta_4 < 10^{-5}$ (Marcus, 1967; Reznik, 1985), then the denominator in expression (7) in the studied interval of concentrations of HCl (1 - 4 mol/dm^3) is near 1. In connection with the absence of reliable data about the value of β_4, and also for the simplification of calculations it is advisable to use the product $K_{ex} \cdot \beta_4 = \bar{K}_{ex}$ instead of K_{ex}. Besides this, equilibrium concentration of extragent in organic phase is possible to express as $[R_3NHCl] = S_o - y_{Ga}$, where S_o - initial concentration of extragent, y_{Ga} - equilibrium gallium concentration in organic phase. Final expression of effective extraction constant of gallium by TOA looks as follows:

$$\bar{K}_{ex} = \frac{D}{[S_o - y_{Ga}] \cdot [Cl^-]^3 \cdot \gamma_{Cl^-}^3} \qquad (8)$$

$\bar{K}_{ex}$ calculated according to equation (8) is equal 13,4 $\pm$ 2,9.

CONCLUSION

Raman spectra of gallium extract with TOA has shown onto the presence of tetrahedral non-solvated anion $[GaCl_4]^-$ in the molecule of extractable complex. ^1H NMR spectra of the same extract evidences about formation of protonated amine form. Thus, gallium extraction by TOA from hydrochloride solutions is going according to anion-exchanging mechanism with the formation of extractable complex with the composition $[R_3NH]^+[GaCl_4]^-$. Calculated effective constant of extraction is equal to 13,4 $\pm$ 2,9.

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RHENIUM EXTRACTION BY TRI-N-OCTYLAMMONIUM HYDROSULPHATE

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ABSTRACT

Rhenium extraction by tri-n-octylammonium hydrosulphate (TOA) from solutions of ammonium perrhenate, rhenium acid, mixture of rhenium and sulphuric acids has been studied by the method of infrared spectroscopy. IR-spectroscopic study of samples of extragents saturated from these solutions during various quantity of stages has shown that rhenium extraction is going according to anion-exchanging mechanism. Equivalence of exchange is supported by chemical analysis of sulphur. By the methods of saturation, isomolar series and dissolving it was found out that monosolvate TOA $HReO_4$ was formed as the result of interaction of TOA hydrosulphate with rhenium.

INTRODUCTION

Amines are widely used for the rhenium extraction from technological solutions. The great part of the papers published is dedicated to the extraction of rhenium by amines in the form of free base (Zelikman and Dragan,1967; Shinde,1984; Shaburova et al,1981). But its application in such form is not desirable for weekly acidic solutions containing sets of elements of II,III and VIII periods. Data on rhenium extraction by salts of tertiary amines are practically absent. In the work of Vinogradova(1971) supposition is made about graded course of the process of rhenium extraction by trialkylamine (TAA) from solutions of sulphuric acid: during the first stage TAA is forming salts with sulphuric acid, and then is changing sulphate or hydrosulphate TAA into perrhenate-ions. Results conforming this supposition are absent. This paper is dedicated to the study of rhenium extraction mechanism by TOA hydrosulphate.

EXPERIMENTAL

Solutions of rhenium acid were prepared from ammonium perrhenate of the type AR-0 by the method of electrodialysis developed at this Institute. Bi-distillated or heavy water was used as dissolver. Concentrations of rhenium and sulphur in organic phase

were defined both on the difference between initial and equilibrium concentrations in aqueous phase and on analysis of organic phase. Quantitative determination of rhenium was made according to usual methods by colorimetric and weight procedures (Borisova, 1974), that of sulphur - by methods of precipitation and titration (Busev,1975). Extragent was saturated by rhenium in 5 stages from 0,16 mol/dm^3 solution of rhenium acid (first set of experiments); mixture containing 0,16 mol/dm^3 of rhenium and 0,25 mol/dm^3 of sulphuric acid (second set) and also from 0,16 mol/dm^3 solution of ammonium perrhenate (third set). Residual contents of aqueous phase after each stage of extraction were eliminated from the extract by centrifuging. IR- spectra of initial extragent and extracts were registered on the infrared spectrophotometer UR-20 with utilization of covers KRS-5.

Composition of the compound forming in the process of extraction was defined by the methods of saturation, isomolar series and dissolving. All conditions characteristic for these methods were satisfied during conducting of experiments.

RESULTS AND DISCUSSION

During extraction from rhenium-containing solutions prepared on the bi-distillated water rhenium concentration in extracts prepared after third stage in first, second and third sets of experiments is 0,49; 0,43; and 0,54 mol/dm^3 respectively and is reaching maximum (1,29 mol/dm^3) just after third stage of extraction.

IR-spectre of initial extragent (Fig. 1-a) is characterized by the collection of absorption bands with maxima at 600, 1060, 1180-1200 cm^{-1} which were caused by deformational and valency vibrations of S-O and S=O bonds in HSO_4^--ions and do not contain absorption bands connected with vibrations of these bonds in sulphate-ions, i.e. TOA hydrosulphate is the extragent.

In the first set of experiments after first stage of extraction in IR-spectre of extract is appearing absorption band conditioned by bond vibrations in perrhenate-ions with maximum at 925 cm^{-1} intensity of which is gradually increasing and becomes maximal already in the spectre of the third example (Fig.1-b). In the region of vibrations of S=O bonds absorption band with maximum at 1100 cm^{-1} which evidences about the presence of sulphate ion in object.

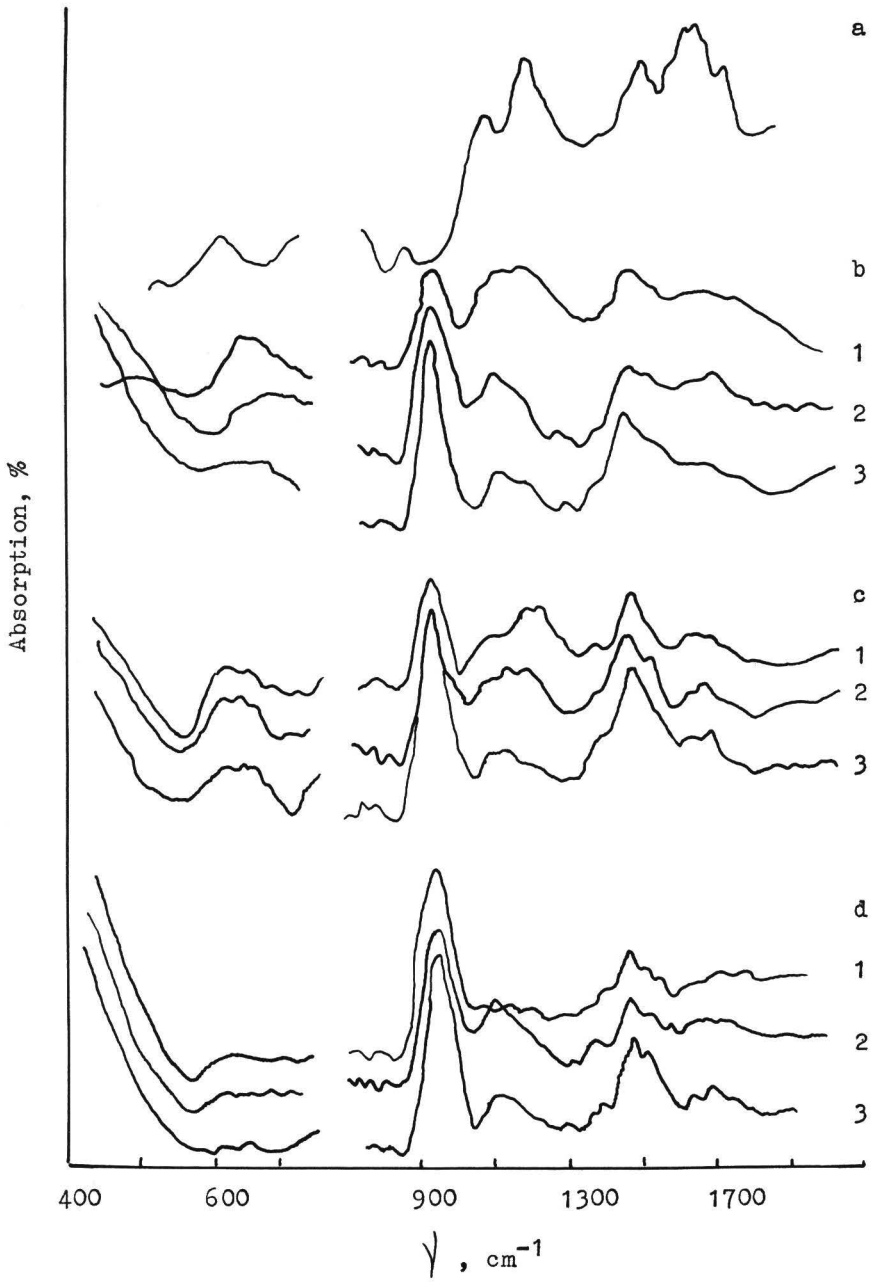


Fig.1. IR-spectra of TOA hydrosulphate(a) and extracts saturated by rhenium from solutions of rhenium acid(b), mixture of rhenium and sulphuric acids(c), perrhenate ammonium(d); 1,2,3 -numbers of stages of extraction.

In case of saturation of extragent with rhenium from sulphuric solutions the transition hydrosulphate to sulphate is delayed. In spectre 1 on the Fig.1-c absorption band intensity in the region 1180-1230 cm^{-1} is higher than that near 1100 cm^{-1}.

In IR-spectra of TOA saturated from the solution of ammonium perrhenate (Fig.1-d) absorption band connected with the vibration of perrhenate-ions is considerably increasing already after the first stage, and that of sulphate- and hydrosulphate-ions - is lowering.

Rearrangement of the part of hydrosulphate-ions to sulphates is taking place in all experiments during the contacting of extragent with rhenium-containing solutions. In dependence on the concentration of sulphuric acid in rhenium-containing solutions the quantity of hydrosulphate- and sulphate-ions in organic phase changes. The solution of the second set has the highest acidity and the third set uses neutral solution. It is possible to expect that during contact of TOA with sulphide solutions in dependence on its acidity, the localization of protons near nitrogen atoms changes and consequently changes electronic density on it. It is reflected on the increase or decrease of basicity of active centres of TOA and on formation of the following forms in highly acidic solutions - $R_3NH...\ HSO_4$ and $R_3N...\ HSO_4$, weakly-acidic and neutral - $R_3NH...\ SO_4$.

Complete saturation of extragent with rhenium is reached on third stage but after the first stage extract of the third set of the experiments contains the highest quantity of absorbed rhenium. At the first set quantity of rhenium absorbed after the first stage is considerably lower and that of sulphate- and hydrosulphate-ions - higher. All foregoing allows to think that before the exchange reaction is going the rearrangement of hydrosulphate-ions to sulphate-ions which are easily exchanging onto perrhenate-ions. Presumably because of high acidity of solution in the first two cases rearrangement of hydrosulphate-ions into sulphate-ions is delayed as does their transition into solution.

It is possible to follow the behavior of protons fixed by the nitrogen atom from TOA amino- group in the process of exchange of perrhenate for sulphate or hydrosulphate-ions. Rhenium extraction is made from solution of rhenium acid prepared on heavy water in conditions analogous with the first set of experiments.

High degree of deuterium exchange was confirmed by spectre of MDCIR (multiple disturbed complete inner reflection) of solution of rhenium acid. Absorption band with maximum at 1210 cm^{-1} (Fig.2, curve 1) corresponds to bond vibration in D_2O.

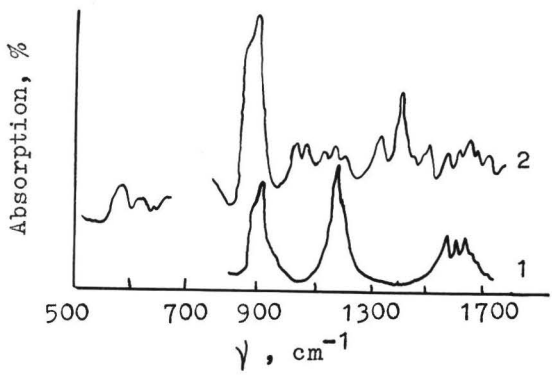


Fig.2. IR-spectra of rhenium acid (1), and extract (2).

Crystal KRS-5 with the angle of 45° between facets was used for the registration of MDCIR-spectra. It was suggested that in case of exchange of protonated forms of ions to deuterated in the spectra of extract must appear absorption bands at least of one isotopic form of hydroxonium ion (H_3O^+, OH_2D^+, OHD_2^+, D_3O^+) or their mixtures. But complete identity of spectra of initial extragent and extract (Fig.1-a, Fig.2, curve 2) and also of spectra of extracts in this and in first experiments does not confirm this, i.e. anionic exchange is provided at the expense of non-protonated ions. High degree of rhenium extraction from ammonium perrhenate solution on the first stage of extraction (third set of experiments) also is the confirmation of this.

Sulphur ions behavior study in the process of extraction has also confirmed anion-exchanging character of interaction of extragent with perrhenate-ions. It has been made a series of experiments with concentrations of TOA hydrosulphate which have been changing from 0,01 to 0,09 mol/dm^3 and the content of rhenium - from 0,09 to 0,01 mol/dm^3. Summarized contents of rhenium and sulphur in extract (after contacting of TOA hydrosulphate

with rhenium-containing solutions) is in accord with TOA concentration in extragent in equilibrium conditions. These data give evidence of equivalent exchange of sulphuric and rhenium acids.

Structure of the compound of TOA with perrhenate-ion defined by methods of saturation, equilibrium shift, isomolar series is corresponding to the composition TOA $HReO_4$.

CONCLUSION

By the studies made it has been found out that rhenium extraction by TOA hydrosulphate was going according to anion-exchanging mechanism with the formation of monosolvate. Rearrangement of hydrosulphate-ions to sulphates-ions is going before the exchange reaction.

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THE HIGH EFFICIENCY SEPARATION OF IRIDIUM FROM RHODIUM BY SOLVENT EXTRACTION USING A MONO N-SUBSTITUTED AMIDE.

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ABSTRACT

Iridium can be separated from rhodium(III) by solvent extraction following oxidation to iridium(IV). The reagents currently employed, however, tend to have disadvantages due either to limited oxidative stability, inadequate selectivity or low distribution coefficients. The extraction of iridium by a novel mono N-substituted amide is described. This reagent is easily prepared in high purity and possesses a high resistance to both hydrolysis and oxidative degradation. It extracts iridium strongly and has an excellent selectivity over both rhodium and over base metals such as copper, nickel, lead and arsenic. The effectiveness of the reagent has been confirmed during extended pilot-plant trials.

1 INTRODUCTION

The separation and subsequent purification of iridium and rhodium is one of the most difficult and costly aspects of the refining of the Precious Metals (PM). Rhodium and iridium are the last of the PM to be separated during refiningand the techniques available to date have been relatively inefficient. As a result there is a major recycle of both metals which contributes significantly to the metal inventory of a PM refinery.

Chloride is the only medium into which all the PM, except silver, can be effectively brought into solution. The separation of the PM from both each other and the accompanying base metals is then achieved by exploiting the differences in the chemistry of the chloro-complexes formed. For reasons which have been discussed elsewhere (Grant, 1990) the other PM are separated first leaving iridium and rhodium together with a number of base metals including copper, nickel, lead and arsenic. Rhodium and iridium are then separated utilising the fact that under oxidising conditions an iridium(IV) chloro-complex ($[IrCl_6]^{2-}$) is formed which can be extracted using an anion-exchange extractant. Rhodium, on the other hand, remains in the trivalent oxidation state mainly as $[RhCl_6]^{3-}$ and $[RhCl_5(H_2O)]^{2-}$ which are both poorly extracted.

2 CURRENT IRIDIUM EXTRACTION OPTIONS

The new Matthey Rustenburg Refiners solvent extraction process employs an amine for the separation of iridium. The extraction is carried out from strong

hydrochloric acid in order to maximise selectivity over rhodium (Figure 1). Despite the apparently low distribution coefficient, some extraction of rhodium still occurs as species which are not easily removed by scrubbing. As a result selectivity over rhodium is incomplete. Amongst the base metals, copper and lead are also extractable. Copper is easily removed using a low acidity scrub. Lead extraction on the other hand improves at low acidity and consequently it cannot be removed in this way. The extraction is therefore carried out under conditions which give a high iridium loading in order to "crowd out" the lead and so minimise co-extraction.

In order to achieve maximum removal of iridium the extraction is carried out under oxidising conditions to counteract reduction of the iridium(IV) by the organic. As iridium(IV) is strongly extracted at all acidities it is then stripped by reduction to iridium(III) which, like rhodium(III), is poorly extracted. The repeated cycling between oxidising and reducing conditions leads to fairly rapid degradation of the amine. Although the extractant is relatively inexpensive, its regular replacement is an additional operating cost.

An alternative flowsheet which was developed by Mintek (Evers et al., 1979) employs a quaternary ammonium ion-exchange resin which has a higher stability. The extraction chemistry is similar to that of an amine extractant although the selectivity over rhodium is poorer. The eluate must therefore be further purified by solvent extraction with tributylphosphate (TBP) prior to the final precipitation. INCO have also investigated the use of TBP (Edwards et al., 1982). A recent paper (Rimmer, 1989) suggests, however, that they currently rely on the traditional technique of precipitation of ammonium hexachloroiridate(IV).

TBP is a weak anion-exchange extractant. At high acidity it extracts a proton by solvation to form an organic cation.

$$n(C_4H_9O)_3PO + H^+ \longrightarrow ((C_4H_9O)_3PO)_nH^+$$

This then extracts iridium by ion-pair formation.

$$2((C_4H_9O)_3PO)_nH^+ + [IrCl_6]^{2-} \longrightarrow (((C_4H_9O)_3PO)_nH^+)_2[IrCl_6]^{2-}$$

Stripping is readily achieved using weak acid to reverse the formation of the organic cation. TBP has a high resistance to oxidation. It is, however, a relatively weak iridium extractant (Figure 2) and Evers et al. (1979) report <90% extraction. Furthermore, the separation factors over copper and lead are poor.

3 MONO N-SUBSTITUTED AMIDE EXTRACTANTS

Di N-substituted amides (RR'NCOR") are attracting increasing interest as alternatives to TBP for the processing of spent nuclear fuels (eg Thiollet,1989) and other metals. As part of a programme sponsored by MRR to develop a "second generation" PM solvent extraction flowsheet, a range of different amides were synthesised and screened. Amongst these, mono N-substituted amides (RHNCOR') proved to be extremely effective reagents for the extraction of the PM hexa-

chlorometallate(IV) complexes (Grant and Murrer, 1988). In particular, they are selective for $[PtCl_6]^{2-}$ over $[PdCl_4]^{2-}$ (separation factor >25) which allows the normal order of extraction to be reversed, resulting in a significant reduction in platinum inventory. They are also highly selective over divalent base metals such as copper and lead which form $[MCl_4]^{2-}$ ions as well as the rhodium(III) chloro-complexes. Consequently they have the ideal extraction properties for an iridium reagent.

3.1 Synthesis

The mono-amides are easily synthesised in high yield from readily available starting materials. A carboxylic acid is first converted to the acid chloride by reaction for example with thionyl chloride.

$$R'COOH + SOCl_2 \longrightarrow R'COCl + SO_2 + HCl$$

This acid chloride is then reacted with a slight excess of primary amine in a diluent such as hexane with triethylamine added as a base.

$$RNH_2 + R'COCl + (CH_3)_3N \longrightarrow RNHCOR' + (CH_3)_3NHCl$$

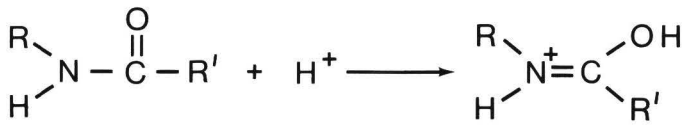
The triethylammonium chloride and the excess amine are then removed by acid washing, followed by alkali to remove any carboxylic acid and unreacted chloride. Finally the hexane is evaporated to yield the mono-amide in high purity (>99%) and yield (>95%).

3.2 Diluent selection and third-phase formation

Due to the poor organic solubility of PM chloro-complexes / extractant ion pairs, highly aromatic diluents such as Solvesso 150 are normally employed. A number of its components are however fairly easily oxidised and will reduce iridium(IV). Consequently the extraction has to be carried out under strongly oxidising conditions to counteract this. Alternative diluents were therefore investigated and a dearomaticised paraffin, Escaid 110, was selected. Under conditions of high loading the organic was highly viscous and third-phase formation could occur. Both were readily overcome by the addition of small quantity of TBP as a modifier. Alternatively 2,6-dimethyl 4-heptanone (di-iso-butyl ketone) can be employed as the diluent without the addition of a modifier.

3.3 Extraction Mechanism

Amides are weak bases which undergo protonation in contact with strong acid.



Consequently, they are similar to TBP in that extraction occurs at high acidity

whilst they can be stripped at low acidity. The variation in distribution coefficient with acidity is, however, far greater than with solvating extractants (Figure 3). As a result they are far stronger extractants than TBP and substantially complete extraction (>99.9%) can be achieved. Due to the very low distribution coefficient at low acidities they are also extremely easy to strip (Figure 4).

3.4 Selectivity

As discussed above the mono-amides offer a very high selectivity. The extraction behaviour of a typical reagent is presented in Figure 3 and shows the very high selectivity over rhodium. With the correct selection of the alkyl substituents, separation factors of $>10^5$ can be achieved. Selectivity over copper and lead is also high with the optimum acidity for extraction at around 5M.

3.5 Pilot plant trials

Following successful completion of bench studies the optimised reagent was tested on a small scale pilot plant for a total of 650 hours operation. The extraction was excellent with the level of iridium relative to rhodium in the raffinate averaging 0.18% with a best result of 0.11%. This compares with an average of 1.2% and a best of 0.5% with the existing amine extractant.

The separation of iridium from rhodium was very high with an average of .013% (best <.007%) rhodium on iridium in the strip compared with an average of 2% (best 0.5%) for the amine. Selectivity over the base metals was excellent with <0.1% lead and <0.01% copper, nickel and arsenic in the strip. The strip was readily processed via the current final purification route to an iridium sponge which was >99.84% pure. The spectrographic analysis of the product is recorded in Table 1. The overall yield of iridium sponge from the feed was >98%.

At the end of the pilot plant trials the organic was analysed by a variety of techniques including capillary GC. All failed to identify any evidence of oxidative degradation of either the amide, modifier or diluent. The amide had, however, started to hydrolyse to the parent acid and amine although the rate was extremely slow (1.3% $annum^{-1}$).

$$RHNCOR' + H_2O \longrightarrow RNH_2 + R'COOH$$

The modifier, TBP, was also undergoing hydrolysis to dibutyl phosphoric acid at roughly the same rate (2% $annum^{-1}$).

$$(C_4H_9O)_3PO + H_2O \longrightarrow (C_4H_9O)_2POOH + C_4H_9OH$$

The diluent was largely unaffected and the only change identified was a slight

TABLE 1

Spectrographic analysis of iridium sponge prepared from the mono N-substituted amide strip liquor.

Element	Percentage	Element	Percentage
Iridium	99.984	Copper	0.0007
Palladium	<0.0001	Iron	0.001
Platinum	0.001	Lead	0.002
Rhodium	0.001	Magnesium	0.0001
Ruthenium	0.003	Nickel	0.0003
Aluminium	0.001	Silver	0.0001
Calcium	0.001	Tin	0.005
Chromium	0.0001		

preferential loss of the more volatile components of the petroleum fraction.

None of these changes had any effect on either the extraction properties or selectivity whilst phase separation remained excellent throughout. There is therefore no reason to believe that the organic should not be capable of achieving a lifetime of a year or more.

The authors wish to thank Matthey Rustenburg Refiners for permission to publish this paper.

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FIGURE 1
Extraction by 0.25M Trioctylamine
in Solvesso 150

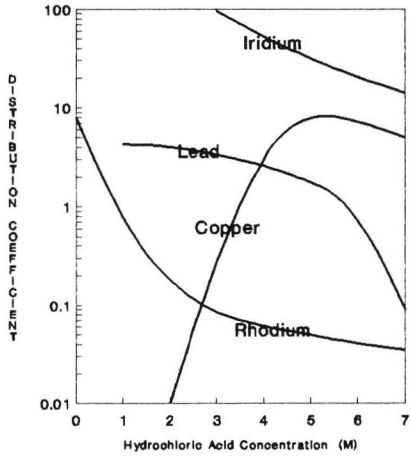


FIGURE 2
Extraction by 2M Tributylphosphate
in Solvesso 150

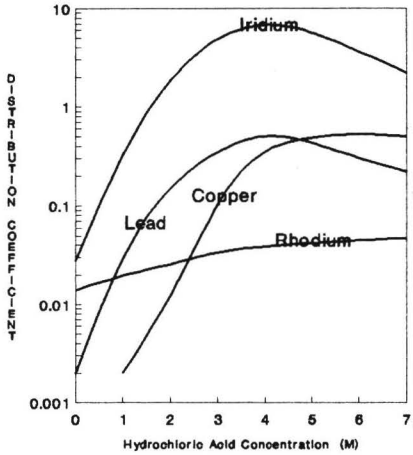


FIGURE 3
Extraction by 0.4M Mono N-Amide
+ 15% TBP in Escaid 110

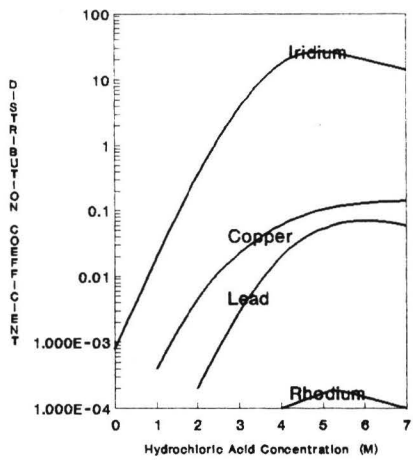
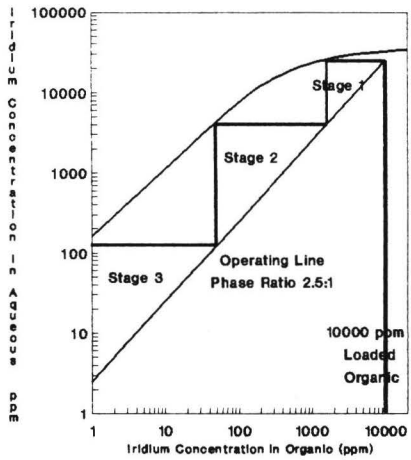


FIGURE 4
Stripping Iridium from 0.4M Mono N-Amide
+ 15% TBP in Escaid 110 Using 0.1M HCl



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EXTRACTION OF LANTHANIDE IONS WITH BENZOYLTRIFLUOROACETONE-TRI–n–BUTYLPHOSPHATE: SYNERGISM AND ANTAGONISM

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Abstract

This paper reports data on the extraction of Eu^{3+}– and Tm^{3+}–ion from aqueous $HClO_4$ – $NaClO_4$ with benzoyltrifluoroacetone (HBTA)/tri–n–butylphosphate (TBP) in benzene. At low concentration the synergism can be explained by the formation of complexes of the Ln–β–diketonate with one and two mole of the synergic coreagent; however, the formation constants of these complexes decrease with increasing concentration of HBTA. This observation, as well as the observed destruction of the synergism at high concentration of TBP, is due to the formation of hydrated species, resulting in a decrease of the activity (the concentration of the "free" extractants). The formation constants of the hydrated complexes were obtained from Karl Fischer titrations in combination with UV and IR spectral data. Taking into account the effect of these species, the extraction data can be fully interpreted assuming the formation of complexes with up to three mole TBP per $Ln(BTA)_3$.

INTRODUCTION

The synergic effect of neutral organophosphorous derivatives in the extraction of metal ions with β–diketones has been the subject of a large number of papers and reviews[1,2], and is generally interpreted by the formation of mixed ligand complexes in the organic phase.

At low concentration of the synergic reagent the data can easily be analyzed by the mass action law to calculate the stability constants of the mixed complexes. However, at high concentration, the distribution ratios show a gradually increasing deviation from the expected behavior, and eventually decrease at very large concentrations of the synergic reagent. Destruction of synergism (antagonism) at high concentration of the synergic reagent has been attributed to the formation of association products with the extracting agent or to the effect of increasing amounts of water in the organic phase[3,4]. The quantitative analysis of these interactions, and their role in the extraction of metal ions is, up till now, very limited.

In view of a quantitative description of the synergism and antagonism in the extraction and separation of lanthanide and actinide ions, this paper reports data for the extraction of Eu^{3+} and Tm^{3+}–ion with HBTA–TBP and on the interaction of the both these reagents with water in benzene. It will be shown that the antagonistic effect can quantitatively be accounted for on basis of the formation constants of the hydrated complexes in the organic phase.

2 EXPERIMENTAL

2.1 Reagents

Commercially available reagents (a.g. products) are purified by classical procedures.

When needed, benzene (Fluka or Baker) was dried by refluxing on sodium metal wire, and subsequently distilled. The radioisotopic mixture $^{152\text{-}154}Eu$ and ^{170}Tm (Radiochemical Centre Ltd., Amersham U.K.), obtained as chlorides in HCl, were converted to the perchlorate form.

2.2 Techniques

The procedure of the the extraction experiments was described previously[5].

The total water content of the organic solutions of HBTA, TBP, and their mixtures, after equilibration with 1M $NaClO_4/HClO_4$ at $p_cH \simeq 3$, was measured by Karl Fischer titration using a coulometric titrator (Metrohm 652 KF). UV spectra were recorded on a Beckman Acta M–IV spectrometer in 10 mm quartz cells at 25 ± 0.1 °C. Infrared spectra were recorded on a Beckman IR 4250 spectrometer in 1 mm quartz Infrasil cells. The pH of the aqueous phase after equilibration with the organic phase was measured using a Corning Model 12 pH meter; mV readings were converted to p_cH values using a calibration plot obtained by measuring reference solutions of known acidity at the same ionic strength.

3 RESULTS and DISCUSSION

3.1 Extraction of Eu^{3+} and Tm^{3+}–ion with HBTA–TBP

It was shown previously that tris–chelates are formed in the extraction of lanthanide ions with strongly acidic β–diketones; addition of TBP results in distribution ratios that are several orders of magnitude larger, due to the formation of mixed complexes according to:

$$Ln_a^{3+} + 3\,HBTA_{o,t} \rightleftharpoons Ln(BTA)_{3,o} + 3\,H_a^+ \qquad (1)$$

$$Ln(BTA)_{3,o} + i\,TBP_o \rightleftharpoons Ln(BTA)_3(TBP)_{i,o} \quad (K_{s,i}) \qquad (2)$$

The synergic effect of TBP on the extraction equilibria can then be formulated as:

$$\frac{[(D/D^o) - 1]}{[TBP]_{o,t}} = K_{s,1} + K_{s,2}\cdot[TBP]_{o,t} + K_{s,3}\cdot[TBP]_{o,t}^2 + \ldots \qquad (3)$$

with D^o and D the distribution ratios in the absence and presence of TBP.

Table 1

Formal formation constants of mixed complexes of $Ln(BTA)_3$ with TBP in benzene.

$[HBTA]_{o,t}$	Eu^{3+}		Tm^{3+}	
M.	$10^4\cdot K_{s,1}$	$10^7\cdot K_{s,2}$	$10^4\cdot K_{s,1}$	$10^6\cdot K_{s,2}$
0.001	4.01 ± 0.85	4.43 ± 0.06		
0.005	4.44 ± 0.69	4.25 ± 0.05		
0.025	5.36 ± 0.50	3.73 ± 0.04	6.28 ± 0.24	3.39 ± 0.20
0.05	3.01 ± 0.49	3.55 ± 0.05		
0.10	2.85 ± 0.64	2.84 ± 0.06	5.35 ± 0.11	2.22 ± 0.09
0.20	2.14 ± 0.43	2.10 ± 0,04		
0.25	1.87 ± 0.15	1.82 ± 0.02	3.84 ± 0.16	1.07 ± 0.14

Up to 0.025 M TBP the plots $(D/D^o-1)/[TBP]_{o,t}$ vs $[TBP]_{o,t}$ are linear, indicating that mixed complexes with up to two mole of TBP are formed; however, the value of $K_{s,1}$ and $K_{s,2}$ decrease with increasing concentration of HBTA (table 1); this fact was not reported by other researchers, because in most studies the synergic effect was measured at only one concentration of the β–diketone. For concentrations larger than 0.025 M the plots become nonlinear, and even decrease for high concentrations of TBP (fig.1.) This behavior, also observed by other groups, is attributed to an increase of the water content of the organic phase; however, data to support this conclusion are scarce, and a quantitative interpretation of the extraction data based on the formation of hydrated species has rarely been attempted.

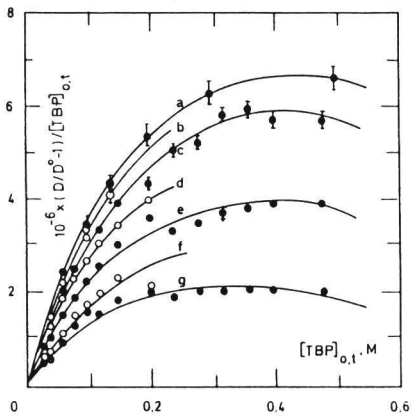


Fig.1: Synergism and antagonism in the extraction of Eu(III) with HBTA/TBP: $[HBTA]_{o,t}$ = 0.001 (a), 0.005 (b), 0.025 (c), 0.05 (d), 0.1 (e), 0.2 (f) and 0.25 M (g).

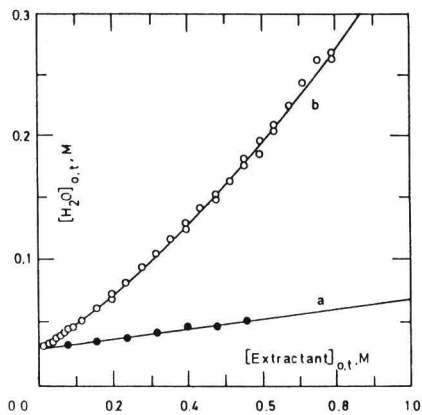


Fig.2: Extraction of water by HBTA (a) and by TBP (b) in benzene (aqueous phase: 1M $NaClO_4$/ $HClO_4$, p_cH = 2.97); points are experimental data, curves are calculated values (cfr. text).

3.2 Extraction of water by HBTA, TBP and HBTA–TBP mixtures

The formation of hydrated complexes in the organic phase can be formulated as:

$$n\ HBTA_o + m\ TBP_o + r\ H_2O_o \rightleftharpoons^{K_{nmr}} (HBTA)_n(TBP)_m(H_2O)_{r,o} \qquad (4)$$

with: $K_{nmr} = \dfrac{[(HBT)_n(TP)_m(H_2O)_r]_o}{[HBTA]_o^n[TBP]_o^m}$; (at low concentration of HBTA and TBP the amount of "free" water in benzene remains constant and is included in the stability constants K_{mnr}.

In absence of TBP, the amount of water increases linearly with increasing concentration of HBTA (fig.2 curve a), thus indicating that only monomeric hydrates are formed. T.V. Healy et al.[3] have shown that HTTA forms a ketohydrate with one mole of water. If a similar complex is formed for HBTA, the mass balance equation of water can be written as:

$$[H_2O]_{o,t} = [H_2O]_o + \frac{K_{101}}{1 + K_{101}}[HBTA]_{o,t} \qquad (5)$$

The formation constant of the ketohydrate (K_{101} = 0.041 ± 0.001) is calculated from the slope of the line; the intercept (0.0293 ± 0.0004) corresponds to the solubility of water in benzene and is in good agreement with values reported in the literature.

The water content as function of the concentration of TBP in absence of HTTA (fig.2 curve b) deviates from a straight line, indicating the formation of hydrated species with more than one mole TBP. The data were analyzed by a non–linear regression method. The best result (the curve in fig 2) was obtained for a model involving two hydrated species: a monomeric monohydrate (K_{011} = 0.203) and a dimeric dihydrate (K_{022} = 0.199).

Further evidence on the formation of TBP–H_2O complexes was obtained from IR data. Spectra of TBP in benzene, equilibrated with a $NaClO_4$–$HClO_4$ solution, vs water saturated benzene as reference, are shown in figure 3. The sharp band at 3690 cm^{-1} corresponds with the stretching vibration of free OH–groups of water bonded to TBP; the broad band at 3470 cm^{-1} is indicative for OH–groups linked to TBP through a hydrogen bond[6].

The concentration of water in mixtures HBTA–TBP in benzene is larger than calculated on basis of the complexes identified in solutions of HBTA and of TBP, indicating the presence of mixed hydrates. The stoichiometry of these complexes was studied using UV spectrometry. The spectrum of HBTA in dry benzene shows a broad band with maximum at 332 nm due to the enol–form. This spectrum remains unchanged when the solution is equilibrated with water: this is not unexpected: it was shown for HTTA in water saturated benzene that less than 5 % of the enol is transformed into ketohydrate, that has a negligible absorbance[3].

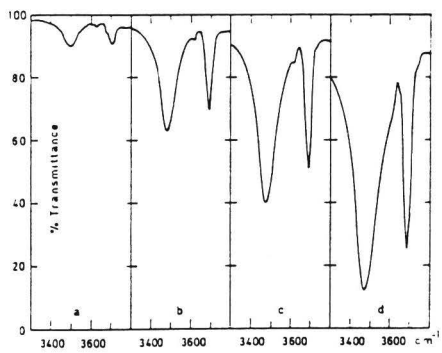


Fig.3: IR spectra of the OH stretching of TBP-H_2O complexes in benzene vs water-saturated benzene as reference solution. $[TBP]_{o,t}$ = 0.016 (a), 0.088 (b), 0.16 (c) and 0.32 M (d).

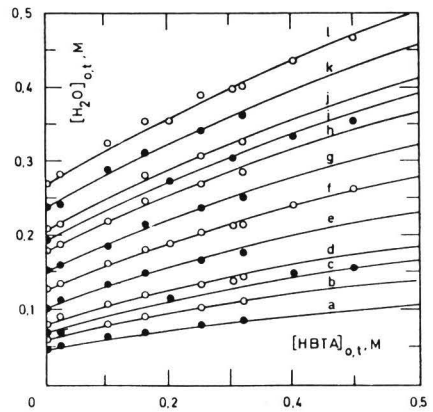


Fig.4: Extraction of water vs HBTA at different concentrations of TBP. $[TBP]_{o,t}$ = 0.10 (a), 0.16 (b), 0.20 (c), 0.24 (d), 0.32 (e), 0.40 (f), 0.48 (g), 0.56 (h), 0.60 (i), 0.64 (j), 0.72 (k) and 0.8 M (l).

The spectrum of HBTA (± 10^{-4} M) in dry benzene is not affected by adding dry TBP. However, if these solutions are equilibrated with an aqueous $NaClO_4/HClO_4$ solution, increasing concentrations of TBP result in a progressive decrease of the absorbance without a

change in the general shape of the absorption band. This indicates the formation of a complexes $(BTA)_1(TBP)_m(H_2O)_r$. At these concentrations of HBTA it is reasonable to supppose that only species with one mole HBTA are formed; the ratio of the absorbances of HBTA solutions without and with TBP (A^o/A) can then be written as:

$$\frac{A^o}{A} = 1 + \frac{K_{111} + K_{112}}{1 + K_{101}} \cdot [TBP]_o + \frac{K_{121} + K_{122}}{1 + K_{101}} [TBP]_o^2 + \ldots \qquad (6)$$

The formation constants of the mixed hydrates are then obtained as the coefficients of a polynome fit of the second degree: $K_{111} + K_{112} = 1.48 \pm 0.22$ and $K_{121} + K_{122} = 0.76 \pm 0.27$. In order to discern whether these species are mono or (and) dihydrates, the concentration of water is calculated by iteration using the mass balance equation for water, but including in it a term for mixed hydrates with two mole of HBTA, since in the Karl Fischer titrations the amount of HBTA is much larger than used for the UV spectrometry:

$$[H_2O]_{o,t} = [H_2O]_o + K_{101} \cdot [HBTA]_o + K_{011} \cdot [TBP]_o + 2 \cdot K_{022} \cdot [TBP]_o^2 + (K_{111} + 2 \cdot K_{112})[HBTA]_o[TBP]_o + (K_{121} + 2 \cdot K_{122})[HBTA]_o[TBP]_o^2 + \sum_m \sum_r \cdot K_{2mr} \cdot r \cdot [HBTA]_o[TBP]_o^m \qquad (7)$$

The best set of values that minimize the difference between the calculated and the measured water content was obtained for $K_{111} = 1.13$; $K_{112} = 0.35$; $K_{121} = 0$; and $K_{122} = 0.76$, and including a mixed hydrate with stoichiometry $(HBTA)_2(TBP)_1(H_2O)_1$ with $K_{211} = 7.0$. This is illustrated in fig.4 where the measured total water content is plotted vs the total HBTA for different concentrations of TBP; the curves in the figure are the calculated values using the constants for simple and mixed hydrates as given in the text.

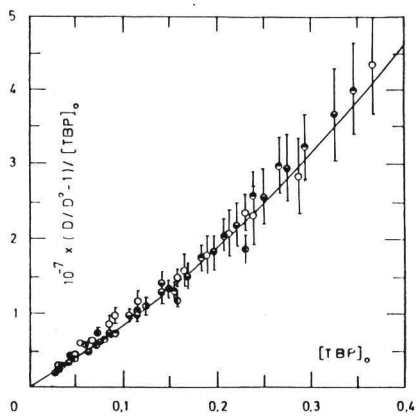


Fig.5: Synergism of TBP in the extraction of Eu(III) according to eq.3, taking into account the different hydrated complexes; points are experimental data (at different concentrations of HBTA); the curve is the best polynome fit.

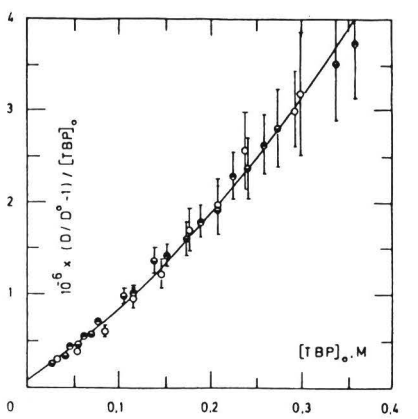


Fig.6: Synergism of TBP in the extraction of Tm(III) according to eq.3, taking into account the different hydrated complexes; points are experimental data (at different concentrations of HBTA); the curve is the best polynome fit.

In order to include the effect of the hydrated species on the synergic extraction of both Eu^{3+} and Tm^{3+}, the distribution data of both metal ions are plotted according to eq.3, but the concentrations of HBTA and of TBP are these of the "free", uncomplexed species. They are calculated from the mass balance equations taking into account all the hydrated species that were shown to exist in benzene. At low concentration of TBP ($[TBP]_0$<0.02 M) the data $(D/D^o - 1)/[TBP]_0$ vs $[TBP]_0$) fit on one straight line; at concentrations larger than 0.02 M, the extraction data show a gradually increasing upward deviation from the linear behavior (see fig.5 and 6), thus indicating that under these conditions mixed complexes are formed with more than two mole of TBP. The complete set of distribution data for both lanthanide ions were analyzed using a second order polynome regression (curves in the figures); the coefficients of the polynome correspond with the stability constants $K_{s,1}$,$K_{s,2}$ and $K_{s,3}$ and are listed in table 2.

Table 2

Stabillity constants for the complex formation of $Ln(BTA)_3$ with TBP in benzene at 25 °C.

	$K_{s,1}$	$K_{s,2}$	$K_{s,3}$
Eu^{3+}	$(4.16 \pm 0.22)\cdot 10^4$	$(7.48 \pm 0.08)\cdot 10^7$	$(1.30 \pm 0.12)\cdot 10^8$
Tm^{3+}	$(7.88 \pm 0.18)\cdot 10^4$	$(5.76 \pm 0.19)\cdot 10^6$	$(1.21 \pm 0.17)\cdot 10^7$

From the present study it follows that the antagonism observed at high concentration of TBP, as well as the dependence of the formation constants of the mixed ligand complexes on the HBTA concentration, can be fully accounted for by the decrease of the activity of both these compounds due to the formation of several hydrated species in the organic phase. If the concentrations of HBTA and TBP are corrected for these hydrated species, the synergic effect of TBP in the extraction Eu^{3+} and Tm^{3+} ion with HBTA can be described quantitatively over the whole concentration range of TBP and at varying concentrations of HBTA by the formation of mixed complexes $Ln_3(BTA)_3(TBP)_i$, with i = 1 to 3.

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EXTRACTION MECHANISM OF Ga WITH 2-BROMODECANOIC ACID

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ABSTRACT

The extraction equilibrium and rate of gallium with 2-bromodecanoic acid were investigated experimentally using octane as a diluent. From the equilibrium study, we have found that two kinds of 2-bromodecanoic acid-gallium complexes are formed in octane depending on the loading ratio of gallium to the extractant. From the results of the equilibrium and rate experiments, we proposed an extraction model. The experimental results on the forward and reverse extraction rates were explained quantitatively by this model.

INTRODUCTION

We have studied the applicability of liquid membrane to a hydrometallurgical process of gallium and indium from the gypsum which is the residue of zinc recovery from Black Ore produced in Akita Prefecture, Japan (Fujinawa et al., 1989; Shono et al., 1989; Hozawa et al.,1987). In the commercial solvent extraction process, Versatic 10, a kind of calboxylic acid, was used as an extractant for the first preconcentration stage. We found 2-bromodecanoic acid(2BDA) was superior to Versatic 10 as an extractant in the liquid membrane system(Shono et al.,1989). The purpose of this work is to make clear quantitatively the extraction mechanism of Ga with 2BDA.

1 EXPERIMENTAL

2-Bromodecanoic acid(2BDA) was synthesized according to Preston et al. (1983) and diluted with octane. The stock solution of gallium was prepared by dissolving gallium metal in perchloric acid. The ionic strength of the aqueous phase was adjusted to 0.1mol/dm^3 by adding sodium perchlorate.

For the equilibrium experiments, the organic and aqueous phases of equal volume(15ml) were shaken together in a 50 ml stoppered conical beaker for a half day. Initial concentration of gallium in the aqueous phase was 0.0025 mol/dm^3. Concentration of metals in the aqueous phase was measured by atomic

absorption spectrometry and that of organic phase was determined by a mass balance equation.

To measure the extraction rate, we used a stirred transfer cell. In the forward extraction rate measurement, the compositions of the two phases were the same as those of the equilibrium measurements. In the reverse extraction rate measurement, 2BDA in the organic phase was loaded with gallium previously and hydrochlolic acid solution was used as the aqueous phase.

All experiments were carried out at 298K.

2 RESULTS AND DISCUSSION

2.1 EXTRACTION EQUILIBRIUM

For the equilibrium of Ga-2BDA system, the followings were assumed. 2BDA exists as dimer in octane and gallium in the aqueous phase forms j-mer complexes with the extractant.

$$j\ Ga^{3+} + j(3+x)/2\ (\overline{HR})_2 \underset{}{\overset{K_{(j,x)}}{\rightleftharpoons}} (\overline{GaR_3 \cdot xHR})_j + 3j\ H^+ \qquad (1)$$

where HR is a monomer of 2BDA and x means the number of coordination of the undissociated extractant in the complex. The equilibrium constant $K_{(j,x)}$ is defined as follows.

$$K_{(j,x)} = \frac{[(\overline{GaR_3\ xHR})_j]\ [H^+]^{3j}}{[Ga^{3+}]^j\ \ [(\overline{HR})_2]^{j(3+x)/2}} \qquad (2)$$

Total concentration of gallium in octane, $[\overline{Ga}]_t$ is expressed as follows.

$$[\overline{Ga}]_t = \sum_j \sum_x j \cdot K_{(j,x)} \cdot [Ga^{3+}]^j \cdot [(\overline{HR})_2]^{j(3+x)/2}\ [H^+]^{-3j} \qquad (3)$$

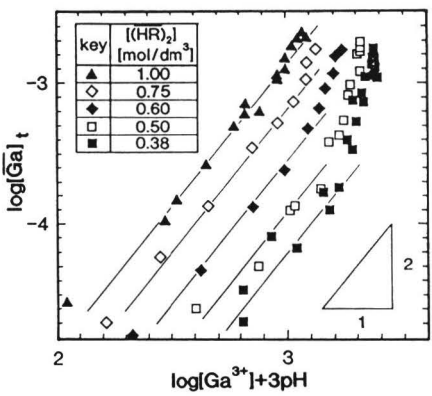


Fig. 1. Determination of value j in Eq.(4) in low loading ratio of Ga to 2BDA.

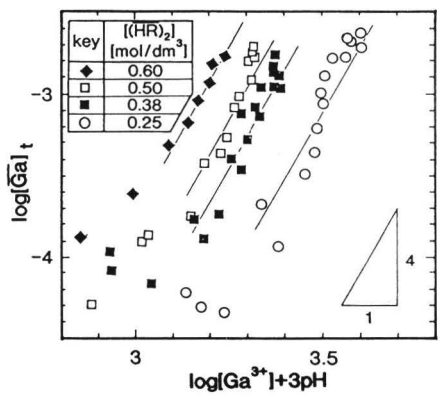


Fig. 2. Determination of value j in Eq.(4) in high loading ratio of Ga to 2BDA.

Supposing that only $(\overline{GaR_3 \cdot xHR})_j$ is the extracted species, the following equation is obtained.

$$\log[\overline{Ga}]_t = j(\log[Ga^{3+}] - 3\log[H^+]) + j(3+x)/2 \cdot \log[(\overline{HR})_2] + \log(j \cdot K_{(j,x)}) \quad (4)$$

The value of j can be determined from the plot of $\log[\overline{Ga}]_t$ against $(\log[Ga^{3+}] - 3\log[H^+])$ under a constant extractant concentration. The results are shown in Figs. 1 and 2. As ionic strength of aqueous phase was constant under the experimental conditions, pH value was used instead of $-\log[H^+]$. We found that there were two values of j depending on the loading ratio of gallium to the extractant. In the low loading ratio, the value of j is 2, while in the high loading ratio, j is 4.

From Eq.(4), we can then decide the x value from the slope of the plot of $(\log[Ga^{3+}] + 3pH)$ against $(\log[(\overline{HR})_2])$ for each value of j under the constant $[\overline{Ga}]_t$. The results are shown in Figs. 3 and 4. The value of the slope in each figure shows (3+x)/2, yielding x=0 and x=-1 for j=2 and j=4 respectively.

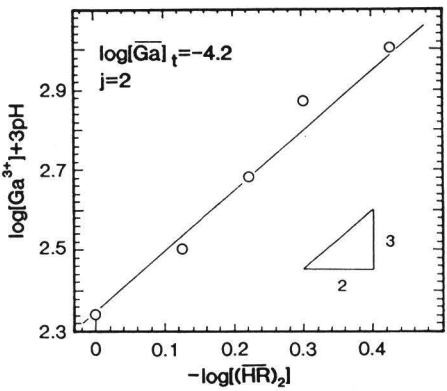


Fig. 3. Determination of value x(j=2).

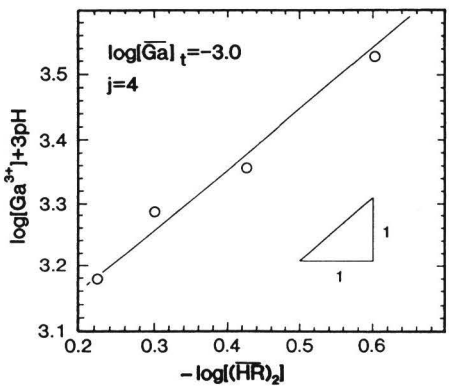


Fig. 4. Determination of value x(j=4).

Consequently, the extraction equilibrium and the equilibrium constants are expressed as follows.

$$2Ga^{3+} + 3(\overline{HR})_2 \underset{\log K_{(2,0)} = -8.6}{\overset{K_{(2,0)}}{\rightleftharpoons}} (\overline{GaR_3})_2 + 6H^+ \quad (5)$$

$$4Ga^{3+} + 4(\overline{HR})_2 + 4H_2O \underset{\log K_{(4,-1)} = -14.3}{\overset{K_{(4,-1)}}{\rightleftharpoons}} (\overline{GaR_2(OH)})_4 + 12H^+ \quad (6)$$

The equilibrium between the dimer $(\overline{GaR_3})_2$ and the tetramer

$(\overline{GaR_2(OH)})_4$ can be considered as follows,

$$2(\overline{GaR_3})_2 + 4H_2O \overset{K_{2to4}}{\rightleftharpoons} (\overline{GaR_2(OH)})_4 + 2(\overline{HR})_2 , \quad (7)$$

where the equilibrium constant K_{2to4} is defined as $K_{2to4} = [(\overline{GaR_2(OH)})_4] \cdot [(\overline{HR})_2]^2 / [(\overline{GaR_3})_2]$ and $\log(K_{2to4}) = 2.97$.

2.2 EXTRACTION RATE

As the next step, we studied the forward and the reverse extraction rates, experimentally. We investigated the experimental dependence of the concentration of concerning chemical species

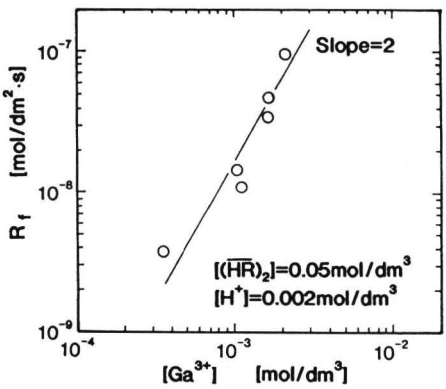


Fig. 5. Effect of Ga concentration in aqueous phase, $[Ga^{3+}]$ on forward extraction rate, R_f.

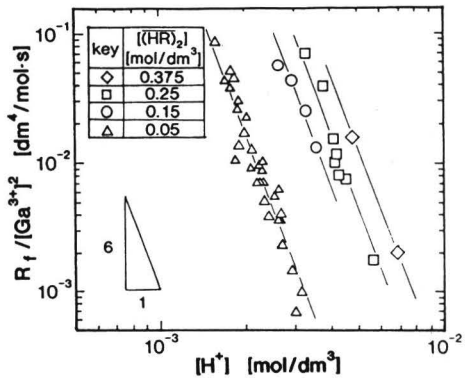


Fig. 6. Effect of proton concentration in aqueous phase, $[H^+]$, on R_f.

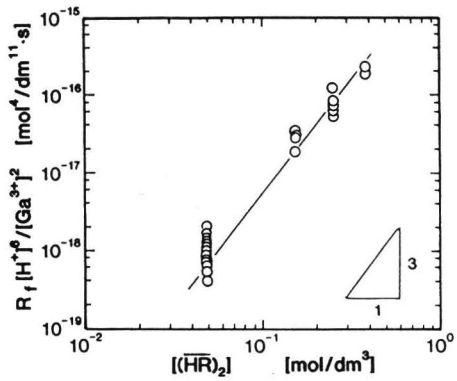


Fig. 7. Effect of extractant concentration in aqueous phase, $[(\overline{HR})_2]$, on R_f.

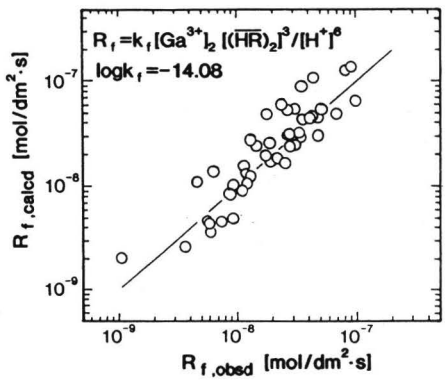


Fig. 8. Comparison between observed and calculated values of forward extraction rate.

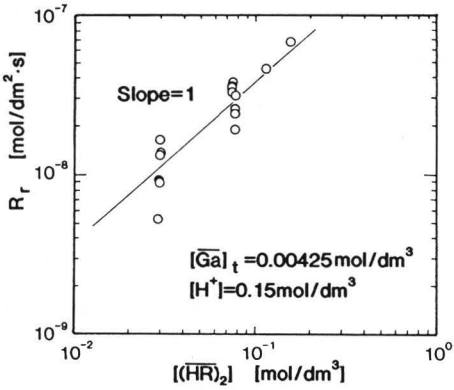


Fig. 9. Effect of extractant concentration in organic phase, $[(\overline{HR})_2]$, on reverse extraction rate, R_r.

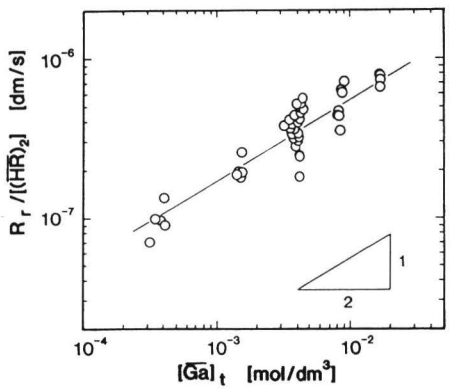


Fig. 10. Effect of Ga concentration in organic phase, $[\overline{Ga}]_t$, on R_r.

on the extraction rate.

Figs. 5, 6 and 7 show the effects of $[Ga^{3+}]$, $[H^+]$ and $[(\overline{HR})_2]$ on the forward extraction rate R_f, respectively. From these results, the following experimental equation was obtained for the forward extraction rate, where k_f is the forward extraction rate constant.

$$R_F = k_f\,[Ga^{3+}]^2\,[(\overline{HR})_2]^3/[H^+]^6 \qquad (8)$$

The observed value of $\log(k_f)$ is -14.08. Fig.8 shows the comparison between the calculated and experimental R_f values.

In the same way, the experimental equation for the reverse extraction rate R_r was determined. Figs. 9 and 10 show the effects of $[(\overline{HR})_2]$ and $[\overline{Ga}]_t$ on R_r, respectively. No dependence of $[H^+]$ on R_r was observed. Because Ga-2BDA complex exists as the tetramer under the experimental conditions, the following equation was obtained for the reverse extraction rate,

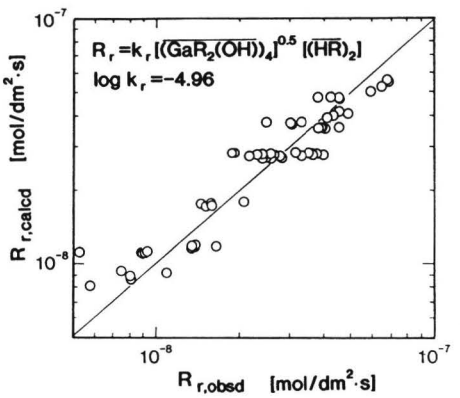


Fig. 11. Comparison between observed and calculated values of reverse extraction rate.

$$R_r = k_r\,[\overline{(GaR_2(OH))_4}]^{0.5}\,[\overline{(HR)_2}], \quad (9)$$

where k_r is the reverse extraction rate constant and $\log(k_r) = -4.96$. Fig.11 shows the comparison between the calculated and experimental k_r values.

2.3 EXTRACTION MECHANISM OF 2BDA-Ga SYSTEM

From the experimental results of both extraction equilibrium and extraction rate, we have assumed that the overall reaction is split into two stages as follows,

$$Ga(H_2O)_6^{3+} + 3/2(\overline{HR})_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ga(H_2O)_3^{3+}\cdot 3R^- + 3H_3O^+ , \quad (10)$$

$$2Ga(H_2O)_3^{3+}\cdot 3R^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (\overline{GaR_3})_2 + 6H_2O . \quad (11)$$

Supposing that Eq.(11) is the rate controlling step, the overall reaction rate is expressed as follows,

$$R = k_2\cdot K_1\cdot[Ga(H_2O)_6^{3+}]^2\cdot[\overline{(HR)_2}]^3/[H_3O^+]^6 - k_{-2}\cdot[\overline{(GaR_3)_2}], \quad (12)$$

where $K_1 = k_1/k_{-1}$. Under the conditions of the reverse extraction rate experiments, most of the Ga-2BDA complex was present as the tetramer in the organic phase, so the second term in the right hand side of Eq.(12) can be rewritten using Eq.(7) as follows,

$$R = k_2\cdot K_1\cdot[Ga(H_2O)_6^{3+}]^2\cdot[\overline{(HR)_2}]^3/[H_3O^+]^6 - k_{-2}\cdot K_{2to4}^{-0.5}\cdot[\overline{(GaR_2(OH))_4}]^{0.5}\cdot[\overline{(HR)_2}] . \quad (13)$$

Apparently, Eq.(13) agrees with the experimental results of Eqs. (8) and (9) on the dependence of each chemical concentration.

3 CONCLUSION

In 2BDA-Ga system, two types of complex, dimer and tetramer, are formed in the organic phase, depending on the loading ratio of gallium to the extractant. The equilibrium and rate equations were obtained experimentally and the extraction mechanism was presented.

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EQUILIBRIUM AND MECHANISM OF EXTRACTION OF GOLD, PALLADIUM AND PLATINUM BY 2-HYDROXY-4-sec.OCTYLOXYL-BENZOPHENOXIME

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ABSTRACT
Extraction performance of Au, Pd and Pt by 2-hydroxy-4-sec.octyloxyl-benzophenoxime was reported. A kinetic catalyst for Pd in this extraction was investigated. The composition and structure of the extracted species was elucidated by equilibrium study, spectroscopic examination in addition to elemental analysis.

INTRODUCTION

Solvent extraction has been developed as one of the most important methods for the separation and purification of precious metals.(Edwards 1983, Ritcey 1979) Although the hydroxyl oxygen and oximido nitrogen atoms are classifield as hard and borderline base, respectively, according to Pearson's scale, however, a series of 2-hydroxy-benzophenoxime derivatives possesses excellent extraction ability for soft-acid type metals including Ag, Hg, Cu and Pd. It can be rationalized either by the inductive effect of benzene ring leading to weaken the hardness of the oxygen atom or by the chelating effect offering higher stability constant of the resulting complex during the extraction process. It is well demonstrated by the practical application of LIX type reagents in the hydrometallurgy of copper based on solvent extraction and electrowinning process in the industrial scale developed as early as late sixties. The structure and separation of geometric isomers of 2-hydroxy-5-octyl-benzophenoxime (N 510) and 2-hydroxy-4-sec.octyloxyl-benzophenoxime (N 530) and their behaviours in copper extraction were reported in our Laboratory.(Chen et al. 1981; Yuan et al. 1989) the structure of the complexes of transition metals with these ligands was also described.(Zhou et al. 1989) In this paper the general performance and kinetic behaviour of Au, Pd and Pt extraction by N510 and N530 were reported. Beside these, the chemical composition of Pd-N530 complex was elucidated based on the slope method and method of continuous variation in addition to elemental analysis as well as UV and IR investigation of the resultant complexes.

1 EXPERIMENTAL

1.1 Stock solutions

Stock solution of Au(III), Pd(II) and Pt(IV) in 2M HCl were prepared by dissolving the pure metal sponge (99.99%) in aqua Regia. The solution was evaporated several times from conc. HCl and the residue was redissolved to make stock solution of 5g. metal per liter of 2M HCl.

Stock solution of Fe(III), Ni(II) and Cu(II) was prepared by dissolving the chloride of these base metals in diluted HCl to obtaine solution containing approximately 5g.M/L HCl. The concentration of metal was then estimated quantitatively by complex titration with EDTA.

1.2 Extractants and kinetic catalysts

Both N510 and N530 are commercially available. Various organic compounds tested as kinetic catalyst were prepared in this Laboratory.

1.3 Analytical methods

Gold was determined quantitatively by the Brilliant Green method,(Fogg 1976) in low concentration. For the high concentration of gold, volumetric titration with potassium bichromate was used. Palladium and platinum were determined by photospectroscopically using N,N'-didodecyl dithio-oxalamide in $CHCl_3$ as reagent. Iron(III), nickel and copper was estimated by complex titration with EDTA.

1.4 Extraction equilibrium

Equal volumes of aqueous and organic solution of known concentration of metal and extractants were shaken together in a separatory funnel using a mechanical shaker at 25+1°C for an appropriate period of time. After phase separation the metal content in aqueous phase was estimated. In case of poor extraction, the metal concentration of both phases were determined. The percentage extraction, Ex %, and extraction coefficient E, were evaluated in the usual manner.

2 RESULTS AND DISCUSSIONS

2.1 Comparison of N510 and N530

The distribution coefficient (D) and separation factor (β) of Au, Pd and Pt in extraction with N510 and N530 from various concentration of HCl were evaluated.

TABLE 1

Extraction behaviours of N510 and N530 in kerosene at 20°C.

Extractant	N510		N530		
[HCl] M	1.0	3.0	1.0	3.0	5.0
D_{Au}	0.156	0.122	0.334	0.317	4.663
D_{Pd}	1.697	0.618	2.702	1.081	0.185
D_{Pt}	0.005	0.005	0.005	0.005	0.076
β Pd/Au	1.09X10	5.07	8.09	3.41	$3.97X10^{-2}$
β Pd/Pt	$3.39X10^2$	$1.23x10^2$	$5.4X10^2$	$6.8X10^2$	2.43

Data on Table 1 demonstrated that the extraction ability of N530 towarding Au and Pd is much greater than that of N510. Meanwhile, the separation factor

between Pd and Pt is much greater than that of N510. Beside these, N530 showed significant D values in Au and Pd extraction even in high HCl concentration (5M). The excellent extraction property of N530 can be rationalized by the substituent effect of the aromatic hydroxyoxime molecule. Since the acidity of the phenolic hydroxyl group is enhanced by the electron withdrawing ability of the ortho-alkoxyl group. In the meantime, the electron density of the oximido nitrogen is increased as the result of the conjugation effect of the alkoxyl group located on the para-position of the oxime moiety.

2.2 Influence of the aqueous acidity

In order to investigate the selectivity of N530 toward Pd, the extraction behaviours of other precious metals including Au and Pt as well as accompanying element Fe(III) by this reagent was examined. The extraction ability of N530 for other accompanying elements such as Cu, Co, Ni, Ca and Zn has been reported by this Laboratory. As shown in Figure 1, with the increase of the aqueous acidity, the percentage extraction of gold due to the fact that in higher acidity,

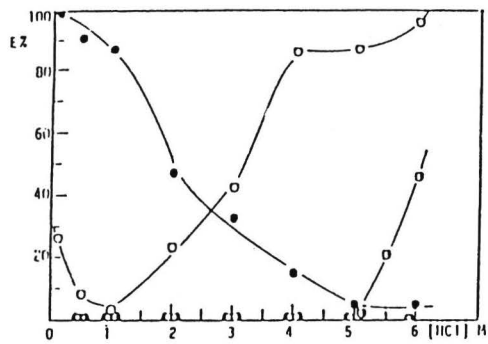


Fig. 1 Extraction performance of N530 in dodecane at 25°C for Au(○), Pd(●), Pt(◐) and Fe(◑).

the dissociation of the phenolic hydroxyl function was depressed. Meanwhile, further increase of the aqueous acidity will bring the enhancement of the extraction ability due to the formation of $HAuCl_4$ species which is favourable to be extracted in this system. Ferric ion behaves similarly, i.e. in the low acidity range, extraction of Fe(III) is extremely low but it turns to comparatively high when the aqueous acidity approaches to 5N. However, Pt is not extracted in the wide range of aqueous acidity since hydroxyoxime is incapable to coordinate Pt ion. Concerning the extraction of Pd by N530, the percentage extraction of this metal is obviously decreased as the increasing of the aqueous acidity as the result of the depression effect on dissociation of the phenolic hydroxyl group of the ligand molecule. Based on these experimental observations, we can predict that N530 is capable to extract selectively Au from Pd or vice versa by adjusting the aqueous acidity. Since Pt and other accompanying base metals are practically

not extracted in these conditions, N530 is therefore can be considered as highly selective reagent in Pd extraction.

2.3 Equilibrium time for Au and Pd extraction

The profile of percentage extraction of Au and Pd as the function of equilibrium time is shown on Figure 2a.It indicates that Au is extracted smoothly and the equilibrium is achieved within one minute. On the other hand, the kinetic behaviour of Pd extraction is not so good, since one hour is required for the equilibrium in 0.5N HCl.

2.4 Kinetic catalysts in Pd extraction by N530

Since N530 is proved to be a powerful extractant for Pd with high selectivity, but the velocity of the process is too slow, a kinetic catalyst should be required for the acceleration of the reaction. For this purpose various types of organic compounds was used for the screening test under standard conditions. The results are summarized on Figure 2b.

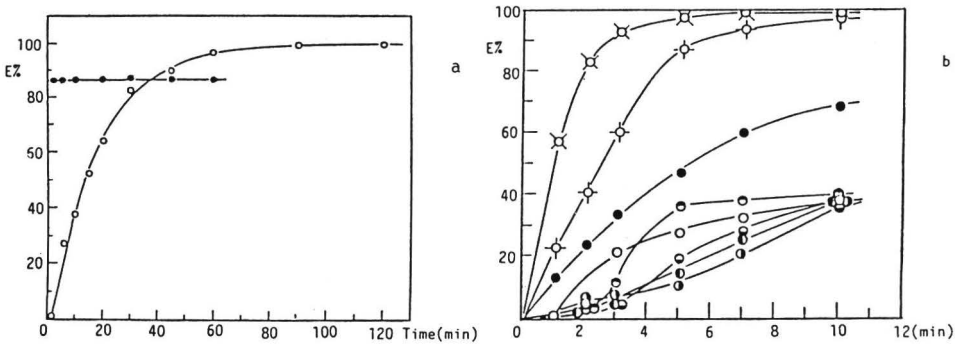


Fig. 2 a. Equilibrium time required for extraction of Au (●) & Pd (○) by N530.

b. Catalytic effect of various reagents in 0.5% of D2EHPA (◒), DLNS(◐), DOAA (◑), DEHDO (◓), Aliquat 336 (●) and ONA (◇) in extraction of Pd by N530. Without addition of catalysts is shown by

As shown in Figure 2b, addition of 0.5% di(2-ethylhexyl)phosphoric acid (D2EHPA), dilaurylnaphthalene sulfonic acid (DLNS) and N,N-di-sec.octylacetamide (DOAA) retarded the process of Pd extraction. 7-Diethyl-7-hydroxy-6-dodecanone oxime (DEHDO), a well-known kinetic catalyst in copper extraction by hydroxyoxime type reagent, provides no significant effect on the velocity of Pd extraction. However, both tricapryl methyl ammonium chloride (Aliquat 336) and 1-octylnonylamine (ONA) shown evident accelerating effect on the extraction velocity of this system. With the aid of 0.5 or 1.0% of amine, the reaction equilibrium achieved within 10 and 5 minutes, respectively. Analogous data were reported.(Freiser et al. 1987)

2.5 Composition of the extracted species N530-Au

In the extraction system, [Au](various conc.),[HCl](5.0M)/[HL](0.1M)n-dodecane,

The plot of log D versus log $[Au]_{(a)}$ was found to be a straight line with slope= 0. It indicates that the D_{Au} in extraction with N530 is independent on $[Au]_{(a)}$ under experimental conditions. In another extraction system, [Au]($5.0X10^{-3}$M), [HCl](5.0M)/[HL](various conc.)in n-dodecane, plotting log D against $\log[HL]_{(o)}$ gave a broken-line graph, in which the slopes are approximately to 1 and 2 in the region of $[HL]_{(o)}$ $5.0X10^{-3}$ to $3.0X10^{-2}$ and $3.0X10^{-2}$ to $1.0X10^{-1}$, respectively. It seems that different species were formed with different ligand concentrations in the organic phase as shown by the following equations:

$$HAuCl_4 + HL \rightleftharpoons HAuCl_4\ HL \qquad (1)$$

$$HAuCl_4 + 2HL \rightleftharpoons HAuCl_4\ 2HL \qquad (2)$$

2.6 Composition of the extracted species N530-Pd

(i)By method of continuous variation.

A series of solution containing $1.0X10^{-3}$— $1.0X10^{-2}$M Pd was prepered and equilibrated with a dodecane solution of N530 so that the molar ratio of Pd and N530 is to be kept constantly. The maximal point of the broken-line graph obtained by plotting $[Pd]_{(o)}$ versus constant molar ratio of $[Pd]_{(a)}$ and $[HL]_{(o)}$ reveals that the composition of the extracted species of N530 and Pd is around 2:1.

(ii)By slope method.

Since we found that N530 is partially dissociated when its concentration is greater than $2.7X10^{-2}$M, the experiments were run under the following conditions: [N530] $2.0X10^{-2}$M, [Pd] $1.0X10^{-3}$M, $[H^+]$ 0.1-1.0M, $[Cl^-]$ 0.1-1.0M. The experimental data demonstrated that the distribution ratio (D) of Pd with N530 was depressed as the increase of $[H^+]$ or $[Cl^-]$ of the equilibrated aqueous phase. The plot of log D versus $\log[H^+]_{(a)}$ or $[Cl^-]_{(a)}$ was found to be a straight line with slope of approximately -2 and -4. In the meantime, D value in Pd extraction is enhanced with the increase of ligand concentration and log D vs. log[HL] plots gave straight line with slope near to 2. The following equation can thus be deduced:

$$PdCl_4^{2-} + 2HL \rightleftharpoons PdL_2 + 4Cl^- + 2H^+ \qquad (3)$$

(iii)By elemental analysis.

The results of the elemental analysis of the extracted complex N530-Pd were shown as follows: C, 63.54%, H, 6.49%, N, 3.65%, Pd 13.64%. The calculated value for $C_{42}H_{52}O_6N_2Pd$: C, 63.96%, H, 6.60%, N, 3.55%, Pd, 13.50%. These data are coincidental with the results obtained by the slope meth and by method of continuous variation. The composition of the extracted species was thus identified as $Pd(C_{21}H_{26}O_3N)_2$.

2.7 Structure of the extracted species N530-Pd

(i)Infra-red spectra.

It was found from the IR studies that the broad absorption band of the associ-

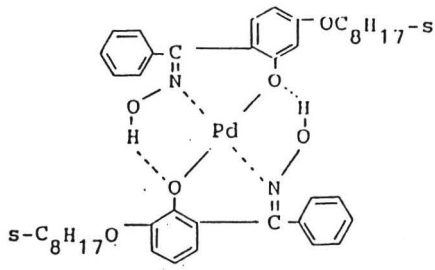
ated phenolic OH group ($3400cm^{-1}$) existing in N530 disappeared in the complex and the characteristic absorption at 408 and $248cm^{-1}$ in the infrared region of the ligand was substituted by new bands at 271 and 365 cm^{-1}, which should be assigned to Pd-O and Pd-N, respectively.(Nakamoto, 1970; Zhou, 1983)

(ii)Utra-violet spectra.

The free ligand N530 showed λ_{max} at 315, 281 and 244nm., where the extracted complex N530-Pd gave a new group of strong absorption at λ_{max} 260, 254, 248, 243, 238 and 211nm, due to the transition of lone pair electron of the coordinated hydroxyl oxygen. The original absorption band near 300nm. of the ligand moved to 366 and 305nm. upon complex formation.

CONCLUSIONS

To sum up, the structure of the extracted complex of N530 with Pd may be deduced as:-



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EXTRACTION OF TITANIUM(IV) FROM HYDROCHLORIC ACID SOLUTIONS BY ACID ORGANOPHOSPHORUS COMPOUNDS

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ABSTRACT
The distribution of titanium(IV) between hydrochloric acid solutions of di-(2-ethylhexyl)-phosphoric acid (DEHPA) or 2-ethylhexyl 2-ethylhexyl-phosphonic acid (EHEHPA) in kerosene or benzene has been investigated under different conditions. The extraction by DEHPA shows that the distribution coefficient decreases with increasing aqueous acidity below 3 mol dm^{-3} and above this acidity rises with acidity. In contrast, although the extraction curve by EHEHPA resembles that by DEHPA, the minimum appears at 2 mol dm^{-3} acid. The efficiency for titanium(IV) of EHEHPA is lower than that of DEHPA at low aqueous acidity, while its order becomes reversely at higher acidity. As a result, it is found that the extraction proceeds in the cation-exchange reaction involving the formation of polymeric titanium-DEHPA or EHEHPA complexes at low aqueous acidity, and in the solvating reaction at higher acidity. This was supported by the infrared spectral results for the organic extracts. Further the kinetic results suggest that titanium(IV) is taken up depending on the rate determining step due to the anation which replaces the hydroxyl group combining with titanium ion by the anion derived from extractant.

1 INTRODUCTION

It is recognized that acid organophosphorus compounds are effective extractants for various metals, particularly di-(2-ethylhexyl)-phosphoric acid (DEHPA, HX) is one of the most frequently used for solvent extractants. We have also used DEHPA as a solvent extractant of uranium(VI) from aqueous acid solutions (Sato, 1962, 1963, 1964, 1965, 1984). In addition the extraction of divalent, trivalent and tetravalent metals has been investigated with DEHPA. This paper extends the work to the extraction of titanium(IV) by DEHPA and 2-ethylhexyl 2-ethylhexyl-phosphonic acid (EHEHPA, HA) from hydrochloric acid solutions in order to obtain further information on metal separation in relation with that from sulphuric acid solutions (Sato et al., 1975).

2 EXPERIMENTAL

Reagents

The DEHPA and EHEHPA (both reagents from Daihachi Chemical Industry Co., Ltd.)

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were purified by washing several times successively with 10 % sodium carbonate solution, 6 mol dm^{-3} hydrochloric acid and water (Sato, 1962). The resulting materials were diluted with purified kerosene (except for infrared (IR) spectrophotometry with hexane). Aqueous titanium solution was prepared by dissolving freshly precipiteted titanium hydroxide gel in hydrochloric acid of required concentration. The gel was obtained by adding aqueous sodium hydroxide to titanium sulphate solution. The aqueous solutions containing titanium chloride in 1 g dm^{-3} were in general used except for loading test. All chemicals were of analytical reagent grade.

Extraction and analytical procedures

Equal volumes (15 cm^3 each) of the aqueous and organic phases were shaken for a decided time in 50 cm^3 stoppered conical flasks in a thermostatted water bath at 20°C, except the experiments on temperature effect. Preliminary experiments showed that the equilibrations were complete in 40 and 300 min. for DEHPA and EHEHPA, respectively. The mixture was centrifuged and separated, and then the aliquots of both phases were pipetted to determine the distribution coefficient (E_a°, the ratio of the equilibrated concentration of titanium in organic phase to that in aqueous phase). Titanium in organic phase was stripped with 1 mol dm^{-3} sodium hydroxide solution. The concentration of titanium in aqueous solution was determined by adding excess of EDTA and back-titrating with zinc sulphate solution at pH 7 to an Eriochrome Black T end-point (Sir et al., 1956). The chloride concentration and water content of the organic phase were determined by the use of Volhard's method in the presence of nitrobenzene and Karl Fischer titration respectively.

Infrared spectrophotometry

Infrared spectra of the organic extracts were determined on JASCO Models IRA-1 (4000-650 cm^{-1}) and IR-F (700-200 cm^{-1}) using a capillary film between thallium halide plates or polyethylene films.

3 RESULTS AND DISCUSSION

3.1 Extraction isotherm by DEHPA

The extraction of titanium(IV) from aqueous solutions containing 1 g dm^{-3} of titanium chloride in hydrochloric acid at various concentrations was carried out with DEHPA in kerosene or benzene at 20°C. The results show that the distribution coefficients decrease with increasing aqueous acidity below 3 mol dm^{-3} and above this acid rises with acidity. This tendency is not greatly influenced by varying the nature of the diluent : although the extraction efficiency for titanium(IV) of DEHPA in kerosene is higher than that in benzene, the shape of the extraction curves resembles each other. The variation of the distribution coefficients by DEHPA is interpreted as follows : at low aqueous acidity

titanium(IV) is extracted by a cation-exchange reaction in which hydrogen ion is liberated, and at higher aqueous acidity by a solvating reaction similar to that with nonionic reagent as TBP. This is confirmed by the following fact : when the results for the extraction of titanium(IV) from aqueous solutions containing 1 g dm^{-3} of titanium chloride in 0.1 mol dm^{-3} hydrochloric acid and lithium chloride at various concentrations with 0.05 mol dm^{-3} DEHPA in kerosene at 20°C are compared with the extraction from hydrochloric acid solution of varying acidity, the distribution coefficient is little influenced by the total chloride ion concentration below 3 mol dm^{-3}. It is thus inferred that the species containing chloride ion is inextractable at low aqueous acidity. In contrast, at the fixed total chloride concentration in 7 mol dm^{-3} the distribution coefficient in the mixture of hydrochloric acid and lithium chloride increases continuously due to a salting-out effect with the total concentration of chloride ion.

However, since the log-log plots of E_a° vs. the initial aqueous hydrochloric acid concentration in the region 0.5 to 2 mol dm^{-3} give a slope of ~2 at constant DEHPA concentration, it seems that the distribution coefficient is inverse second-power hydrogen ion dependent. Besides, there is no simple aquated titanium(IV) ion because of the extremely high charge-to-radius ratio; in aqueous solutions, hydrolyzed species occur and basic oxo salts or hydrated oxides may precipitate. Further a titanyl ion, TiO^{2+}, does not appear to exist in either solutions or in crystalline salts. As the species $[Ti(OH)_2(H_2O)_4]^{2+}$ is generally considered to be the prevailing species in dilute aqueous solutions of titanium salt (Sato et al., 1975), the initial decrease in the distribution coefficient at low aqueous acidity is governed by an ion-exchange reaction

$$Ti(OH)_2^{2+}(a) + n(HX)_2(o) \rightleftharpoons TiOX_{2n-2}(o) + 2H^+(a) + H_2O(a) \qquad (1)$$

where $(HX)_2$ refers to the dimeric reagent, and (a) and (o) denote aqueous and organic phases respectively. This leads

$$\log 2^n E_a^\circ = \log K + n \log(C_S - 2nC_{Ti}) - 2 \log C_H \qquad (2)$$

in which K is the equilibrium constant, C_S the total extractant concentration, C_{Ti} the titanium concentration in organic phase and C_H the aqueous acidity. Log-log plots of E_a° vs. $(C_S - 2nC_{Ti})/C_H^{2/n}$ at constant hydrochloric acid concentrations at 0.1-3 mol dm^{-3} show that Eqn. (2) is satisfied for n=1 at $[HCl]_{init\ aq} \leq 1$ mol dm^{-3} and n=2 at $[HCl]_{init\ aq} > 1$ mol dm^{-3} giving the straight lines with the slopes of ~1 and ~2 respectively. Hence the following equilibrium equations are given for the extraction of titanium(IV) from hydrochloric acid solutions below 3 mol dm^{-3} by DEHPA : when the DEHPA is present in excess, the monomeric species is formed according to the cation-exchange reaction

$$Ti(OH)_2^{2+}(a) + 2(HX)_2(o) \rightleftharpoons TiOX_4(o) + 2H^+(a) + H_2O(a), \qquad (3)$$

and in addition the extraction at higher titanium concentration proceeds in the reaction involving the formation of a polymeric titanium-DEHPA complex

$$TiOX_4H_2(o) + Ti(OH)_2^{2+}(a) + (HX)_2(o) \rightleftharpoons (TiO)_2X_6H_2(o) + 2H^+(a) + H_2O(a). \quad (4)$$

Therefore Eqs. (3) and (4) may be written by the general expression

$$mTi(OH)_2^{2+}(a) + (m+1)(HX)_2(o) \rightleftharpoons (TiO)_mX_{2(m+1)}H_2(o) + 2mH^+(a) + mH_2O(a) \quad (5)$$

where $m \geq 1$.

At higher aqueous acidity, if the extraction involves the combination n' molecules of the DEHPA dimer, which is bonded as the monomer 2HX, with the titanium species by a reaction similar to that for TBP

$$Ti(OH)_2Cl_2(a) + n'(HX)_2(o) \rightleftharpoons Ti(OH)_2Cl_2 \cdot 2n'HX(o), \quad (6)$$

we have

$$\log 2^{n'}E_a^\circ = \log K_2 + 2n' \log(C_S - 2n'C_{Ti}) \quad (7)$$

where K_2 is constant. Log-log plots of E_a° vs. $(C_S - 2n'C_{Ti})$ at 3-10 dm^{-3} acid concentrations give the straight lines with a slop of ~1 for n'=1. Accordingly the extraction at higher aqueous acidity is expressed as

$$Ti(OH)_2Cl_2(a) + (HX)_2(o) \rightleftharpoons Ti(OH)_2Cl_2 \cdot 2HX(o). \quad (8)$$

When the molar ratios of DEHPA concentration, chloride ion concentration and water content to the titanium concentration in the organic phase as a function of initial aqueous titanium concentration at hydrochloric acid concentrations in 1 and 10 mol dm^{-3} were determined with 0.03 mol dm^{-3} DEHPA in kerosene at 20°C, it was found that the former and latter approach the limiting values of 2 : 0 : 0 and 2 : 2 : 0 respectively. This suggests that the polymeric species $TiOX_2$ and the complex $Ti(OH)_2Cl_2 \cdot 2HX$ are formed in the extractions at low and higher aqueous acidities respectively, although they have no coordinated water. Additionally, at the same hydrochloric acid concentrations, the variation in the titanium concentration at a fixed total concentration of [Ti]+[HX]=0.03 mol dm^{-3} was followed by the method of continuous variations. A maximum at the molar ratio [HX]/[Ti] ~2 was observed in the extractions at low and higher aqueous acidities, in agreement with the results for loading test.

Consequently, it is seen that in the extraction at low aqueous acidity the equilibrium equation from hydrochloric acid solutions agrees with that from sulphuric acid solutions, and that at higher aqueous acidity the former corresponds to the latter (Sato et al., 1975).

3.2 Infrared spectral studies

The organic extracts from aqueous solutions containing titanium chloride in

1 and 10 mol dm^{-3} hydrochloric acid with 0.05 mol dm^{-3} DEHPA were examined by infrared spectrophotometry.

With increasing the concentration of titanium in the organic phase in contact with an aqueous solutions in 1 mol dm^{-3} hydrochloric acid, the OH stretching bands at 2680 and 2350 cm^{-1}, which are ascribed to the hydrogen bond in the formation of DEHPA dimer, and the OH bending band at 1690 cm^{-1} decrease in the intensity. Simultaneously the P → O stretching band at 1230 cm^{-1} shifts to lower frequencies. In addition, the band at 840 cm^{-1}, which probably results from the Ti-O-Ti bridging band formed according to Eq. (5), and the Ti-O stretching band at 330 cm^{-1} appear. In contrast, the Ti-Cl stretching band at 250 cm^{-1} is observed in the extraction at hydrochloric acid concentration in 10 mol dm^{-3}. These results confirm that titanium extracted into DEHPA by the cation-exchange or solvating reactions, Eqs. (3), (4), (5) and (7), is bonded to the phosphoryl oxygen atom, suggesting that the extracted species exist as the complexes $TiOX_4H_2$, $(TiO)_2X_6H_2$ and $Ti(OH)_2Cl_2 \cdot 2HX$ which display a coordination of six in an octahedral arrangement.

3.3 Temperature effect

The extractions of titanium(IV) from hydrochloric acid solutions in 1 and 10 mol dm^{-3} with 0.05 and 0.01 mol dm^{-3} DEHPA in kerosene, respectively, were carried out at temperature between 10 and 40°C. The results indicate that the distribution coefficient for titanium(IV) decreases with rising temperature. This extraction behaviour corresponds to that from sulphuric acid solution at higher acidity (Sato et al., 1975).

3.4 Extraction isotherm by EHEHPA

When the extration of titanium(IV) from aqueous solutions containing 1 g dm^{-3} titanium chloride in hydrochloric acid at various concentrations was carried out with EHEHPA in kerosene at 20°C, it was found that the extraction behaviour of titanium(IV) by EHEHPA is close to that by DEHPA, although the former efficiency is lower than the latter one at aqueous acidity below 3 mol dm^{-3} while above this acidity the order reverses. These phenomena are analogous to the other instances for the extraction by EHEHPA (Sato, 1984, 1989; Sato et al., 1989). In addition, as the extraction of titanium(IV) by DEHPA from hydrochloric acid solutions is similar to that from sulphuric acid solutions (Sato et al., 1975), it is supposed that the extraction of titanium(IV) by EHEHPA from sulphuric acid solutions resembles that from hydrochloric acid.

3.5 Kinetic study

The extraction of titanium(IV) from hydrochloric acid solutions by DEHPA and EHEHPA is rather slow to attain to the equilibrium state, although the extraction rate by DEHPA is faster than that by EHEHPA. Accordingly a kinetic investigation was carried out in order to elucidate the mechanism of reaction in these extraction systems. As a result, it was found that the rate of forward reaction in

cation-exchange at low aqueous acidity is proportional to first order with respect to the concentrations of titanium and DEHPA or EHEHPA and to inverse first order with respect to the hydrogen ion concentration.

On the basis of kinetic results, therefore, it is presumed that the extraction of titanium from hydrochloric acid solutions by DEHPA or EHEHPA proceeds in the rate determing step by the anation which replaces the hydroxyl group combining with titanium ion by the anion, R_2H^- where R=X or A, at the interface between aqueous and organic phases.

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DILUENT EFFECT ON THE HEAT CHANGE IN SOLVENT EXTRACTION OF DIVALENT COPPER, ZINC AND CADMIUM AND URANIUM(VI) FROM HYDROCHLORIC ACID SOLUTIONS BY HIGH-MOLECULAR WEIGHT AMINES

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ABSTRACT
In the extraction of divalent copper, zinc and cadmium and uranium(VI) from hydrochloric acid solutions by trioctylamine hydrochloride (TOAHCl) and trioctylmethylammonium chloride (TOMAC) in various organic solvents such as benzene, chlorobenzene, o-dichlorobenzene, toluene, m-xylene, nitrobenzene, carbon tetrachloride and 1,2-dichloroethane, the heat change associated with the uptake of their metals has been examined by using a twin type isoperibol calorimeter. It was found that the dependence of apparent molar heat change (the value of the heat change detected with regard to the concentration of metal reacted, ΔQ) on the aqueous chloride concentration could be attributed to the change in the distribution of metal chloride species in the aqueous phase. From the values of ΔQ obtained, it is considered that in the extraction by TOMAC, ΔQ correlates with the solubility parameter of diluent, suggesting that the organic phases may be regarded as regular solutions, while in the extraction by TOAHCl, no clear-cut relation holds between ΔQ and the solubility parameter of diluent.

1 INTRODUCTION

In previous papers (Sato et al., 1981, 1983a,b, 1985), dependency of the distribution coefficient and the change in enthalpy estimated from the distribution data by the use of Van't Hoff plot on solubility parameter of diluent has been investigated for the extraction of divalent metals and uranium(VI) from hydrochloric acid solutions by trioctylmethylammonium chloride (TOMAC, $R_3R'NCl$) and trioctylamine (TOA, R_3N) in various diluents. Calorimetry has been applied to measure the heat change directly associated with metal extraction (Sato et al., 1982, 1984). With regard to application of titration-calorimetry to solvent extraction, there are only a few papers (Grauer et al., 1973; Marcus et al., 1973, 1974, 1976: Kertes et al., 1978). This work is, therefore, undertaken by calorimetry to elucidate further the diluent effect in the extraction of divalent copper, zinc and cdmium and uranium(VI) from hydrochloric acid solutions by TOA and TOMAC.

2 EXPERIMENTAL

Reagent

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The high purity TOA and TOMAC (> 99 %, Koei Chemical Co., Ltd.) were used without further purification. Their extractants were diluted with the various organic solvents such as benzene, chlorobenzene, o-dichlorobenzene, toluene, m-xylene, nirobenzene, carbon tetrachloride and 1,2-dichloroethane. The concentration of TOMAC was determined by Volhard's method. A solution of TOA was shaken with a slight excess of dilute hydrochloric acid to form R_3NHCl (TOAHCl) (Sato, 1965). Aqueous solutions of divalent metals were prepared by dissolving their chlorides ($CuCl_2 \cdot 2H_2O$, $ZnCl_2$, $CdCl_2 \cdot 2.5H_2O$ and $UO_2Cl_2 \cdot 2H_2O$) at 0.1, 0.05, 0.05 and 0.05 mol dm^{-3} respectively, in hydrochloric acid and/or lithium chloride of the selected concentration. Other chemicals used were of analytical reagent grade.

Extraction and Analytical Procedures

The distribution coefficient was obtained as described previously (Sato et al., 1977a). The concentration of metal in aqueous solution was determined by EDTA titration using XO (xylenol orange) for copper, zinc and uranium and Cu-PAN for cadmium as indicator (Kinnunen et al., 1957; Sato et al., 1984b).

Calorimetric Measurement

The measurement of heat change Δ_q associated with extraction of metal was carried out at 25°C using a twin type isoperibol calorimeter, TIC-221 (Tokyo Riko Co., Ltd), equipped with integrator and designed to have highly sensitive thermistors (0.067°C/mV) and a very rapid response. Each vessel is of 100 cm^3 capacity. Each of the various diluents (70 cm^3) containing 0.05 mol dm^{-3} of extractant and an aqueous solution of hydrochloric acid and/or lithium chloride containing no metal (15 cm^3) are introduced into the sample reaction vessel, while the same volumes of organic solvent in the absence of extractant and the aqueous solution are placed in the reference vessel. Metal chloride solutions each of 4 cm^3 containing hydrochloric acid and/or lithium chloride, adjusted to the same concentrations as those of the aqueous solutions in both vessels, are placed in the inner glass cells separated from the mixed solutions. At a quasi-adiabatic state, which is attained in 12 h by agitating the solutions with a Teflon-coated stirring bar at 360 rev min^{-1}, the extraction is performed by contacting metal chloride solutions with the mixed solutions. Although independent of the concentration of hydrochloric acid in aqueous phase under the conditions mentioned above, most of the metal is taken up into the organic phase. After equilibrium, portions of the organic phase are pipetted to assay the concentration of metal reacted. Moreover, it is confirmed that at a constant acid concentration the heat change rises with increasing concentration of metal reacted, indicating that the heat change arising from the dilution of metal chloride solution and from a slight difference in the concentration of acid are compensated experimentally. The total heat change of the system is determined by

introduction of an exact and known amount of heat with the aid of a precisely calibrated electrical heater in the sample reaction vessel.

The heat of solution for extractant into organic solvent was measured at 25°C using the same apparatus.

3 RESULTS AND DISCUSSION

3.1 Extraction system by TOMAC

In the extraction of zinc(II) of 0.0125-0.05 mol dm^{-3} from hydrochloric acid solutions with 0.05 mol dm^{-3} TOMAC in benzene, it is found that the observed heat change varies with the concentration of acid in aqueous phase in spite of almost the same amount of zinc extracted into organic phase. The heat change is endothermic at 0.1 mol dm^{-3} hydrochloric acid, but above this acid mol dm^{-3} hydrochloric acid. In the latter concentration range of hydrochloric concentration it increases exothermally with increasing aqueous [HCl] to a maximum which occurs at 2 mol dm^{-3} hydrochloric acid, and then falls again. This phenomenon is more clarified by the plot of the apparent molar heat change (the value of the change in heat obtained with regard to the concentration of metal reacted, ΔQ) against initial aqueous [HCl]. Similar trend is also observed in the case of other diluents used. In the extraction from mixed solutions of 0.01 mol dm^{-3} hydrochloric acid and lithium chloride with 0.05 mol dm^{-3} TOMAC in benzene, ΔQ increases exothermally with increasing aqueous [Cl]. Its behaviour follows closely the heat change for the extraction from hydrochloric acid solutions in the absence of lithium chloride, although no maximum is given in the range of [Cl] up to 4 mol dm^{-3}. It is thus perceived that up to 2 mol dm^{-3} hydrochloric acid the increase in ΔQ depends on the aqueous [Cl], suggesting that the distribution of the species $ZnCl_j^{(2-j)+}$ in aqueous phase affects the heat change associated with zinc(II) extraction. At higher [HCl] above 2 mol dm^{-3}, the decrease in ΔQ arises from the formation of the spesies such as $R_3R'NCl \cdot HCl$ (Sato et al., 1975) in organic phase. This is proved by the fact that the molar ratios $[HCl]_{org}/[R_3R'NCl]_{org}$ at 0.5, 1, 2, 3, 5 and 7 mol dm^{-3} in equilibrated organic phase are found to be 0.038, 0.080, 0.16, 0.28, 0.69 and 1.6, respectively.

The change in enthalpy for stepwise formation of the species $ZnCl^+$, $ZnCl_2$ and $ZnCl_3^-$ in aqueous phase at μ = 3.0 ((Na,H)Cl + $NaClO_4$) has been estimated to 5.44, 37.1 and 0 kJ mol^{-1}, respectively, at 25°C (Gerging, 1969). Taking into consideration of these results and stability constants for $ZnCl_j^{(2-j)+}$ in aqueous phase (Sato et al., 1977b, 1982b, 1984b) it is evident that the apparent molar heat change varies with aqueous [Cl]. Accordingly the hypothetical steps which contain the reactions in aqueous phase should be considered for the theoretical estimation of ΔQ associated with zinc(II) extraction by TOMAC in various

diluents. These hypothetical steps provide the relation

$$\Delta Q = -(1/n_t) \sum_{j=0}^{3} \Delta n_j \Delta h_j - Y \qquad (1)$$

where $Y = f_d$ + const in the term f_d depending on the kind of diluent, Δn_j and n_t are initial concentration of the species $ZnCl_j^{(2-j)+}$ and total [Zn] in aqueous phase, respectively, and Δh_j refers to the change in enthalpy for the respective steps, $ZnCl_j^{(2-j)+}(aq) + (4-j)\ Cl^-(aq) \rightarrow ZnCl_4^{2-}(aq)$. Here it is noticed that Y corresponds to the change in enthalpy estimated by using Van't Hoff equation.

Eq. (1) is applied to the estimation of the total heat change associated with zinc(II) extraction with 0.05 mol dm^{-3} TOMAC in benzene, putting -3.4 kJ mol^{-1} obtained from the distribution data into Y. Linear least squares yield the values of Δh_0, Δh_1, Δh_2 and Δh_3 to be 6.67 $\pm$ 1.74, 4.26 $\pm$ 3.24, -37.2 $\pm$ 18.4 and -111.7 $\pm$ 26.1, respectively, in which the degree of formation of the species $ZnCl_j^{(2-j)+}$ is calculated using the overall stability constants (Sato et al., 1977b, 1982, 1984b). Calculated heat change fits to the experimental one. From Δh_j's value obtained, the change in enthalpy for stepwise formation of the species $ZnCl_j^{(2-j)+}$ is calculated to be 2.42 ($ZnCl^+$), 41.5 ($ZnCl_2$), 74.8 ($ZnCl_3^-$) and -111.7 kJ M^{-1} ($ZnCl_4^{2-}$), respectively. Magnitude of the change in enthalpy for the stepwise formation of the species $ZnCl^+$ and $ZnCl_2$ agrees with those at μ = 3, supporting that the heat change detected is considered as the sum of the change in enthalpy over the respective steps and that the variation in ΔQ is accounted for the change in the distribution of the species $ZnCl_j^{(2-j)+}$ in aqueous phase as a function of aqueous [Cl].

In the extraction of zinc(II) from hydrochloric acid solutions with 0.05 mol dm^{-3} TOMAC in various diluents, ΔQ at 0.5 and 1 mol dm^{-3} hydrochloric acid gave the respective values of 35.7 and 49.0 (1,2-$C_2H_4Cl_2$), 34.6 and 44.3 ($C_6H_5NO_2$), 14.2 and 23.7 (o-$C_6H_4Cl_2$), 6.73 and 17.9 (C_6H_5Cl), 3.34 and 11.3 (C_6H_6), 2.65 and 9.16 ($C_6H_5CH_3$), 2.43 and 8.59 (m-$C_6H_4(CH_3)_2$) and 1.29 and 7.89 kJ mol^{-1} (CCl_4). The value of ΔQ is in the order 1,2-$C_2H_4Cl_2$ > $C_6H_5NO_2$ > o-$C_6H_4Cl_2$ > C_6H_5Cl > C_6H_6 > $C_6H_5CH_3$ > m-$C_6H_4(CH_3)_2$ > CCl_4 depending on the nature of diluent. The difference btween ΔQ at 0.5 and 1 mol dm^{-3} hydrochloric acid, which is 13.5 kJ mol^{-1} for 1.2-$C_2H_4Cl_2$, is more than twice as large as 6.51 kJ mol^{-3} for m-$C_6H_4(CH_3)_2$ which gives the smallest one of all. One of the reason for this gap is considered as due to the difference trend in increase of the amount of hydrochloric acid extracted into organic phase with increasing initial aqueous [HCl]. However, since the present evidence is not enough to take into account of such effect, the values of Y for respective diluents are estimated as $-\Delta h_4$ in the step, $R_3R'NCl \cdot nHCl(org) \rightarrow R_3R'NCl(org) + nHCl(aq)$, of invariance independent of aqueous [HCl] throughout the present treatment for the data. Parameter Y at 1 mol dm^{-3} hydrochloric acid is evaluated to be -3.4 (C_6H_6), -1.26

($C_6H_5CH_3$), -0.69 (m-$C_6H_4(CH_3)_2$), -10.0 (C_6H_5Cl), -15.8 (o-$C_6H_4Cl_2$), -36.4 (C_6H_5-NO_2), -41.1 (1,2-$C_2H_4Cl_2$) and 0.01 kJ mol^{-1} (CCl_4), respectively, by the use of Δh_j's values estimated for benzene.

By assuming a regular solution, the parameter Y is related with the solu-parameter :

$$(Y - Y_s)/(\delta_d - \delta_s) = (f_d - f_s)/(\delta_d - \delta_s)$$
$$= (V_c\Phi'_d{}^2 - 2V_e\Phi_d{}^2)(\delta_d + \delta_s) + 2(2V_e\Phi_d{}^2\delta_e - V_c\Phi'_d{}^2\delta_c) \quad (2)$$

where V, δ and Φ (Φ') decote molar volume, solubility parameter and volume fraction, respectively, subscripts c, e, d and s stand for the complexes formed in the organic phase, extractant, diluent and the diluent chosen as standard, respectively. The plots of $(Y - Y_s)/(\delta_d - \delta_s)$ vs. $(\delta_d + \delta_s)$ using $C_6H_5NO_2$ as standard reveal a linear relationship, indicating that the Eq. (2) is satisfied for the extraction of zinc(II) from hydrochloric acid solutions by TOMAC in various diluents (except 1,2-$C_2H_4Cl_2$). Similarly the linear relation is also maintained in the extraction systems of copper(II), cadmium(II) and uranium(VI) by TOMAC, although the Y is replaced by the $-\Delta Q$. The obtained values are thus put into Eq. (2), and the parabolic relations are derived as follows :

$$Y = -4.69\delta_d{}^2 + 75.4\delta_d - 301, \quad (3)$$
$$Y = -8.02\delta_d{}^2 + 141\delta_d - 524, \quad (4)$$
$$Y = -3.25\delta_d{}^2 + 51.4\delta_d - 216 \quad (5)$$

and

$$Y = -8.96\delta_d{}^2 + 162\delta_d - 724 \quad (6)$$

for zinc(II), cadmium(II) and copper(II) and uranium(VI) at 1, 0.5, 2 and 1 mol dm^{-3}, respectively, with TOMAC concentration in 0.05 mol dm^{-3}.

In comparison of the result obtained by means of the temperature-dependence of the distribution coefficient (Sato et al., 1981, 1983a) with that by calorimetry, it is concluded that the Y correlates with the solubility parameter of diluent, supporting that the regular solution theory accounts for the diluent effect on the extraction of divalent copper, zinc and cadmium and uranium(VI) from hydrochloric acid solutions by TOMAC.

3.2 Extraction system by TOA

Similarly the heat change associated with the uptake of the metal was examined for the extraction of zinc(II) from aqueous solutions containing zinc chloride in hydrochloric acid or 0.1 mol dm^{-3} hydrochloric acid and lithium chloride with 0.05 mol dm^{-3} TOAHCl in benzene at 25°C. The plots of the ΔQ as the function of initial concentration of total chloride in aqeuous phase give the following results : the maximal exotherm appears at 3 mol dm^{-3} acid similar to that of TOMAC, and the heat change increases exothermally with the total aqueous [Cl] when a part of hydrochloric acid is replaced by lithium chloride. Besides, for the extraction of zinc(II) from 1 mol dm^{-3} hydrochloric acid with 0.05 mol dm^{-3} TOAHCl in various diluents, ΔQ gave the values of 27.2, 27.5, 24.4, 30.0, 29.1,

38.1, 30.7 and 21.7 kJ mol^{-1} in C_6H_6, $C_6H_5CH_3$, m-$C_6H_4(CH_3)_2$, C_6H_5Cl, o-$C_6H_4Cl_2$, $C_6H_5NO_2$, 1,2-$C_2H_4Cl_2$ and CCl_4 respectively. Accordingly Y is estimated to be the respective values of -19.6 (C_6H_6), -19.9 ($C_6H_5CH_3$), -16.8 (m-$C_6H_4(CH_3)_2$), -22.4 (C_6H_5Cl), -21.5 (o-$C_6H_4Cl_2$), -30.5 ($C_6H_5NO_2$), -23.1 (1,2-$C_2H_4Cl_2$) and -14.1 kJ mol^{-1} (CC_4). Hence it is seen that a parabolic dependency of Y on solubility parameter of diluent similar to that by TOMAC (Sato et al., 1985) exists apparently in the extraction by TOAHCl. However, since the plots of $(Y - Y_s)/(\delta_d - \delta_s)$ vs. $(\delta_d + \delta_s)$ using nitrobenzene as standard don't give a straight line, it is thought that Eq. (2) is not satisfied, suggesting that non-random interactions btween diluent and R_3NHCl and/or the species $(R_3NH)_2ZnCl_4$ are present. Similar tendency is also observed in the extraction system of copper(II), cadmium(II) and uranium(VI) by TOAHCl, although the Y is replaced by the $-\Delta Q$. In comparison with the results for the dependency of distribution coefficients on the solubility parameter of diluent, it is also presumed that the extraction of divalent metals (copper, zinc and cadmium) and uranium(VI) from hydrochloric acid solutions by TOA in organic solvents is not regarded as regular solution.

Furthermore, when the plots of ΔQ vs. the heat of dissolution of TOMAC or TOAHCl to organic solvent, ΔQ_s, were checked in the extraction of zinc(II) from 1 mol dm^{-3} hydrochloric acid solution with 0.05 mol dm^{-3} TOMAC or TOAHCl in various diluents, it was found that there is a linear relationship between ΔQ and ΔQ_s. From this it is deduced that the kind of extractants affects on the extraction of metal more than the nature of diluent.

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EXTRACTION OF LANTHANUM(III) AND YTTRIUM(III) FROM AQUEOUS THIOCYANATE SOLUTIONS BY NEUTRAL ORGANOPHOSPHORUS COMPOUNDS

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ABSTRACT
The extraction of lanthanum(III) and yttrium(III) from aqueous solutions containing hydrochloric acid in the presence of potassium thiocyanate by tributyl phosphate (TBP) or trioctyl phosphine oxide (TOPO) in benzene has been investigated under different conditions. The infrared (IR) and nuclear magnetic resonance (NMR) spectral studies have been carried out for the organic extracts. The distribution coefficients of lanthanum(III) and yttrium(III) for TBP increase monotonously with increasing aqueous thiocyanate concentration at a constant hydrochloric acid concentration, and decrease with increasing hydrochloric acid concentration at a constant thiocyanate concentration. As a result, it is found that the equilibrium equations by TBP are expressed as follows : $M^{3+}(aq) + 3NCS^{-}(aq) \rightleftharpoons M(NCS)_3(aq)$, $M(NCS)_3(aq) + 4TBP(org) \rightleftharpoons M(NCS)_3 \cdot 4TBP(org)$ where M = La or Y. Similar results were also obtained in the extraction by TOPO, although the extraction efficiency of TOPO is higher than that of TBP. The IR results indicate that the thiocyanate ion coordinates to metal ions through the nitrogen atom and metal ions combine with the phosphoryl oxygen atom of extractants, corresponding to the NMR ones.

1 INTRODUCTION

Thiocyanate has been utilized as a selective complexing agent in the spectrophotometric determination of cabalt(II) and as a selective extraction for the separation of divalent transition metals and so on (Wilson et al., 1963; Skey, 1967; O'Neill et al., 1976). We have also investigated the extractions of thorium(IV), uranium(VI), titanium(IV), vanadium(IV) and zirconium(IV) from aqueous solutions containing hydrochloric acid in the presence of potassium thiocyanate by a high-molecular weight quaternary ammonium compound (Sato, 1972, 1979; Sato et al., 1973, 1974, 1976 and 1977). Therefore the present paper extends the work to the extraction of lanthanum(III) and yttrium(III) from aqueous solutions containing hydrochloric acid in the presence of potassium thiocyanate by tributyl phosphate (TBP) and trioctyl phosphine oxide (TOPO) in relation to the separation of rare earth elements.

2 EXPERIMENTAL

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Chemicals

TBP (Daihachi Chemical Industry Co., Ltd.) was purified by the usual method (Alcock et al., 1956), and TOPO (Hokko Chemical Industry Co., Ltd.) was used without further purification. TBP and TOPO were diluted and dissolved, respectively, in benzene. The stock solutions of lanthanum and yttrium were prepared by dissolving their chlorides prepared by dissolving their oxides (Shinetsu Chemical Industry Co., Ltd.) in concentrated hydrochloric acid and evaporating hydrochloric acid for selected concentration, in hydrochloric acid solution containing potassium thiocyanate of the required concentration. Generally the aqueous metal concentration was 1 g dm^{-3} lanthanum or yttrium chloride. Other chemicals were of analytical reagent grade.

Extraction and analytical procedures

Equal volumes (15 cm^3 each) of the aqueous and organic phases were shaken for a decided time in 50 cm^3 stoppered conical flasks in a thermostatted water bath at 20°C, except the experiments on temperature effect. Preliminary experiments showed that the equilibrations were complete in 10 min. The mixture was centrifuged and separated, and then the aliquots of both phases were pipetted to determine the distribution coefficient (E_a°, the ratio of the equilibrated concentration of lanthanum or yttrium in organic phase to that in aqueous phase). Lanthanum or yttrium in organic phase was stripped with 1 mol dm^{-3} hydrochloric acid. The concentration of yttrium in aqueous solution was determined by EDTA titration using xylenol orange (XO) as indicator (Kinnunen et al., 1957). The concentrations of chloride and thiocyanate in the organic phase were determined as described previously (Sato et al., 1973), and the water content of the organic phase by Karl-Fisher's titration method.

IR and NMR spectral measurements

Infrared (IR) spectra of the organic extracts were determined on JASCO Models IRA-1 (4000-650 cm^{-1}) and IR-F (700-200 cm^{-1}) using a capillary film between thallium halide plates or polyethylene films. Nuclear magnetic resonance (NMR) spectra were obtained for the organic extracts dissolved in carbon tetrachloride using JEOL Model JNM-PMX60SO NMR spectrometer in the use of tetramethylsilane as an internal reference.

3 RESULTS AND DISCUSSION

3.1 Extraction isotherms by TBP

The extraction of lanthanum(III) and yttrium(III) from aqueous solutions containing hydrochloric acid in the presence of potassium thiocyanate at different concentrations by TBP in benzene gave the result that the distribution coefficient increases monotonically with increasing aqueous thiocyanate concentration at a constant hydrochloric acid concentration, and decreases with increasing hydrochloric acid concentration at a constant thiocyanate concen-

tration, In contrast, the extraction of lanthanum(III) and yttrium(III) from aqueous chloride solutions containing hydrochloric acid and lithium chloride at different concentrations in the presence of potassium thiocyanate by TBP in benzene showed the result that the distribution coefficient is not appreciably influenced by chloride concentration, suggesting that the extracted species contains no chloride. For these extraction systems,the log-log plots of E_a° vs. $[NCS^-]_{init\ aq}$ give the straight lines with a slope of ~ 3, indicating that three thiocyanate groups combine with lanthanum and yttrium ions.

In the extraction of yttrium(III) from aqueous solutions containing 0.01 mol dm^{-3} hydrochloric acid in the presence of potassium thio cyanate with 4.8-57 % TBP (v/v) in benzene, the log-log plots of E_a° vs. $[TBP]_{init}$ at a constant concentration of potassium thiocyanate in 1-9 mol dm^{-3} show the straight lines with a slop of ~ 4 : e.g., the slopes of 3.8, 3.9, 3.8, 3.8, 3.9, 3.7 and 4.2 at the concentrations of potassium thiocyanate in 1.0, 2.0, 3.0, 4.0, 5.0, 7.0 and 9.0 mol dm^{-3} respectively. Similarly the extraction of lanthanum(III) from aqueous solutions containing 0.05 mol dm^{-3} hydrochloric acid in the presence of potassium thiocyanate with 4.8-93 % TBP in benzene gives the straight lines with a slope of ~ 4 for the log-log plots of E_a° vs. $[TBP]_{init}$ at a constant concentration of potassium thiocyanate in 0.1-10 mol dm^{-3}. It is therefore considered that lanthanum(III)- and yttrium(III)-thiocyanato complexes are associated with four molecules of TBP. Accordingly if we assume that the extraction of lanthanum (III) and yttrium(III) from aqueous solutions in the presence of thiocyanate by TBP proceeds according to a solvating reaction, the equilibrium equation is expressed as follows :

$$M^{3+}(a) + 3NCS^-(a) \rightleftharpoons M(NCS)_3(a) \quad (1)$$

$$M(NCS)_3(a) + 4TBP(o) \rightleftharpoons M(NCS)_3 \cdot 4TBP(o) \quad (2)$$

where M=La or Y, and (a) and (o) represent aqueous and organic phases respectively. This is supported by the results for the continuous variation of $[M]_{org}$ as the functions of molar fractions $[M]_{init\ aq}/([M]_{init\ aq} + [NCS^-]_{init\ aq})$ and $[M]_{init\ aq}/([M]_{init\ aq} + [TBP]_{init})$ at the fixed total concentrations of $[M]_{init\ aq} + [NCS^-]_{init\ aq} = 0.5$ mol dm^{-3} and $[M]_{init\ aq} + [TBP]_{init} = 0.2$ mol dm^{-3} respectively : the values of $[M]_{org}$ give the maxima at the former and latter molar fractions of 0.25 and 0.2, respectively. In addition, the stoichiometry of the extracted species was examined by a loading test of lanthanum or yttrium to the organic phase. As a result, it was found that in the extraction of yttrium(III) from aqueous solutions containing 0.01 mol dm^{-3} hydrochloric acid in the presence of 7.0 mol dm^{-3} potassium thiocyanate with 19 % TBP in benzene, the variation of the composition in the organic phase approaches a limiting value of the molar ratio [Y]/[NCS]/[TBP]/[H_2O] in 1 : 3 : 4 : 0,which suggests the formation of the species $Y(NCS)_3 \cdot 4TBP$, with increasing the aqueous

lanthanum concentration. In the same manner, the extraction of lanthanum(III) from aqueous solutions containing 0.05 mol dm^{-3} hydrochloric acid in the presence of 8.0 mol dm^{-3} potassium thiocyanate with 9.5 % TBP in benzene gave the result that the organic phase as a function of the aqueous yttrium concentration approaches a limiting value of the molar ratio [La]/[NCS]/[TBP]/[H_2O] in 1 : 3 : 4 : 0 too.

3.2 IR spectra

The organic extracts of lanthanum(III) and yttrium(III) from aqueous solutions containing 0.05 and 0.01 mol dm^{-3} hydrochloric acid in the presence of 8.0 and 7.0 mol dm^{-3} potassium thiocyanate with 9.5 and 19 % TBP, respectively, in benzene were examined by IR spectroscopy. With increasing the aqueous lanthanum or yttrium concentration, the spectra of the organic extracts show the following results in addition to the absorptions of the alkyl groups due to TBP : the OH stretching band at 3520-3400 cm^{-1} and the bending band at 1640 cm^{-1} decrease in those intensities, indicating that the extracted species contains no coordinated water; the P - O stretching band of water-saturated TBP at 1270 cm^{-1} shifts to lower frequencies; the La-O and Y-O stretching bands appear at 365 and 360 cm^{-1} respectively; the CN stretching band appears at 2060 cm^{-1}, and the NCS bending band at 480-465 cm^{-1}, implying that the thiocyanate ion coordinates to lanthanum or yttrium through the nitrogen atom. These results confirm that lathanum and yttrium extracted into TBP by a solvating reaction in Eq. (2) are bonded to the phosphoryl oxygen atom, suggesting that the extracted species exist as the complexes $La(NCS)_3 \cdot 4TBP$ and $Y(NCS)_3 \cdot 4TBP$ displaying the coordination number of seven (Matsumoto et al., 1989a,b).

The organic phases for the repeated extractions of lanthanum(III) from aqueous solution containing 0.05 mol dm^{-3} hydrochloric acid in the presence of 8.0 mol dm^{-3} potassium thiocyanate with 93 % TBP were examined by NMR spectroscopy. The NMR spectrum for water saturated TBP shows a sharp peak at 9.09 (τ value) in a doublet due to the methyl protons, a multiplet at 8.50, which arises from most of the methylenic protons, and a quartet at 5.92 from the methylenic protons attached to the carbon atoms immedeately adjacent to oxygen atoms; in addition, the water proton resonance at 6.60 indicates the formation of the compound $TBP \cdot H_2O$ (Sato, 1970). In the extraction of aqueous solution containing hydrochloric acid in the presence of potassium thiocyanate alone, the water proton signal is shifted to 6.20, confirming the formation of a hydrogen bond in the compound $HNCS \cdot TBP$ (Yoshida, 1962). The organic solution from the extraction of lanthanum (III) reveals the water proton resonance at 6.21 and its signal decreases in intensity, corresponding to the IR results.

3.3 Temperature effect

The extraction of lanthanum(III) from aqueous solution containing 0.05 hydrochloric acid in the presence of 8.0 mol dm^{-3} potassium thiocyanate with 9.5 %

TBP in benzene was carried out at temperature between 10 and 50°C. The result indicates that the distribution coefficient for lanthanum(III) decreases with rising temperature. The heat of reaction ($-\Delta H$, change in enthalpy) is estimated to be 54.8 kJ mol^{-1}. The similar temperature effect was also observed in the extraction of yttrium(III) from aqueous solution containing 0.01 mol dm^{-3} hydrochloric acid in the presence of 4.0 mol dm^{-3} potassium thiocyanate with 9.5 % TBP in benzene. However, since the heat of reaction for the extraction of yttrium(III) is estimated to be 32.4 kJ mol^{-1}, it is inferred that the extraction from aqueous thiocyanate solutions by TBP of yttrium(III) is more easy than that of lanthanum(III), corresponding to the distribution data.

3.4 Extraction isotherms by TOPO

In the extraction of lanthanum(III) from aqueous solutions containing hydrochloric acid in the presence of potassium thiocyanate at different concentrations by TOPO in benzene, the distribution coefficient increases with increasing aqueous thiocyanate concentration at a constant TOPO concentration. The extraction behaviour of lanthanum(III) by TOPO is similar to that by TBP, although the extraction efficiency for lanthanum(III) of TOPO is higher than that of TBP. When the extraction of lanthanum(III) from aqueous solutions containing hydrochloric acid and lithium chloride at different concentrations in the presence of potassium thiocyanate is carried out by TOPO in benzene, the distribution coefficient is not appreciably influenced by chloride concentration.

Besides the log-log plots of E_a° vs. $[TOPO]_{init}$ gave the straight lines with a slope of ~ 4. In addition the continuous variation of $[La]_{org}$ as the function of $[La]_{init\ aq}$ shows that the molar ratios of $[La]_{init\ aq}/[KNCS]_{init\ aq}$ and $[La]_{init\ aq}/[TOPO]_{init}$ indicate the maxima at 1/3 and 1/4 at the fixed total concentrations of $[La]_{init\ aq} + [KNCS]_{init\ aq}$ and $[La]_{init\ aq} + [TOPO]_{init}$, respectively. Also the loading test of lanthanum in the organic phase as a function of $[La]_{init\ aq}$ reveals that the molar ratio [La]/[NCS]/[TOPO]/[H_2O] in the organic phase approaches a limiting value of 1 : 3 : 4 : 0. These results suggest that the stoichiometric composition of the extracted species is $La(NCS)_3 \cdot 4TOPO$.

Hence the extraction of lanthanum(III) from aqueous solutions in the presence of thiocyanate by TOPO is expressed by the following equilibrium equation similar to Eq. (2) :

$$La(NCS)_3 + 4TOPO(org) \rightleftharpoons La(NCS)_3 \cdot 4TOPO. \qquad (3)$$

The IR spectra of the organic extracts of lanthanum(III) from aqueous solutions containing hydrochloric acid in the presence of potassium thiocyanate with TOPO in benzene show the shift of the P → O stretching band of TOPO at 1146 cm^{-1} to the lower frequency at 1119 cm^{-1}, the La-O stretching band at 390

cm^{-1}, the CN stretching band at 2050 cm^{-1}, and the NCS bending band at 478 cm^{-1}. The result implies that the thiocyanate ion coordinates to lanthanum through the nitrogen atom, and that lanthanum(III) extracted into TOPO by a solvating in Eq. (3) is bonded to the phosphoryl oxygen atom. From this it is deduced that the extracted species exists as the complex $La(NCS)_3 \cdot 4TOPO$ displaying the coordination number of seven (Matsumoto et al., 1989a,b), corresponding to the NMR spectral result.

In contrast, when the temperature effect on the extraction of lanthanum(III) from aqueous solutions containing hydrochloric acid in the presence of potassium thiocyanate by TOPO in benzene was examined at temperature between 10 and 50°C, it was found that the distribution coefficient decreases with rising temperature.

Similar results are also obtained in the extraction of yttrium(III) from aqueous solutions containing hydrochloric acid in the presence of potassium thiocyanate by TOPO in benzene, but the extraction efficiency of TOPO for yttrium(III) is larger than that for lanthanum(III). Therefore it is seen that the extraction of lanthanum(III) and yttrium(III) from aqueous solutions containing hydrochloric acid in the presence of potassium thiocyanate by TOPO resembles that by TBP, although the former extraction efficiency is larger than the latter one.

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SEPARATION OF NEODYMIUM FROM ITS CONCENTRATE USING 20% SAPONIFIED DI-(2-ETHYL HEXYL) PHOSPHORIC ACID IN KEROSENE AS AN EXTRACTANT

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ABSTRACT

Extractions of Nd by 20% saponified di-(2-ethyl hexyl) phosphoric acid (1.0 M) in kerosene containing 5% (v/v) isodecanol were carried out from aqueous solutions in HCl medium. Distribution coefficients of the metal ions were determined as a function of initial concentration of HCl for different initial concentrations of metal ions. Similar distribution data for La, Ce, Pr and Sm were generated using the distribution data of Nd and the separation factors for Nd-La, Nd-Ce, Nd-Pr and Sm-Nd. On the basis of these data the empirical mathematical models were made to predict the extraction behaviour of these metal ions at various initial acidities and metal concentrations. Incorporating these models a computer program has been written to calculate the concentrations of these metal ions in the organic and aqueous phases at various stages of extractions and scrubbings in a counter-current solvent extraction cascade. Using this program the conditions such as number of extraction and scrubbing stages, initial acidity of the feed and scrub solutions, Nd concentration in the scrub and organic to aqueous phase ratio have been determined to get the desired purity (>95%) and recovery (>80%) of Nd in the organic phase. Under the predetermined conditions, counter-current extractions and scrubbings were carried out using mini mixer-settler. The results obtained are in good agreement with the predictions, indicating the feasibility of the process.

INTRODUCTION

Separation of individual rare earths (RE) by solvent extraction (SX) technique using di-(2-ethyl hexyl) phosphoric acid (DEHPA) and alkyl phosphonic acid (PC 88A) or its equivalents is by now the most widely used industrial practice. However, these extractants function as cation exchangers and the liberated acid due to metal extraction adversely affect the metal extraction. This problem is overcome by converting these acids to alkali salt form by saponification with $NaOH/NH_4OH$. Often partial saponification is preferred for operational reasons. Amongst the rare earths, separation of Nd from Pr is difficult due to low separation factor (β). A systematic study has been carried out by us on the separation of Nd from lighter rare earths mixture (La,Ce,Pr, Nd and Sm) in HCl medium using 1.0 M DEHPA in kerosene containing 5% (v/v) isodecanol, after 20% saponification with NH_4OH.

2 MECHANISM OF EXTRACTION

The extraction of RE by DEHPA under normal conditions of use can be expressed as.

$$M^{+3} + 3\,\overline{(HG)}_2 \rightleftharpoons \overline{M(HG_2)_3} + 3\,H^+ \qquad (1)$$

where M^{+3} is a trivalent RE ion, $\overline{(HG)}_2$ is a dimer molecule of DEHPA in kerosene and $\overline{M(HG_2)_3}$ is the RE complex with DEHPA in solvent phase. When partially neutralised DEHPA is used for RE extraction, it is assumed that the NH_4^+ ions are first replaced by RE ions in preference to H^+ ions. Thus, the acidity of the aqueous solution remains under control and extraction of RE is improved. The extraction coefficient (D) of RE depends on the initial acidity (H_i) and the initial metal ion concentration (C_i) provided the extractant concentration $[\overline{(HG)}_2]$ is constant which is normally the case since it is in large excess. Hence, an empirical mathematical equation showing D as a function of H_i and C_i would prove helpful.

3 EXTRACTION DATA

For deriving mathematical models one has to generate large volume of data for each individual RE. The data D vs H_i were experimentally determined for Nd only, varying H_i from 0.05 to 0.5 M and C_i from 0.05 - 0.25 M at a constant organic/aqueous (O/A) phase ratio (R) equal to 1. The H_i values were corrected using the expression $H_i = H_i(\text{expt}) - R * 0.2$. The data obtained are shown in Table 1.

TABLE 1

Data of distribution coefficient (D) vs initial acidity (H_i) for various Nd concentrations.

20 % Saponified DEHPA (1M) Phase Ratio O/A = 1

Nd	0.05 M		0.15 M		0.25 M	
	H_i	D	H_i	D	H_i	D
	-0.1	76.5	-0.19	3.93	-0.15	0.97
	0.2	8.25	-0.1	1.82	-0.1	0.88
	0.3	1.74	0.2	0.58	0.2	0.34
	0.4	0.20	0.4	0.30		

Similar data for La, Ce, Pr and Sm were generated using an equation (2) derived by Thakur, 1990 for this purpose. This equation can be utilised if we know the separation factor (β) for various pairs of RE under study. In our case we have utilised the β values reported by Pierce and Peck, 1963 [β(Nd-La) = 8.42, β(Nd-Ce) = 2.83, β(Nd-Pr) = 1.35, β(Sm-Nd) = 6.58].

The distribution data generated experimentally for Nd , was substituted in the following equation

$$[H_2^+]_i = \{[H_1^+]_i + A*(1- \beta^{1/3})\} / \beta^{1/3} \quad (2)$$

where $[H_1^+]_i$ is the corrected initial acidity of Nd solution at which the D value has been determined, $[H_2^+]_i$ is the calculated initial acidity for another RE of interest (La, Ce, Pr) at which the D value for that RE would be identical to that of Nd. Data for Sm were generated using the same equation as above but $[H_1^+]_i$ is the calculated initial acidity of Sm solution and $[H_2^+]_i$ is the corrected initial acidity of Nd solution. In other words, this equation helps to generate sets of data, D vs H_i, for each of the individual RE without carrying out any experiments, provided the experimental data of one of the rare earths are known. In the above equation β is the separation factor of the pair of elements - Nd and the other RE of interest, and

$$A = 3 * C_i * D_1 * R / (D_1 * R + 1) = 3 * C_i * D_2 * R / (D_2 * R + 1)$$

where C_i is the initial concentration of the metal ion which would be the same for both the elements, and $D_1 = D_2$. Using the equation (2) data on D vs H_i have been generated for La,Ce,Pr and Sm, and as an example, the derived data of Pr have been shown in Table 2.

TABLE 2.

Data of distribution coefficient (D) vs initial acidity (Hi) for various Pr concentrations.

20% Saponified DEHPA (1M) Phase Ratio O/A = 1

Pr	0.05 M		0.15 M		0.25 M	
	H_i	D	H_i	D	H_i	D
	-0.105	76.5	-0.206	3.93	-0.171	0.97
	0.167	8.25	0.062	1.822	-0.124	0.88
	0.263	1.14	0.164	0.579	0.162	0.34
	0.359	0.20	0.351	0.293	0.355	0.08
					0.539	0.04

4 DERIVATION OF MATHEMATICAL MODELS

The data D vs H_i, obtained for the various RE at C_i (0.05, 0.15 and 0.25 M), were curve fitted using least square method with the help of a micro computer using software "GRAPHPACK' to get an exponential fit

$$D = A * e^{(B * H_i)} \quad (3)$$

where A and B are arbitrary constants depending on the metal, C_i and H_i. The values of A and B (Table 3) for the fitted curves showed a significant dependence on C_i. Hence the data on A vs C_i and B vs C_i were once again fitted to the following general equations

$$A = A_1 * C_i^{(A_2)} \quad (4)$$

$$B = B_1 * C_i^{(B_2)} \quad (5)$$

where A_1, A_2, B_1 and B_2 are arbitrary constants which depend on the particular metal. Substituting the values of A and B from equations (4) and (5) in equation (3) we get the overall general equation

$$D = A_1 * C_i^{(A_2)} * e^{(B_1 * C_i^{(B_2)} * H_i} \quad (6)$$

This is the general mathematical model derived for the extraction behaviour of RE under our experimental conditions. Based on the data generated the mathematical models derived for La, Ce, Pr, Nd and Sm are shown in Table 4. These models have been utilised in a computer program developed for simulation studies on separation of Nd from a mixture of LRE.

TABLE 3

Curve fitting parameters (A,B) of exponential fit $D = A*e^{(B*H_i)}$ for the curves D vs H_i for different initial rare earths (La, Ce, Pr, Nd, Sm) concentrations $(C)_i$.

Rare Earth Metal	Initial Concn.[M]	A	B
Lanthanum	0.05	8.976	-19.35
	0.15	0.657	-6.00
	0.25	0.212	-6.034
Cerium	0.05	17.67	-19.52
	0.15	0.99	-5.05
	0.25	0.364	-5.214
Praseodymium	0.05	29.27	-12.52
	0.15	1.421	-4.73
	0.25	0.498	-4.699
Neodymium	0.05	34.56	-11.53
	0.15	1.454	-4.212
	0.25	0.569	-4.464
Samarium	0.05	75.44	-6.74
	0.15	2.737	-2.77
	0.25	1.061	-3.04

5 DISTRIBUTION OF INDIVIDUAL RE FROM A MIXTURE OF LRE

To calculate the distribution of individual RE in two phases from LRE mixture the following assumptions have been made. (1) The C_i of each RE is assumed to be equal to the sum of the concentrations of LRE. (2) The mole fraction of individual RE in solvent phase is assumed to be the same as in the aqueous feed solution. Based on these assumptions the distribution of each RE present in the two phases is determined.

6 COMPUTER PROGRAM FOR CALCULATIONS

A program has been written in FORTRAN incorporating the mathematical models given in Table 4. Provision has been made in the program to calculate the concentration of each of the LRE present in the solvent and aqueous phases at any phase ratio and to correct the acidity at various stages of counter-current extraction due to changes in the neutralisation level of DEHPA as a result of metal extraction. This program is available on request.

TABLE 4

Mathematical models for the extraction behaviour of LRE (La, Ce, Pr, Nd, Sm) using 20 % saponified DEHPA (1.0M) in kerosene with 5 % (v/v) isodecanol

$$D(La) = 0.008 * C_i^{-2.33} * e^{(-1.74 * C_i^{-0.778})} * H_i$$

$$D(Ce) = 0.011 * C_i^{-2.446} * e^{(-1.255 * C_i^{-0.880})} * H_i$$

$$D(Pr) = 0.0127 * C_i^{-2.569} * e^{(-1.664 * C_i^{-0.653})} * H_i$$

$$D(Nd) = 0.013 * C_i^{-2.605} * e^{(-1.562 * C_i^{-0.642})} * H_i$$

$$D(Sm) = 0.0208 * C_i^{-2.708} * e^{(-1.230 * C_i^{-0.544})} * H_i$$

7 PROCESS OPTIMISATION FOR Nd RECOVERY

The computer program was utilised to carry out simulation studies to obtain a Nd rich fraction assaying >95% Nd_2O_3 at an overall recovery of >80% under conditions shown in Table 5. The process parameters were optimised to suit the micro mixer-settler assembly consisting of a 4-stage unit for extraction and two 10-stage units to give 20 stages of scrubbing. Part of the Nd recovered was recycled for scrubbing of the extract. The experimental results are shown in Table 6 and compared with the computed values. The results obtained using 20% saponified DEHPA have shown the feasibility of obtaining >95% pure Nd_2O_3 at about 80% recovery.

TABLE 5

Optimised parameters for purity of Nd_2O_3 > 95% at a recovery of > 80% for the specified feed composition

Feed composition	No. of stages	Solution flows
0.374 M LaCl3	extraction : 4	feed soln. : 1 vol.
<0.001 M CeCl3	scrubbing : 20	scrub soln.: 2 vol.
0.064 M PrCl3		solvent : 9 vol.
0.200 M NdCl3		
<0.001 M SmCl3		
0.010 M HCl		
Scrub composition		
Nd concn. : 0.1 M		
HCl concn. : 0.7 M		

TABLE 6

Composition of the extract and the raffinate after equilibration using the conditions mentioned in Table 5 (mixer-settler used)

	Experimental	Computed	% Recovery of Nd	% Purity w.r.t. Pr
Nd (M) raffinate	0.013	0.007		
Pr (M) raffinate	0.013	0.015		
Ce (M) raffinate	-	-		
La (M) raffinate	0.123	0.125		
Sm (M) raffinate	-	-		
Nd (M) extract	0.043	0.042		
Pr (M) extract	0.0023	0.0022	81.0	~95.0
Ce (M) extract	-	-		
La (M) extract	<0.001			
Sm (M) extract	-	-		

8 CONCLUSIONS

The methodology followed for studying the RE extraction and the assumptions made in developing the computer program for 20% saponified DEHPA have been proved to be correct. The conditions of extractions and scrubbings can be predetermined with the help of computer program to get the desired purity and recovery of Nd for the specified feed composition. The saponification helps in improving the recovery of Nd considerably. The process is feasible for getting >95% purity of Nd_2O_3 in the extract with a recovery of >80%.

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SOLVENT EXTRACTION OF PALLADIUM (II) FROM AQUEOUS CHLORIDE MEDIA WITH LIX 63

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ABSTRACT

The kinetic aspect of palladium (II) extraction from chloride solutions with 5,8-diethyl-7-hydroxy-6-dodecanone oxime (H_2Ox) (active component of LIX 63) in dodecane was studied.

The extraction rate of Pd(II) was measured using an ARMOLLEX cell and a high stirred cell. The experimental results are explained by an interfacial reaction model in which the formation of the 1:2 Pd:LIX complex at the interface is rate determining. The formation of $PdCl_3(H_2Ox)_2^-$ occurs in the bulk aqueous phase and is fast. $PdCl_3(H_2Ox)_2^-$ then slowly reacts with H_2Ox adsorbed to form $PdCl_2(H_2Ox)_2$ at the interface. For high HCl concentrations this compound enters the organic phase without any change, whereas for low HCl concentrations it is transformed into $Pd(HOx)_2$ before its transfer into the organic medium.

1) INTRODUCTION

LIX 63 (H_2Ox) is an α-hydroxyoxime which extracts palladium with high distribution ratios and exhibits an interesting selectivity with respect to platinum (1,2). Several authors (3,4,5) have studied the extraction kinetics of different metals, mainly copper, by LIX 63 and LIX 65N. LIX 63 alone gives very slow extraction rates and it seems interesting to find out the causes of this phenomenon in the case of palladium (II) which has not been studied yet. The aqueous medium is hydrochloric acid which is of industrial interest.

Thermodynamic studies previously performed (6) lead to the following extraction mechanisms :

- <u>for low HCl concentrations</u>

$$PdCl_n^{(2-n)+} + 2\,\overline{H_2Ox} \longleftrightarrow \overline{Pd(HOx)_2} + n\,Cl^- + 2\,H^+$$

with $n <= 3$

Pd(II) is found in hydrochloric acid solutions under different forms depending on chloride ion concentration ($PdCl_n$). $\overline{H_2Ox}$ represents free monomeric LIX 63 in the organic phase (LIX 63 is in apolar diluents, mainly under trimeric and monomeric forms and it is supposed that only the latter can extract Pd(II)).

- for high HCl concentrations

$PdCl_4^{2-}$ is the only Pd species existing in the aqueous phase

$PdCl_4^{2-} + 2\,\overline{H_2Ox} <----> \overline{PdCl_2(H_2Ox)_2} + 2\,Cl^-$

An ARMOLLEX cell with constant interfacial area and a highly stirred cell are used to measure the extraction rate of palladium. The palladium concentration in the organic phase is continuously recorded versus time for the ARMOLLEX cell ; in the other cell samples of the aqueous phase are analysed.

In a previous paper (6) we have shown that the chemical reactions are always limiting even for very small rotation rates. So in this work we study the influence of chemical parameters (Cl^-, H^+, $\overline{H_2Ox}$, Pd) on the extraction rate in order to establish the kinetic equations.

2) MATHEMATICAL TREATMENT

The distribution ratios are under our conditions always very high. We can then ignore the reverse reaction. The forward reaction is supposed to be pseudo-first order according to palladium. So $dy/dt = k_f x$ where x and y are the Pd(II) concentrations at the time t in aqueous and organic phases respectively.

Integrating this equation with $y = 0$ for $t = 0$ and $x = 0$ at equilibrium leads to : $\ln (1 - y/y_{eq}) = - k_f t$ for equal volumes of both phases.

For each experiment $\ln(1 - y/y_{eq})$ is plotted versus time. If a straight line is obtained, the pseudo-first order assumption is proved to be true.

The slope of the straight line k_f is the apparent kinetic constant which depends on the following chemical parameters: Cl^-, H^+, $\overline{H_2Ox}$. It is then possible to determine the kinetic equation expressed as : $r = k \times [H^+]^m\,[Cl^-]^n\,\overline{[H_2Ox]}^p$ where r is the extraction rate and [X] indicates the concentration of the compound X.

3) DETERMINATION OF THE KINETIC LAW

* determination of m (stirred cell, $\overline{[H_2Ox]} = 0.01$ mol/L)

For the two acidity ranges, k_f does not depend on $[H^+]$. So m is equal to 0 in both cases as it can be seen on the following tables.

$[Cl^-] = 0.14$ mol/L

$[H^+]$ mol/L	0.14	0.74	0.94	1.34	1.74	2
$k.10^3\ s^{-1}$	6.6	5.83	5.33	4.67	5.17	6.6

$[Cl^-]$ = 2 mol/L

$[H^+]$ mol/L	0.06	0.26	0.46	0.86	1.26	1.66
$k.10^4\ s^{-1}$	6.7	7.3	8.3	9.5	12.6	13.2

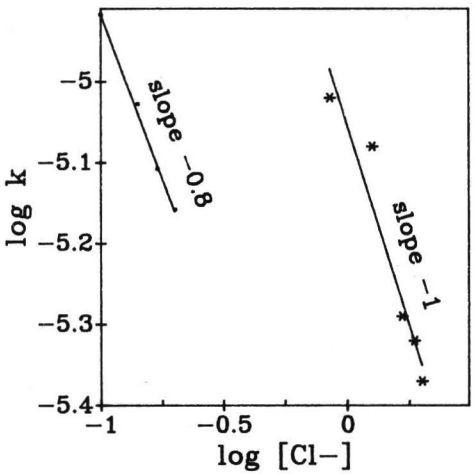


Fig 1: influence of [Cl−] on the extraction rate of Pd(II)

. [H+] = 0.15 mol/L

*** [H+] = 1 mol/L**

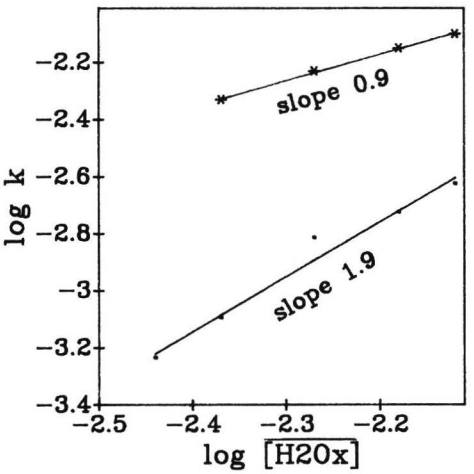


Fig 2: influence of $\overline{[H2Ox]}$ on the extraction rate of Pd(II)

. [HCl] = 1 mol/L

*** [HCl] = 0.1 mol/L**

* <u>determination of n</u> (ARMOLLEX cell, $\overline{[H_2Ox]}$ = 0.01 mol/L)

For $[H^+]$ = 1 mol/L and $[Cl^-]$ varying from 0.9 to 2 mol/L, log k_f = f (log $[Cl^-]$) is a straight line which slope is - 1 (figure 1). In this case n is equal to -1.

On the other hand for acidities close to 0.1 mol/L, the slope is found to be - 0.8. This result is attributed to the fact that in the aqueous phase two different species $PdCl_3^-$ and $PdCl_4^{2-}$ exist. It would be more realistic to express the kinetic law with the concentration of one of the complexes, for instance $[PdCl_3]$; this concentration can be expressed as following: $[PdCl_3^-] = x\ (1 + K_4\ [Cl^-])^{-1}$, where K_4 is the constant of the following equilibrium:

$PdCl_3^- + Cl^- <----> PdCl_4^{2-}$.

k_f is found to be proportional to $(1 + K_4 [Cl^-])^{-1}$.

* determination of p (stirred cell)

For HCl 1 mol/L, p is close to 2 whereas it is equal to 1 for HCl 0.1 mol/L (figure 2).

In conclusion we have ascertained two different kinetic laws:

HCl 1 mol/L $\quad r = k \times [Cl^-]^{-1} \overline{[H_2Ox]}^2$

HCl 0.1 mol/L $\quad r = k \times (1 + K_4 [Cl^-])^{-1} \overline{[H_2Ox]}$

4) INTERPRETATIONS

In a previous paper (6) we have examined the H_2Ox distribution between the two phases and its adsorption at the interface.

H_2Ox under its monomeric form is slightly soluble in the aqueous media. Its distribution ratio was measured at 25°C ; it was found to be 1140. The solubility increases with increasing acidity due to the protonation of H_2Ox which appears beyond 0.1 mol/L : $H_2Ox + H^+ <----> H_3Ox^+$

With regards to the adsorption of H_2Ox at the interface the following conclusions should be mentioned :

* at high acidities the adsorbed predominant species is H_3Ox^+ and the interface is far from saturation ; there is a very small number of molecules of H_2Ox adsorbed

* at low acidities H_3Ox^+ does not exist. H_2Ox is the only adsorbed species at its saturation concentration, i.e. when the concentration of $\overline{H_2Ox}$ is increased in the organic phase the concentration of adsorbed H_2Ox remains constant.

We can propose the following mechanisms:

$\overline{H_2Ox} <----> H_2Ox$

$PdCl_3^- + Cl^- <----> PdCl_4^{2-}$

$PdCl_3^- + H_2Ox <----> PdCl_3(H_2Ox)^-$

The last reaction occurs in the bulk aqueous phase since H_2Ox exits in it. The three reactions are valid for both acidity ranges.

The complex 1:2 formation reaction is the limiting step. It occurs probably at the interface since the extraction rate depends on the interfacial area.

$PdCl_3(H_2Ox)^- + (H_2Ox)_{ad} <----> PdCl_2(H_2Ox)_{2\ ad} + Cl^-$

The difference between the two kinetic laws (different orders with respect to $[H_2Ox]$) is explained as following : at low acidity $[H_2Ox]_{ad}$ is constant (saturation of the interface) while at high acidities this concentration is very small and proportional to $[H_2Ox]$ according to the Langmuir equation.

The subsequent steps are fast and depend on the acidity of the aqueous phase:

HCl 1 mol/L $PdCl_2(H_2Ox)_{2\ ad} <----> \overline{PdCl_2(H_2Ox)_2}$

HCl 0.1 mol/L $PdCl_2(H_2Ox)_{2\ ad} <----> \overline{Pd(HOx)_2} + 2\ Cl^- + 2\ H^+$

The elimination of H^+ and Cl^- is not possible when the aqueous phase is too rich in these compounds.

We have ascertained two different kinetic mechanisms which could lead to useful informations on the LIX 63 properties as extractant. It seems however interesting to focus further investigations on the interfacial phenomena which is very complicated in order to understand precisely all the causes of the kinetics slowlyness.

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Solvent Extraction 1990, T. Sekine (Editor)

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SEPARATION AND PURIFICATION OF VANADIUM AND MOLYBDENUM BY SOLVENT EXTRACTION AND SUBSEQUENT REDUCTIVE STRIPPING

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ABSTRACT

The solvent extraction of pentavalent vanadium and hexavalent molybdenum by tri-n-octylmethylammonium chloride(TOMAC) from neutral solutions and subsequent selective stripping were studied. It was found that vanadium was extracted preferentially as compared to molybdenum by an anion exchange mechanism. The extracted pentavalent vanadyl anion was reduced to the form of tetra- or trivalent cations by contacting a solution containing a reduction agent such as L-ascorbic acid or by two-phase electrolysis using a platinum electrode. These method enables only the vanadium to be stripped selectively by reduction, with the molybdenum remaining in the organic phase. The appropriate selection of the reducing condition and of the solution pH gave high separation efficiency and percentage recovery. A separation efficiency of 1.64×10^4 was obtained by chemical-reductive stripping from an aqueous solution containing an initially equal concentration of both metals by single extraction followed by single selective stripping. The electro-reductive stripping was also found to enhance the stripping percentage of vanadium.

INTRODUCTION

Recently, much attention has been paid to rare metals as new industrial materials and solvent extraction method is known to be one of the most effective methods for their separation and purification. A solvent extraction process used for rare metals normally consists of three stages; extraction, scrubbing and stripping. Usually, separation is effected at the extraction stage on the basis of difference in distribution ratio between the metals in the feed solution. When selective stripping of the required metal can be included, it results in a much higher separation efficiency.

In the Purex process for the recovery of plutonium and uranium from waste nuclear fuels, plutonium was stripped selectively by either chemical(Rydberg, 1957 and Tsujino et al., 1976) or electrochemical reduction(Baumgartner et al., 1978). Reduction of extracted metals is very effective in the stripping operation, since the reduced metal just acts as a different metal in the extraction systems.

In this work, the separation and purification of vanadium and molybdenum by solvent extraction using tri-n-octylmethylammonium chloride(TOMAC) as extractant and subsequent selective stripping of vanadium by chemical and electrochem-

ical reduction were investigated.

2 EXPERIMENTAL

TOMAC(Koei Kagaku Kogyo Co., Ltd.) was purified and diluted with benzene. Aqueous stock solutions of vanadium and molybdenum were prepared by dissolving sodium metavanadate($NaVO_3$) and sodium molybdate($Na_2MoO_4 \cdot 2H_2O$) respectively in distilled water.

Organic and aqueous feed solutions were mixed at volume ratios of 1:1 and shaken for about 2 hours for equilibration at 25°C. The two phases were separated and the extraction percentage, E, was determined.

Stripping was carried out by shaking equal volumes of the metal loaded organic solution and aqueous solution together for about 2 hours at 25°C. L-ascorbic acid was used as a reduction agent. Figure 1 shows the electrochemical cell for electro-reductive stripping, which have two compartments separated by a cation exchange membrane(Aldrich Nafion417) and is equipped with platinum electrodes. The working electrode is 12 x 2 cm platinum mesh(40 mesh). Equal volumes(15 ml) of the metal-loaded organic and aqueous solutions were agitated and electrolized in the cathodic compartment. The vanadium and molybdenum concentrations in the aqueous solutions were determined by means of an inductively coupled argon plasma atomic emission spectrophotometer(ICP, Nippon Jarrell-Ash ICAP-575MarkII).

3 RESULTS AND DISCUSSION

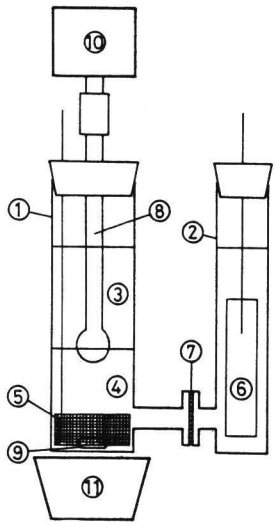
3.1 Extraction behavior of vanadium and molybdenum by TOMAC

Figure 2 shows the performance of vanadium and molybdenum extraction from mixed solutions containing equal quantities of each metal(ca. 0.01 mol/l) as a function of the equilibrium pH. An equilibrium pH of 7 to 8 should be employed for the effective separation of the two metals. With a TOMAC concentration of 0.015 mol/l and an input aqueous pH value of 7.0, the resulting equilibrium pH value was ca. 7.4. Under these conditions, the extraction percentages for vanadium and molybdenum were greater than 98 % and less than 8 %, respectively, and the concentration of vanadium in the organic phase(ca. 9.3×10^{-3} mol/l) was more than 12 times greater than that of molybdenum(ca. 7.6×10^{-4} mol/l). More than 92 % molybdenum remained in the raffinate aqueous solution; in molar terms, its quantity was more than 50 times greater than that of vanadium.

3.2 Chemical-reductive stripping of vanadium

To improve the separation of the two metals, the scrubbing of molybdenum and/or the selective stripping of vanadium is needed. The method of selective stripping of vanadium by chemical reduction was investigated.

When hydrochloric acid was used as the stripping solution, it was seen in



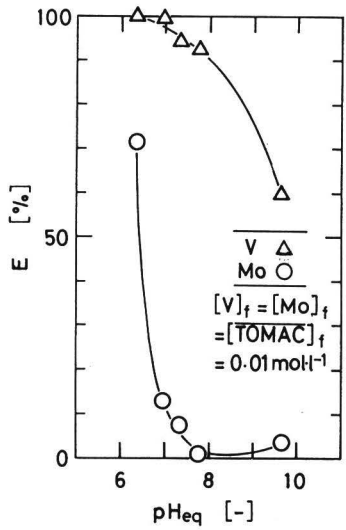


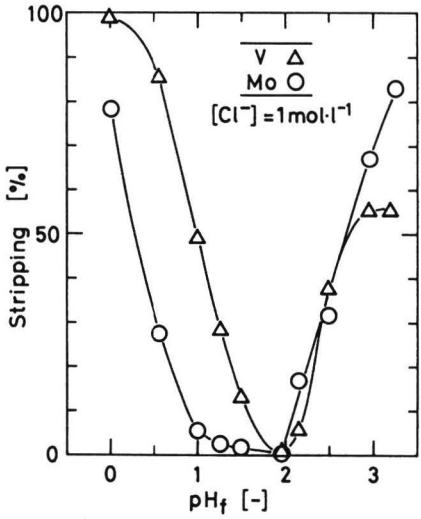
Fig. 1. Two compartment electrochemical cell for electro-reductive stripping. 1: Cathodic compartment, 2: Anodic compartment, 3: Organic phase, 4: Aqueous phase, 5: Cathode(Pt mesh), 6: Anode(Pt plate), 7: Cation exchange membrane, 8: Agitator, 9: Stirring bar, 10: Stirring motor, 11: Magnetic stirrer.

Fig. 2. Relationship between equilibrium pH and extraction performance of vanadium and molybdenum.

Fig. 3 that the stripping performance was a minimum value at pH_f = 2 (pH_{eq} = ca. 2.3) and less than 1 % of both metals transferred into the stripping solution. This minimum stripping is likely caused by the very stable structure of the pentavalent vanadyl ion and hexavalent molybdate ion at this pH in the organic phase. At this pH, the effect on the stripping performance of the addition of L-ascorbic acid as a reduction agent was investigated. The results are shown in Fig. 4. The stripping of vanadium was remarkably enhanced, whereas that of molybdenum was insensitive to the addition of the reduction agent. The spectroscopic analyses showed that the pentavalent vanadium was reduced to a mixed state of tetra- and trivalent vanadium by L-ascorbic acid, where the reduced vanadium species existed as cations such as VO^{2+}(tetravalent) and V^{3+}(trivalent). TOMAC is basically an anion exchanger and acts as an extractant for anionic species. Consequently, these cationic species are hardly extracted.

The separation efficiency, which was defined as the molar ratio of vanadium to molybdenum, in the resulting stripping solution showed a maximum at pH values of 1.8-2. The effect of the composition of the stripping solution on the stripping performance is shown in Table 1. With 1 mol/l L-ascorbic acid solu-

tion, the percentage stripping for vanadium reaches 91.3 % and a separation efficiency of 6.47 x 10^3 is obtained. With decreasing the concentration of the reduction agent, the stripping performance for both metals decreases. However the separation efficiency increases up to a value of 1.64 x 10^4 with further decrease in concentration of the reduction agent to 0.01 mol/l.



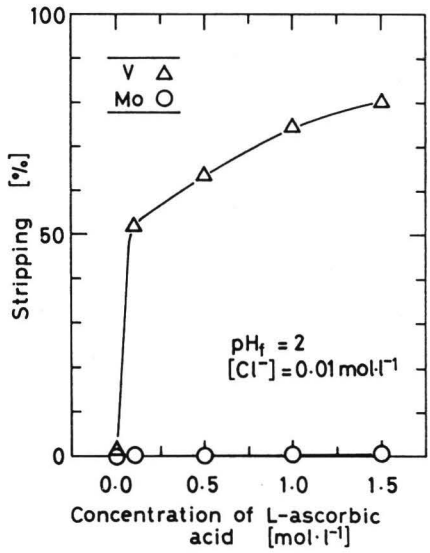


Fig. 3. Effect of stripping solution pH on stripping performance of vanadium and molybdenum.

Fig. 4. Effect of addition of L-ascorbic acid on stripping performance of vanadium and molybdenum at pH 2.

TABLE 1

Stripping performance of vanadium and molybdenum, and separation efficiency at various conditions. The organic solution used contains 9.26 x 10^{-3} mol/l vanadium and 7.59 x 10^{-4} mol/l molybdenum. Each stripping solution contains 0.01 mol/l hydrochloric acid.

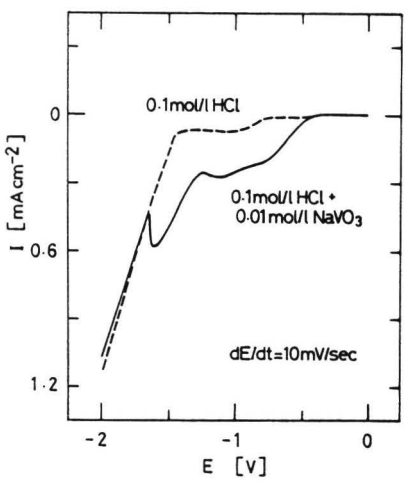
Concentration of L-ascorbic acid [mol/l]	pH_f [-]	Stripping [%]		Separation efficiency [-]
		V	Mo	
0.1	2.03	64.7	0.048	1.64 x 10^4
0.5	1.91	85.0	0.074	1.40 x 10^4
1.0	1.83	91.3	0.172	6.47 x 10^3

3.3 Electro-reductive stripping of vanadium

Since electrical conductivity of benzene is too much small to reduce the vanadyl ion in the organic phase at the organic solution/electrode interface, cathodic reduction must occur at the aqueous electrolyte/electrode interface in the two-phase electrolysis system, as the case of uranium reduction(Feess et al., 1982). Thus, mass transfer of vanadyl ion from the organic into aqueous phase should be required. Hydrochloric acid solution of pH 2 is not suitable stripping solution in this case, because the vanadyl ion hardly moves into the aqueous phase. Thus, 0.1 mol/l HCl solution was applied in this study.

Figure 5 shows the current-voltage curve obtained by using platinum electrodes in 0.1 mol/l HCl solution containing 0.01 mol/l $NaVO_3$. The reduction current of pentavalent vanadium is seen, and it is found that 1.5 V is the suitable electrolysis voltage to reduce the vanadyl ion sufficiently without considerable hydrogen generation.

The relationship between the electrolysis time and stripping performance of vanadium and molybdenum at agitation speed of 300 rpm is shown in Fig. 6. The data at time = 0 show the stripping performance at equilibrium without electrolysis. The enhancement of vanadium stripping was seen, and the reduced vanadium species was characterized as VO^{2+} by spectroscopic analysis. The stripping percentage of molybdenum was ca. 1 % and not effected by electrolysis.



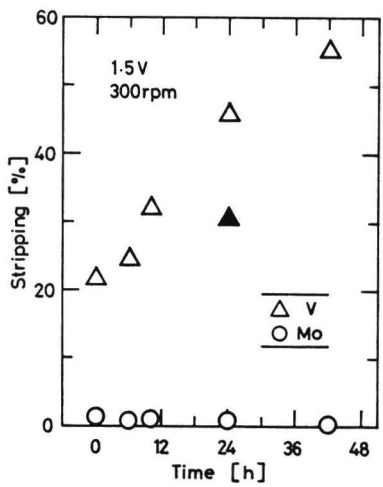


Fig. 5. Current-voltage curve obtained in 0.1 mol/l HCl solution.

Fig. 6. Effect of electrolysis time on stripping performance of vanadium and molybdenum. Closed key shows a datum obtained by electrolysis without agitation.

The agitation speed of both phases quite influenced the stripping performance. The datum obtained by electrolysis without agitation(only the aqueous phase was stirred by the stirring bar) is also shown in Fig. 6 with the closed key. The stripping of vanadium remarkably decreases, indicating that the mass transfer of vanadyl ion at the organic/aqueous solution interface is the rate controlling step. Thus, it is expected that the increase in the agitation speed brings about the increase in the stripping rate. In order to obtain the greater stripping percentage and stripping rate of vanadium, the electrochemical cell shown in Fig. 1 should be improved to make the stronger agitation possible.

4 CONCLUSIONS

The separation and purification of vanadium and molybdenum by solvent extraction and subsequent reductive stripping was studied and the following results were obtained.

(i) Vanadium was extracted from neutral solutions preferentially by TOMAC as compared to molybdenum.

(ii) The extracted vanadium was selectively stripped by the chemical reduction method, in which the vanadium was changed from a pentavalent anion to tetra- or trivalent cations. The highest separation efficiency obtained by extraction followed by this selective stripping process was 1.64×10^4.

(iii) The electro-reductive stripping of vanadium was found to be also applicable in this process. In this study, the stripping percentage of greater than 50 % was obtained for vanadium.

5 ACKNOWLEDGEMENT

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EXTRACTION OF Sc, Y, AND LANTHANOIDS BY QUATERNARY AMMONIUM SALTS

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ABSTRACT
The separation of Sc and Y from the lanthanoids by extraction with various quaternary ammonium salts was investigated. Aliquat-336, Methyltrioctylammonium nitrate (MTOA), Methyldibutylhexadecylammonium nitrate (MDBHDA) and Tributyl-hexadecylammonium nitrate (TBHDA) were used as extractants. The synthesis of MDBHDA and TBHDA from industrial products is described. From the results obtained in the extraction studies of REE as a function of the parameters of aqueous and organic phases we have determined the optimal separation conditions. The salting-out action on these systems of a great number of cations such as Al^{3+}, Fe^{3+}, Mg^{2+}, Cu^{2+}, Ni^{2+}, Li^{+} , Cs^{+} , was investigated. For the derivation of the functional dependences of the separation factors for the REE the microviscosity of ions was used.

INTRODUCTION

Quaternary ammonium salts (QAS) are widely used in the technology of rare metals. In particular, they are promising chemicals for the separation of rare earth elements (REE) because the extraction of lanthanoids strongly depends on their atomic number. As regards Sc, it must be noted that its extraction with QAS is less investigated. In this paper we have studied the separation of Sc, Y and lanthanoids from solutions of various salting-out agents using different QAS (Aliquat-336, MTOA, MDBHDA, TBHDA). MDBHDA and TBHDA were synthesized using industrial products. As already known, the REE are extracted by QAS from HNO_3 solution with small distribution coefficients. Maeck et al. (1961) have shown that Sc, Y and lanthanoids can be extracted by symmetric QAS (tetrapropyl, tetra-butyl and tetrahexyl) into methyl isobutyl ketone with an efficiency below 1%. In order to increase the extraction efficiency the salting-out agents are necessary. Usually $LiNO_3$ or NH_4NO_3 are used for this purpose. Here we studied the salting-out action of the cations Al^{3+}, Fe^{3+}, Ce^{3+}, Mg^{2+}, Cu^{2+}, Ni^{2+}, Li^{+} and Cs^{+}. The salting-out effects depend on the cation charge and radius, on the cation hydration or on the density of the hydration shell. We have used the viscosity of the first hydration shells (microviscosity) for the explanation of the salting-out effect.

2 EXPERIMENTAL

2.1 Synthesis of QAS

Early we have synthesized a commercially simple preparable tertiary amine Dibutylalkylamine, alkyl- = $C_{10\cdots18}$ (I) which are proved as an extractant for

Fe-III from $AlCl_3$-solutions and for the preparation of ammoniumparatungstate containing low amounts of alkaline ions. As a corresponding reference amine we did use Dibutylhexadecylamine (II) which is isomer to Trioctylamine and possessing quite equal extraction characteristic like this. The preparation of the corresponding quaternary ammonium compounds, especially the methyl-derivatives in comparison with MTOA or Aliquat-336 was realised by methylation of amine I and II with dimethylsulfate DMS or with butylbromide. We obtained: $C_{16}(C_4)_2CH_3N^+$ (MDBHDA), $C_{16}(C_4)_3N^+$ (TBHDA). Despite using excess of DMS we did obtain only quarternisation of 2/3 of amine present. Repeating the DMS procedure resulted 90% QAS. We expect, that in case of availability of methylchloride the aklylation will give quite better results.

2.2 Extraction experiments

For the extraction the QAS was dissolved in m-xylene and after the addition of 2% ethylhexanol, transferred to nitrate by shaking successive with equal amounts of 0.5M HNO_3 and 3M NH_4NO_3. In the extraction experiments $^{44,46}Sc$, ^{88}Y, ^{139}Ce, ^{143}Pm, ^{145}Sm, ^{152}Eu, $^{151,153}Gd$, ^{160}Tb, ^{170}Tm, ^{169}Yb and ^{173}Lu were used as radiotracers. After the dissolution of the nitrates of REE in a solution of the salting-out agent in 0.02M HNO_3 an equal volume of extractant was added and the mixture was shaken for 20 min at room temperature. Aliquots were taken from both organic and aqueous phases and the γ-activity of the samples was measured.

3 RESULTS

At first the extraction isotherm was determined. Using Ce as an example, the dependence of the distribution coefficients on the concentration of the extracted element was investigated in the extraction by Aliquat-336 and MDBHDA. The data (Fig. 1) show that K_d practically remains constant for Ce concentrations of up to $1 \cdot 10^{-2}$ mol·l^{-1} in the case of Aliquat-336 and $3 \cdot 10^{-2}$ mol·l^{-1} for MDBHDA. It seems that at saturation the compounds $(R_4N)_4Ce(NO_3)_7$ and $(R_4N)_7Ce(NO_3)_{10}$ are formed in the organic phase for Aliquat and MDBHDA respectively. Using this method Stepanov et al. (1987) have obtained an extracted compound $(R_4N)_6Sc(NO_3)_9$ for Sc, but at saturation of the extractant in the organic phase $(R_4N)_3Sc(NO_3)_6$.

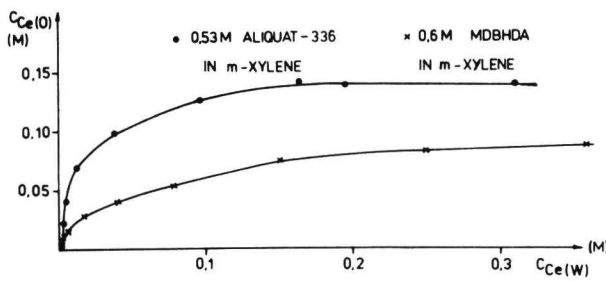


Fig. 1. Extraction isotherms for Ce.

It is usually supposed that lanthanoids are extracted as penta- or hexanitrate complexes (Shmidt, 1980, pp.102–110). The slope analysis in the extraction systems of Ce, Sc, Y with MTOA and TBHDA gives straight line functions with a slope $n \approx 1$ (Table 1). Ce, Y, Sc are in carrier-free trace amounts.

TABLE 1

The slopes of the functions of log K_d from log C_{QAS} for the REE with MTOA and TBHDA in a concentration range of 0.1 to 0.56 $mol \cdot l^{-1}$.

Element	n	
	MTOA	TBHDA
Ce	1.01 ± 0.14	0.87 ± 0.16
Y	1.01 ± 0.03	—
Sc	0.74 ± 0.06	1.23 ± 0.09

This indicates that in our solutions the nitrates of QAS are associated in a degree higher than two. Studying the distribution coefficients of REE in the extraction with QAS in a system of 0.8 $mol \cdot l^{-1}$ $Al(NO_3)_3$, we have found that Sc lies between Sm and Gd, but Y is over Tm (Fig. 2).

Under these conditions the separation factors decrease in the order Aliquat-336 $\approx$ MTOA $>$ MDBHDA $\geq$ TBHDA, as is seen from Table 2.

TABLE 2

Separation factors for Eu, Y and Sc from Ce by extraction with different QAS, aqueous phase: 0.8 $mol \cdot l^{-1}$ $Al(NO_3)_3$, 0.02 $mol \cdot l^{-1}$ HNO_3.

QAS	δ Ce/Eu	δ Ce/Y	δ Ce/Sc
Aliquat-336	17.9	126.5	30.3
MTOA	16.2	117.4	31.4
MDBHDA	9.5	28.8	7.7
TBHDA	3.3	11.2	4.4

Furthermore, the influence of the salting-out agents on the distribution coefficients and separation factors were investigated. The extraction efficiency increases with the concentration of the salting-out agent $Al(NO_3)_3$. The distribution coefficients for Ce reached values larger than 100 for 0.53 $mol \cdot l^{-1}$ Aliquat -336 and higher than 10 for 0.6 $mol \cdot l^{-1}$ MDBHDA at $Al(NO_3)_3$ concentration of 1.5 mol l^{-1}. But the separation factors decrease for $\delta_{Ce/Y}$ from 200 at $C_{Al(NO_3)_3}$ = 0.5 $mol \cdot l^{-1}$ to 19 at $C_{Al(NO_3)_3}$ = 1.5 $mol \cdot l^{-1}$ in the extraction system with Aliquat-336. Using different salting-out agents we have found the distribution coefficients for Ce, as shown in Table 3.

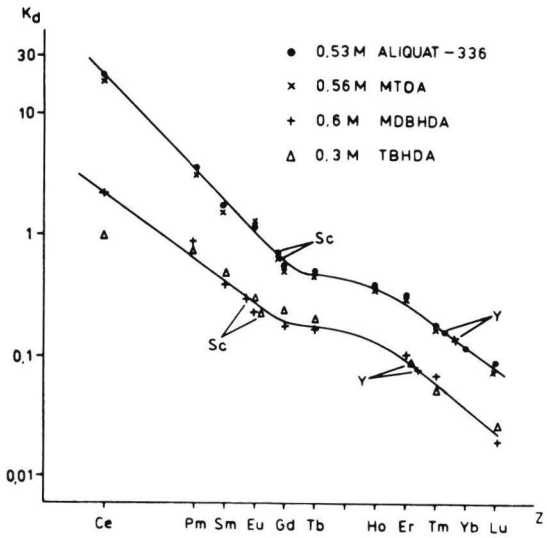


Fig. 2. Distribution coefficients of REE as a function of atomic number.

Aqueous phase:

0.8M $Al(NO_3)_3$, 0.02M HNO_3

TABLE 3

Extraction of Ce by various QAS in m-xylene at salting-out concentrations of 0.5 mol·l^{-1} and TOA in toluene at salting-out concentrations of 1.5 mol·l^{-1}.

Salting-out cation	$\eta_i \cdot 10^4$ (kg m^{-1} s^{-1})	K_{dCe}			
		Aliquat 0.53M	MDBHDA 0.6M	TBHDA 0.3M	TOA 1.5M
Al^{3+}	76.61	10.50	0.45	0.25	2.63
Fe^{3+}	54.00	1.81	0.27	0.08	
Mg^{2+}	44.42	1.15	0.17	0.08	1.20
Cu^{2+}	41.13	0.90	0.16	0.07	
Ni^{2+}	36.98	0.80	0.14	0.06	
Li^{+}	30.02	0.22	0.11		0.28
Ce^{3+}	29.93	0.16	0.10		
Cs^{+}	5.20	0.06	0.02		0.08
NH_4^{+}		21.60	2.61		

For the derivation of the functional dependences of the salting-out action, empirical methods are of great importance. The use of the parameter determining quantitatively the influence of ions on the solvent properties can have an advantage. As such a parameter, we have recommended the viscosity of the hydration shell (microviscosity) of the cations (Gorski, 1989). The microviscosity (η_i) characterizes the total influence of the ion on the solvent, η_i was calculated for a great number of cations by Gorski (1980). The data given in

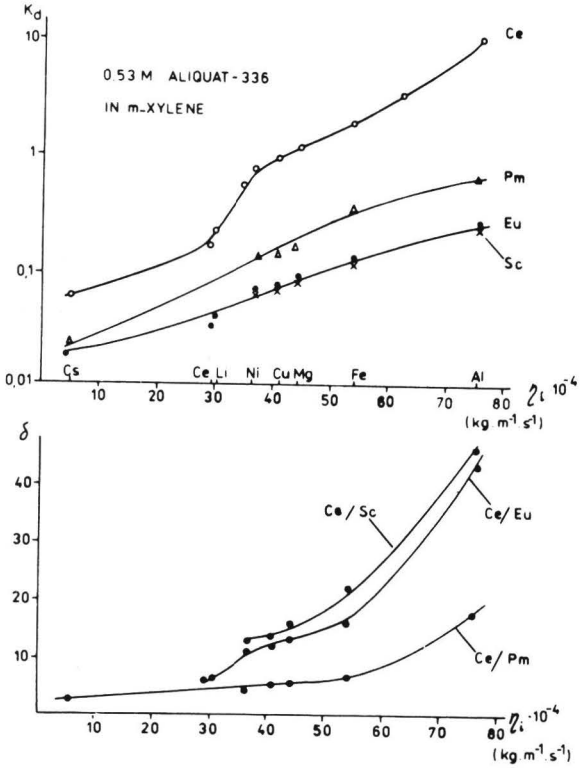


Fig. 3. Distribution coefficients and separation factors as a function of the microviscosity of salting-out cations.
Aqueous phase:
0.5M salting-out agent
0.02M HNO_3

Table 3 shows that the distribution coefficients in the extraction of Ce with different QAS and also with trioctylamine decrease with the microviscosities of salting-out cation. From Fig. 3 it is seen that the separation factors for Ce/Sc, Ce/Pm, Ce/Eu depend in the same manner on the microviscosity of the salting-out cations.

4 CONCLUSIONS

The results have shown that the extraction efficiency for the QAS synthesized by us is lower than that for the commonly used Aliquat-336, but the distribution coefficients are high enough for the quantitative extraction of the light lanthanoids so that separation from Y and Sc is possible. For this purpose the salting-out agent concentrations of up to 0.8 $mol \cdot l^{-1}$ $Al(NO_3)_3$ are necessary. The best results can be obtained using $Al(NO_3)_3$, NH_4NO_3 or $Fe(NO_3)_3$.

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EXTRACTION AND SEPARATION OF TUNGSTEN WITH 3-HYDROXY-2-METHYL-1-(4-TOLYL)-4-PYRIDONE

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ABSTRACT

The extraction of tungsten(VI) and tungsten(V) from aqueous hydrochloric acid solutions with 3-hydroxy-2-methyl-1-(4-tolyl)-4-pyridone (HY) dissolved in chloroform was studied. Tungsten(VI) is quantitatively extracted with HY as a complex with the formula WO_2Y_2. Tungsten(V) is quantitatively extracted with HY only after complexation with thiocyanate ions as a mixed ligand W(V)-NCS-HY complex. The extraction of tungsten(VI) with HY is very simple, fast and selective and the extraction of tungsten(V) as a mixed ligand complex is also applicable for the spectrophotometric determination of tungsten in the organic phase. Tungsten(V) can be also extracted with HY without the presence of thiocyanate ions, but not quantitatively.

INTRODUCTION

In our previous paper (Tamhina and Herak, 1977a, 1977b) it has been reported that 3-hydroxy-2-methyl-1-phenyl-4-pyridone (HX) is a very suitable agent for the selective extraction of tungsten(VI) and that tungsten(V) can be extracted with HX only in the presence of an excess of thiocyanate as a mixed ligand thiocyanate-HX complex.

We now report the extraction of tungsten with 3-hydroxy-2-methyl-1-(4-tolyl)-4-pyridone (HY) from three different systems: V(VI)-HCl-HY, W(VI)-HCl--$SnCl_2$-HY and W(VI)-HCl-$SnCl_2$-KNCS-HY. The results show that HY is better extractant for tungsten than HX. HY reacts with W(VI) in more acidic solutions and can extract tungsten in the presence of a reduction agent. The composition of the mixed ligand thiocyanate-HY complex of tungsten(V) is different from that of the HX complex and tungsten(V) can also be extracted with HY without the presence of thiocyanate.

2 MATERIALS AND METHODS

2.1 Reagents

Standard tungsten solution (0.01 M) was prepared by dissolving sodium

tungstate in water and standardized gravimetrically by the 8-hydroxyquinoline method (Vogel, 1961, p. 567.). HY was synthesized as described previously (Jakopčić et al, 1977) and used in a chloroform solution, The other chemicals used were of analytical reagent grade.

2.2. Apparatus

Absorption spectra and absorbance measurements of solutions were made on a Perkin-Elmer Hitachi-200 spectrophotometer.

2.3 Determination of distribution ratios

Two equal volumes (5 ml) of the organic and aqueous solutions were shaken with a mechanical shaker for 30 min although the equilibrium was attained more rapidly. Tungsten concentrations in the aqueous phases were determined spectrophotometrically with rhodamine B (Pollock, 1958) and those in the organic phases were calculated from the differences between the initial and the final aqueous values.

2.4 Procedure for the spectrophotometric determination of tungsten as a mixed ligand thiocyanate-HY complex

A solution containing 10-150 μg of tungsten(VI), 0.6 ml of 10% $SnCl_2$, 2.2 ml of conc. solution HCl, 0.5 ml of 30% KSCN and water to bring the total volume to about 5 ml was placed in a 50-ml conical flask. After the addition of 5 ml of $5x10^{-3}$ M HY in chloroform the solution was shaken for 30 min with a mechanical shaker. After the phases were separated, the absorbance of the organic phase was measured at 406 nm against a reagent blank.

3 RESULTS AND DISCUSSION

3.1 Extraction of tungsten(VI) with HY

The extraction of tungsten(VI) with HY dissolved in chloroform as a function of the hydrochloric acid concentration was studied (Fig. 1(a)). Tungsten(VI) was quantitatively extracted from the aqueous solutions in the range 0.8-8 M hydrogen ion concentration. On decreasing the acid concentration, the extraction of tungsten decreased and at $1x10^{-3}$ M acid practically all the tungsten was retained in the aqueous phase. The same results were obtained by conducting the experiments at constant ionic strength. Reextraction of tungsten was carried out with 8M NaOH. In a single shaking only about 30% of tungsten was passed into the aqueous phase. Quantitative reextraction of tungsten could be

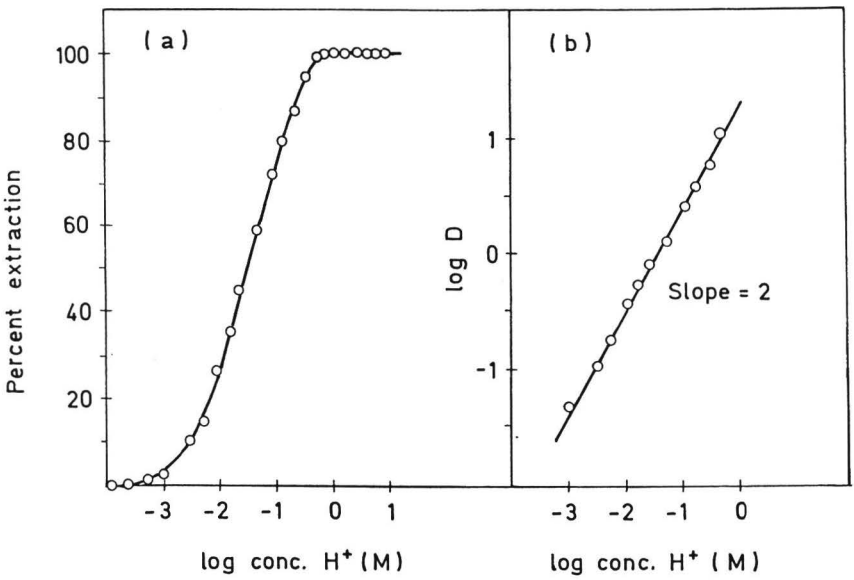


Fig. 1. The dependence of the percent of extraction (a) and the distribution ratio (b) of tungsten(VI) on the hydrogen ion concentration. W(VI) conc. 1.6×10^{-4} M, HY conc. 1×10^{-3} M.

achieved if the organic phase was repeatedly reextracted with four fresh portions of 8M NaOH.

In order to obtain quantitative extraction of tungsten from the optimal acidity (0.8-8 M HCl) the concentration of HY must be at least three times higher than that of tungsten as shown in Fig. 2(a).

The relationships between log $D_{W(VI)}$ and log HY_{org} determined from the aqueous phase of constant acidity are shown in Fig. 2(b). A second-power extractant dependency was found, indicating that two molecules of the extractant were bonded to one atom of tungsten. Since low tungsten concentrations were extracted from the high acidities, it can be assumed that WO_2^{2+} ions were present in the solution (Cotton and Wilkinson, 1972). This was confirmed by relationships between log $D_{W(VI)}$ and log hydrogen ion concentration in the aqueous phase in the range 1×10^{-3}-0.8 M HCl. $D_{W(VI)}$ was second-power dependent upon the hydrogen ion concentration (Fig. 1(b)), indicating that two protons were needed for the formation of one tungsten(VI) ion which would

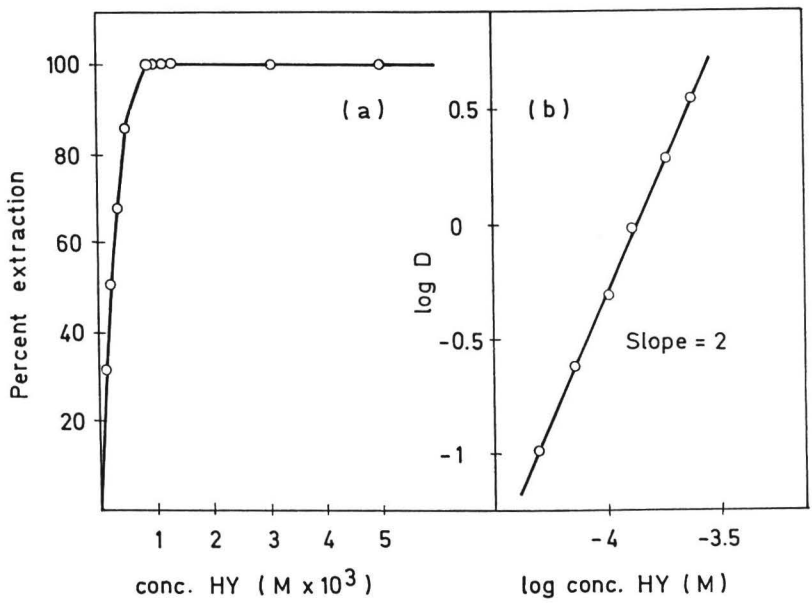


Fig. 2. The dependence of the percent of extraction (a) and the distribution ratio (b) of tungsten(VI) on the HY concentration.
W(VI) conc. 1.6×10^{-4} M, HCl conc. 1.0 M.

react with extractant. The formation of this tungsten(VI) ion (WO_2^{2+}) in the aqueous phase and the formation of the extractable complex may be shown as:

$$H_2WO_{4(aq)} + 2H^+_{(aq)} \rightleftarrows WO^{2+}_{2(aq)} + 2H_2O \quad (1)$$

$$WO^{2+}_{2(aq)} + 2HY_{(o)} \rightleftarrows WO_2Y_{2(o)} + 2H^+_{(aq)} \quad (2)$$

The extracted WO_2Y_2 complex has maximum absorption at 307 nm, but absorbances are not reproducible.

The extraction of tungsten described above is very simple, fast and selective. Only a few metals are extracted with HY. The difference in the extraction properties of tungsten and these metals can be utilized for their separation. From 6-8 M hydrochloric acid solutions tungsten could be quantitatively extracted (Fig. 1(a)) while Zr(IV), Hf(IV), Nb(V), U(VI), Fe(III), Th(IV), Cu(II) and Ga(III) remained in the aqueous phase. Only Mo(VI), V(V) and Ti(IV) are partially co-extracted with tungsten. A large concentration

of anion can also be present in the aqueous solution of tungsten.

3.2 Extraction of tungsten(V) with HY

Reduction of tungssten(VI) to tungsten(V) with tin(II) chloride was studied in hydrochloric acid media. Following the addition of hydrochloric acid and tin(II) chloride, potassium thiocyanate was introduced and the thiocyanate complex formed was extracted with HY in chloroform. The yellow mixed ligand complex in the organic phase has maximum absorption at 338 and 406 nm (Fig. 3). The absorption spectra of the organic phase without the presence of thiocyanate and with a different thiocyanate concentration (Fig. 3) show that W(V) can also be extracted with HY without the addition of thiocyanate as W(V)-HY complex. The extracted W(V)-HY complex has maximum absorption at 335-340 nm, but absorbances are not reproducible. Contrary to this tungsten(V) can be extracted with HX only as a mixed thiocyanate-HX

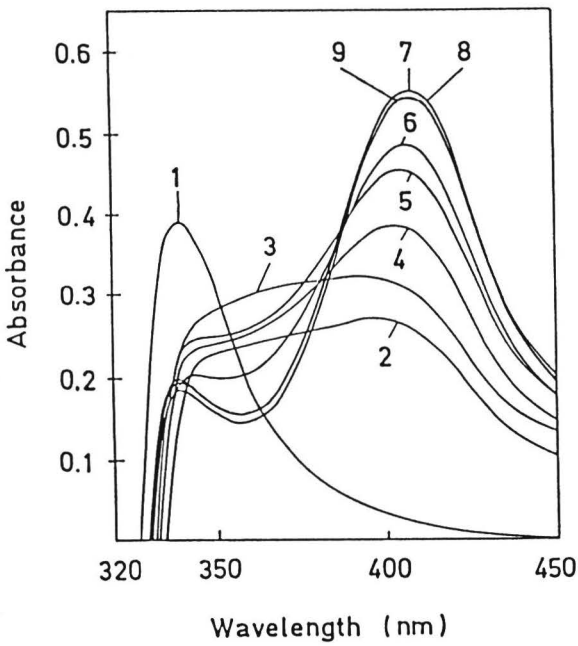


Fig. 3. The dependence of the absorption spectra of the organic phase on thiocyanate ion concentration.
Tungsten conc. 5×10^{-5} M, 5.2 M HCl, 1.5 % $SnCl_2$, 5×10^{-3} M HY.
(1) without thiocyanate. Thiocyanate concentration: (2) 0.1 %; (3) 0.2 %; (4) 0.3 %; (5) 0.5 %; (6) 0.8 %; (7) 1.0 %; (8) 1.2 %; (9) 1.5 %.

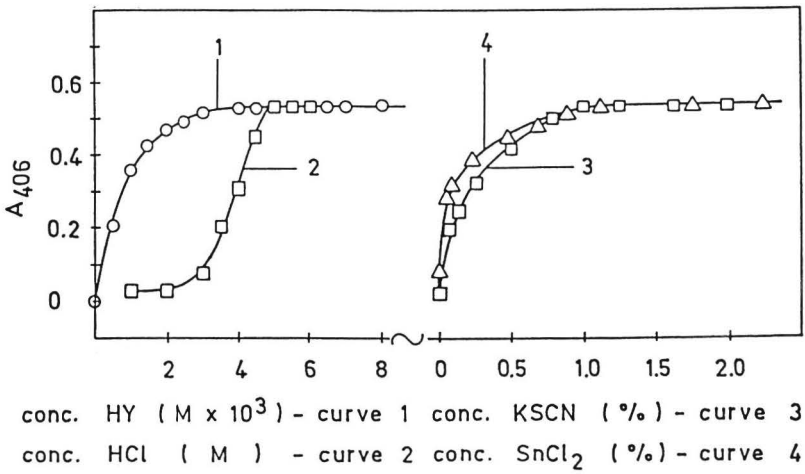


Fig. 4. The dependence of W(V)-NCS-HY complex formation on various parameters. Tungsten conc. $5x10^{-5}$ M.

complex and HX extracted tungsten without the presence of thiocyanate only as W(VI)-HX complex formed without the presence of tin(II) chloride (Tamhina and Herak, 1977a, 1977b). The optimal concentrations for the formation of the mixed ligand complex and for the spectrophotometric determination of tungsten are: 5-6 M hydrochloric acid, >1% tin(II) chloride, >1% potassium thiocyanate in the aqueous phase and $>3x10^{-3}$ M HY in chloroform (Fig. 4). The molar absorptivity at 406 nm is $1.1x10^4$ $dm^3mol^{-1}cm^{-1}$. The molar ratio of W:HY in mixed ligand complex is 1:1 and molar ratio of W:NCS could not be determined.

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EXTRACTIONS OF PRECIOUS METAL IONS WITH TRIS(2,6-DIMETHOXYPHENYL)-PHOSPHINE AND ITS DERIVATIVES FROM HYDROCHLORIC ACID SOLUTIONS

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ABSTRACT

Extraction ability of tris(2,6-dimethoxyphenyl)phosphine, $(2,6\text{-MeOPh})_3P$, toward precious metal ions such as Au(III), Pd(II), Pt(II) and Pt(IV) has been investigated from hydrochloric acid solutions. Nearly 100% extraction of Au(III) was achieved over a wide range of HCl concentrations. The percentage extraction of Pt(IV) was almost constant over HCl concentrations from 0.1 to 6.0 M, whereas those of Pt(II) and Pd(II) were decreased with an increase of HCl concentration. The Pd(II) and Pt(IV) transferred into the organic phases could be recovered by back-extraction with 0.5 M HCl and 2.0 M $HClO_4$, respectively. Moreover, Au(III) was found to be extracted selectively in the presence of 1000-fold amounts of Cu(II) over Au(III). The quaternary phosphonium salts of $(2,6\text{-MeOPh})_3P$ have been prepared and employed as ion-pair extractants toward these metal ions. In addition, a novel anion exchange resin having quaternary phosphonium salts as a functional group has been synthesized and found to be effective for separation of Au(III) in the presence of large amounts of Cu(II).

INTRODUCTION

Triphenylphosphine(Ph_3P, TPP) has been used as an extractant for noble metal ions such as Pt(II), Pd(II), Rh(III) and Ir(III) (Mojski, et al., 1979, Mojski, 1980). In previous papers (Yamashoji, et al., 1988, 1989), the liquid-liquid extraction behaviour of a series of methoxy-substituted triarylphosphines for Ga(III) from HCl solutions has been reported. The highly basic compounds, tris(2,6-dimethoxyphenyl)phosphine, $(2,6\text{-MeOPh})_3P$ and tris(2,4,6-trimethoxyphenyl)phosphine, $(2,4,6\text{-MeOPh})_3P$ exhibited the highest extraction abilities among the triarylphosphines.

This paper describes the preparation of quaternary phosphonium salts of $(2,6\text{-MeOPh})_3P$ with alkyl bromides, dibromoalkanes and chloromethylated polystyrene and extraction behaviour of $(2,6\text{-MeO-Ph})_3P$ and its phosphonium salts toward precious metal ions such as Au(III), Pd(II), Pt(II) and Pt(IV) from HCl solutions. In addition recovery of the metal ions transferred into the organic phases will be described.

EXPERIMENTAL

Materials

Tris(2,6-dimethoxyphenyl)phosphine, $(2,6\text{-MeOPh})_3P$, was prepared according to the literature method (Wada et al., 1985). The phosphonium salts were prepared by the reaction of $(2,6\text{-MeOPh})_3P$ with perchloric acid, alkyl bromides, dibromoalkanes and chloromethylated polystyrene. A typical example of the preparation is as follows. For $[(2,6\text{-MeOPh})_3PC_{12}H_{25}]^+Br^-$, dodecyl bromide(12.5 g, 5 mmol) was added to a toluene solution (30 ml) of $(2,6\text{-MeOPh})_3P$ (2.2 g, 5 mmol) and the mixture was refluxed for 6 h with stirring. After the solution had been cooled to room temperature, the resulting white precipitate was filtered, air-dried, and then recrystallized from ethanol. All the compounds were obtained in 60 - 98% yields and identified by the elemental analyses.

An anion exchange resin was prepared as follows. Chloromethylated polystyrene beads (3% DVB, 5.0 g) and $(2,6\text{-MeOPh})_3P$ (15 g) were stirred in dioxane (700 ml) at 70 °C for 24 h. After filtration, the beads were subsequently washed with dioxane, 1 M HCl, deionized water, dioxane and ether, and dried in vacuo. The yield was ca. 10 g. The ion exchange capacity of the resin was roughly evaluated to be ca. 1 meq P^+/g from the recovered phosphine. The preparation scheme for the quaternary phosphonium salts used in the present work is shown in Fig. 1.

Standard solutions of metal ions were prepared by dissolving

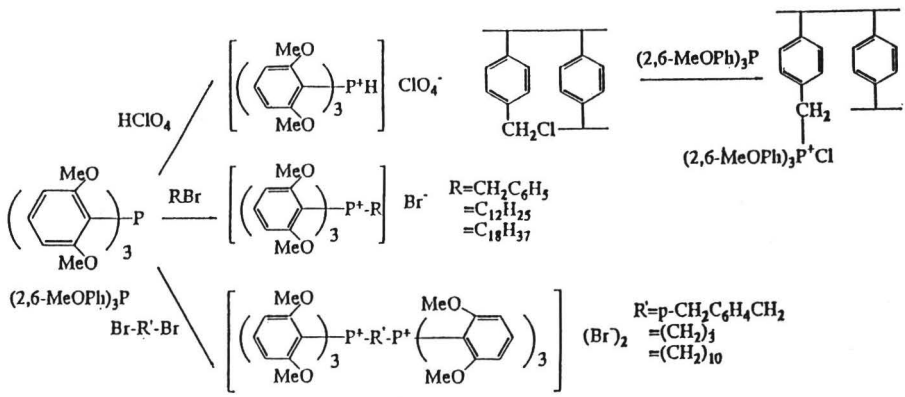


Fig. 1. Preparation scheme for quaternary phosphonium salts of $(2,6\text{-MeOPh})_3P$.

$NaAuCl_4$, K_2PdCl_4, K_2PtCl_4 or $H_2PtCl_6 \cdot 6H_2O$ in 0.1 M HCl and used after dilution to the required concentration.

Extraction procedure and analyses

Equal volumes (5 ml) of aqueous and organic phases were placed into a glass tube (10 ml) with a stopper and shaken for 30 min at 25±0.1 °C. After the phases had been separated, the concentration of the metal ion remaining in the aqueous phase was determined by atomic absorption spectrometry (a Nippon Jarrell Ash AA-8500 Mark II spectrometer), except for platinum, which was determined spectrophotometrically by the tin(II) chloride method. An aliquot (4 ml) from the organic solution was shaken with an aqueous stripping solution (4 ml) containing a stripping agent for 30 min at 25±0.5 °C, and the back-extracted metal ions in the aqueous phase were measured.

Adsorption capacities of the anion exchange resin toward metal ions were determined as follows. In a batch system, the resin (50 mg) and an aqueous solution of metal ion (5×10^{-4} M, 10 ml) were placed into a glass tube (10 ml) with a stopper and it was shaken for an appropriate time at room temperature. After the resin was filtered off, the concentration of the metal ion remaining in the filtrate was determined. In a column system, the resin (3.0 g) was loaded with 0.1 M HCl in a column (8x100 mm) and allowed to stand for 24 h. Aqueous solutions of metal ions in 0.1 M HCl were passed through the column at a flow rate of 0.5 ml/min. The concentrations of the metal ions in the effluents were determined by atomic absorption spectrometry. The elution of the Au(III) adsorbed on the resin was carried out with an aqueous solution of 0.5 M NH_3-0.1 M NH_4Cl at a flow rate of 0.75 ml/min.

RESULTS AND DISCUSSION

Figure 2 shows the extraction isotherms of precious metal ions with $(2,6\text{-MeOPh})_3P$ from HCl solutions. Nearly 100% extraction of Au(III) was attained over the HCl concentration range from near 0 to 6 M when equal amounts of the extractant and the metal ion were used. On the other hand, the extractions of Pd(II) and Pt(II) depend on the HCl concentration in the aqueous phase, whereas that of Pt(IV) hardly depends on it. The extraction of Pd(II) decreases steeply with increasing HCl concentration and is almost zero above ca. 1.0 M HCl. The extraction of Pt(II) decreases slowly with increasing acid concentration, but that of Pt(IV) is constant over the range of acid concentrations studied.

Absorption spectroscopic data for the Pd(II)-HCl system indicate that the Pd(II) ion may exsist mainly as tetrachloropalladate(II), $[PdCl_4]^{2-}$, in solutions of 1.2 M HCl and above (Droll et al., 1957, Yamashoji et al., 1990). This may cause the decrease in the extraction of Pd(II) with increasing HCl concentrations.

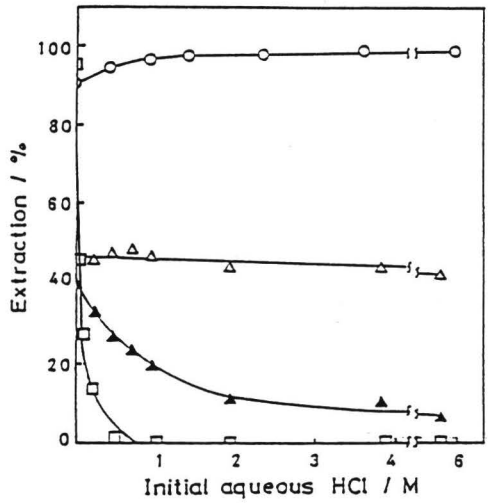


Fig. 2. Effects of HCl concentration on extractions of Au(III), Pt(II), Pt(IV) and Pd(II) with $(2,6\text{-MeOPh})_3P$.

Au(III) and Pd(II) : 1 x 10^{-4} M, Pt(II) and Pt(IV) : 1 x 10^{-3} M
$(2,6\text{-MeOPh})_3P$: 1 x 10^{-4} M [for Au(III) and Pd(II)]
$(2,6\text{-MeOPh})_3P$: 1 x 10^{-3} M [for Pt(II) and Pt(IV)]
(○) : Au(III), (▲) : Pt(II), (△) : Pt(IV), (□) : Pd(II)
Solvent : CH_2ClCH_2Cl

In previous papers(Yamashoji et al., 1989, 1990), the extraction of the metal ions such as Ga(III) and Fe(III) with this extractant from HCl solutions has been reported to proceed via the formation of ion-pairs between their chloro complex anions and the phosphonium cation, $[(2,6\text{-MeOPh})_3PH]^+$, on the basis of NMR and IR spectroscopic data. Thus, several phosphonium salts of $(2,6\text{-MeOPh})_3P$ (see Fig. 1) were prepared and their extraction abilities toward the metal ions were examined as ion-pair extractants. The singly charged cationic phosphonium salts exhibited almost the same extraction ability as those obtained with the parent phosphine, except for $[(2,6\text{-MeOPh})_3PH]^+ClO_4^-$. The extraction ability of this extractant is high for Au(III) but very low for other metal ions. This phosphonium perchlorate was found to distribute predominantly in the organic phase from the UV spectrophotometry. This may cause the decreases in the extraction of the metal ions with the exception of Au(III), i.e., Au(III) can be selectively extracted with this perchlorate. On the other hand, the doubly charged cationic phosphonium salts exhibited superior extraction ability than $(2,6\text{-MeOPh})_3P$ and the singly charged cationic one. In particular, the Pd(II) was almost quatitatively extracted with $\{[(2,6\text{-MeOPh})_3P]_2(CH_2)_3\}^{2+}(Br^-)_2$.

In order to recover the metal ions after extraction with (2,6-MeOPh)$_3$P, back-extractions were examined by shaking the organic phases with aqueous solutions containing suitable stripping agent. Nearly 90% recovery of Pd(II) was achieved by using 0.5 M HCl. The Pt(IV) was also back-extracted with 2.0 M $HClO_4$. However, the Au(III) was not back-extracted with mineral acids of various concentrations.

We have found that (2,6-MeOPh)$_3$P readily reacts with chloromethylated polystyrene to give the resin containing quaternary phosphonium salts as a functional group. Thus, its adsorption ability toward metal ions has been studied as an anion exchange resin. The batch system results show that this resin can adsorb selectively Au(III) over Cu(II). We have applied it to the separation of Au(III) from Cu(II) in 0.1 M HCl by a column method.

Figure 3A shows the break-through curves for adsorption of Au(III) and Cu(II) on the resin. It can be seen that Au(III) was completely adsorbed on the resin, whereas Cu(II) was not adsorbed on it even in the presence of 10-molar fold amounts over Au(III). Figure 3B shows the elution curve of the Au(III) adsorbed on the resin with 0.5 M NH_3-0.1 M NH_4Cl solution. About 75% Au(III) was recovered, and the resin was regenerated with a treatment of 1.0 M HCl. These results indicate that the present anion exchange resin can be useful for selective separation of Au(III) in the presence of large amounts of Cu(II).

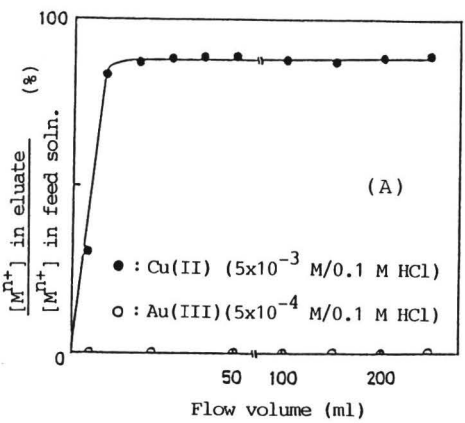


Fig. 3A. Break through curves for adsorption of Cu(II) and Au(III) on the resin in a column method.
Resin; 3.0 g, Flow rate: 0.5 ml/min.

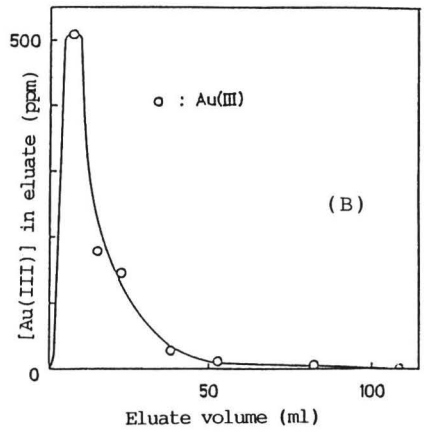


Fig. 3B. Elution curve of Au(III) adsorbed on the resin with 0.5 M NH_3-0.1 M NH_4Cl solution.
Resin: 3.0 g, Flow rate: 0.75 ml/min.

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A STUDY OF THE EXTRACTION KINETICS OF LANTHANUM (Ⅲ) WITH PRIMARY AMINE N1923 SULFATE*

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ABSTRACT

The extraction kinetics of lanthanum (Ⅲ) with primary amine N1923 in n－heptane has been determined using the growing drop method at 25 ℃ . The effect of temperature and the influence of the concentrations of La (Ⅲ) , N1923, SO_4^{2-} and pH on the rates of extraction were examined. The apparent activation energy were found to be 66.0 KJ $\cdot mol^{-1}$. It is suggested that the rate controlling steps may be the chemical reaction of $LaSO_4^+$ with N1923 at the interface.

INTRODUCTION

Primary amine N1923 (RNH_2) is a efficient extractant for separating thorium (IV) from rare earth element (Ⅲ) and iron (Ⅲ) .The extraction mechanism of rare earth (Ⅲ) , iron (Ⅲ) and thorium (IV) from sulfuric acid solutions by N1923 has been reported (Li et al ., 1987). But studies of the extraction kinetics have not been reported so far . Kinetics studies can help to understand the mechanism of extraction . On the other hand , N1923 is a good surface active reagent, so the extraction rates of some phosphorous based extractants may be enhanced by use of primary amine as a organic phase additive . In this paper , the authers try to approach the extraction kinetics of lanthanum (Ⅲ) with N1923.

1 EXPERIMENTAL

1.1 Reagents

Primary amine N1923 with an average molecular weight of 280.69 was available from the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, the contents of nitrogen and primary are 4.99% and 99% respectively. Lanthanum(Ⅲ) sulfate solu-

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tion was prepared by dissolving Lanthanum(Ⅲ) oxide as 99.9% pure in sulfuric acid. All other reagents were analytical grade purity products.

1.2 Experimental method and instruments

The growing drop technique was used as described (Sun et al., 1989). According to the extraction system in present work, the extraction rate of lanthanum(Ⅲ) sulfate with N1923 can be expressed as follows:

$$\log\frac{A}{t} = \log K + a\log[La^{3+}] + b\log[(RNH_3)_2SO_4]_{(o)} + c\log[H^+] + d\log[SO_4^{2-}] \qquad (1)$$

Where A is the absorbance of the organic phase loading La (Ⅲ) and is used to express the concentration of La (Ⅲ) in organic phase; t is the growing time of the drop ; a , b , c and d are the orders of the reaction ; $(RNH_3)_2SO_4$ indicates the Primary amine N1923 Salt. (o) indicates the organic phase.

The concentration of La (Ⅲ) was determined by spectrophotometric method with chlorophosphonazo－DBC as spectrophotometer (Ren et al ., 1987).

2 RESULTS AND DISCUSSIONS

2.1 Effect of $[La^{3+}]$ on the extraction rate

Fig. 1 gives the extraction rate of La (Ⅲ) as a function of La (Ⅲ) concentration. The slope of the straight line is determined to be 0.82, which indicates that the extraction rate is first order with respect to La (Ⅲ).

2.2 Effect of $[(RNH_3)_2SO_4]_{(o)}$ on the extraction rate

The reaction order with respect to extractant was shown in Fig. 2.Slope is 1.35 near to 1.5, i. e. d＝1.5 for N1923.

2.3 Effect of $[SO_4^{2-}]$ on the extraction rate

As seen from Fig. 3, the slope of the straight line is 0.88, which suggests that the extraction rate is first order with respect to sulfate ion.

2.4 Effect of pH values on the extraction rate

The result indicates that the effect of pH values on the extraction rate is not large.

2.5 Effect of temperature on the extraction rate

The plot of $\log\frac{A}{t}$ versus 1/T is shown in Fig. 4. The activation energy was calculated to be 66.0 KJ • mol^{-1} according to the Arrhenius equation.

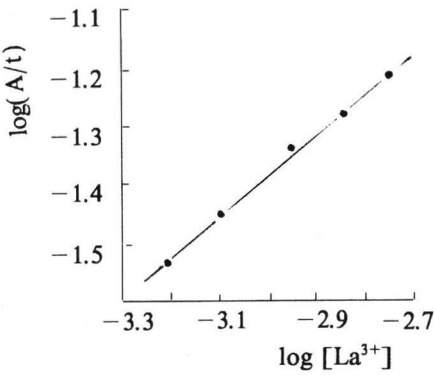


Fig. 1 Re lationship of $\log\frac{A}{t}$ to $\log [La^{3+}]$
$[(RNH_3)_2SO_4]_{(0)} = 0.011 mol/dm^3$
$[SO_4^{2-}] = 0.10\ mol/dm^3$
pH = 5.80

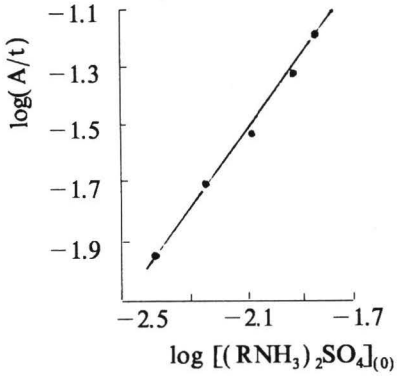


Fig. 2 Relationship of $\log\frac{A}{t}$ to $\log [(RNH_3)_2SO_4]_{(0)}$
$[La^{3+}] = 1.6 \times 10^{-3}\ mol/dm^3$
$[SO_4^{2-}] = 0.10\ mol/dm^3$
pH = 5.70

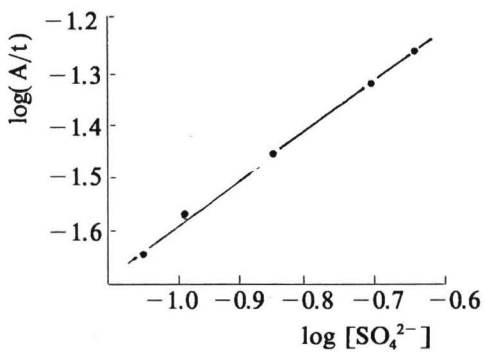


Fig. 3 Relationship of $\log\frac{A}{t}$ to $\log [SO_4^{2-}]$
$[(RNH_3)_2SO_4] = 0.011 mol/dm^3$
$[La^{3+}] = 1.5 \times 10^{-3} mol/dm^3$
pH = 4.00

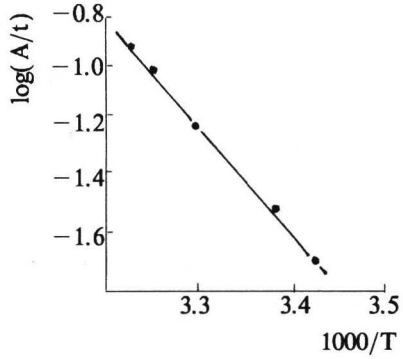


fig. 4 The effect of temperature on the extraction rate
$[(RNH_3)_2SO_4] = 0.011\ mol/dm^3$
$[La^{3+}] = 1.9 \times 10^{-3} mol/dm^3$
$[SO_4^{2-}] = 0.10 mol/dm^3$
pH = 5.70

2.6 The extraction mechanism

In the present work, the rate controlling steps for the extraction mechanism may be the following interfacial reactions (Gai et al., 1987; Sun et al., 1989):

$$(RNH_3)_2SO_{4(i)} + LaSO_4^+ + SO_4^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (RNH_3)_2La(SO_4)_{3(i)}^-$$

$$(RNH_3)_2La(SO_4)_{3(i)}^- + 1.5\,(RNH_3)_2SO_{4(o)} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (RNH_3)_3La(SO_4)_{3(o)} + (RNH_3)_2SO_{4(i)} + \frac{1}{2}\,SO_4^{2-}$$

Where k is rate constant; (i) and (o) denote interfacial and organic phase species respectively.

The forward initial rate of this extraction process can be expressed as follows:

$$R = \frac{K[LaSO_4^+][SO_4^{2-}][(RNH_3)_2SO_4]_{(o)}^{\frac{3}{2}}}{k_{-1} + k_2[(RNH_3)_2SO_4]_{(o)}^{\frac{3}{2}}} \qquad (2)$$

Where $K = k_1 k_2 [(RNH_3)_2SO_4]_{(i)}$.

In the experimental conditions, the rate of La (Ⅲ) from the aqueous to the organic phase is faster than the reverse rate, i. e. $k_{-1} >> k_2[(RNH_3)_2SO_4]_{(o)}^{\frac{3}{2}}$. Thus considering $[LaSO_4^+] \approx [La^{3+}]$ (Wang et al., 1960), the extraction rate equation can be written as:

$$R = K'[La^{3+}][SO_4^{2-}][(RNH_3)_2SO_4]_{(o)}^{\frac{3}{2}} \qquad (3)$$

where $K' = K/k_{-1}$. This equation well represents the experimental result, and the extraction mechanism is in agreement with similar thermodynamic studies.

3. CONCLUSIONS

The extraction kinetics of lanthanum (Ⅲ) with primary amine N1923 has been studied. The results show that the controlling steps of this extraction process are in the interface and the forward initial rate equation is

$$R = K'[La^{3+}][SO_4^{2-}][(RNH_3)_2SO_4]_{(o)}^{\frac{3}{2}}$$

The activation energy is 66.0 KJ • mol^{-1}.

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SYNERGISTIC EXTRACTION OF CADMIUM(Ⅱ) FROM THIOCYANIDE WITH PRIMARY AMINE N1923 AND DBBP*

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ABSTRACT

The synergistic extraction of Cd(Ⅱ) from thiocyanide solution with primary amine N1923 and DBBP in heptane has been investigated. The synergistic complex of Cd(Ⅱ) with RNH_3NO_3 and DBBP has been determined to be $(RNH_3)Cd(SCN)_3$ DBBP by the methods of constant mole , slope analysis and IR spectra. Moreover, the equilibrium constants of synergistic reactions have been calculated also.

INTRODUCTION

Although the synergistic extraction of Cd(Ⅱ) from hydrochloric acid solution with primary amine and neutral organophosphorus compounds has been reported (Ma et al.,1989), the synergistic extraction of Cd(Ⅱ) from thiocyanide solution with primary amine and neutral organophosphorus compounds has not been reported yet. In order to study the effect of different anions on the extraction of Cd(Ⅱ) and the formation of Cd(Ⅱ) complexes with more reagents at various conditions, thus the synergistic extraction of Cd(Ⅱ) from thiocyanide solution with primary amine N1923 and DBBP in heptane has been investigated in greater detail.

1 EXPERIMENTAL

1.1 Reagents

Primary amine N1923 with an average molecular weight of 280.69 was available from the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, the contents of nitrogen and primary amine were 4.99 and 99% respectively. DBBP was provide by Mobil Chemical Industry Co.. All other chemicals needed were analytical reagents.

1.2 Experimental method and instruments

Equal volumes of the aqueous and organic phase were placed in a thermostatic box at

* The Project Supported by National Natural Science Foundation of China.
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25± 1℃ for 30 min, and were shaken for 30 min. The concentration of Cd(II) in the aqueous phase was determined by the titrimetric method of EDTA with indicator of Xylenol Orange. The IR spectra were measured on a DIGILAB FTS−20 spectrophotometer.

2 RESULTS AND DISCUSSIONS

2.1 Extraction of Cd(II) from thiocyanide solution with RNH_3NO_3 alone.

Fig. 1 shows that the logarithm of the distribution ratio of Cd(II) vary with the logarithm of RNH_3NO_3 concentration and the slope of the straight line obtained in Fig. 1 is 1, considering the polymerization degree of amine salts in octane (Le, 1983), which suggests that two RNH_3NO_3 molecules are complexed to each cadmium thiocyanate molecules. In order to test the result above, the composition of extracted complex is determined by the method of continuous variation As seen from Fig. 2, the maximum of Cd(II) concentration in organic phase appeared at the mole ratio of Cd (II) and RNH_3NO_3 1: 2. The result agrees with the suggestion of Fig. 1. Thus, the formula of the extracted complex can be shown to be $(RNH_3)_2Cd(SCN)_4$ and the extraction reaction may be represented by the following reaction:

$$(RNH_3NO_3)_{2(0)} + Cd(SCN)_4^{2-} \underset{}{\overset{K_1}{\rightleftharpoons}} (RNH_3)_2Cd(SCN)_{4(0)} + 2NO_3^- \qquad (1)$$

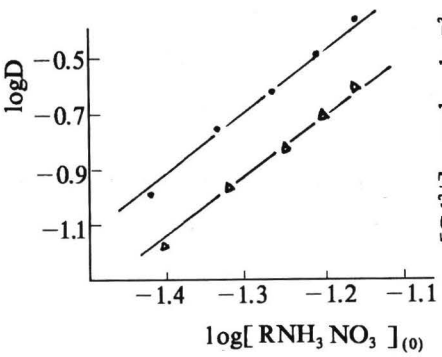


Fig. 1 Plots of logD vs $\log[RNH_3NO_3]_{(0)}$
$[SCN^-] = 1.0$ mol • dm^{-3}
●: $[Cd^{2+}] = 0.0488$mol • dm^{-3}
Δ: $[Cd^{2+}] = 0.0430$mol • dm^{-3}

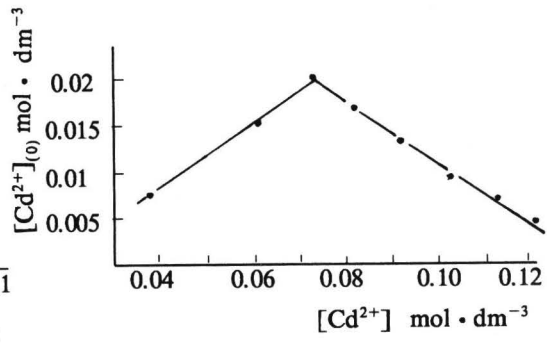


Fig. 2 Method of continuous variation to determine composition of extraction species at constant $[SCN^-] = 1.0$ mol • dm^{-3}

The equilibrium constant K_1 can be expressed as

$$K_1 = D_i[NO_3^-]^2 \ (1 + \sum_{i=1}^{4} \beta_i[SCN^-]^i) \ / \beta_4[SCN^-]^4[(RNH_3NO_3)_2]_{(0)} \qquad (2)$$

where D_1 stands for distribution ratio of Cd(II) with primary amine N1923 and β represents the overall stability constant of Cd(II) with thiocyanic ions.

2.2 Extraction of Cd(II) from thiocyanide solution with DBBP alone

Fig. 3 shows that the logarithm of the distribution ratio of Cd(II) vary with the

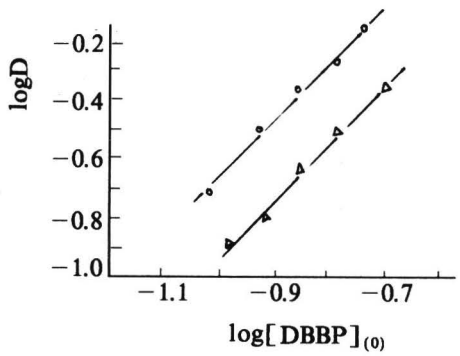


Fig. 3 Plots of logD vs $\log[DBBP]_{(0)}$
$[SCN^-]=1.0$ mol · dm^{-3}, Δ: $[Cd^{2+}]=0.0510$mol · dm^{-3}
$[SCN^-]=0.4982$mol · dm^{-3}, o: $[Cd^{2+}]=0.03008$mol · dm^{-3}

logarithm of DBBP concentration and the slope of the straight line obtained in Fig. 3 is 2 which suggests that the extraction reaction can be expressed as

$$Cd(SCN)_2+2DBBP_{(0)} \underset{}{\overset{K_2}{\rightleftharpoons}} Cd(SCN)_2\cdot 2DBBP_{(0)} \qquad (3)$$

the equilibrium constant K_2 can be represented by

$$K_2=D_2(1+\sum_{i=1}^{4}\beta_i[SCN^-]^i)/\beta_2[SCN^-]^2[DBBP]^2_{(0)} \qquad (4)$$

2.3 Synergistic extraction of Cd(II) from thiocyanide solution with RNH_3NO_3 and DBBP

In this experimental conditions, the pH values in aqueous phase have not practically effect on the synergistic extraction of Cd(II). Accordingly, the following experiment is at constant pH value hereafter. At constant aqueous conditions and DBBP concentration, the concentration of RNH_3NO_3 is changed, then a series of $D_{tot.}$ has been obtained; Under similar circumstances, the concentration of DBBP is changed at constant aqueous conditions and RNH_3NO_3 concentration, a series of $D_{tot.}$ has been obtained again. In the light of $D_{tot.}=D_1+D_2+D_{12}$, the $D_{12}=D_{tot.}-D_1-D_2$. $\log D_{12}$ is plotted against the logarithm of the amine nitrate salt concentration or DBBP concentration in Fig. 4 and Fig. 5 respectively, and slope of the straight lines are 0.5 and 1 respectively. Considering the polymerization degree of amine salts in Octane (Le, 1983), the

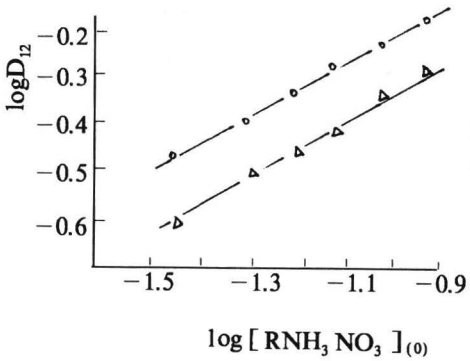


Fig. 4 Plots of $\log D_{12}$ vs $\log[RNH_3NO_3]_{(0)}$
$[SCN^-]=1.0$ mol · dm^{-3}
$[DBBP]_{(0)}=0.10$mol · dm^{-3}
o: $[Cd^{2+}]=0.0510$mol · dm^{-3}
Δ: $[Cd^{2+}]=0.0506$mol · dm^{-3}

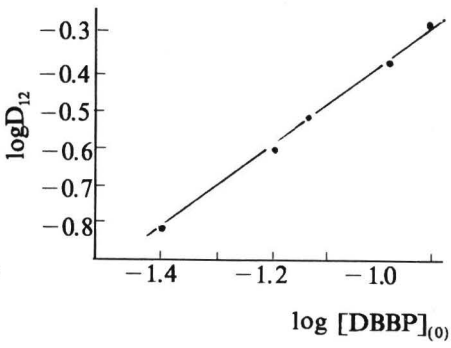


Fig. 5 Plot of $\log D_{12}$ vs $\log[DBBP]_{(0)}$ at constant
$[RNH_3NO_3]_{(0)}=0.15$mol · dm^{-3}
$[SCN^-]=1.0$ mol · dm^{-3}
$[DBBP]_{(0)}=0.10$mol · dm^{-3}
$[Cd^{2+}]=0.04995$ mol · dm^{-3}

synergistic reaction of Cd(Ⅱ) from thiocyanide solution can be represented by the following reaction,

$$1/2(RNH_3NO_3)_{2(0)}+Cd^{2+}+3SCN^-+DBBP_{(0)} \overset{K_{12}}{\rightleftharpoons} (RNH_3)Cd(SCN)_3DBBP_{(0)}+NO_3^- \quad (5)$$

the equlilbrium constant K_{12} can be expressed as

$$K_{12}=D_{12}(1+\sum_{i=1}^{4}\beta_i[SCN^-]^i/[NO_3^-][SCN^-]^3[(RNH_3NO_3)_2]^{1/2}_{(0)}[DBBP]_{(0)} \quad (6)$$

The organic phase synergistic reaction can be represented by

$$(RNH_3)_2Cd(SCN)_{4(0)}+DBBP_{(0)} \overset{\beta_{12}}{\rightleftharpoons} (RNH_3)Cd(SCN)_3DBBP_{(0)}+SCN^- \quad (7)$$

and the equilibrium constant β_{12} can be expressed as

$$\beta_{12}=K_{12}[RNH_3NO_3/2]^{1/2}_{(0)}/K_1\beta_4 \quad (8)$$

2.4 Calculation of the equilibrium constants of extraction reactions

Under the present experimental conditions, in the light of β_i(Högfeldt, E., 1982) ($\log\beta_1=1.89$, $\log\beta_2=2.78$, $\log\beta_3=2.85$, $\log\beta_4=2.26$) and pertinent values of equation (2)、(6) and (8), the equilibrium constants K_1、K_2、$K_{12}$and β_{12} are calculated to be $\log\bar{K}_1=1.48$、$\log\bar{K}_2=1.62$、$\log\bar{K}_{12}=3.48$、$\log\bar{\beta}_{12}=0.33$ respectively.

2.5 Studies on the IR spectra of the extracted species

The results of IR spectra of the extracted species show that the RNH_3^+ group is still present in the synergistic complex; the shift of the P=0 stretching frequency from 1250cm^{-1} to $\nu_{P=0}$: 1234cm^{-1}, which indicates that the P=0 group is involved in

bonding. This could be attributed to the coordination with metal through the oxygen atom of P=0 group, which is supported evidence obtained above.

3 CONCLUSIONS

By the methods of slope and constant mole, the composition of extracted complexes has been determined. The equilibrium constants of synergistic reactions have been calculated and the studies on the IR spectra of the extracted complexes are carried out.

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EXTRACTION OF SCANDIUM(Ⅲ) FROM NITRATE-THIOCYANATE SOLUTIONS WITH PRIMARY AMINE N1923 *

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ABSTRACT

The extraction of scandium(Ⅲ) from nitrate－thiocyanate solutions with primary amine N1923 has been investigated. The results suggest that scandium(Ⅲ) is extracted into organic phase in $Sc(OH)_2^+$ form and synergistic effect is observed. By the methods of slope continuous variation and the determination of pH values, the extraction reactions of scandium(Ⅲ) have been determined. In addition, the equilibrium constants and the thermodynamic functions of the extraction reactions have been calculated.

INTRODUCTION

Scandium, which is lack and expensive metal in rare metals, has widely been used and and applied(Chen, 1982). But the source of scandium has mainly been obtained from the by－products of other ores, it seems necessary for the recovery and refinement of scandium accordingly. As the tendencies of the intense hydration and forming complex appear(Aveston, 1966), the reported works of scandium extraction have been much small and in sulphate solutions mainly. The extraction of scandium(Ⅲ) from nitrate－thiocyanate solutions has not been reported so far. In this paper, the authors try to approach the extraction mechanism of scandium(Ⅲ) from nitrate－thiocyanate solutions with primary amine N1923 in detail.

1 EXPERIMENTAL

1.1 Reagents

Primary amine N1923 with an average molecular weight of 280.69 was available from the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, the contents of nitrogen and primary amine are 4.99% and 99% respectively. Scandium thiocyanate was prepared by the method of literature (Audrieth, 1950; Zhang et al., 1982) All other chemicals needed are analytical reagents.

* The Project Supported by National Natural Science Foundation of China.

1.2 Experimental method and instruments

Equal volumes of the aqueous and organic phase were placed in a thermostatic box at 25± 1 ℃ for 30 min, and shaken for 15 min. The concentration of Sc(Ⅲ) in the aqueous phase were determined as described (Li et al., 1986), the concentration of Sc(Ⅲ) in the organic phase were obtained by difference method . Primary amine concentration was titrated with the standard HCl solution with indicator of Bromocresol Green , the primary amine titrated was equilibrated with HNO_3 • Spectrophotometer was produced by Shanghai analytical instrument factory .

2 RESULTS AND DISCUSSIONS

2.1 Effect of pH values on the extraction of Sc(Ⅲ) with RNH_3NO_3

As seen from Fig. 1, the distribution ratios of Sc (Ⅲ) from nitrate−thiocyanate solution increased with the pH values and tend to smooth after increasing of pH value to 5, which suggests that the extraction of both Sc(Ⅲ) and HSCN occured at lower pH value; As increasing of pH values, the contents of HSCN in solutions were reduced, that is, the extraction of Sc(Ⅲ) compared with HSCN was increasing. Slope of the straight line in Fig. 1 is determined to be 1,which shows that OH^- ion take part in the extraction of Sc(Ⅲ), due to the $Sc(OH)_x^{3-x}$ hydration complex formed.

Fig. 2 shows the similar result to Fig. 1, and slope of the straight line is 2 approximately, which suggests that Sc(Ⅲ) is extracted into organic phase in $Sc(OH)_2^+$ form.

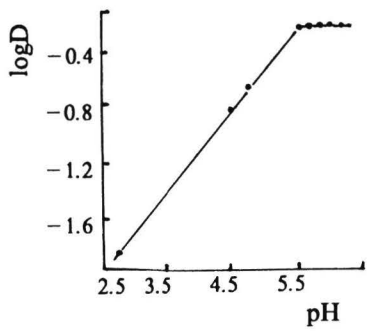


Fig. 1 Relationship of logD to pH
$[Sc^{3+}]=2.74\times10^{-4}$ mol • dm^{-3}
$[SCN^-]=0.90$ mol • dm^{-3}
$[NO^-_3]=8.28\times10^{-4}$ mol • dm^{-3}
$[RNH_3NO_3]_{(0)}=0.1006$ mol • dm^{-3}

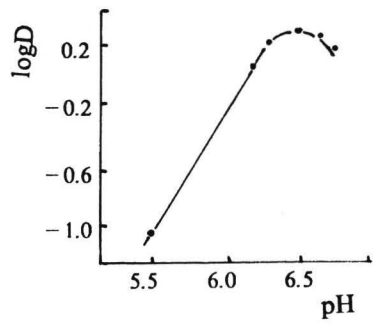


Fig. 2 Relationship of logD to pH
$[Sc^{3+}]=2.74\times10^{-4}$ mol • dm^{-3}
$[SCN^-]=0.90$ mol • dm^{-3}
$[RNH_3NO_3]_{(0)}=0.1006$ mol • dm^{-3}

2.2 Effect of SCN^- ion on the extraction of scandium

As seen from Fig. 3 and Fig. 4, the slopes of the straight lines were determined to be 1,which shows that the molecular number of SCN^- in the extraction reactions is 1.

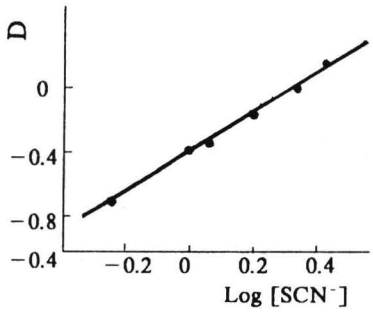


Fig. 3 Effect of $[SCN^-]$ on D
$[Sc^{3+}]=2.59\times10^{-4}$mol • dm^{-3},pH=4.00
$[RNH_3NO_3]_{(0)}=0.1006$ mol • dm^{-3}

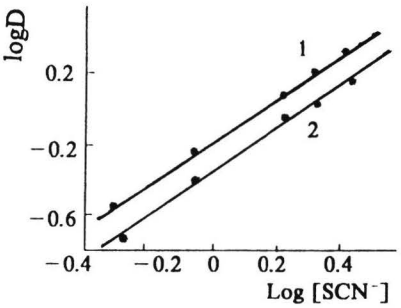


Fig. 4 Plots of LogD vs Log $[SCN^-]$
$[Sc^{3+}]=2.60\times10^{-4}$mol • dm^{-3},pH=4.20
$[RNH_3NO_3]_{(0)}=0.1002$ mol • dm^{-3}
1: $[NO_3^-]=7.8\times10^{-4}$ mol • dm^{-3}
2: $[NO_3^-]=0.20$ mol • dm^{-3}

The result, as for the scandium thiocyanate solution, which is in accordance with the conclusion of extracted complex $Sc(OH)_2^+$ is different from the extraction of Sc(Ⅲ) with di(3,5,5— trimethylhexyl) amine in sulphate solution(Cattrall et al., 1970), i. e., Sc(Ⅲ) was extracted into organic phase in $Sc(OH)^{2+}$ form. This phenomena could be due to main species $Sc(OH)_2^+$ presented.

2.3 Effect of $[NO_3^-]$ on the extraction of scandium(Ⅲ)

The effect of NO_3^- concentration on the extraction of Sc(Ⅲ) in Fig. 5 with the slope of straight line is 1, the result suggests that the molecular number of NO_3^- in the extraction reaction of Sc(Ⅲ) is 1.

2.4 Effect of the ratios of SCN^- and NO_3^- concentrations on the extraction of scandium (Ⅲ)

The result in Fig. 6 indicates that the synergistic effect has been observed and the maxmum of the plot is 1 in the ratio of $[SCN^-]$ and $[NO_3^-]$, which demonstrates the similar molecular number of SCN^- and NO_3^- in the extraction reaction.

2.5 Effect of $[RNH_3NO_3]$ on the extraction of scandium (Ⅲ)

Fig. 7 and Fig. 8 show that the logarithms of the distribution ratios of Sc(Ⅲ) vary with the logarithms of $[RNH_3NO_3]$ and the slope of the straight line obtained is 2 and 1

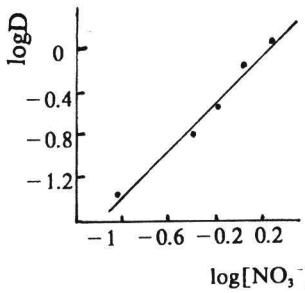


Fig. 5 Plot of logD vs $\log[NO_3^-]$
$[S_C^{3+}]=2.60\times10^{-4}$mol·dm^{-3}, pH=4.20
$[RNH_3NO_3]_{(0)}=0.1002$ mol·dm^{-3}
$[SCN^-]=0.50$ mol·dm^{-3}

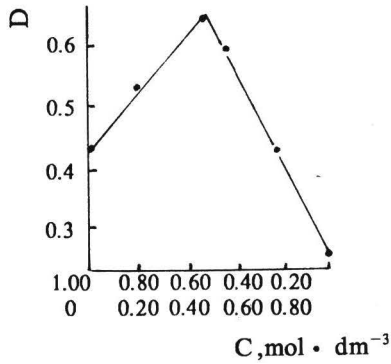
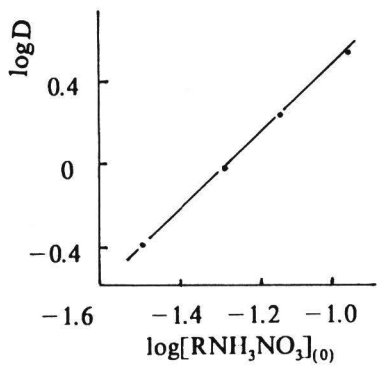


Fig. 6 Plot of $[SCN^-]/[NO_3^-]$ vs D
$[Sc^{3+}]=2.60\times10^{-4}$mol·dm^{-3}, pH=4.20
$[RNH_3NO_3]_{(0)}=0.1006$ mol·dm^{-3}

respectively. Considering the polymerization degree of amine salts in octane (Le, 1983), then the composition of extracted complexes of Sc (Ⅲ) in two systems is $(RNH_3NO_3)_4 Sc(OH)_2SCN$ and $(RNH_3NO_3)_2 \cdot Sc(OH)(SCN)NO_3$ respectively.



[Fig. 7 Plot of logD vs $\log[RNH_3NO_3]_{(0)}$
$[Sc^{3+}]=2.59\times10^{-4}$mol·dm^{-3}
pH=4.00, $[SCN^-]=2.50$mol·dm^{-3}

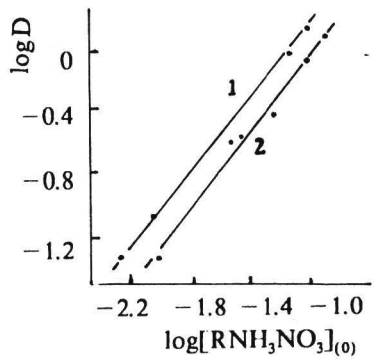


Fig. 8 Plots of logD vs $\log[RNH_3NO_3]_{(0)}$
$[Sc^{3+}]=2.60\times10^{-4}$mol·dm^{-3}, pH=4.20
$[SCN^-]=2.00$ mol·dm^{-3} $[NO_3^-]$:
1: 0.20mol·dm^{-3}; 2: 7.8×10^{-4}mol·dm^{-3}

2.6 Calculation of equilibrium constants and thermodynamic functions of the extraction reactions

The extraction reactions of Sc(Ⅲ) in two systems can be proposed as follows:

$$Sc(OH)_2^+ + SCN^- + 2(RNH_3NO_3)_{2(O)} \overset{K_1}{\rightleftharpoons} (RNH_3NO_3)_4 \cdot Sc(OH)_2SCN \quad (1)$$

$$Sc(OH)_2^+ + SCN^- + NO_3^- + (RNH_3NO)_{2(O)} \overset{K_{12}}{\rightleftharpoons} (RNH_3NO)_2Sc(OH)(SCN)NO_{3(O)} \quad (2)$$

In the experimental conditions, considering the overall stability constants of Sc (Ⅲ) with hydroxide ion OH^-, thiocyanide ion SCN^- and nitrate ion NO_3^- (Högfeldt, 1982a, b; Sillen, 1964) respectively, then the equilibrium constants of Eq (1) and Eq (2) have been calculated to be $\log K_1 = 35.25 \pm 0.05$ and $\log K_{12} = 33.74 \pm 0.06$ respectively.

The slope of straight line of $\log D_1$ and $\log D_{12}$ plotted against the reciprocal of the temperature is calculated to be 248.8 and 492.9 respectively using the least square method, thus the thermodynamic functions of the extraction reactions in two systems can be calculated to be $\Delta H_1 = -4.76 KJ \cdot mol^{-1}$, $\Delta H_{12} = -9.44 KJ \cdot mol^{-1}$, $\Delta G_1^0 = -RTLnK_1 = -201.27 KJ \cdot mol^{-1}$, $\Delta G_{12}^0 = -192.64 KJ \cdot mol^{-1}$, $\Delta S_1 = -(\Delta G^0 - \Delta H_1)/T = 658.99 J \cdot mol^{-1} \cdot K^{-1}$. $\Delta S_{12}^0 = 614.35 J \cdot mol^{-1} \cdot K^{-1}$.

3. CONCLUSIONS

(1). The extraction of Sc (Ⅲ) with RNH_3NO_3 from thiocyanate and nitrate-thiocyanate solutions has been studied and the composition of extracted complexes has been proposed.

(2). The results of the extraction of Sc(Ⅲ) in this experimental process show that Sc(Ⅲ) is extracted into organic phase in $Sc(OH)_2^+$ form and the synergistic effect of SCN^- and NO_3^- on the extraction of Sc(Ⅲ) has been observed.

(3). The extraction reactions by the methods of slope, continuous variation of pH values have been determined. The equilibrium constants and thermodynamic functions of extraction reactions have been calculated as well.

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SYNERGISTIC EXTRACTION OF ZINC THIOCYANATE WITH PRIMARY AMINE N1923 AND TBP*

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ABSTRACT

The synergistic extraction of zinc thiocyanate from nitric acid solution with primary amine N1923 and TBP has been investigated. By the methods of slope analysis and constant mole, the composition of extracted complexes has been determined. The dependence of temperature on the synergistic extraction of zinc thiocyanate and IR spectra of the synergistic complexes have been studied. The equilibrium constants and the thermodynamic functions of the synergistic reaction have been calculated as well.

INTRODUCTION

The binary synergistic system of primary amine and neutral organophosphorus reagents has been reported to be much smaller (Mooiman et al., 1986; Yu et al., 1989), after the synergistic extraction of zinc and cadmium chloride with primary amine and neutral organophosphorus reagents has been studied by the present authors (Ma et al., 1989 a,b), in order to study the effect of Zn(II) by primary amine and neutral organophosphorus reagents, the synergistic extraction of zinc thiocyanate by primary amine N1923 (RNH_2) and tributylphosphate(TBP) from nitric acid solution has been therefore investigated in greater detail. Moreover, the extraction of zinc thiocyanate by TBP, which has not been reported yet, has been also studied.

1 EXPERIMENTAL

1.1 Reagents

Primary amine N1923 with an average molecular weight of 280.69 was available from the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, the contents of nitrogen and primary amine were 4.99% and 99% respectively. TBP, analytical reagent, after washed three times with 4% sodium hydroxide, followed to neutral with water of removing ions, distilled by means of reduce pressure and distillate of 119 ℃ /1

* The Project Supported by National Natural Science Foundation of China.

mmHg was obtained, then was dried with anhydrous sodium sulfate. The physical parameters of TBP were determined to be $d_4^{20}=0.9772$, $n_D^{25}=1.4230$. Zinc thiocyanate solution was prepared using zinc nitrate with a certain amounts of potassium thiocyanate, that is , the mole ratio of zinc and thiocyanic ion is 1: 5, since zinc nitrate has not been extracted with primary amine N1923 according to preexperimental result. All other chemicals were analytical reagents.

1.2 Experimental method and instruments

Equilibrium studies were carried out at 25± 1℃ using equal volumes of aqueous and organic solutions and an equilibration time of 15min. The Zn(Ⅱ) concentrations in the aqueous phase were determined by the titrimetric method of EDTA with indicator of Xylenol Orange; Stock amine nitrate solutions in heptane were prepared by using the amine and equilibrating the solution with an equivalent amount of aqueous nitric acid. The IR spectra were measured on a DIGILAB FTS−20 spectrophotometer.

2. RESULTS AND DISCUSSIONS

2.1 Extraction of zinc thiocyanate with TBP in heptane

Fig. 1 shows that the logarithms of the distribution ratios of Zn(Ⅱ) vary with the logarithms of TBP concentration and the slope of the straight line obtained is 3 which suggests that three TBP molecules are complexed to each zinc thiocyanate molecules. In order to prove the result above, the composition of extracted complex is determined by the method of continuous variation. As seen from Fig. 2, the maximum of Zn

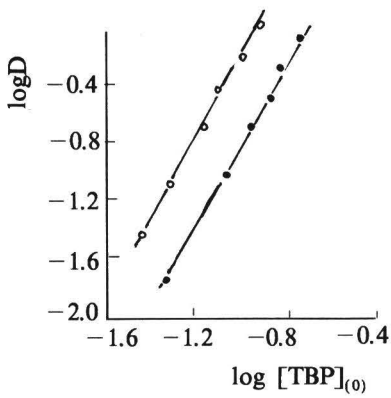


Fig. 1 Plots of logD vs log[TBP]$_{(0)}$ [SCN$^-$]=0.20,pH=3.53, [Zn^{2+}]: ● −0.03864mol • dm^{-3} o −0.02311mol • dm^{-3}

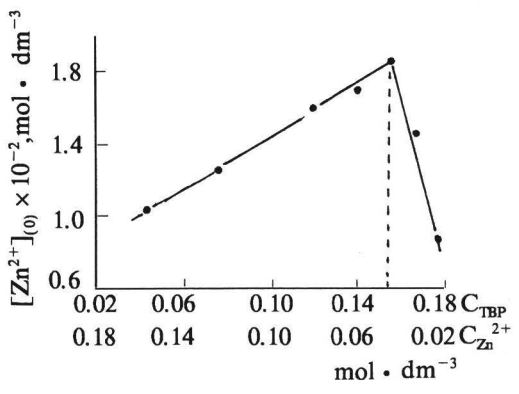


Fig. 2 Method of continuous variation to determine composition of extraction species at constant [SCN$^-$]=0.20mol • dm^{-3}

(Ⅱ) concentration in organic phase appeared at the mole ratio of Zn(Ⅱ) and TBP 1:3. Thus, the formula of the extracted complex can be shown to be $Zn(SCN)_2 \cdot 3TBP$ and the extraction reaction may be represented by the following reaction, viz.

$$Zn(SCN)_2 + 3TBP_{(0)} \rightleftharpoons Zn(SCN)_2 \cdot 3TBP_{(0)} \quad (1)$$

the equilibrium constant K_2 can be expressed as

$$K_2 = D_2 (1 + \sum_{i=1}^{4} \beta_i [SCN^-]^i) / \beta_2 [SCN^-]^2 [TBP]^3_{(0)} \quad (2)$$

2.2 Synergistic extraction of zinc thiocyanate with RNH_3NO_3 and TBPin heptane

Previous investigation (Le, 1983) has been reported for the extraction of zinc thiocyanate with primary amine N1923 alone. In order to ascertain the synergistic effect of Zn(Ⅱ) with N1923 and TBP, it is first necessary to know the synergistic diagram of Zn(Ⅱ). As seen form Fig. 3, the synergistic effect is observed obviously. Moreover, the pH values in aqueous phase have not practically effect on the synergistic extraction of Zn (Ⅱ). Accordingly, the following experiment is at constant pH=3.53 hereafter.

2.3 Calculation of equilibrium constants

At constant aqueous conditions and TBP concentration, the concentration of RNH_3NO_3 is changed, then a series of $D_{tot.}$ has been obtained; Under similar circumstances, the concentration of TBP is changed at constant aqueous conditions and

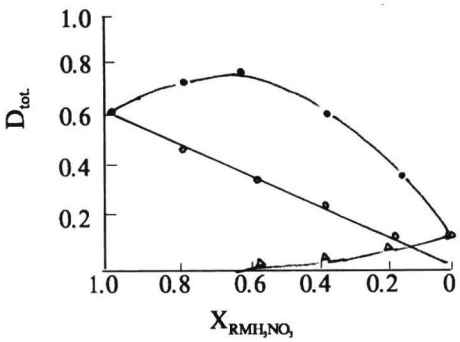


Fig. 3 Plots of $D_{tot.}$ vs $X_{RNH_3NO_3}$ at $C_{Zn^{2+}} = 0.03864 mol \cdot dm^{-3}$
$pH = 3.53, [SCN^-] = 0.20 mol \cdot dm^{-3}$ $\Delta - TBP + Zn(SCN)_2$,
$o - RNH_3NO_3 + Zn(SCN)_2$, $\bullet - RNH_3NO_3 + TBP + Zn(SCN)_2$

RNH_3NO_3 concentration, a series of $D_{tot.}$ has been obtained again. In the light of $D_{tot.} = D_1 + D_2 + D_{12}$, $\log D_{12}$ is plotted against the logarithm of the amine nitrate salt concentration or TBP concentration in Fig. 4 and Fig. 5 respectively, and slope of the straight line is 1, Considering the polymerization degree of amine salts, the synergistic reaction of Zn(Ⅱ) from thiocyanate system can be represented by the following reaction, i. e.

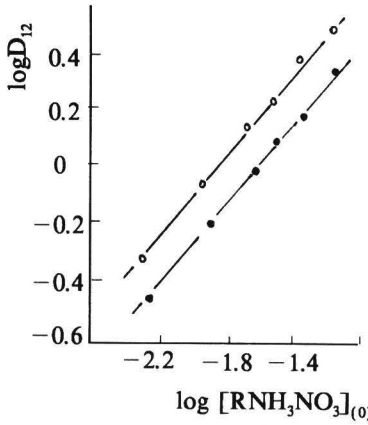


Fig. 4 Plots of $\log D_{12}$ vs $\log[RNH_3NO_3]_{(0)}$ at constant $[TBP]_{(0)}$ • $-0.06 mol \cdot dm^{-3}$, o $-0.08 mol \cdot dm^{-3}$.

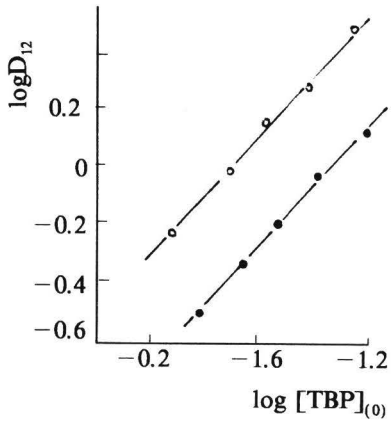


Fig. 5 Plots of $\log D_{12}$ vs $\log [TBP]_{(0)}$ at constant $[RNH_3NO_3]_{(0)}$ • $-0.04 mol \cdot dm^{-3}$, o $-0.06 mol \cdot dm^{-3}$.

$$Zn(SCN)_4^{2-} + (RNH_3NO_3)_{2(0)} + TBP_{(0)} \xrightleftharpoons{K_{12}} (RNH_3)_2Zn(SCN)_4 \cdot TBP_{(0)} + 2NO_3^- \quad (3)$$

the equilibrium constant K_{12} can be expressed as

$$K_{12} = D_{12}(1 + \sum_{i=1}^{4} \beta_i [SCN^-]^i)[NO_3^-]^2 / \beta_4 [SCN^-]^4 [(RNH_3NO_3)_2]_{(0)} [TBP]_{(0)} \quad (4)$$

According to the various extracted species in organic phase, the synergistic reactions in organic phase can be represented by

$$(RNH_3)_2Zn(SCN)_{4(0)} + TBP_{(0)} \xrightleftharpoons{\beta_{12}'} (RNH_3)_2Zn(SCN)_4 \cdot TBP_{(0)} \quad (5)$$

$$(RNH_3NO_3)_{2(0)} + Zn(SCN)_2 \cdot 3TBP_{(0)} + 2SCN^- \xrightleftharpoons{\beta_{12}''} (RNH_3)_2Zn(SCN)_4 \cdot TBP_{(0)} + 2TBP_{(0)} + 2NO_3^- \quad (6)$$

$$(RNH_3NO_3)_{2(0)} + (RNH_3)_2Zn(SCN)_{4(0)} + 2SCN^- + Zn(SCN)_2 \cdot 3TBP_{(0)} \xrightleftharpoons{\beta_{12}'''} 2(RNH_3)_2Zn(SCN)_4 \cdot TBP_{(0)} + 2NO_3^- + TBP_{(0)} \quad (7)$$

the equilibrium constants β_{12} for which are given by equation(8) $-$(10) respectively.

$$\beta_{12}' = K_{12}/K_1 \quad (8)$$

$$\beta_{12}'' = (K_{12}/K_2)/(\beta_4/\beta_2) \quad (9)$$

$$\beta_{12}''' = (K_{12}^2/K_1K_2)/(\beta_4/\beta_2) \quad (10)$$

Under the present conditions, replacing $[NO_3^-]$ by $[RNH_3NO_3]$ from literature data for β_i (Högfeldt, 1982) and pertinent values of equation (2)、(4)and (8)—(10), the equilibrium constants K_1、K_2、K_{12} and β_{12} are calculated to be $\log\bar{K}_1 = 0.50$、$\log\bar{K}_2 = 3.02$、

$\log\bar{K}_{12}=2.41$, $\log\bar{\beta}'_{12}=1.91$, $\log\bar{\beta}''_{12}=0.42$, $\log\bar{\beta}'''_{12}=2.05$ respectively.

2.4 Calculation of the thermodynamic functions of the extraction reaction

The slope of straight line of log D_{12} plotted against the reciprocal of the temperature is calculated to be 329.68 using the least square method, then the thermodynamic functions of the extraction reaction can be calculated to be $\triangle H_{12}=-6.31KJ \cdot mol^{-1}$, $\triangle G^0_{12}=-13.75KJ \cdot mol^{-1}$ and $\triangle S^0=7.44KJ \cdot mol^{-1} \cdot K^{-1}$ through Gibbs-Helmholtz formula respectively.

2.5 Studies on the IR spectra of the extracted species

The results of IR spectra of the extracted species show that the RNH^+_3 group is still present in the synergistic complexes. The shift of the P=O stretching frequency from $1281cm^{-1}$ to $1242cm^{-1}$ indicates that the P=O group is involved in bonding. This could be attributed to the coordination with metal through the oxygen atom of P=O group. Moreover, the shift of the P=O stretching frequency from $1281cm^{-1}$ in the ligand TBP to $1265cm^{-1}$ in the extracted complex with TBP and zinc thiocyanate suggests that TBP intensively coordinates with zinc ion. In a word, RNH_3NO_3 and TBP are involved in the formation of the synergistic complex from the supported evidence obtained above.

3 CONCLUSIONS

The synergistic effect of zinc thiocyanate with primary amine N1923 and TBP in heptane is observed obviously. By the methods of slope and constant mole, the composition of extracted complexes has been determined. The equilibrium constants and the thermodynamic functions of the synergistic reactions have been calculated and the studies on the IR spectra of the extracted complexes are carried out.

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SYNERGISTIC EXTRACTION OF ZINC(Ⅱ) AND CADMIUM(Ⅱ) WITH DI (1-METHYL-HEPTYL) METHYL PHOSPHONATE AND PRIMARY AMINE N1923

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ABSTRACT

The extractions of Zn(Ⅱ) and Cd(Ⅱ) from hydrochloride midia with di-(1-methyl-heptyl) methyl phosphonate (B) and primary amine N1923 hydrochloride salt (RNH_3Cl) in heptane have been studied, synergistic effects are observed and the order is Zn(Ⅱ) > Cd(Ⅱ). The composition of synergistic extracting complexes was identified as $(RNH_3Cl)_{3/2}ZnCl_2B$ and $(RNH_3Cl)_2CdCl_2B$ by the methods of slope and constant mole, synergistic extraction reactions and their equilibrium constants were determined, thermodynamic functions of the systems were calculated as well.

1 INTRODUCTION

Di (1-methyl-heptyl) methyl phosphonate (denoted as B) is a useful extractant for the separation of metal ions (Hu et al., 1981), and primary amine N1923 hydrochloride salt (denoted as RNH_3Cl) is widely used for the extraction of metal ions as well (Le et al., 1987a, b). But the synergistic extraction of metal ions with B and RNH_3Cl has not been reported so far. As a part of a systematic study of the synergistic extraction of metal ions with mixtures of neutral organophosphorus extractants and ions association extractants (namely BC species for metal ions) in this paper, the synergistic extraction of Zn(Ⅱ) and Cd(Ⅱ) from hydrochloride media with B and RNH_3Cl in heptane has been studied in detail .

2 EXPERIMENTAL

Di (1-methyl-heptyl) methyl phosphonate (B) and primary amine N1923(RNH_2)

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were supplied by Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. B was purified to reach >99% purity by a reported method (Hu et al., 1981). The contents of nitrogen and primary amine for RNH_2 are 4.99% and 99% respectively. Zn (Ⅱ) and Cd(Ⅱ) solutions were prepared from analytical grade reagents, the ionic strengths were maintained at 1.5 with NaCl, and initial concentrations in the aqueous phase were $C_{Zn(Ⅱ)}=2.09\times10^{-2}$mol · dm^{-3}(pH=2.88) and $C_{Cd(Ⅱ)}=2.15\times10^{-2}$mol · dm^{-3}(pH=3.31) respectively. All other chemicals needed are of analytical pure grade.

The procedures for the extraction and the analytical methods (including appuratus) are the same as described previously (Ma et al., 1989), temperature and time of the extracting equilibrium were 30± 1 ℃ and 40 min respectively.

3 RESULTS AND DISCUSSION

3.1 Synergistic effect of extraction of Zn(Ⅱ) and Cd(Ⅱ) with B and RNH_3Cl

The total concentration of "B+RNH_3Cl" in organic phase has been maintainted to be 0.20 mol · dm^{-3} during the experimental processes, the ratio of RNH_3Cl and B concentration has changed, then the synergistic extracting diagram of the distribution ratio (D_t) versus mole fraction (X_{RNH_3Cl}) has been obtained (Fig. 1). The results show that synergistic effect is present in the extraction of Zn(Ⅱ) and Cd(Ⅱ) with B and RNH_3Cl, coefficient of the synergistic extraction ($R=D_{max}/D_{plus}$) of Zn(Ⅱ) and Cd (Ⅱ) can be calculated to be $R_{Zn}=2.46$, $R_{Cd}=2.26$ (Xu et al., 1984), from which we

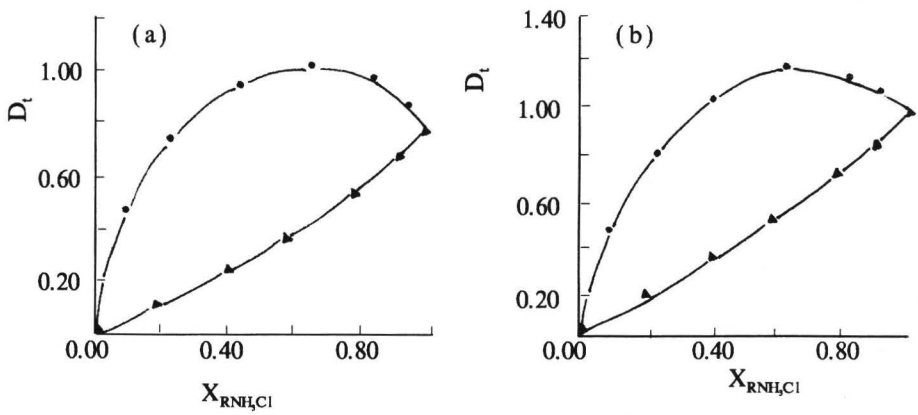


Fig. 1 Plots of Dt vs X_{RNH_3Cl}

(a): ▲ —RNH_3Cl –Zn(Ⅱ); ● —B–RNH_3Cl–Zn(Ⅱ)

(b): ▲ —RNH_3Cl –Cd(Ⅱ); ● —B–RNH_3Cl–Cd(Ⅱ)

could see that i. e., the order of the synergistic effect is Zn (Ⅱ) > Cd (Ⅱ). It indicates that the synergistic effect is weaker which is the synergistic effect is weaker, for the metal ion extracted strongly while the metal ion extracted weakly exhibits stronger synergistic effect (Li et al., 1981).

3.2 Mechanism of the synergistic extraction of Zn(Ⅱ) and Cd(Ⅱ) with B and RNH_3Cl

Under the conditions investigated in this study, the extraction of Zn(Ⅱ) and Cd (Ⅱ) by B was confirmed to be negligible ($D_B < 10^{-3}$). Previous investigation (Le et al., 1987a, b) have shown that the extraction reactions of Zn(Ⅱ) and Cd(Ⅱ) by RNH_3Cl from hydrochloride media are as follows:

$$MCl_2 + (RNH_3Cl)_{3(0)} \underset{}{\overset{Kc}{\rightleftharpoons}} (RNH_3Cl)_3MCl_{2(0)} \quad (1)$$

(M = Zn and Cd)

Since $D_B \approx 0$, the distribution ratio of binary synergistic extraction can be expressed as $D_{BC} = D_t - D_B - D_C \approx D_t - D_C$. At constant aqueous phase and B or RNH_3Cl concentrations, $\log D_{BC}$ is plotted against $\log[RNH_3Cl]_{(0)}$ or $\log[B]_{(0)}$ in Fig. 2,3 respectivelg, and the slope of the straight lines is determined to be x = 0.6, y = 1.2 (M = Zn) and x = 0.7, y = 1.3 (M = Cd). Considering the polymerization degree of RNH_3Cl in heptane (Le et al., 1987a) and Eq. (1), the synergistic extraction of Zn(Ⅱ) and Cd(Ⅱ) can be represented by the following reaction:

$$MCl_2 + x(RNH_3Cl)_{3(0)} + yB_{(0)} \underset{}{\overset{K_{BC}}{\rightleftharpoons}} (RNH_3Cl)_{3x}MCl_2By_{(0)} \quad (2)$$

$$(M = Zn: x = \frac{1}{2}, y = 1;\ M = Cd: x = \frac{2}{3}, y = 1)$$

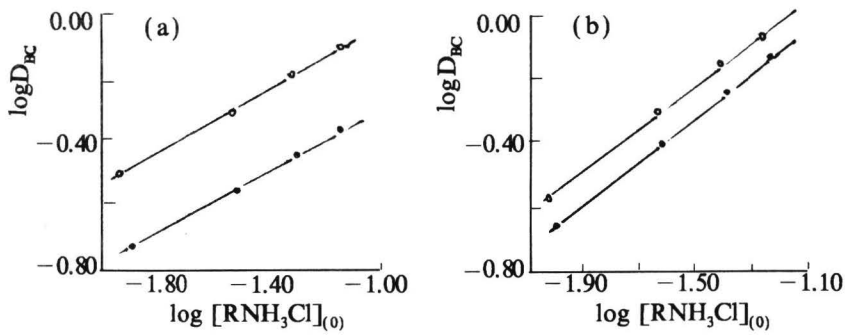


Fig. 2 Plots of $\log D_{BC}$ vs $\log [RNH_3Cl]_{(0)}$ at constant C_B
• —0.08 mol • dm^{-3}; ○—0.12 mol • dm^{-3};
(a): B—RNH_3Cl —Zn (Ⅱ); (b): B—RNH_3Cl—Cd (Ⅱ)

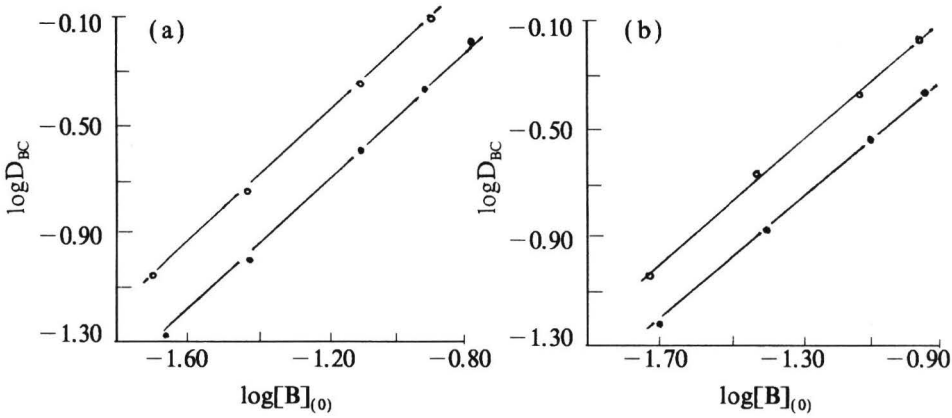


Fig. 3 Plots of $\log D_{BC}$ vs $\log[B]_{(0)}$ at constant C_{RNH_3Cl}

• —0.04 mol • dm^{-3} ; o —0.08 mol • dm^{-3} ;

(a): B−RNH_3Cl−Zn (II); (b): B−RNH_3Cl−Cd (II)

The addition reaction of synergistic extractiny complexes in the organic phase can be written as:

$$(RNH_3Cl)_3MCl_{2(0)} + B_{(0)} \overset{\beta}{\rightleftharpoons} (RNH_3Cl)_{3x}MCl_2B_{(0)} + z(RNH_3Cl)_{3(0)} \quad (3)$$

(M=Zn: $x=\frac{1}{2}$, $z=\frac{1}{2}$; M=Cd: $x=\frac{2}{3}$, $z=\frac{1}{3}$)

3.3 Calculation of equilibrium constants of the synergistic extraction reactions

From some published data for the overall stability constants of Zn(II) and Cd(II) with chloride ion Cl^- (Sillen, 1971 and Sato et al., 1977), the equilibrium constants of Eq. (1) −(3) have been calculated to be $\log K_C = 1.64 \pm 0.06$ (M=Zn), $\log K_C = 1.38 \pm 0.04$ (M=Cd); $\log K_{BC} = 2.10 \pm 0.06$ (M=Zn), $\log K_{BC} = 2.08 \pm 0.06$ (M=Cd); $\log\beta = 0.46$ (M=Zn) and $\log\beta = 0.70$ (M=Cd).

3.4 Effect of temperature and calculation of thermodynamic functions of the synergistic extraction reaction

Fig. 4 is the plots of $\log D_{BC}$ versus the reciprocal of temperature, the results show that the synergistic reactions are exothemic ones. The slope of straight line is calculated to be (a) 763.5, (b) 260.5 using the least square method, thus the thermodynamic functions of the synergistic extraction reactions can be calculated to be $\triangle H_{Zn} = -2.303R[\triangle \log D_{BC}/\triangle(1/T)] = -14.62$ KJ • mol^{-1}, $\triangle H_{Cd} = -14.56$ KJ • mol^{-1}, $\triangle G_{Zn} = -RT\ln K_{BC}^{Zn} = -12.18$ KJ • mol^{-1}; $\triangle G_{Cd} = -12.07$ KJ • mol^{-1}, $\triangle S_{Zn} = -(\triangle G_{Zn} - \triangle H_{Zn})/T = -8.05$ J • mol^{-1} • K^{-1} and $\triangle S_{Cd} = -8.22$ J • mol^{-1} • K^{-1}.

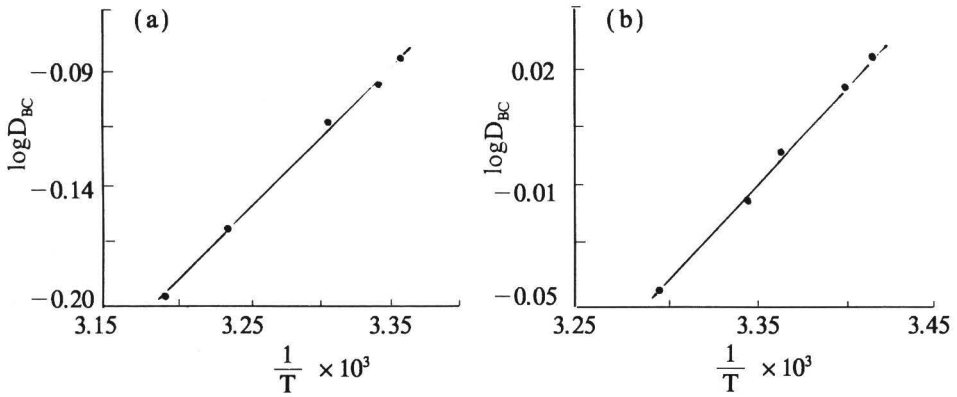


Fig. 4 Plots of $\log D_{BC}$ vs $1/T$

C_B=0.12 mol • dm^{-3} ; C_{RNH_3Cl}=0.08 mol • dm^{-3} ; (a): Zn(Ⅱ); (b): Cd(Ⅱ)

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PROBLEMS IN THE SEPARATION OF RARE EARTHS FROM HCl LEACHED MONAZITE SOLUTION

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ABSTRACT

Monazite is found in many areas of the world, and is ,in Australia, a potential source for most of the rare earths. A major problem in the processing of such a mineral is the attendant quantities of radionuclides, particularly thorium, which are present. Thus the process development requires technology for its processing and the isolation of the radionuclides for safe storage or disposal, as well as the separation of the rare earths by solvent extraction.

The paper briefly describes the caustic treatment of a concentrate and the controlled leaching in HCl to isolate the thorium and uranium and solubilize the rare earths. Solvent extraction studies were initially with DEHPA and later compared with other alkyl- phosphate esters. The selection of the extractant, requirement for a modifier, and the effect of feed pH, solvent concentration, stagewise extraction and kinetics were investigated as affecting extraction and discrimination. Scrubbing and stripping are also included. Consideration of the physical-chemical problems as related to the equipment selection is also an important aspect in the process optimization in order to optimize separation efficiencies and minimize the formation of stable emulsions and cruds.

1. INTRODUCTION

Australia produces about 10,000 t/y of monazite [RE, Y, Th, PO4] as a by-product of its mineral sands industry, all of which is exported. However, a number of companies are assessing the feasibility of rare earths production in Australia.

One problem associated with monazite feed stocks from Australian beach sands is the presence of thorium (5-8%) and uranium (0.2-0.3%). Although both thorium and uranium can be recovered by solvent extraction, the absence of a market for thorium and the small tonnages of uranium means that it is more practical to leave the radioactivity in the residue.

Rare earths can be recovered by solvent extraction from sulphate, nitrate, or chloride solutions. The sulphate system is usually used in the recovery of rare earths as a by-product from uranium processing. The nitrate system leads to high purity products

and permits the use of a wider selection of extractants, but is more expensive and less desirable on environmental grounds. It was in the above context (development of improved technology which meets economic and environmental constraints) that a project was initiated by the Australian Nuclear Science and Technology Organization (ANSTO),to develop suitable techniques for rare earths recovery from chloride systems.

In the optimization of a rare earth circuit, like most solvent extraction circuits, there are a number of parameters and variables that have to be considered, in three general areas:

a) Process Selection - extractant, diluent, modifier and equipment.

b) Operating Parameters - pH, phase ratio, solvent concentration, temperature, scrub solution and conditions, stripping solution and conditions, and phase continuity.

c) Effects of Process Conditions - kinetics, equilibrium, stages, selectivity, solvent poisoning, physical aspects (cruds, third phase, precipitates, emulsions, coalescence).

The subject of this paper is therefore the consideration of some of the above in the development of the extraction and separation of rare earths from chloride solutions resulting from monazite processing.(Page constraints limits the amount of detail that can be presented here).

2. PROCEDURE AND EQUIPMENT

2.1 Cracking and Leaching

The initial work at ANSTO was to develop the cracking procedure for treating a monazite concentrate to solubilize the rare earth values. The object was to produce leach solution for feed to solvent extraction investigations. The alkaline cracking process used on the -10 to -44 micron concentrate employed a NaOH:ore ratio of 1.5:1, at 140-150 °C and 50-60 % NaOH for 2-3 hours reaction time. The cake is selectively leached of rare earths using HCl to pH 3-4. (See Fig. 1.).

2.2 Solvent Extraction

The initial solvent extraction tests were performed in separatory funnels. The typical feed solutions used in the bench-scale investigations and that in the continuous testing had the following analyses, in g/L:

La	63.1	Eu	0.17	Er	0.31
Ce	130.6	Gd	5.22	Tm	0.067
Pr	14.0	Tb	0.60	Yb	0.085
Nd	52.6	Dy	1.44	Lu	0.011
Sm	8.5	Ho	0.25	Y	4.47

The initial shake-out tests were at phase ratios of A/O 1/1 for a 2 minute contact time. Solvent concentrations were varied from 5-30% by volume, in Shellsol 2046 diluent. Initially no modifier was used but it was found that multi-stage contacts with certain extractants required the addition of 3-5% TBP. DEHPA was first examined because of its past acceptance and personal experience. Subsequently other possible reagents were investigated, including Hostarex PA 216 (Hoechst),(di-2-ethylhexyl phosphate mixture) and Ionquest 801 (Albright & Wilson),(2-ethylhexyl phosphonic acid).

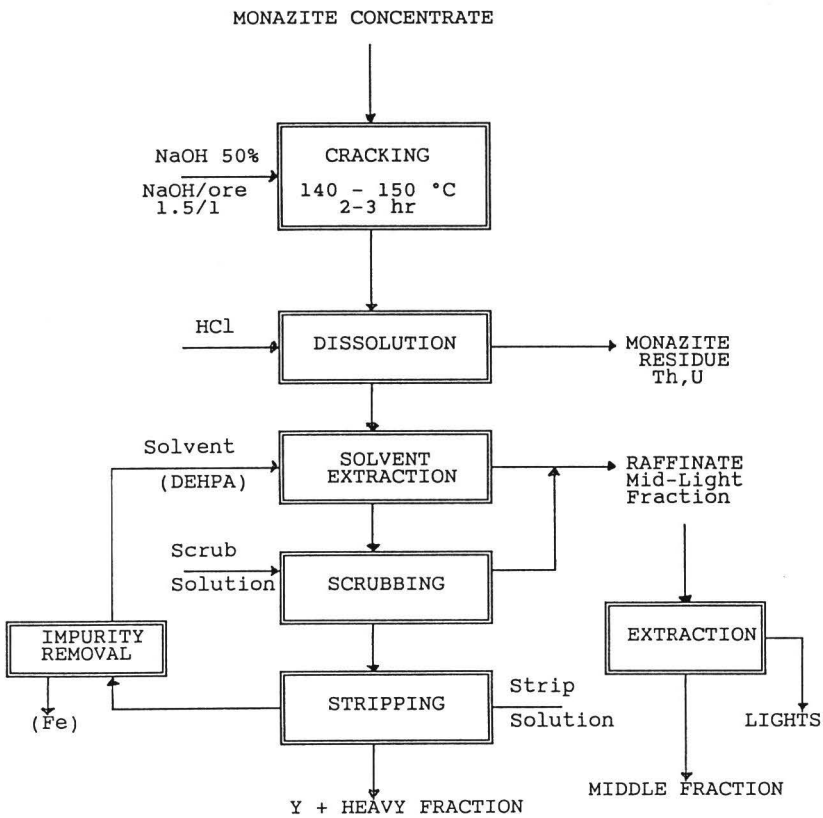


Fig. 1 Monazite Processing Schematic Flowsheet

Mixer-settlers as well as sieve-plate pulse columns were evaluated for performance in a small pilot plant investigation.

3. RESULTS

3.1 Comparison of Some Extractants

Three phosphorus-based extractants were evaluated in the selection process. All extractants were 5 vol. percent in Shell 2046 diluent, A/O 1/1 and the contact time was 60 seconds. Both DEHPA and Hostarex PA 216 required TBP addition to enhance phase separation and inhibit rare earth precipitation. Ionquest 801 was considered the best and did not require the modifier. Data are given in Table 1.

Table 1 Comparison of Some Extractants

Extractant	Tot. Loading (g/L)	Discrimination Y/La	Y/Ce	Y/Gd	Y/Ho	Y/Tm	Y/Lu
DEHPA	2.85	16.1	5.0	12.2	27.9	39.4	39.4
PA 216	2.78	15.3	7.7	12.1	27.4	37.5	37.3
Ionquest 801	2.36	141.1	18.8	6.8	29.7	16.6	12.8

All extractants were 5% by vol. in Shellsol 2046 diluent, A/O ratio 1/1, contact time 60 seconds.

3.2 Phase Separation

The order of phase separation was:

Ionquest 801 > Hostarex PA 216 > DEHPA

3.3 Modifier Requirement

Without the addition of a modifier such as TBP, on successive stage contacts there was a precipitation of rare earths in the DEHPA system, and to a lesser degree in the Hostarex PA 216 system. However in the Ionquest 801 system no modifier was required, and clear phases resulted.

3.4 Comparison and Ranking of Diluents

A number of diluents, with varying composition of aromatic, naphthenes, and paraffins , were selected for an evaluation and comparison. These were ranked according to the phase separation, total loading and Y discrimination over total rare earths. The results showed that Shellsol 2037, nil aromatics was the best

overall(Shelley and Quan,ISEC'90). Selection criteria will of course change,based on the weighting importance in the ranking parameters. The chemical composition of the aqueous and the diluent as well as the distillation range of the diluent will influence the overall performance.

3.5 Solvent Concentration, pH and Selectivity

At high solvent concentration (30% DEHPA in Shellsol 2046) there was no difference in selectivity over the pH 1-3 range. As the solvent concentration was decreased to 5% DEHPA (at feed pH 3.2) the selectivity increased.

3.6 Stagewise Extraction

A comparison of stagewise loading indicated continued loading and extraction of the heavy portion plus yttrium, and rejection of the lighter fraction of the rare earth series. (Fig. 2).

3.7 Temperature, Solvent Concentration and Kinetics

There was very little difference, chemically, in the extraction rate (30 or 60 sec) over the 20-50 °C range. However the higher temperature enhanced the phase separation. Higher extractions for DEHPA , compared to Ionquest 801, were obtained over the solvent concentration range 10-30%.

3.8 Scrubbing

Important considerations in obtaining the desired purity include scrub solution type and pH phase ratio,and phase continuity.These parameters are controlled to initially reject, for example, the light fraction, and obtain an upgraded heavy fraction.

3.9 Stripping and Product Recovery

Important considerations include: a) solution type and concentration; b) possible selectivity; c) compatibility with recycle streams; d) compatibility of strip solution with product required; and e) technical, economic and environmental viability.

3.10 Physical-Chemical Problems

There are a number of problems that relate to both the satisfactory physical and chemical operation of a rare earth circuit, and these include: a) third phase; b) emulsion;c) cruds; d) precipitates; e) co-extraction of impurities; and f) equipment selection and mode of operation.

Contactor selection can be an important aspect in the optimization of a multi-separation process such as required for rare earths. In using mixer-settlers, many are required, and the high shear of agitation can often cause cruds. Differential contactors,

such as sieve-plate pulse columns can provide many stages while minimizing shear and therefore crud and emulsions. The latter are also extremely easy to control.

4. CONCLUSIONS

The design and operation of a rare earth circuit can only be accomplished by considerable attention to most of the more important aspects in the design of complex solvent extraction flowsheets. Not only do the upstream and downstream portions of the process need to be considered with respect to chemistry and metallurgy, but also the reagent selection, equipment selection and the overall optimization of the operational variables.

5. ACKNOWLEDGEMENTS

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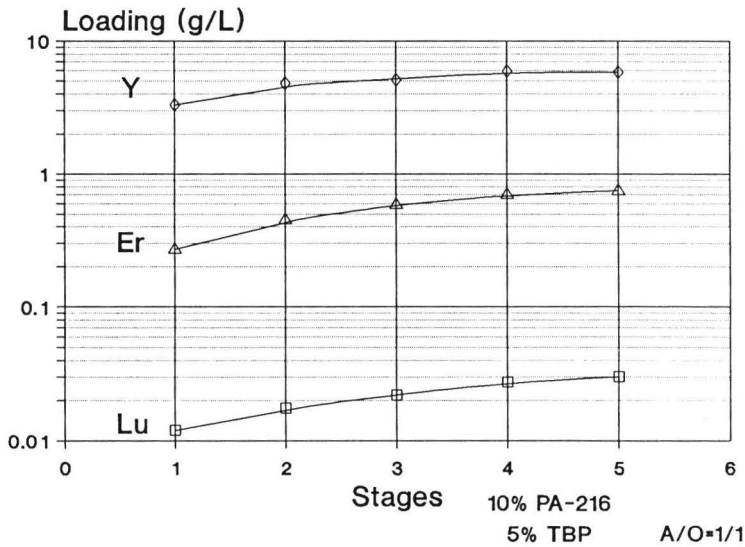


Fig. 2 Stagewise Loading of Rare Earths

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EXTRACTION OF RARE EARTH ELEMENTS WITH P-(1,1,3,3-TETRAMETHYLBUTYL)PHENYL 2-ETHYLHEXYL PHOSPHORIC ACID

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ABSTRACT

Di(2-ethylhexyl)phosphoric acid (HDEHPA) is one of the commonest extractants for the extraction of rare earth elements. But in this case, alkali is necessary for pH adjustment. Therefore, to prepare a new extractant which reduce the consumption of the alkali, we synthesized four different types of organophosphoric acids having higher extraction efficiencies than HDEHPA and compared the extraction efficiencies of them. The result seems to indicate that an additivity of substituent effect can be applied to the extraction efficiency of an organophosphoric acid. Considering the high extraction efficiency and the ease of back-extraction, we have chosen p-(1,1,3,3-tetramethylbutyl)phenyl 2-ethylhexyl phosphoric acid (HOφEHP) as a studying extractant. The separation factors between rare earth elements of this extractant are not higher than those of HDEHPA. So, HOφEHP is unsuitable for the purification of individual rare earth elements, but is expected to be applicable to the recovery of them from acidic solutions. As an application of this extractant, we tried to use it for the recovery of Y from the leach liquor obtained by the decomposition of Xenotime with H_2SO_4, and 100% Y could be recovered without any addition of alkali.

When H_2SO_4 was used as a stripping acid, rare earth elements were back-extracted efficiently as a precipitate of the rare earth sulphates with only equivalent consumption of H_2SO_4. Therefore, combined with this solid back-extraction technique, HOφEHP is expected to provide an economical method for the recovery of rare earth elements.

1. INTROCUCTION

Many kinds of extractants have been studied for the extraction of rare earth elements, such as alkyl phosphoric acids, alkyl phosphonic acids, carboxylic acids, amines, etc. Among them, di(2-ethylhexyl)phosphoric acid (HDEHPA ;structure is shown in Fig.1) has a high separation efficiency and is well-known as an extractant for the separation and purification of their individual elements. But in the case of HDEHPA, alkali is necessary for pH adjustment because metal extraction lowers the pH value in the aqueous phase. The consumption of the alkali is not neglected in the economical viewpoint. Therefore, in order to reduce the consumption of the alkali, we researched an extractant which has a higher extraction efficiency than HDEHPA.

DESIGN OF EXTRACTANTS

The extraction efficiency of an organophosphoric acid [(GO)(G'O)P(O)OH] is considerably affected by the structure of its substituent(G). For example, the branching of the alkyl group leads to a substantial decrease of the extrac-

tion efficiency for rare earth elements (Baes, 1962; Kolarik and Pankova, 1966), and aryl group increases the extraction efficiency more than alkyl group does (Peppard, 1958; Sistokova et al., 1969).

In order to prepare an extractant which has a higher extraction efficiency in comparison with HDEHPA, we designed and synthesized four different types of organophosphoric acids considering the above-mentioned facts, i.e., di-straight-alkyl, branched-alkyl aryl, straight-alkyl aryl and di-aryl type) and studied them for the extraction of rare earth elements (Fig 1).

2. EXPERIMENTAL

2.1 Synthesis of extractants

HDEHPA and HDBPA were prepared by reaction of $POCl_3$ with the corresponding alcohol followed by hydrolysis of the chloride formed (Kolarik and Pankova, 1966).

HDOϕP was prepared by reaction of $POCl_3$ with p-(1,1,3,3-tetramethylbutyl)-phenol in the presence of $AlCl_3$ (Sistokova et al., 1969).

HOϕEHP and HOϕBP were synthesized from $POCl_3$, p-(1,1,3,3-tetramethylbutyl)-phenol and corresponding alcohols in the presence of $AlCl_3$ using a modified procedure in the literature (Orloff et al., 1958; Sistokova et al., 1969).

2.2 Analytical Procedure

The solutions of rare earth elements were prepared by dissolving high purity oxides in HCl. Their metal ion concentration was determined by EDTA titration. The equilibrium lanthanide concentration of the aqueous and organic phase was determined by ICP-AES (SEIKO SPS1200).

3. RESULT

3.1 Comparison of the extraction efficiencies of these extractants

We estimated the extraction efficiencies of these extractants by comparing a batch extraction rate of La. From the result shown in Fig.2, the extraction efficiencis of these extractants prove to be in the order ;

$$\text{HDEHPA} < \text{HDBPA} < \text{HO}\phi\text{EHP} < \text{HO}\phi\text{BP} < \text{HDO}\phi\text{P}$$

The order of the three di-alkyl or di-aryl phosphates (HDEHPA, HDBPA and HDOϕP) was in accord with the literature (Baes, 1962). The other two alkyl aryl phosphates (HOϕEHP,HOϕBP) lie between the corresponding di-alkyl phosphate and di-aryl phosphate. This result seems to indicate that an additivity of substituent effect can be applied to the extraction efficiency of an organophosphoric acid. From the viewpoint of making a more efficient extractant than HDEHPA, di-aryl and straight-alkyl aryl type (HDOϕP, HOϕBP) are suitable for the purpose,

as shown in Fig.2. But it is expected that their high extraction efficiencies make it impossible to back-extract rare earth elements, especially heavy rare earths, from them. Therefore, we have chosen HOϕEHP, a milder extractant than HDOϕP or HOϕBP, as a studying extractant.

3.2 Application of HOϕEHP

(i) Separation efficiency of HOϕEHP. The separation factors between Sm and Nd($\beta_{Sm,Nd}$), Nd and Ce($\beta_{Nd,Ce}$), Ce and La($\beta_{Ce,La}$) were measured in the case of HOϕEHP and compared with those of HDEHPA (TABLE 1).

TABLE 1 Separation factors of HOϕEHP and HDEHPA

extractant	$\beta_{Sm,Nd}$	$\beta_{Nd,Ce}$	$\beta_{Ce,La}$
HOϕEHP	2.67	1.32	2.31
HDEHPA	8.09	2.06	3.15

1M HOϕEHP,HDEHPA in kerosen soln.
0.05M La,Ce,Nd,Sm in HCl soln.
O/A= 1

The β values of HOϕEHP are much smaller than those of HDEHPA. Therefore, HOϕEHP is unsuitable for the purification of individual rare earth elements, but is expected to be applicable to the recovery of them from acidic solutions such as metalliferous effluents and wastes.

(ii) Extraction of Y from an acidic solution. We tried to apply HOϕEHP to the recovery of Y from the leach liquor, an acidic solution, obtained by the decomposition of Xenotime with H_2SO_4 (see Fig.3). The experiments were made by 3 stage countercurrent extraction using HOϕEHP and HDEHPA, respectively. The result is shown in Fig.3.

With HDEHPA, only 63% of Y was extracted. But with HOϕEHP, 100% of Y was extracted without any addition of alkali.

(iii) Back-extraction from loaded HOϕEHP. At first, we applied 6M HCl to back-extract Y from the loaded HOϕEHP resulting from the above experiment because in general, 5~6M HCl or HNO_3 is used as a stripping acid for HDEHPA. However, only 40% of Y was back-extracted (see TABLE 2). It means that the high extraction efficiency of HOϕEHP needs a large amount of HCl to back-extract Y and then, makes the extraction process expensive.

Therefore, we tried the solid back-extraction technique with H_2SO_4 for the stripping. In this technique, back-extracted rare earth elements precipitate as sulphates in H_2SO_4 solution, which promotes the back-extraction furthermore. By

recycling the H_2SO_4 after filtration of the precipitate, the consumption of H_2SO_4 is reduced to an equivalent amount of stripped rare earth elements, thus it provides an economical back-extraction method (Minagawa and Kaneko, 1983; Kaneko, 1988). The experiment was carried out with varying phase ratio. The result (see TABLE 2) shows that most of Y can be back-extracted irrespective of O/A ratio.

TABLE 2 Back-extraction of Y from loaded HOφEHP

STRIPPING ACID	O/A RATIO	BACK-EXTRACTION RATE(%)
6M HCl	1.0	39.6
50% H_2SO_4	5.0	99.9
	3.0	100
	2.0	100
	1.0	100
	0.5	100

4. CONCLUSION

We prepared a new organophpsphoric acid, HOφEHP (p-(1,1,3,3-tetramethylbutyl) -phenyl 2-ethylhexyl phosphoric acid) having a higher extraction efficiency than HDEHPA. Although HOφEHP is not suitable for the purification of rare earth elements because of its low separation efficiency, it could extract rare earth elements from a highly acidic solution to which HDEHPA cannot be applied, without any addition of alkali.

Combined with the solid back-extraction technique, it is expected to provide an economical method for the recovery of rare earth elements. A typical flow of the extraction process using HOφEHP is shown in Fig.4.

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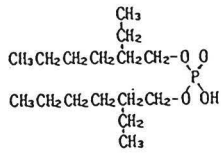
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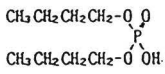
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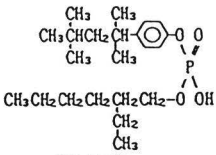
Fig.1 Structural formulas of the extractants studied



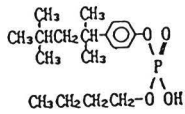
HDEHPA
Di(2-ethylhexyl)phosphoric acid



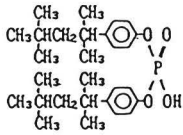
HDBPA
Di-n-butyl phosphoric acid



HOφEHP
p-(1,1,3,3-tetramethylbutyl)phenyl 2-ethylhexyl phosphoric acid

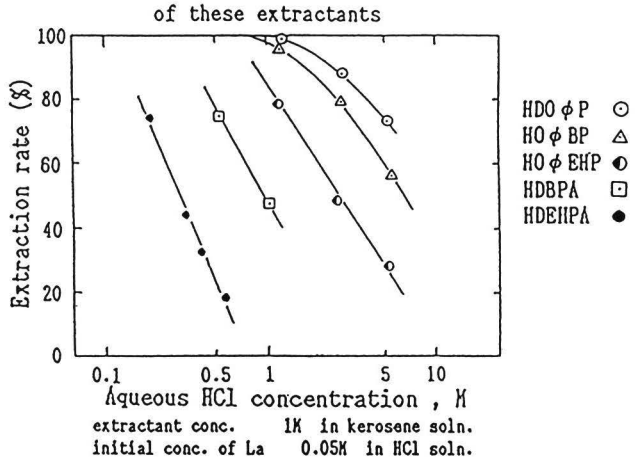


HOφBP
p-(1,1,3,3-tetramethylbutyl)phenyl n-butyl phosphoric acid



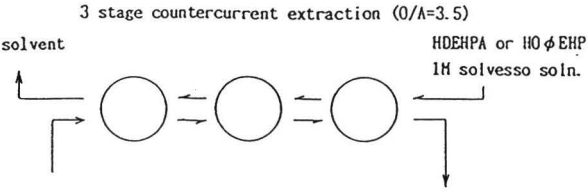
HDOφP
Di-p-(1,1,3,3-tetramethylbutyl)-phenyl phosphoric acid

Fig.2 Comparison of the extraction efficiencies of these extractants



extractant conc. 1M in kerosene soln.
initial conc. of La 0.05M in HCl soln.

Fig. 3 Extraction of Y from the leach liquor



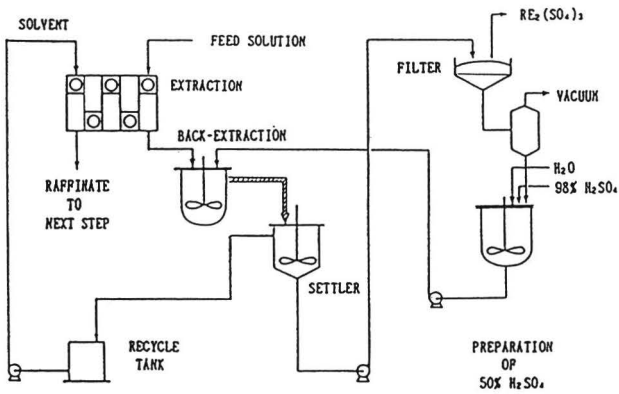
Composition of the leach liquor

La	0.21 (g/l)
Ce	0.38
Pr	0.11
Nd	0.48
Sm	0.38
Gd	2.04
Dy	2.63
Er	2.14
Y	18.14
H_2SO_4	2.0 (mol/l)

Extraction rate of Y (%)

HDEHPA	63.1
HOφEHP	100

Fig. 4 Flow Diagram of rare earths recovery



Solvent Extraction 1990, T. Sekine (Editor)

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SOLVENT EXTRACTION OF RARE-EARTH METALS BY CARBOXYLIC ACIDS

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ABSTRACT

The solvent extraction of the trivalent lanthanides and yttrium from nitrate media by solutions of carboxylic acids in xylene has been studied. Both commercially available carboxylic acids such as Versatic 10 and naphthenic acids, as well as model compounds of known structure, such as 2-ethylhexanoic and and 3-cyclohexylpropanoic acids, were used. In some cases, extraction from sulphate and chloride solutions was also investigated. The dependance of the extraction properties of the carboxylic acids on the atomic number of the lanthanide metal shows a distinct relationship to the steric bulk of the carboxylic acid molecule (which can be quantified by means of the steric parameter, E'_s of the substituent alkyl group). Thus for sterically hindered acids ($-E'_s > 2$) the $pH_{0,5}$ of extraction decreases more or less continuously from lanthanum through to lutetium, and the behaviour of yttrium most closely resembles that of the middle lanthanides, such as gadolinium or terbium. For straight-chain and other non-hindered acids ($-E'_s < 1$), the $pH_{0,5}$ values begin to increase again after the middle of the lanthanide series, and the behaviour of yttrium most closely resembles that of the lighter lanthanides, such as cerium and praseodymium. The stoichiometries of the extracted complexes for representative light (La), middle (Gd) and heavy (Lu) rare earths were investigated by the slope analysis technique for both Versatic 10 and 3-cyclohexylpropanoic acids. It was found that monomeric complexes of the type $LnA_3.(HA)_3$ were extracted by Versatic 10 acid, whereas with 3-cyclohexylpropanoic acid dimeric complexes of stoichiometry $[LaA_3.(HA)_3]_2$, $[GdA_3.(HA)_3]_2$ and $[LuA_3.(HA)_2]_2$ were formed.

INTRODUCTION

Although carboxylic acids have not been studied as comprehensively for the extraction of rare-earth metals as their organophosphorus counterparts, some fundamental studies have been conducted in the past. Preston (1985) described the extraction of representative rare earths by both Versatic 10 and naphthenic acids, and Korpusov *et al.* (1974) conducted an investigation on rare-earth extraction by monocarboxylic acids with different hydrocarbon substituent groups.

Reagents of the carboxylic acid type are relatively inexpensive and readily available, and have found some application in commercial processes. For example, Versatic acid has been used by Thorium Ltd. in England for the production of pure europium(III), lanthanum(III) and yttrium(III) oxides. (Brown and Sherrington, 1979; Sherrington, 1983).

A fundamental study on the extraction of rare-earth metals, using both commercial carboxylic acids and model compounds of known structure, was therefore conducted to gain further insight into the extraction chemistry in these systems.

2. EXPERIMENTAL

Initial aqueous phases contained 0,05M rare earths as nitrates, chlorides or sulphates in sodium nitrate, sodium chloride or lithium sulphate of 1,00M ionic strength. Metal concentrations were decreased to 0,01M in slope-analysis experiments.

Equal volumes (100 ml) of the aqueous and organic phases were stirred magnetically for 3-5 minutes in a water-jacketed glass vessel at 20,0 ± 0,01°C. After each pH adjustment (done with 10M NaOH or 5M LiOH) samples (3-5 ml) were withdrawn from each phase, and metal concentrations in the aqueous phase were determined by titration against a 0,010M EDTA solution, using xylenol orange as indicator.

Organic phases contained 0,25M-1,00M carboxylic acid in xylene of analytical grade.

3. RESULTS AND DISCUSSION

3.1 *Effect of carboxylic acid structure*

The steric bulk of carboxylic acids can be quantified by means of the steric parameter of the substituent alkyl group ($-E'_s$) (MacPhee *et al.*, 1978 and Panaye *et al.*, 1980). The carboxylic acids used (with $-E'_s$ values in parentheses) were : Versatic 10 (3,63), 2-ethylhexanoic (2,03), iso-nonanoic (0,93), cyclohexanexcarboxylic acid (0,69), 3-cyclohexylpropanoic (0,34), n-octanoic (0,31) and n-hexanoic acids (0,31).

The extraction of the trivalent rare earths and yttrium from nitrate solutions by carboxylic acids is shown in Fig. 1.

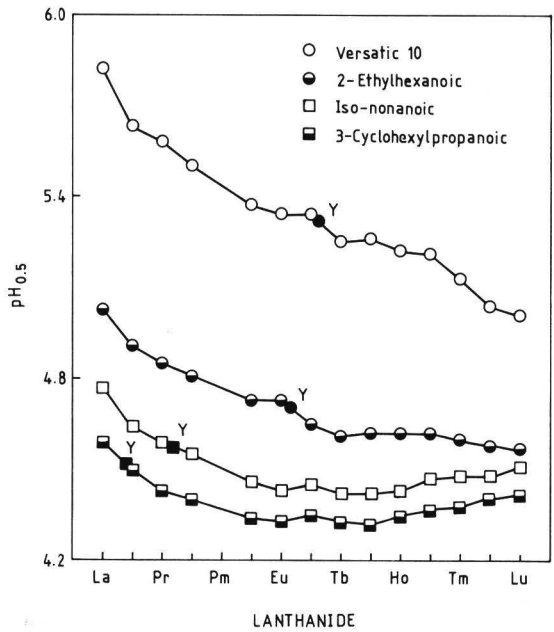


Fig. 1. The extraction of trivalent rare earths and yttrium from nitrate solutions by 0,5M carboxylic acids in xylene at 20°C. Aqueous phases: 0,05M $Ln(NO_3)_3$ in 1,00M $NaNO_3$.

It can be seen that for sterically hindered acids ($-E'_s > 2$)such as Versatic 10 and 2-ethylhexanoic acids the $pH_{0,5}$ values decrease more or less continuously from lanthanum through the lutetium, following the same order of decrease as the ionic radii with increasing

atomic number (Shannon, 1976). The behaviour of yttrium most closely resembles that of the middle lanthanides. Lutetium is more strongly extracted than lanthanum due to increase in electrostatic attraction with decreasing cationic radius through the series, and hence an increase in stability of the complexes. For less sterically hindered acids ($-E'_s < 1$) such as iso-nonanoic and 3-cyclohexylpropanoic acids, the $pH_{0,5}$ values decrease from lanthanum to the middle rare earths, after which they begin to increase again through to lutetium.

Comparative extractions from chloride and sulphate solutions with Versatic 10 and iso-nonanoic acids were done. Little difference between the $pH_{0,5}$ values for nitrate and chloride solutions was observed ($pH_{0,5}$ (Cl^-) - $pH_{0,5}$ (NO_3^-) = 0,01 to 0,12 pH units). A significant difference ($pH_{0,5}$ (SO_4^{2-}) - $pH_{0,5}$ (NO_3^-) = 0,47 to 0,65 pH units) was observed between $pH_{0,5}$ values for nitrate and sulphate solutions, due to the stronger complexation of sulphate ions with lanthanide ions in the aqueous phase, resulting in the inhibition of metal extraction.

3.2 *Effect of steric hindrance*

The effect of steric hindrance in the carboxylic acids on lanthanide extraction was examined by means of correlations of $pH_{0,5}$ values with the steric parameter of the substituent alkyl group (Fig. 2).

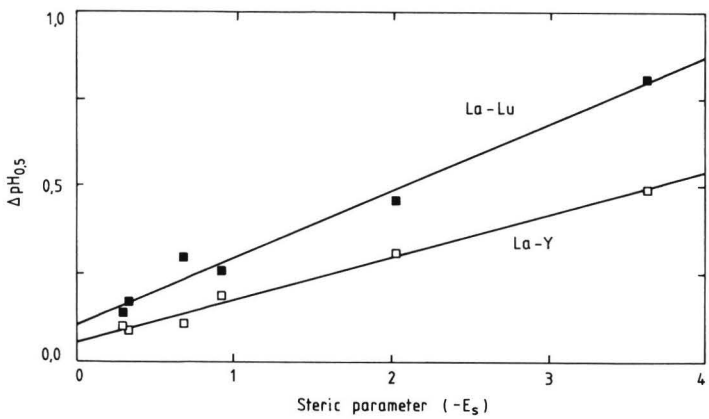


Fig. 2. Difference between $pH_{0,5}$ values for lanthanum and lutetium and of lanthanum and yttrium as a function of the steric parameter of the substituent alkyl group in carboxylic acids.

The difference between the $pH_{0,5}$ values for lanthanum and lutetium was found to increase linearly with increasing steric parameter. With straight-chain or non-hindered acids ($-E'_s < 1$), the behaviour of yttrium most closely resembles that of the lighter lanthanides (Ce and Pr). As the steric parameter of the substituent alkyl group increases the $pH_{0,5}$ values for the extraction of yttrium moves progressively towards those of the heavier lanthanides, such that a linear correlation between $\Delta pH_{0,5}$(La-Y) and steric parameter was also obtained.

3.3 *Slope analysis treatment*

The stoichiometries of the extracted complexes of La, Gd and Lu for Versatic 10 and 3-cyclohexylpropanoic acids in xylene were investigated by the slope analysis technique. The general equation for the extraction of a trivalent lanthanide Ln^{3+} by a carboxylic acid H_2A_2 can be written as

$$jLn^{3+} + \overline{xjH_2A_2} = \overline{(LnA_3 \cdot (HA)_{(2x-3)})_j} + 3jH^+ \quad (1)$$

where bars denote the presence of the species in the organic phase; j is the degree of polymerization; and x is the number of carboxylic ligands per metal ion extracted. It can be shown that:

$$\log [Ln]_{org} = j(\log[Ln]_{aq} + 3pH) + xj \log[H_2A_2] + \log K_E \quad (2)$$

Values for j can then be derived from the slopes of the plots of log $[Ln]_{org}$ versus log $[Ln]_{aq}$ + 3pH at constant $[H_2A_2]$ (Korpusov *et al.*, 1974). An example of such a plot for the extraction of La, Gd and Lu by 3-cyclohexylpropanoic acid is shown in Fig. 3.

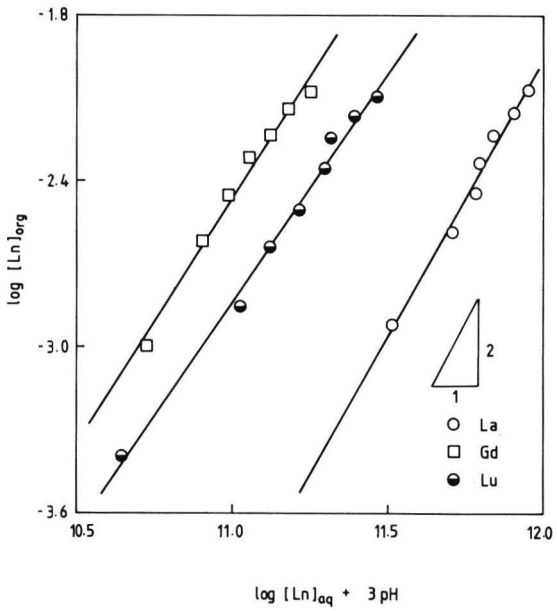


Fig. 3. Determination of the degree of polymerization (j) for the extraction of lanthanum, gadolinium and lutetium by 0,5M 3-cyclohexylpropanoic acid in xylene at 20°C. Aqueous phases: 0,01M $Ln(NO_3)_3$ in 1,00M $NaNO_3$.

The following expression can also be derived from equation (1).

$$\log K_E = \log D - 3jpH - (j-1)\log[Ln]_{aq} - xj \log (H_2A_2) \quad (3)$$

indicating that values for x can be determined from the slopes of the plots of log D-(j-1) $\log[Ln]_{aq}$ versus $\log[H_2A_2]$ at constant pH (slopes = xj). Values for j and x for the extraction of La, Gd, and Lu by Versatic 10 and 3-cyclohexylpropanoic acids are given in Table 1.

TABLE 1

Values for j and x obtained for the extraction of rare earths by carboxylic acids

Rare earth	j		x	
	Versatic 10 acid	3-Cyclohexyl-propanoic acid	Versatic 10 acid	2-Cyclohexyl-propanoic acid
La	0,88	2,05	3,20	3,02
Gd	0,93	1,71	3,27	2,92
Lu	0,85	1,62	2,86	2,54

The results in Table 1 show that with Versatic 10 acid, monomeric complexes of the type $LnA_3.(HA)_3$ are extracted in all cases. With 3-cyclohexylpropanoic acid it appears that dimeric complexes of stoichiometry $[LnA_3.(HA)_3]_2$ are extracted in the case of La and Gd, whereas complexes of the type $[LuA_3.(HA)_2]_2$ are formed in the extraction of the smaller lutetium cation. This distinct difference in extraction behaviour between sterically hindered acids (Versatic 10) and those with low steric hindrance (3-cyclohexylpropanoic acid) shown in Figure 1 can be rationalized. The $pH_{0,5}$ data for the extraction of the trivalent lanthanides by Versatic 10 acid approximate to a straight line. Since 3-cyclohexylpropanoic acid is a stronger acid than Versatic 10 acid, a downward displacement of $pH_{0,5}$ values would be expected (pK_a difference). Also there is a further stabilization effect due to the dimerization of the extracted metal complex that occurs with 3-cyclohexylpropanoic acid. This stabilization becomes progressively less favourable as the size of the lanthanide cation decreases, with the result that the $pH_{0,5}$ data take the form of a curve with a shallow minimum near the middle of the series.

The proposed structures for the extracted complexes are shown in Fig. 3.

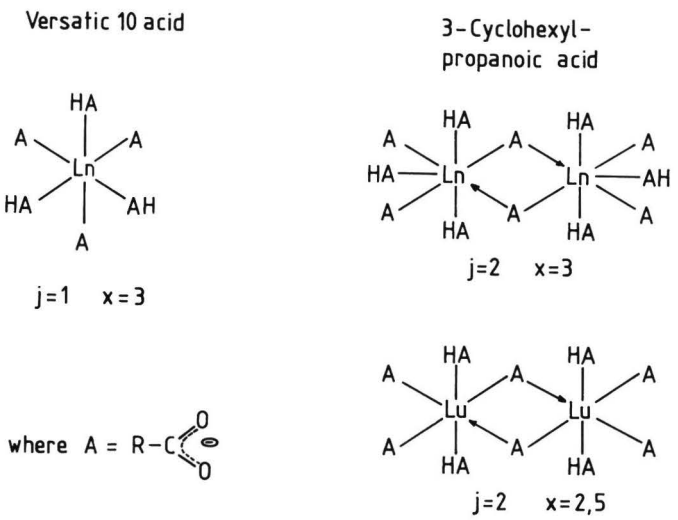


Fig. 3. Structures of extracted organic complexes for lanthanum, gadolinium and lutetium.

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SOLVENT EXTRACTION OF PALLADIUM BY PYRIDINE CARBOXYLIC ESTERS

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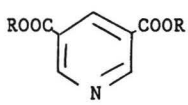
ABSTRACT

The extractant ACORGA CLX50 and related compounds, developed originally for the extraction of copper from chloride leach solutions[1,2], have proved to be strong extractants for palladium and of potential application in the separation of platinum group metals (PGMs) by solvent extraction. The pyridine dicarboxylic ester extractant ACORGA CLX50 is highly selective over other metals with the exception of copper which if present in the process stream is coextracted with the palladium. A clean separation of these metals is readily obtained however, by selective stripping of the organic phase. It is believed that removal of both copper and palladium from PGM process streams should allow a more efficient separation of the remaining precious metals.

INTRODUCTION

The traditional method of processing ores and residues containing Platinum group metals is based on digestion of the ore with aqua regia after which some of the nitric acid may be evaporated off to give a solution of the various metals present in an aqueous chloride medium. These are mainly the precious metals Pt, Pd, Rh, Ru, Ir, Au, Ag, and the base metals Ni, Cu, Fe, and Pb. The metals are then separated by precipitation techniques, e.g. by successive additions of ammonia to precipitate the chloro amine complexes of platinum and palladium followed by cementation[3-5]. More recently there has been interest in solvent extraction methods, particularly for the isolation of palladium. Various processes have been published and a number are believed to be in current operation. For example, fatty amines or amine derivatives may be used to coextract both platinum and palladium as ion pairs of the amine salts[6].
e.g. $[BH^+]_2\ [PdCl_4]^{2-}$ and $[BH^+]_2\ [PtCl_6]^{2-}$.
After stripping, thioethers may be used to reextract and hence isolate the palladium, though the kinetics of extraction are reportedly slow[6]. It is claimed that both α and β- hydroxyoximes may also be used for palladium extraction though they apparently suffer from the problems of slow rates of extraction and difficulty in stripping[7].

The extractant ACORGA CLX50, based on a diester of pyridine 3,5 dicarboxylic acid is a strong extractant for palladium and offers a number of significant advantages over other reagents for the isolation of palladium by solvent extraction.



ACORGA CLX50

EXPERIMENTAL

The extractant solution used in this work comprised a 50 % v/v solution of the reagent ACORGA CLX50 in Escaid 100, which is an approximately 0.5molar concentration of the active component. The aqueous feed solutions were based on PGM process feeds containing a range of precious and base metals including palladium and copper in an aqueous ammonium chloride medium . Metals were analysed by means of Inductively Coupled Plasma Emission Spectroscopy.

Selectivity

A precious metals process solution containing relatively high concentrations of palladium and copper was equilibrated by vigorous stirring for 30 minutes with an equal volume of extractant solution containing ACORGA CLX50 after which the organic phase was analysed. The results are presented in table 1. and illustrate the strong extraction of both palladium and copper with high selectivity over other metals.

TABLE 1 Selectivity of ACORGA CLX50 for copper and palladium (all metals mg/l)

Metal	Pd	Pt	Au	Rh	Ru	Ir	Ag	Cu	Pb	Ni	Fe	Cl^-	pH
Feed	6920	90	20	335	400	22	40	7640	965	4900	9065	3.13M	0
Organic loading	6320	2	4	<1	<2	<5	<1	6280	6	5	2		

Selective Stripping

Though copper and palladium are coextracted by CLX50 with high selectivity over other metals, a good separation of copper and palladium may still be obtained by means of selective stripping. It has been found that if a kerosene solution of ACORGA CLX50 bearing both copper and palladium is contacted with water, substantially all of the copper is stripped into the aqueous phase leaving the palladium behind in the organic phase. The palladium may then be recovered from the organic phase by contacting with a suitable stripping medium such as dilute aqueous ammonia solution. This is illustrated by the experiment described below.

Equal volume portions of an Escaid 100 solution of ACORGA CLX50 and of an aqueous platinum group metals process solution were stirred together vigorously for 30 min at 25°C. The aqueous and organic phases were then separated and samples of each retained for analysis . A portion of the metal bearing organic solution was then contacted with two separate equal volume portions of water at 25°C. The aqueous fractions were combined and samples of both the aqueous and organic solutions set aside for analysis. A portion of the water stripped

organic solution was then contacted with two separate equal volume portions of dilute ammonia solution (9% w/v). Again the aqueous fractions were combined and samples of both the organic and aqueous fractions sampled and analysed. The analysis of the various fractions at different stages of these operations is given in Table 2.

TABLE 2 Extraction and selective stripping of metals from ACORGA CLX50. All concentrations in mg per litre.

	Aqueous		Organic	
	Cu	Pd	Cu	Pd
Aqueous Feed	7635	6920		
Organic after extraction			4035	5925
After stripping 2x with water	2033	<1	1	5995
after stripping 2x with dilute ammonia	-	2815	-	26

The analysis of the organic and aqueous phases after stripping with water clearly illustrates the effectiveness of the separation of copper and palladium. Palladium is recovered with high efficiency giving a virtually barren organic by stripping with dilute (9%) ammonia. Acidification of the aqueous phase with dilute hydrochloric acid following stripping gives a yellow precipitate analysed as $(NH_3)PdCl_2$.

Extraction Isotherms

Various volume ratios of extractant solution and aqueous feed were charged to glass vessels and stirred vigorously in a thermostated bath at 25°C for 30 minutes, the phases separated and analysed for both copper and palladium. The isotherms for coextraction of palladium and copper are shown in Fig 1.

Stripping

A strip isotherm could not be generated because at every strip phase ratio evaluated the palladium in the organic phase was reduced to an extremely low level. For example when a 50% solution of ACORGA CLX50 loaded with palladium was contacted with a 10% ammonia solution at the highest organic to aqueous phase ratio examined (4:1) the following result was obtained:

Palladium in organic phase 15 ppm

Palladium in aqueous phase 65 g/l

This demonstrates that stripping of palladium from ACORGA CLX50 by ammonia solution is extremely facile and capable of producing high aqueous

concentrations of palladium as well as giving virtually complete regeneration of the extractant.

Analysis of Extraction Isotherm Data

The metal distribution data (isotherms) for the coextracted metals have been interpreted using the ICI Minchem II computer program[8] to give predicted metal recoveries. Organic to aqueous phase ratios have been computed to give high recovery of both copper and palladium.

Extraction stage efficiencies of 95% have been assumed for copper and 85% for palladium to account for its slower extraction kinetics and to illustrate the remarkably high recoveries that are still theoretically attainable at these lower efficiencies.

Two different feed solutions have been examined (A and B) and in each case an organic to aqueous phase ratio computed to give a satisfactory copper recovery in three extraction stages. This O/A ratio has then been used to compute the palladium recovery.

The computed data are shown in Table 3 and the McCabe-Thiele construction for recovery of palladium from feed solution A shown in Fig 2. All concentrations are in gl^{-1} unless stated otherwise.

TABLE 3. Computed McCabe-Thiele data for extraction of Copper and Palladium.

	Feed A		Feed B	
	Cu	Pd	Cu	Pd
Metal in feed	7.64	6.92	73.5	28.0
Metal in raffinate	0.12	4.4 ppm	0.09	14 ppm
% recovery	98.4	99.9	99.9	99.95
O/A phase ratio	2.5	2.5	7.0	7.0

These computed data for each of the process streams show that if three stages of extraction are used then not only is a very high proportion of the copper extracted, but palladium may be reduced to ppm levels, equivalent to recoveries exceeding 99.5%. Laboratory experiments based on batchwise contacts confirm that recoveries of this order are attainable.

Rate of extraction of Palladium

An investigation was made of the rate of extraction of palladium and copper from the aqueous feed solution of composition "A" used in previous experiments by a 50% solution of ACORGA CLX50 in Escaid 100. The standard ICI method[9] was used based on stirring equal volume portions of the two solutions at 1270 rpm in a baffled 1 litre vessel at 25°C.

The data are presented in table 4 below and shown graphically in fig. 3.

Table 4 Rates of extraction of copper and palladium by ACORGA CLX50.

Time (min)	COPPER	PALLADIUM		
	Cu organic (g/l)	Pd organic (g/l)	Pd aqueous (g/l)	% Pd extn. equilibrium
0	0	0	7.07	0
0.5	4.96	2.28	4.85	31.5
1	4.65	3.42	3.83	45.9
2	4.32	4.74	2.42	65.9
5	3.98	6.72	0.75	89.4
10	3.80	6.95	0.175	97.5
30	3.81	7.28	25ppm	99.65
60	3.81	7.16	20ppm	99.71
180	3.84	7.32	15ppm	99.78

The rate of extraction of palladium is slower than for copper but still very fast compared with other known palladium extractants giving almost 98% extraction in 10 minutes. It is also apparent that some of the copper that is initially extracted is subsequently displaced by palladium and therefore that in the presence of copper the rate of extraction of palladium will depend on a ligand exchange reaction.

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Note - The word ACORGA is a registered trade mark of ACORGA Ltd., a wholly owned subsidiary of Imperial Chemical Industries Plc

Fig 1. Extraction Isotherms - Coextraction of Pd and Cu

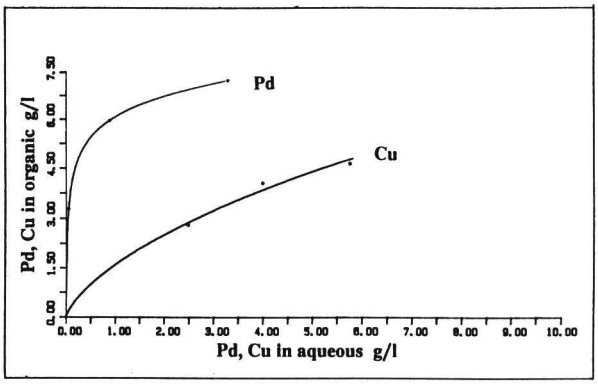


Fig 2. Extraction of Palladium by 50% ACORGA CLX50 from mixed Pd , Cu solution, 3.2 M chloride

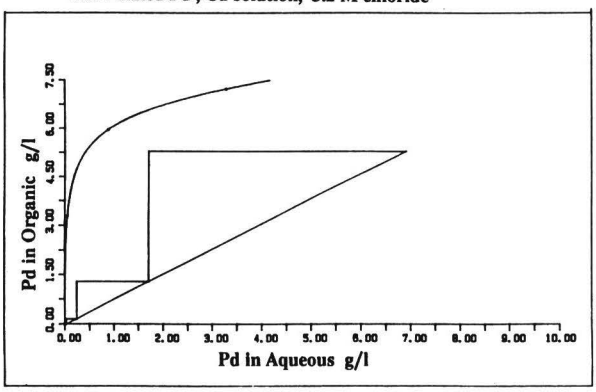
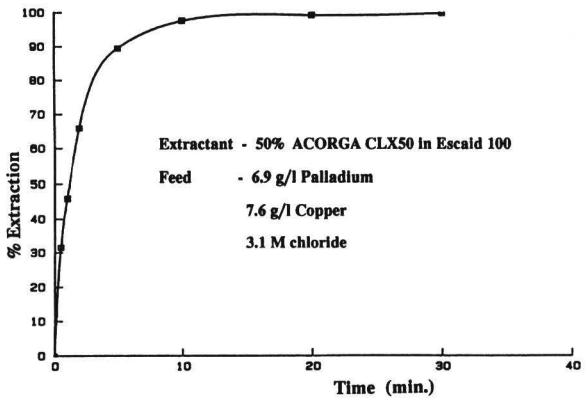


Fig 3. Rate of extraction of Palladium by Acorga CLX50



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SOLVENT EXTRACTION SEPARATION OF URANIUM(VI) WITH DIBENZO-24-CROWN-8 FROM HYDROCHLORIC ACID MEDIA

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ABSTRACT

Solvent extraction separation studies of uranium(VI) were carried out with DB-24-Crown-8 in nitrobenzene. Uranium was quantitatively extracted from 7-10 M hydrochloric acid with 0.01 M DB-24-C-8 in nitrobenzene. Uranium was stripped from the organic phase with 2 M nitric acid and determined spectrophotometrically at 530 nm with PAR. Uranium(VI) was separated from several elements in binary mixtures and also from multicomponent mixtures. The method was extended to the analysis of uranium in monazite sand and syenite rock sample.

INTRODUCTION

In view of nuclear industry, separation of uranium from associated elements is very important. Very recently Deorkar & Khopkar (1989) used crown ethers for the extraction analysis studies of uranium. In liquid-liquid phase transfer studies of uranium perchlorate Aarts et al (1987) found that crown ethers with 27 or more ring atoms are the best hosts to transfer uranium salts from an aqueous to organic phase. Synergistic extraction studies of uranium(VI) with crown ethers have been reported in presence of di(1-methyl heptyl) methyl phosphonate by Quian et al (1986). Dicyclohexano derivatives of crown ethers have been used for the extraction of uranium (VI) by Wang et al (1987) and Xu et al (1986) from hydrochloric acid media.

So far no systematic efforts have been made for the use of Dibenzo-24-crown -8 for the extractive separation of uranium (VI) from associated elements. This paper presents systematic investigations of solvent extraction separation of uranium (VI) from associated elements with Dibenzo-24-crown-8 in nitrobenzene as diluent from hydrochloric acid medium. The method has been extended to the separation of uranium (VI) from large number of elements and also to the analysis of uranium in real samples.

2 EXPERIMENTAL SECTION

2.1 Apparatus and Reagents

Zeiss spectrophotometer (German), a digital pH meter (Model LI-120 ELICO, India) with glass and calomel electrodes, a digital flame photometer (PEI, Model, No.041 India) and wrist action flask shaker were used.

About 2.166 g of uranyl nitrate hexahydrate (Anala R.B.D.H.) was dissolved

in 1000 mL of distilled water containing 1% nitric acid. The solution was standardised gravimetrically as given in Vogel (1975). It contained 1 mg mL^{-1} of uranium (VI), diluted solutions containing 50 µg mL^{-1} of U (VI) were prepared by appropriate dilution.

Crown ethers ($1x10^{-2}$M in nitrobenzene) included, 18-crown-6 (Fluka,A.G.), 12-crown-4, 15-crown-5, DB-18-crown-6, DC-18-crown-6, DB-24-crown-8 and DC-24-crown-8 (Aldrich) and were used without further purification.

2.2 General Procedure

To an aliquot of solution containing uranium (VI) (50-90 µg), hydrochloric acid was added so as to have its concentration of 7 M in a total volume of 10 mL. The solution was then transferred to a separating funnel and was equilibrated with 10 mL. of $1x10^{-2}$ M suitable crown ether with nitrobenzene as the diluent for 10 min on a wrist action flask shaker. The two phases were allowed to settle and separate. Uranium (VI) was stripped from the organic phase with 10 mL of 2 M nitric acid. It was then determined spectrophotometrically with PAR at 530 nm as per Pollard et al (1959). The concentration of uranium (VI) was calculated from the calibration curve.

3 RESULTS AND DISCUSSION

3.1 Extraction of Uranium as a function of hydrochloric acid concentration

The extraction of uranium was studied at various hydrochloric acid concentrations. (Fig.1) The optimum acid concentration for the quantitative extraction of uranium was ascertained by extraction with $1x10^{-2}$ M different crown ethers in nitrobenzene as the diluent. The hydrochloric acid concentration was varied from 1-10 M. It was found that DB-24-crown-8 was suitable for the quantitative extraction of uranium from 6M-10M hydrochloric acid concentration. The extraction of uranium was 76% at 6M HCl with 18-crown-6, 90% at 9M HCl with DB-18-crown-6, 84% with DC-18-crown-6 and 88% with DC-24-crown-8 at 5-6M HCl. There was no extraction with 12-crown-4, 15-crown-5 in the concentration range of 1-10 M hydrochloric acid. For further studies DB-24-crown-8 in nitrobenzene was used and the extraction studies were carried out at 7 M HCl concentration. In order to study the effect of anion on the extraction of uranium, an attempt was made to extract uranium from $1x10^{-2}$ M picric acid with $1x10^{-2}$ M DB-24-crown-8 in nitrobenzene. It was found that there was no extraction of uranium from $1x10^{-2}$ M picric acid media. This condition was exploited for the separation of uranium from other elements.

3.2 Effect of Crown Ether Concentration

The optimum concentration of DB-24-crown-8 required for the quantitative extraction of uranium was ascertained by extracting uranium at 7 M hydrochloric acid with varying concentration of DB-24-crown-8 in the concentration range of $1x10^{-4}$ M to $1x10^{-1}$M. The extraction started at $1x10^{-4}$ M and was

quantitative with 10 mL of $4x10^{-3}$ M of DB-24-crown-8. For further studies 10 mL of $1x10^{-2}$ M DB-24-crown-8 in nitrobenzene was used.

3.3 Effect of various diluents

The extraction of uranium was carried out with DB-24-crown-8 at 7 M hydrochloric acid with various solvents as diluent such as benzene, toluene, xylene, carbontetrachloride, chloroform, methylenechloride, ethylenechloride, tetrachloroethane, nitrobenzene and nitromethane. The phase volume ratio was maintained at unity. The studies revealed that there was quantitative extraction of uranium with nitrobenzene and nitromethane as diluent, whereas with rest of the solvents the extraction was less than 5%. Further studies were carried out with nitrobenzene as diluent.

3.4 Nature of the Extracted Species

An attempt was made to ascertain the probable composition of the extracted species by extracting uranium at 7 M hydrochloric acid with varying concentration of DB-24-crown-8 in nitrobenzene. The plot of log D vs log [DB-24-crown-8] showed a slope of 1.88. Hence the probable composition of the extracted species was 1:2 (UO_2Cl_2:2DB-24-C-8).

3.5 Period of Equilibration and Choice of Stripping Agents :

In order to ascertain the optimum period of extraction the equilibrations were performed for various periods of time (1-60 min). It was found that with 1 min of equilibration there was quantitative extraction of uranium. Further studies were carried out with 10 min equilibration period.

After extraction of uranium from 7 M hydrochloric acid with DB-24-crown-8 in nitrobenzene as diluent, uranium from the organic phases was stripped with various stripping agents in the concentration range of 0.01 M-10 M. The stripping of uranium was quantitative with 0.01 M-2 M hydrochloric acid, 0.5-4 M nitric acid, 4-8 M sulfuric acid, 0.01-0.1 M acetic acid,with 6 M perchloric acid stripping was only 86%, with 7 M-8 M hydrobromic acid there was back extraction of uranium into the organic phase due to formation of extractable bromo-complex. With water also there was quantitative stripping of uranium from the organic phase.

3.6 Separation of Uranium from Binary Mixtures :

Uranium was extracted in presence of various ions. The tolerance limit was set as the amount of foreign ions required to cause ± 2% error in the recovery of uranium. Amongst the transition metals tungsten (VI), zirconium (IV) and molybdenum (VI) were tolerated in 1:1 ratio. Cobalt (II) and yttrium (III) were tolerated in 1:6 ratio. Alkali and alkaline earth metals were tolerated in higher ratios. For beryllium and vanadium (V) the tolerance limit was less (1:2). Most of the non transition elements, anions and anions of organic acids

were tolerated in higher ratios. Amongst the diverse ions only molybdenum(VI) and iron(III) were co-extracted with uranium and their tolerance limit was very low.

3.7 Separation of Uranium from Multicomponent Mixtures :

Uranium(VI) was extracted with DB-24-crown-8 in nitrobenzene from 7 M hydrochloric acid. Under this condition there was no extraction of barium and rubidium but from $1x10^{-2}$M picric acid there was quantitative extraction of barium and rubidium with DB-24-crown-8 in nitrobenzene. This property was exploited for the separation of uranium from multicomponent mixtures using DB-24-crown-8. A mixture of uranium(VI), barium and thorium was separated by extracting uranium(VI) from 7 M hydrochloric acid with $1x10^{-2}$M DB-24-crown-8. When barium and thorium still remained in the aqueous phase, barium was extracted with $1x10^{-2}$M DB-24-crown-8 in nitrobenzene from $1x10^{-2}$M picric acid whereas thorium remained in the aqueous phase. Uranium(VI) and barium from the respective organic phases were stripped with 2 M nitric acid. In the same manner as above, uranium(VI) was separated from other multicomponent mixtures (Table 1).

TABLE 1

Analysis of Uranium (VI) in Tertiary Mixtures

No.	Mixture	Taken mg.	Found mg.	% Recovery	Extractant	Stripping agent
1.	U	0.05	0.05	100	DB-24-C-8, 7M HCl	2M HNO_3
	Ba	1.00	1.00	100	DB-24-C-8, 0.01M Picric acid	2M HNO_3
	Th	0.50	0.50	100	Aqueous phase	-
2.	U	0.05	0.050	100	DB-24-C-8, 7M HCl	2M HNO_3
	Rb	1.00	0.990	99	DB-24-C-8, 0.01M Picric Acid	2M HNO_3
	Sr	0.50	0.500	100	Aqueous phase	-
3.	U	0.05	0.05	100	DB-24-C-8, 7M HCl	2M HNO_3
	Ba	1.00	1.00	100	DB-24-C-8, 0.01M Picric Acid	2M HNO_3
	Ce(III)	0.50	0.50	100	Aqueous phase	-
4.	U	0.05	0.05	100	DB-24-C-8, 7M HCl	2M HNO_3
	Rb	1.00	0.98	98	DB-24-C-8, 0.01M Picric Acid	2M HNO_3
	Th	0.50	0.50	100	Aqueous phase	-
5	U	0.05	0.05	100	DB-24-C-8, 7M HCl	2M HNO_3
	Ba	1.00	0.99	99	DB-24-C-8, 0.01M Picric Acid	2M HNO_3
	Sr	0.50	0.49	98	Aqueous phase	-

No.	Mixture	Taken mg.	Found mg.	% Recovery	Extractant	Stripping agent
6.	U	0.05	0.05	100	DB-24-C-8, 7M HCl	2M HNO_3
	Rb	1.00	1.00	100	DB-24-C-8, 0.01M Picric Acid	2M HNO_3
	La	1.00	0.99	99	Aqueous phase	-
7.	U	0.05	0.05	100	DB-24-C-8, 7M HCl	2M HNO_3
	Ba	1.00	1.00	100	DB-24-C-8, 0.01M Picric Acid	2M HNO_3
	Ru	1.00	1.00	100	Aqueous phase	-
8.	U	0.05	0.05	100	DB-24-C-8, 7M HCl	2M HNO_3
	Ba	1.00	1.00	100	DB-24-C-8, 0.01M Picric Acid	2M HNO_3
	La	1.00	1.00	100	Aqueous phase	-
9.	U	0.05	0.05	100	DB-24-C-8, 7M HCl	2M HNO_3
	Ba	1.00	1.00	100	DB-24-C-8, 0.01M Picric Acid	2M HNO_3
	Cr(III)	1.00	1.00	100	Aqueous phase	-
10.	U	0.05	0.05	100	DB-24-C-8, 7M HCl	2M HNO_3
	Ba	1.00	0.98	98	DB-24-C-8, 0.01M Picric Acid	2M HNO_3
	Y	0.20	0.20	100	Aqueous phase	-

3.8 Application to Analysis of Uranium from Geological Samples :

Syenite rock sample (SY-II) was brought into solution as per the procedure described by Mohite et al.(1985). 1.0 g of monozite sample was dissolved in a mixture of nitric acid and sulfuric acid. Silica was separated by filtration and the solution was diluted to 100 mL with distilled water. In case of syenite rock iron was removed beforehand by an ether extraction from a sample solution of 6 M hydrochloric acid and then it was used for uranium extraction. To an aliquot of solution containing uranium, 2 mg of EDTA was added to mask other elements and then extracted with $1x10^{-2}$M DB-24-crown-8 in nitrobenzene from 7 M hydrochloric acid. Under these conditions thorium, cerium, yttrium, calcium, sodium were not extracted. From the organic phase uranium was stripped with 2 M nitric acid and determined spectrophotometrically. The amount of uranium found in syenite rock sample was 284 ppm as against the standard value of 280 ppm. In monozite sand it was 0.29% as against the standard value of 0.30%.

4 CONCLUSIONS

The important feature of this method is that it permits the separation of uranium from thorium, cerium, barium, rubidium, strontium, lanthanum, yttrium,

chromium which are usually associated with nuclear fission product. The method is applicable to the analysis of uranium in geological samples. The extractant DB-24-crown-8 in nitrobenzene can be reused repeatedly. The method is very simple, rapid, selective and reproducible.

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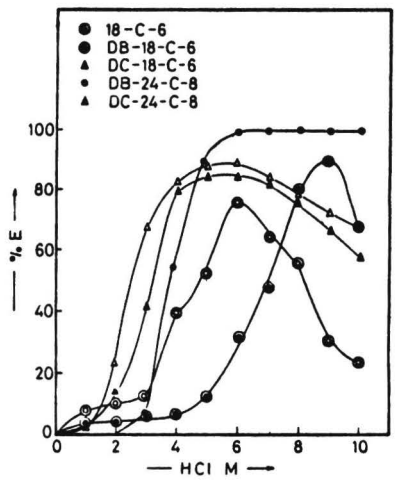


Fig. 1 - Extraction of uranium as a function of HCl concentration with various crown ethers with nitrobenzene as diluent.