

INTERNATIONAL SOLVENT EXTRACTION CONFERENCE

ISEC'80

PROCEEDINGS

- 14. Nuclear Processes
- 15. Physical Chemistry
- 16. Extractants and diluents
- 17. Metal Extraction
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INTERNATIONAL SOLVENT EXTRACTION CONFERENCE

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Nuclear Processes

Session 14

Co-chairmen : J.D. Navratil (Atomic Energy Agency, Vienna, Austria)
E. Detilleux (Eurochemic, Mol, Belgium)

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A MODIFIED THOREX-FLOWSHEET FOR REPROCESSING DENATURED
URANIA/THORIA FUEL

H.J. von Wachtendonk and E. Merz

Institute for Chemical Technology
Kernforschungsanlage Jülich GmbH,

5170 Jülich
Federal Republic of Germany

ABSTRACT

The THOREX process has been developed to separate thorium, uranium and fission products with the aid of tri-n-butylphosphate, TBP, which forms extractable complexes with uranium, thorium and plutonium moreover. In the presented new flowsheet the uranium concentration of the feed solution is considerably higher and the thorium concentration a little lower than in the THOREX feed solution, but the total heavy metal concentration remains approximately constant. No severe alternations to the THOREX process are necessary to achieve a complete separation of thorium, uranium and fission products.

1. INTRODUCTION

Various combinations of fissile and fertile materials can be used in existing reactor systems to generate nuclear energy. Increasing interest has recently been devoted towards thorium utilization for concepts involving denatured uranium-thorium fuel cycles in the context of non-proliferation considerations. Two versions of uranium-topped thorium cycles have been considered for application in high temperature gas-cooled reactors, which differ in the enrichment level of the fresh fuel. In the so-called HEU/Th cycle, highly enriched uranium containing about 93 % U-235 or a pure U-233 equivalent is used for topping, whereas in the MEU/Th cycle, the fissile uranium isotope content in the fuel is adjusted to ≤ 20 % for U-235 and ≤ 13 % for U-233, respectively, in order to assure that it is non weapons usable without isotopic separation [1].

Whether the denatured U-233 cycle would offer any greater proliferation resistance than the U/Pu cycle has, according to the INFCE investigations [2], come up with the conclusion that there is only little difference, if one is considering the complete fuel cycle including uranium enrichment. Therefore, the interest in applying denatured thorium fuel cycles has in the meanwhile greatly disappeared. One of the main reasons for this is the fact that there are several serious problems in the required three-way separation of large quantities of uranium, thorium and plutonium. This paper can only serve as a first attempt to identify the performance of a solvent extraction system in which the three elements, U, Th and Pu are all present in significant quantities. A final judgement would require considerable research and development effort far beyond our present knowledge.

2. COMPOSITION OF SPENT HTR FUEL ELEMENTS

The principal composition of typical HEU and MEU mixed (Th,U) O_2 spent fuel elements is shown in figure 1. For the sake of an attractive fuel economy, a mixed fuel concept composed of three different fuel element compositions is proposed, thus the percentage numbers in figure 1 are representing average mass balance values of close to equilibrium cycles [3].

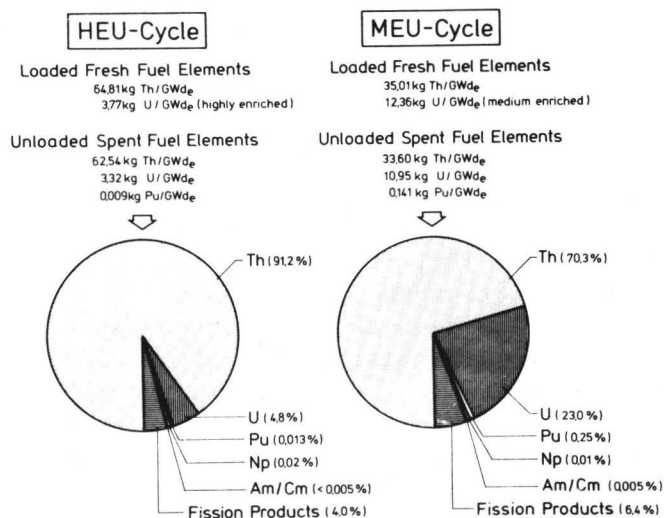


FIG. 1

Chemical composition of fresh and spent HTR fuel elements

It is important to note that in the HEU cycle the ratio of Th:U in irradiated fuel is approximately 1:20 in contrast to 1:3 in the MEU concept. Another important difference is the roughly 20 times higher Pu content in the spent MEU fuel as compared to the HEU fuel.

3. BASIC CONSIDERATIONS CONCERNING ACTINIDE EXTRACTION WITH TRI-N-BUTYL-PHOSPHATE

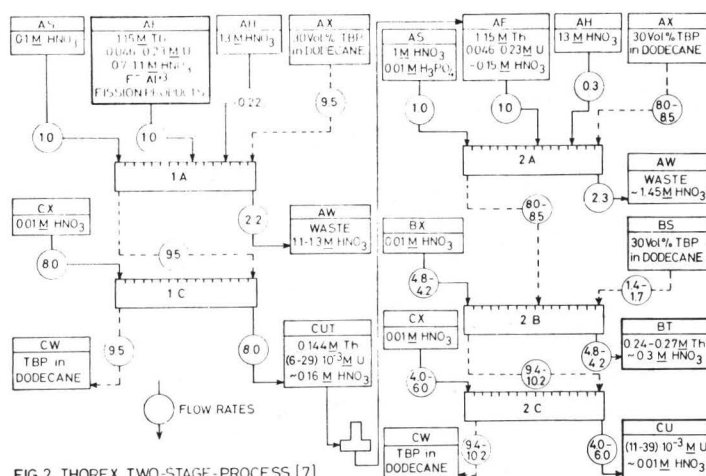
The THOREX process has been developed to separate thorium, uranium and fission products, since these two elements, just as plutonium, form easily extractable complexes with tri-n-butylphosphate, TBP, in a nitrate system. It has primarily be utilized for the isolation of large quantities of U-233 from irradiated thorium.

Examples of its successful application are the reprocessing of more than 850 tons of irradiated thorium in the existing USAEC PUREX plants at Savannah River and Hanford, yielding 1.4 tons of purified U-233 [4,5]. Since the burnup of the fuel was rather low, the concentration of uranium in the irradiated thorium did scarcely exceed 0.2 %. This implies that in the TBP solvent extraction one has to deal in practice with only a one component system, namely thorium. The influence of uranium on the distribution of thorium is negligible. Because uranium nitrate exhibits a higher distribution coefficient between an aqueous solution and a TBP/dodecane solvent, the uranium coextraction is complete at the same time.

Preverentially, the flowsheets first developed at the Knolls Atomic Power Laboratory and at the Oak Ridge National Laboratory had been applied,

adding aluminum nitrate to the feed solution thus acting as a salting-out reagent. This measure had the disadvantage of increasing the bulk of high level wastes. To avoid this drawback, ORNL developed in the late 1950's the so-called Acid THOREX process, in which nitric acid is substituted for most of the aluminum nitrate. In a few of the campaigns this advanced technique has been applied successfully. It must be noted, however, that a complete renunciation for any salting out reagent than pure nitric acid does not give satisfactory extraction yields in case of thorium, due to its relatively poor distribution coefficients.

The need for reprocessing of fuel with a larger U content arised for the first time from the primary fuel loading of Consolidated Edison Co.'s Indian Point-1 nuclear power plant. The fresh fuel was composed of 94 % Th and 6 % U. Pilot scale reprocessing development was executed at the Oak Ridge National Laboratory which came up with the ORNL-Acid THOREX process [6]. It allows processing of thorium feed solutions close to 10 % uranium content. A typical feed solution may contain: 267 g Th/l; ≤ 20 g U/l; ~ 0.15 M HNO_3 . Mostly 30 % TBP/dodecane solvent was applied.



When the necessity for capabilities to reprocess spent fuel from HTR's came up in the Federal Republic of Germany with the advent of the HTR commercialization, own R&D activities were started based upon U.S. experience available hithertoo. Farbwerke Hoechst in cooperation with KFA have optimized the Acid THOREX process in order to enable handling high concentrations of fission products present in fuel with rather high burnups and uranium concentrations of up to 20 % in thorium [7]. The proposed flowsheet is presented in figure 2.

To overcome the problem of a third phase formation, the thorium content of the feed solution was limited to ≤ 1.15 M. For completion of already published data for the formation of a second organic phase, additional experiments have been performed for the system 5 vol.% TBP/dodecane as a function of temperature and Th concentration. The results are shown in figure 3.

The individual straight lines were obtained applying equalization calculation with the measured values ($c = \text{mol/l}$; $T = ^\circ\text{C}$). In figure 4 limiting thorium concentrations in different TBP-AMSCO 125-82 AS mixtures are plotted as a function of equilibrium aqueous acidity [10]. The maximum thorium loading of the organic phase containing 30 % TBP by volume is 65 g/l or 0.28 moles/l respectively.

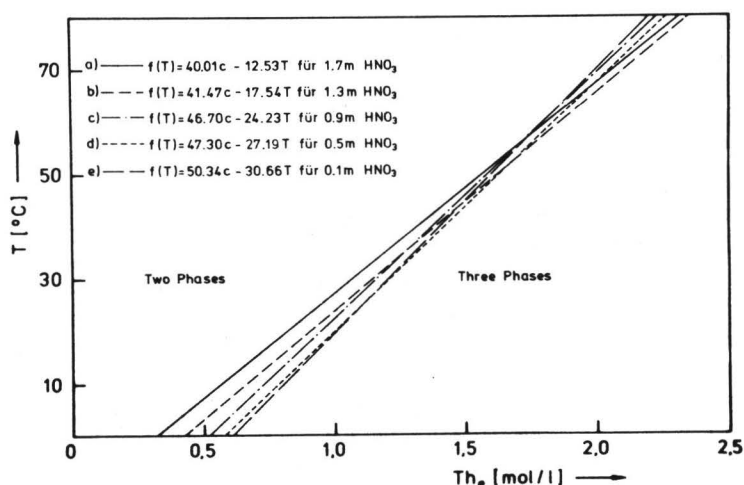


FIG. 3

Second organic phase limits in 5 vol.% TBP/dodecane [9]

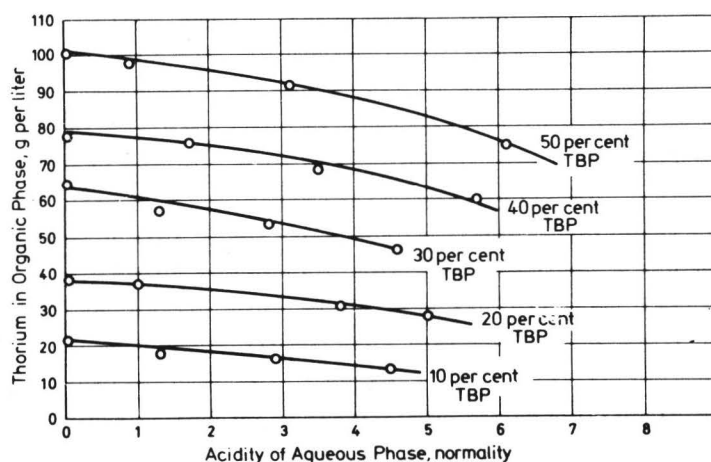


FIGURE 4. LIMITING THORIUM CONCENTRATIONS IN TBP-A14SCO 125-82 AS
A FUNCTION OF EQUILIBRIUM AQUEOUS ACIDITY [10]

This two stage THOREX process is suitable for reprocessing of all HEU thorium fuel types considered so far. The trace quantities of neptunium present as $Np(V)$ ions in the process solution are not extracted in the co-decontamination cycle and follow therefore the fission products more or less quantitatively into the high-radioactivity waste stream. Plutonium trace quantities are distributed to about 90 % in the Th product and the rest of approximately 10 % in the U product applying the flowsheet mentioned. In case a purification of the two product streams is required according to specifications, an extraction chromatographic separation procedure has been developed by our laboratory [8].

4. THE MULTICOMPONENT EXTRACTION

In order to separate feed solutions arising from irradiated MEU/Th fuel, the established two stage THOREX process is no longer applicable without further modifications due to the higher uranium as well as plutonium content in the feed solution. The possibility to overcome the problem by utilizing

feed solutions adjusted to acceptable Th:U ratios by diluting the dissolver solution with pure inactive thorium nitrate to yield U concentrations < 20 % is - though theoretically feasible - to reject from an economic point of view.

In the prevailing multicomponent system the elements Th, U, Pu as well as HNO_3 are competing with the complex ligand TBP. Uranium exhibits the highest extractability into the organic phase. Consequently, it is salted-out from the aqueous phase by these components. Figure 5 illustrates the minimum amount of solvent required for a complete uranium extraction, thus determining the slope of the operating line. Hence, the fundamentals for the uranium distribution may be derived. Taking the resulting slope $o/a = 0.89$, already two theoretical stages are sufficient for a 99 % U recovery.

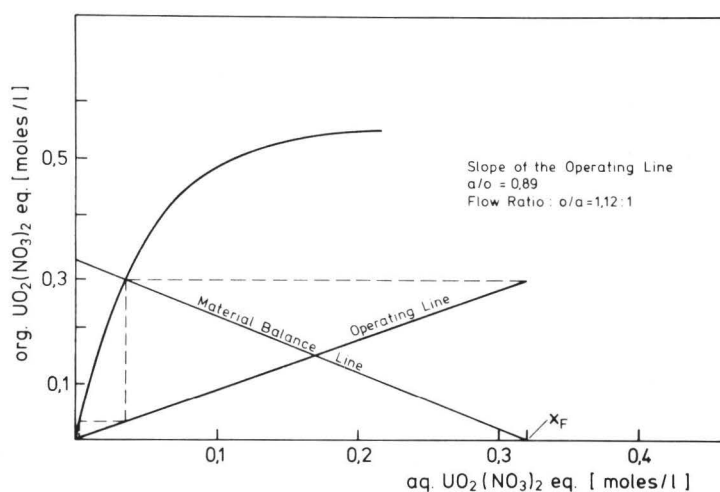


FIG. 5

Estimation of the minimum flowratio for a complete uranium recovery

With the corresponding flowratio $a/o = 1.12$ the thorium can't be extracted quantitatively. Furthermore, in the second extraction stage thorium would form a second organic phase which will cause a breakdown of the mentioned process. As conclusion, a single extraction of uranium leaving all other components including thorium behind in the aqueous phase will not succeed with 30 % by volume TBP in n-dodecane.

Because it is intended to recover each valuable element, a different flowsheet has to be applied, where the thorium content will determine the flowratio. Limiting factors for the thorium loading of the organic phase are the formation of a second organic phase on the one hand and the displacement of thorium from the organic phase by uranium on the other hand. Figure 6 presents the different equilibrium lines of thorium in presence of uranium concerning to the first four extraction stages. The intersections of the material balance lines with the equilibrium lines specify the composition of the organic phase with the corresponding aqueous phase. From these points and the initial feed concentration different minimum flowratios can be derived. The resulting operating line with the lowest slope determines the operating conditions of the extractor. Only in this case the thorium can be extracted totally without any trouble for the mentioned process. The deciding stage is the feed stage, where uranium is present in the highest concentra-

tion. The slope of the operating line amounts to $a/o = 0.105$ which corresponds to a flowratio of organic to aqueous phase of 9.5 to 1.

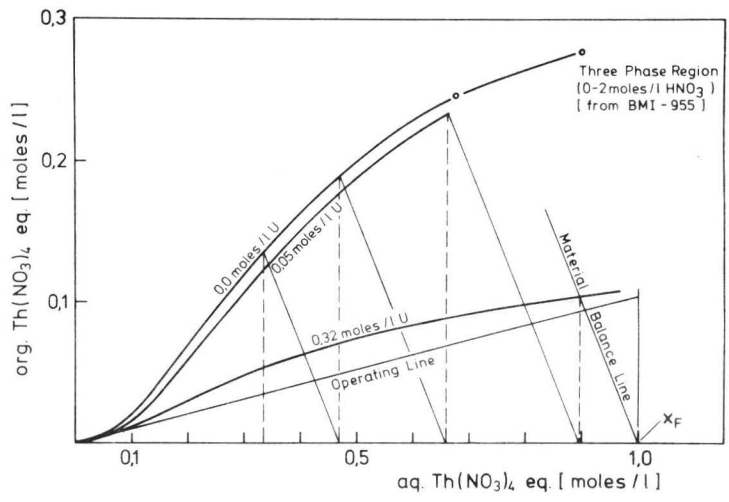


FIG. 6
 Estimation of the minimum flowratio for a complete thorium and uranium recovery

But even with this flowratio thorium isn't extracted quantitatively, because the equilibrium lines intersect with the operating line at an aqueous thorium concentration of about 0.05 moles/l (figure 7).

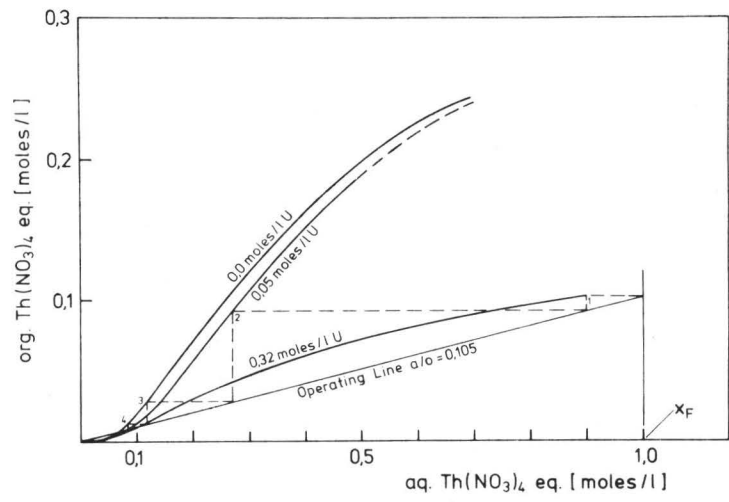


FIG. 7
 Extraction system for thorium

The resulting thorium loss is intolerable high, therefore it is necessary to use a salting agent in a later extraction stage. In the applied mixer settler nine extraction stages are disposable. After four theoretical extraction stages the point of intersection of the equilibrium line with the operating line is nearly attained. Further extraction stages do not raise the yield of thorium markedly. It is opportune to introduce the salting agent at this place. Because of the lower efficiency of the mixer stages five real extraction stages are recommended before the salting nitric acid is added (figure 8). Only a low flux of 13 molar nitric acid is necessary to achieve an acid concentration of about 2 or 3 moles/l in the sixth extraction stage.

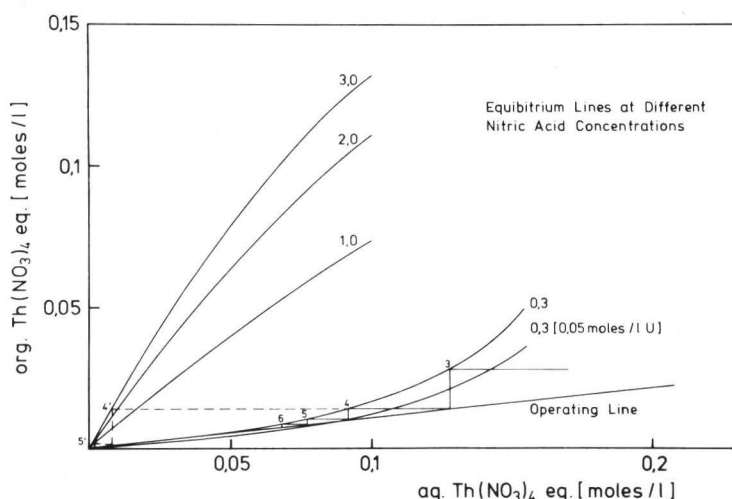


FIG. 8

Effect of the addition of salting nitric acid

This acid concentration is sufficient to allow a complete extraction of thorium in the last three extraction stages. The waste solution will then contain an acid concentration of about 1.3 moles/l.

5. CONCLUSION

The total heavy metal concentration in the feed solution of spent MEU fuel elements is similar to the well known two stage THOREX process (figure 2). No severe alternations to the THOREX process are necessary to achieve a complete extraction and separation of thorium and uranium with the new process. Further improvements of the new flowsheet are presented.

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THE EXTRACTION-CHROMATOGRAPHY METHOD FOR RECOVERY OF
TRANSPLUTONIUM ELEMENTS FROM IRRADIATED TARGETS IN A
LARGE LABORATORY SCALE

V.B.Dedov, V.N.Kosyakov, V.M.Semochkin,
I.K.Shvetsov, N.G.Yakovlev
Kurchatov Atomic Energy Institute

Moscow, USSR

ABSTRACT

Examples of recovery and purification of gram quantities of curium-244 as well as milligrams of californium-252 and berkelium-249 given in this report demonstrate the possibilities of the extraction chromatography. Some features of this method are also considered.

1. INTRODUCTION. The quantity of transplutonium elements (TPE) accumulated in nuclear power reactors as WWR will reach some kilograms per year for 1 Gwt(e) (1) and a construction of large plants will be required for their recovery. To solve this problem, national programs of the TPE production have been developed in a number of countries. These elements are produced by special irradiation of starting materials (heavy isotopes of Pu, Am, Cm) in high flux reactors followed by a chemical recovery and separation. It is necessary to study properties and possibilities using TPE isotopes in different fields of science and technology.

The irradiation and recovery processes are periodical and have rather small scale. As a rule, the quantity of starting materials after irradiation does not exceed some tens of grams, and that of accumulated TPE isotopes, for example californium-252, reaches only tens of milligrams and depends on the irradiation conditions.

On the basis of a long-term experience in reprocessing of irradiated targets for the recovery and purification of TPE isotopes we can recommend to use the extraction-chromatography method. The first results on the recovery and separation of TPE weight quantity by using extraction chromatography were published in ref (2), but the authors did not give any description of the columns and of the conditions used to carry out the process.

W. Muller et al (3) carried out purification of Am and Cm on the scale of tens of grams by extraction chromatography.

A one step scheme with application of extraction chromatography was used for the recovery of TPE isotopes from an irradiated target containing 203 mg of Cm isotopes (4).

A rather detailed description of the extraction chromatographic reprocessing of irradiated plutonium targets is also given in paper (5).

Examples of recovery and purification of gram quantities of curium-244 and milligrams of californium-252, given in this report demonstrate the possibilities of the extraction chromatography. Some features of this method are also considered.

2. EXPERIMENTAL

2.1. Requirements for an organic phase carrier.

The essence of this method is that an organic compound-extractant is retained on the hydrophobic carrier placed in a usual chromatographic column, with an aqueous phase passing through it.

Therefore the basic factor of this process is the distribution of the matter between two liquid phases, one of which is movable (aqueous) and the other (organic) is fixed on the carrier.

The process can also be performed with a reverse arrangement of the phases, but this version is not considered in the present report. The carrier properties must meet the following requirements:

1. Changes in its composition and properties caused by organic compounds, mineral acids and gamma-, alpha-radiation should be minimum.

2. A desirable quantity of extractant should be retained on its surface.

3. It should practically play no role in the sorption mechanism of extracting elements.

4. Its mechanical strength should be sufficient so that the sorbent weight and pressure would not cause compression of the sorbent and as a result, a significant increase in resistance to passage of the aqueous phase.

5. It must enable a remote replacement of the organic phase.

In our opinion silicagels of various types meet all these requirements. Undoubtedly application of carriers of other types, such as kieselguhr, fluoroplastic, copolymer styrene and divinylbenzene etc. is possible if the experiment conditions do not require keeping some of the above limitations.

2.2. Sorbent preparation.

The granular silicagel is powdered and fractions with particles of desired sizes are selected. The fractions obtained are scrubbed with conc. hydrochloric acid until iron is completely removed and with distilled water to neutral reaction and then are dried at 110-115°C for 2-3 hours.

The carriers can be made hydrophobic by treatment with dimethyldichlorosilane for better retainment of the organic phase. The treatment can be carried out in the gas or liquid phases. In the first case the carrier is placed above dimethyldichlorosilane and kept for several days; in the second case it is treated with 3-5% dimethyldichlorosilane solution in an easily volatile diluent (chloroform, ether etc.). After hydrophobisation the carriers are dried, calcinated at 250-280°C for 6-7 hours.

The sorbent itself can be prepared by two methods: "dry" and "wet". In the former method the carrier powder is mixed with two extractant diluted by a volatile solvent, which is removed by drying. As a result the dry powder of the sorbent is formed, and the particles are covered with the extractant.

In the "wet" method the carrier without the extractant is placed in a column which is sealed at the top and at the bottom by filters of some inert material. Then the column is evacuated and loaded with the extractant through the lower outlet till a complete carrier saturation with the organic phase. The extractant excess is removed by scrubbing with 10-15 column volumes, for example, 1 M NH_4NO_3 at a low pressure. In the case of the hydrofobicated carrier the loss of organic phase is practically not observed. Impregnation levels of unhydrofobicated silicagel are TOA=23-27%, TBP=22-34%, HDEHP=28-33% and for hydrofobic silicagel they are TO=43-45%, TBP=29-36%, HDEHP=45% of carrier volume, respectively.

It should be emphasized that the latter method of the sorbent preparation allows to carry out replacement of the extractant by a remote method without demounting the column. The organic phase is eluted from the carrier with the volatile solvent, the column is dried by vacuum and then the carrier is saturated with the organic phase as described above.

2.3. Examples of extraction chromatography application.

In view of shortlength of the present report the most interesting stages of the general schemes of irradiated targets reprocessing are only given here.

2.3.1. Group separation of transplutonium elements and rare-earth elements. 7.3g of heavy plutonium isotopes and 0,44g of americium and curium isotopes were separated in reprocessing the irradiated targets with initial plutonium-239 load. The fraction of Am (44.8% wt²⁴²Am, 48.5% wt²⁴³Am) and Cm (6.6% wt²⁴⁴Cm) contained also the rare earth fission products.

An attempt to separate TPE and REE by Tramex-process in mixer-settler did not appear quite satisfactory because of the corrosion of some apparatus parts and the TPE purification factor was only 100. The residual activity was approximately 2Ci and the volume of hydrochloric solution was 7 l.

The subsequent purification was carried out with the HDEHP-ammonium thiocyanate system (6) by the extraction-chromatographic method. The process scheme is given in figure 1. After the solution acidity was decreased down to pH=1, the solution volume was equal to 9 l. This solution was injected into the column loaded with silicagel particles 0.2 mm in diameter impregnated with HDEHP. Because of the high specific activity of the isotopes loaded the bright glow and escape of gas bubbles were observed in the sorption zone but it did not affect the experiment in any way.

In the first run the TPE recovery from thiocyanate solution was carried out using a one-step extractor and TBP in decane as extractant. The subsequent investigations of this process showed that it is better to use the diisoamyl ether of methylphosphonic acid for this purpose. This extractant has a distribution coefficient for TPE of about 2000. This enables to recover TPE by extraction chromatography.

The purification factor of TPE from fission products was better than $2 \cdot 10^4$ including the purification by tramex-process.

Recently the extraction chromatographic version of Talspeak-process has been applied for the group separation of TPE and REE (2) .

2.3.2. Separation of curium and californium.

The targets containing Pu-242, Am-241,243 and Cm-244 were irradiated in the high flux reactor SM-2 for a long time and then they were subject to the combined chemical reprocessing by the method described in (2) .

The Cm-Cf fraction was a 1 M nitric acid solution of volume 2.2 l and contained 3 g of Cm-244 and 1.44 mg of Cf-252. This solution was evaporated down to a 0.5 l volume and then the hydroxide of TPE was precipitated with a water solution of sodium oxide, it was washed with water and with acetone dissolved in 3 M nitric acid.

The acid was removed by evaporation, the residue was dissolved 100 ml of H₂O and then 50 ml of 1,5 M HNO₃ was added to obtain 0.5 M nitric acid. This solution resembles "a boiling one" because of the radiolytic gases were charged into the column for separation of Cm and Cf. In this process two columns were successively used, their sorption beds being 210 mm high, and they were 56 mm in diameter. Such arrangement of the columns allowed the remote control of this process.

The sorbent was a glass powder with particles of 0.2 mm in diameter. The operations are shown schematically in figure 2. The velocity through the columns was controlled by a pressure a little in excess of the atmospheric pressure and was kept at a value of 300 ml/hr. The elution of Cm was carried out with 0.5 M and that of Cf, with 3 M nitric acid. The Cm fraction volume was equal to 3.8 l and contained 99.72% of Cm and 0.17% of Cf; the Cf fraction volume was equal to 2.3 l and contained 99.83% of Cf and 0.28% of Cm. Thus the purification factors were for californium from curium better than $4 \cdot 10^2$, and for curium from californium better than $6 \cdot 10^2$.

2.3.3. Extraction of TPE from solutions, containing strong complexing agents.

For the group separation of TPE and REE we apply an extraction chromatographic version of the so called Talspeak-process 2,7,8, in which the extraction of the TPE from the complexone solution (1 M HLact + 0,08 M DTPA) is achieved by using trioctylphosphine oxide (TOPO) as an extractant after the preliminary addition of aluminium nitrate up to the concentration of 1 M. As it was shown by special experiments addition of aluminium decreases the pH of the complexone solution from 3.2 to 0.5 and the extraction efficiency of the TPE by TOPO sharply increases (by a factor of about 10^6).

The observed increase in the distribution coefficients seems to be due to several reasons:

- 1) aluminium nitrate is a strong salting out agent;
- 2) considerable increase in the acidity of the solution results in the suppression of the dissociation of DTPA and, therefore, in a decrease in the complex formation with TPE;
- 3) at high aluminium concentrations a competitive bounding of the complexing agents takes place.

In practice the following procedure was applied. The "complexone" solution (1 M HLact + 0,08 M DTPA) containing TPE obtained as a result of Talspeak-process after addition of aluminium nitrate passed through a column filled with silicagel impregnated with 30% TOPO in benzene. The silicagel volume was usually 1/20 of the initial solution volume. Then the column was washed with the pure solution of complexone containing aluminium and 4 M solution of NH_4NO_3 for the removal of the rest of the complexone and aluminium. The back extraction of TPE is performed with 6 M nitric acid (5-6 column volumes). The sorption zone of TPE and its movement along the column could be followed visually by watching the bright red glint of curium.

The extraction by TOPO with aluminium nitrate addition has the following advantages in comparison with the extraction by HDEHP with preliminary acidification:

- 1) the absence of the acidification stage, when a precipitate can be formed;
- 2) the possibility to concentrate the product;
- 3) a high purification factor ($\sim 10^3$) of TPE from zirconium and other fission and corrosion products.

This method was successfully applied for the purification of gram quantities of curium and milligram quantities of californium.

2.3.4. Recovery of ^{249}Bk from irradiated targets.

For the recovery of ^{249}Bk from the irradiated targets (^{242}Pu and isotopes of Am and Cm) an oxidation-reduction method is applied which is based on the extraction of Bk(IV) by HDEHP and selective back extraction of Bk(III) by a "complexone"

solution (2) . This method (so called Okvibek-process*) have been developed at our laboratory in 1969. The flow sheet of the extraction chromatography version of Okvibek-process is shown in FIG.3. This method permits with one column to attain the quantitative recovery of Bk with the simultaneous efficient purification not only from trivalent actinides and lanthanides but from curium as well.

The extraction of Bk from the "complexone" solution (DTPA in lactic acid) was accomplished with a column with TOPO, as it was discussed above. The additional purification of Bk from Zr and other fission and corrosion products (not less than 10^3) is performed at this stage.

The extraction chromatographic version of the Okvibek-process has been successfully applied since 1969 for Bk recovery in remote chemical processing irradiated targets containing gram quantities of ^{244}Cm , when specific activity (relating to α -radiation) reaches 50 Ki/l. The maximum dimensions of the columns applied were 30 mm in inner diameter and 300 mm in bed height. The high purification of Bk reached in this process allows to limit the hot cell operations by performing only the first cycle, and to perform the following purification stages already in glove box.

2.3.5. TPE concentrating.

In the laboratory practice wastes and washing solutions with relatively low content of TPE are often to be regenerated. Due to high values of the distribution coefficients of TPE,

TOPO can also be used. Preliminary experiments have shown that up to 300 column volumes of "complexone" solution with aluminium can be passed through TOPO column (20% wt on silicagel or polyethylene) till TPE break-through.

The method of concentrating is as follows. Aluminium nitrate is added to the solution to be processed, the quantity of the former is sufficient to precipitate hydroxide (~ 0.3 mg/ml). After the hydroxide has been separated, it is washed and then dissolved in a minimum volume of concentrated nitric acid. The solution obtained is evaporated to dryness and the salt is dissolved in the total volume of the "complexone" solution (1 M HLact + 0.07 M DTPA), which provides about 1 M aluminium concentration. Then the solution passes through the column filled with silicagel (or polyethylene powder) containing 20wt% of TOPO. The column dimensions are chosen so that the filled volume would be about 1/300 of the passed solution volume. Back extraction of TPE is performed with 6 M nitric acid (5-6 column volumes).

The total concentrating factor in using this technique is higher than 10^3 . It should be noted the concentration process is accompanied by efficient purification from many possible impurities such as Fe, Al, Cu, Zr and so on.

* Okvibek - is an abbreviation of the Russian name of the process Oxidation-Reduction Berkelium Recovery by Extraction with Complexone.

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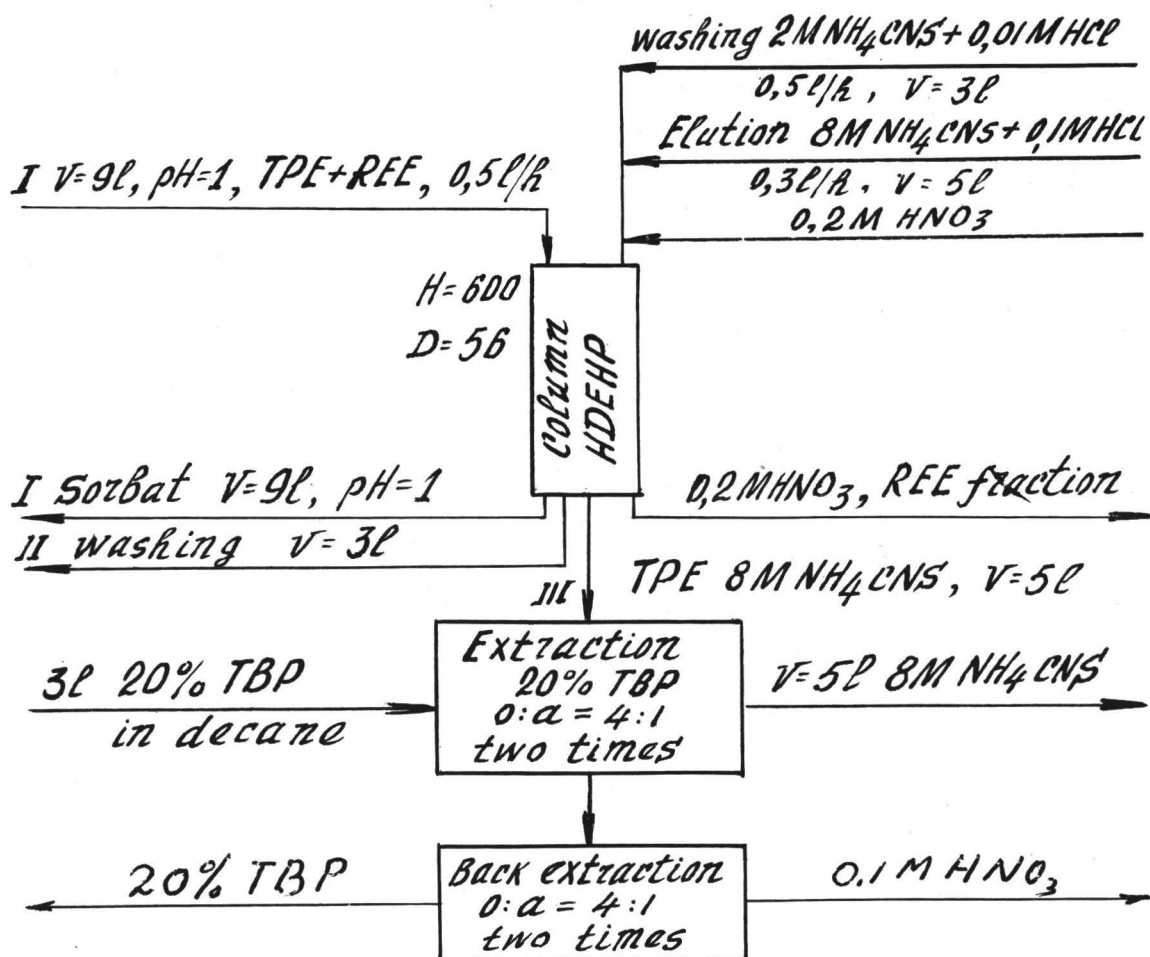


Fig. 1. The group separation of TPE and REE with system HDEHP- NH_4CNS

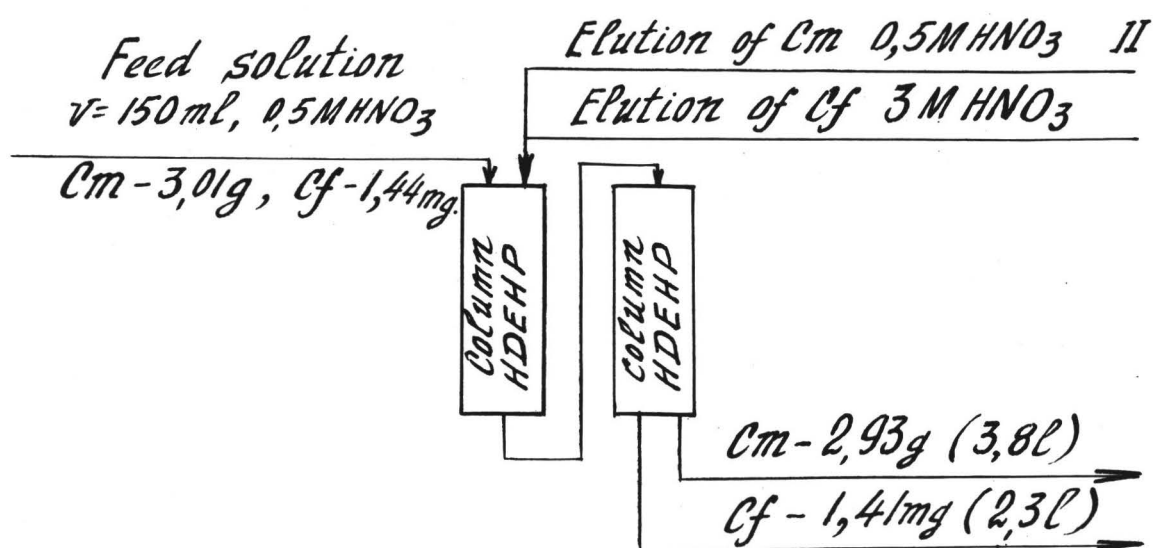


Fig. 2. Separation of Cm and Cf

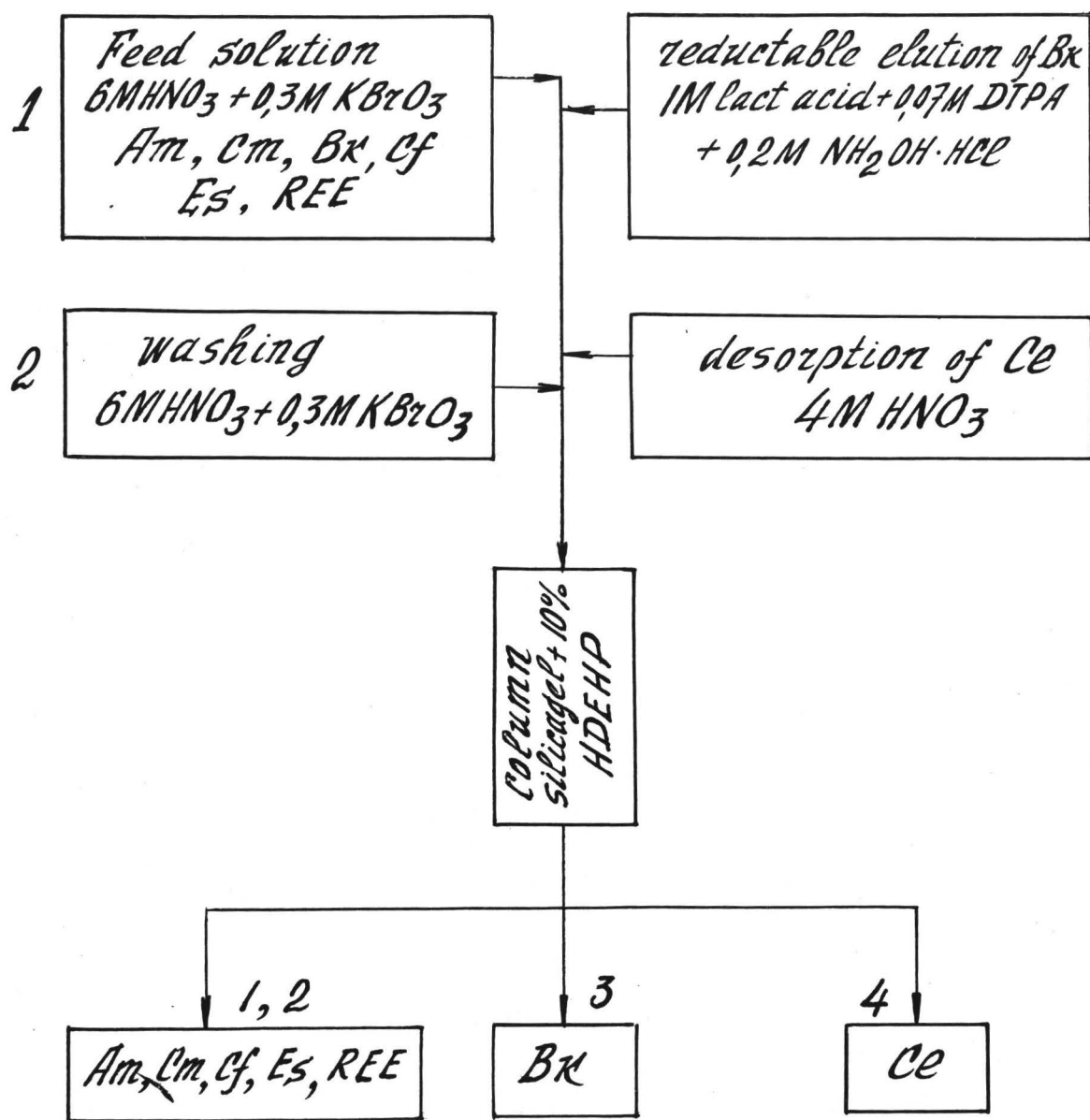


Fig. 3. Scheme of extraction-chromatographic separation method of Bk-249.

REMOVAL OF ACTINIDES FROM NUCLEAR FUEL REPROCESSING WASTES:
A PILOT PLANT STUDY USING NON-RADIOACTIVE SIMULANTS

(H. R. Maxey, D. B. Chamberlain,
L. D. McIsaac, and G. J. McManus, Exxon
Nuclear Idaho Company, Idaho Falls, Idaho)

ABSTRACT

Nuclear fuel reprocessing wastes generated at the ICPP contain small amounts of actinides, primarily Pu and Am. Removal of these actinides reduces the long term storage hazards of the waste. The development of a flow-sheet to remove trivalent actinides is discussed in this paper. Pilot plant studies used actinide simulants. As a result of these studies, the Height of a Transfer Unit (HTU) was selected as the better measure of pulse column separation efficiency.

INTRODUCTION

The Idaho Chemical Processing Plant (ICPP), located at the Idaho National Engineering Laboratory near Idaho Falls, Idaho is a multipurpose reprocessing facility for Department of Energy (DOE) fuels containing highly enriched uranium. Fuels routinely processed at the ICPP include stainless-steel-clad fast-reactor fuels, aluminum-clad test-reactor fuels, and zirconium-clad fuels for which the enrichment before burnup varies from 50% to 93%. The stainless-steel-clad fuel is electrolytically dissolved in HNO_3 , the aluminum-clad fuels are dissolved in HNO_3 - $\text{Hg}(\text{NO}_3)_2$, and zirconium-clad fuels are dissolved in HF. These multi-head-end dissolver solutions provide the feed for a multiple-solvent extraction system that is composed of a first cycle of tributyl phosphate (TBP) extraction followed by two cycles of methyl-isobutyl ketone extraction(1). The uranyl nitrate product from the extraction system is denitrated in a fluidized-bed to UO_3 for shipment. Dissolved aluminum and zirconium fuels are processed concurrently. A typical raffinate from such processing, designated coprocessing waste, is presented in Table 1. This stream is solidified to a free flowing granular material, called calcine, in a fluidized bed.

The presence of small amounts of actinide elements, primarily americium and plutonium, in this calcine causes it to be classified by the DOE as a transuranic waste. Such classification could require geologic disposal of

TABLE 1

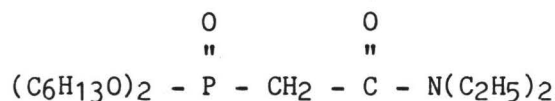
TYPICAL COMPOSITION OF ICPP COPROCESSING RAFFINATE

Macroconstituents		Actinides, g/l	
H ⁺ , M	1.62	Total U	2.0x10 ⁻⁴
Al ⁺³ , M	0.67	²³⁷ Np	1.24x10 ⁻⁶
Zr ⁺⁴ , M	0.45	²³⁸ Pu	3.70x10 ⁻⁴
F ⁻ , M	3.21	²³⁹ Pu	1.09x10 ⁻³
B ⁺³ , M	0.20	²⁴⁰ Pu	2.92x10 ⁻⁴
NO ₃ ⁻ , M	2.36	²⁴¹ Pu	1.29x10 ⁻⁵
Lanthanides, g/l	0.20	²⁴² Pu	4.33x10 ⁻⁵
Hg ⁺² , M	0.002	²⁴¹ Am	3.53x10 ⁻⁵
		²⁴³ Am	9.77x10 ⁻⁷
		²⁴⁴ Cm	5.87x10 ⁻⁷

the waste. The radioactive decay of these actinides in calcine is represented in Figure 1. The figure illustrates that, without removal of the actinides, the calcine is a transuranic waste for over 125,000 years. By removing the actinides from the calcine, the remaining fission product wastes could be stored in existing surface facilities until they decay to an acceptable level, typically 500 years. The actinide fraction could be stored geologically, or fabricated into fuel elements and fissioned as fuel in a fast reactor. Our pilot plant studies have established the feasibility of this process in pulsed extraction columns.

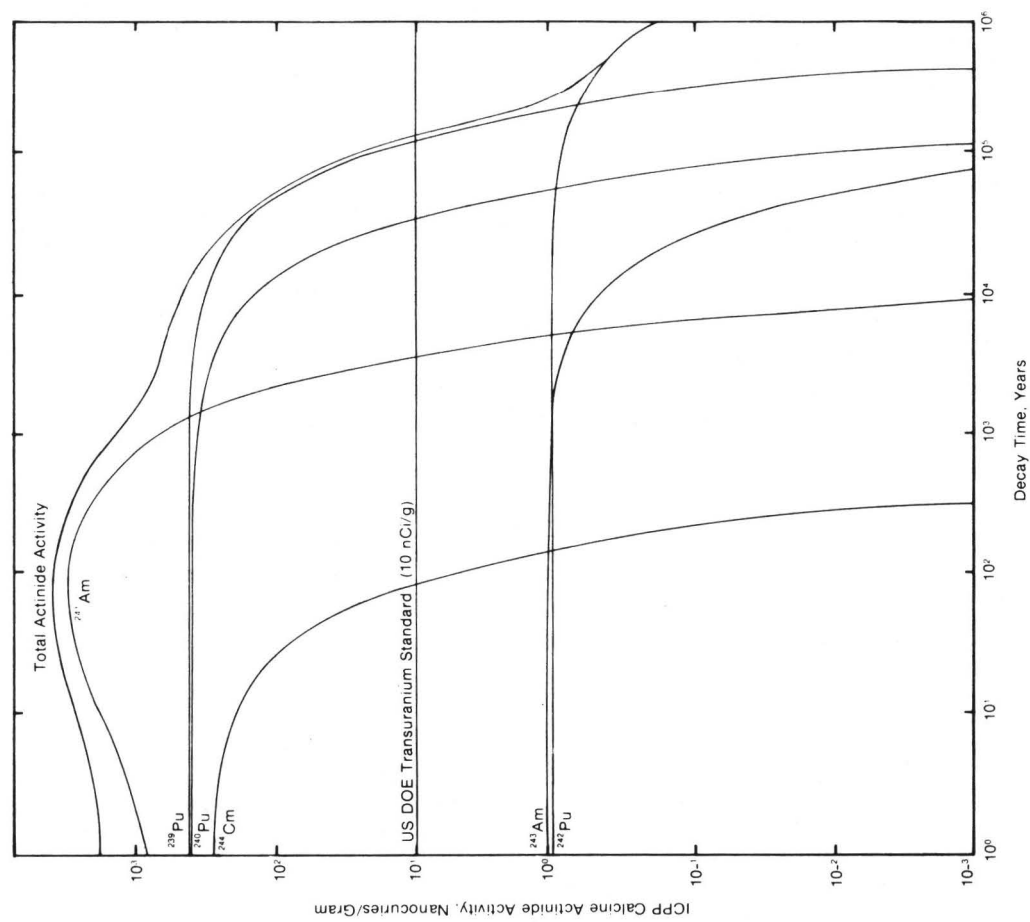
PROCESS CHEMISTRY

Dihexyl-N, N-diethylcarbamylnmethylenephosphonate (DHDECMP) is the extractant used in this process. DHDECMP is a bidentate organophosphorous compound with the following structure:

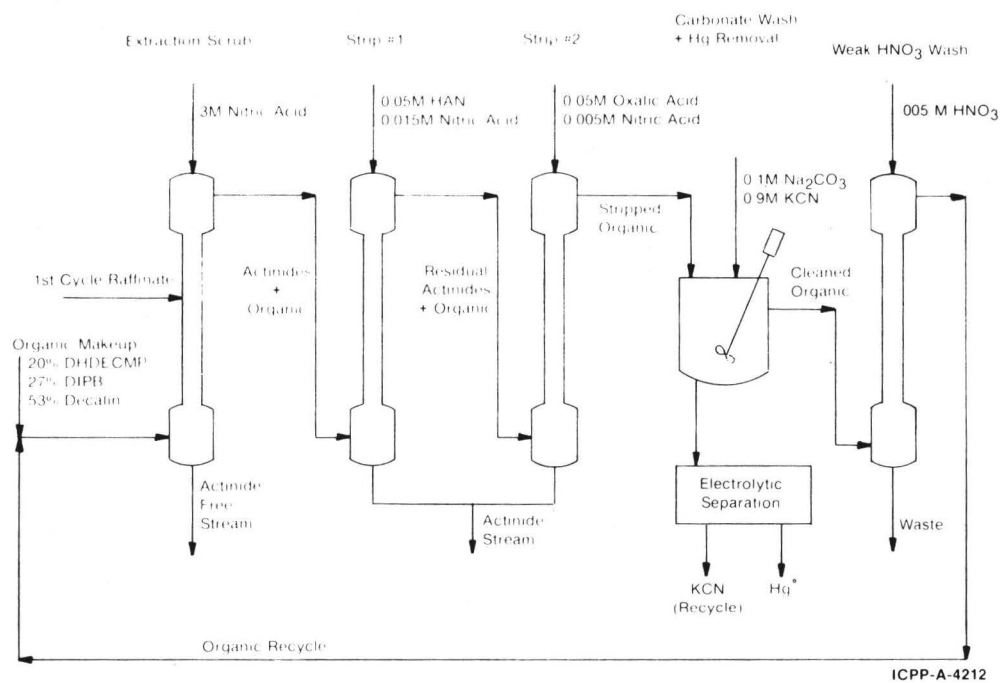


The selectivity of DHDECMP for trivalent actinides is the chemical basis for this process. Schulz(2) and McIsaac have reported on the synthesis and purification of DHDECMP and the effects of extractant concentration, diluent, temperature, contact time, and HNO₃ concentration upon extraction. The complexing and extraction of the actinide Americium (Am) can be represented by the mechanism shown in equation (1):





ICPP-A-4499
Fig. 1. Actinide Decay in ICPP Calcine



ICPP-A-4212
Fig. 2. Conceptual Actinide Removal Process

While the extraction of other actinides may differ in detail, they all proceed by the formation of a neutral species and are dependent upon nitrate and extractant concentrations. Thus, a high aqueous phase HNO_3 concentration promotes extraction, while stripping of the actinides from the pregnant organic is achieved by a low-aqueous phase concentration.

By using a mixed diluent of decalin and di-isopropylbenzene (DIPB), a favorable distribution coefficient of actinides without the formation of a second organic phase is attained. A 20 volume percent DHDECMP solution in a 2:1 solution of decalin-DIPB has a density of 0.9 and a viscosity of 3.0 centipoise at 20°C. The hydraulic properties of the system have proven to be acceptable. In addition, these diluents are inexpensive, and their flash points are in excess of 60°C.

PROCESS FLOWSHEET

The flowsheet of the actinide removal process is shown in Figure 2. The principal features of this process are as follows: a separation of the actinides from the TBP raffinate in column I; a stripping of the actinides from the pregnant organic in column II; a second stripping in column III to recover the Pu and U chemically unremovable in column II; removal of solvent degradation products in mixer-settler; a wash of the solvent prior to recycle to column I.

The feed solution, a TBP raffinate, is described in Table 1. This feed is contacted countercurrently by the DHDECMP solvent which removes actinides, lanthanides, and some HNO_3 from the chemically unadjusted feed. Because of its high feed concentration, a greater mass of Zr is extracted than that of the actinide/lanthanide fraction, even though its distribution coefficient is less than 0.01. For this reason, the pregnant organic is scrubbed with 3M HNO_3 to preferentially remove the Zr. Hydroxyl Amine Nitrate (HAN) reduces Pu to Pu(III) allowing most of it to be stripped in Column II along with the Am, HNO_3 and the lanthanides.

The subsequent unit operations are used to recover the solvent for reuse as an extractant, an essential feature of a solvent extraction flowsheet. Radiation from fission products in the aqueous feed promotes the formation of organic complexes of Pu which are not reduced with HAN strip solution. For this reason, a second strip, using oxalic acid ($\text{HO}_2\text{C}\cdot\text{CO}_2\text{H}$) is necessary. Hg, present as an aluminum cladding dissolution catalyst, is complexed by cyanide allowing it to be stripped away in a mixer-settler. Acidic organic degradation products are produced by the radiolytic degradation of the DHDECMP in the presence of acid, and are removed by a Na_2CO_3 neutralization in the same mixer-settler. A weak HNO_3 wash is used to polish the solvent prior to recycling to the extraction column.

SMALL-SCALE FLOWSHEET DEVELOPMENT

Much of the process chemistry was established using single separatory funnel extractions. Plant scale operations undoubtedly will operate countercurrently, so two types of laboratory experiments were performed on a countercurrent basis. A "batch pseudo countercurrent extraction," or a "simulated column," is a separatory funnel cascade(3) in which liquids are

repeatedly transferred from one funnel to another. Once chemical steady-state is achieved, the liquids in the separatory funnels have all physical properties which would be encountered in a multistage process. By using small amounts of chemicals, stagewise distribution coefficients and material balances can be determined and undesirable side effects, such as third phase formation, can be determined before costly pilot plant work is undertaken.

Over 80 percent of the actinide content of ICPP calcine is due to the isotopes of Am and Pu. Consequently, the extraction of these solutes down to the concentration range necessary to produce "actinide-free" wastes is a major goal of this project. The separation of Pu from ICPP coprocessing raffinates is represented as McCabe-Thiele operating diagrams for Pu and HNO_3 in Figures 3 and 4, respectively. These figures are representative of the data also collected for Am and for Ce, which was used as an actinide simulant in our pilot plant work. From these experiments, we concluded: (1) the extractable species behave as ideal solutes, as evidenced by the straight equilibrium lines; (2) the extraction and scrub sections operate efficiently, because of pinches for actinides in the scrub section and HNO_3 and Zr in the extraction section; (3) two stages of scrubbing remove the co-extracted Zr; and, (4) the actinide free raffinate can be produced. The pregnant organic was effectively stripped in a five stage simulated column.

Virtually all experiments in this program were performed with nonradioactive solutions containing actinides. Since the presence of β - γ activity may cause unfavorable changes in equilibrium or the formation of highly stable organic complexes, which may not follow the design flowsheet, some experiments using actual ICPP raffinates were necessary. One of us (Lyle McLissac) has used a miniature mixer-settler which is small enough to be placed in a shielded cell. This mixer-settler has six extraction stages and two scrub stages. Using one liter of ICPP coprocessing raffinate as feed, chemical steady state was reached in the mixer-settler in ten hours. The results of this test are presented in Table 2. It is evident that the actinide-free raffinate was produced. A six stage strip mixer-settler was used to remove the actinides from the pregnant organic. Oxalic acid, present in the strip raffinate, caused the lanthanides to precipitate. Consequently, provision was made in the flowsheet for two strips.

TABLE 2
RESULTS OF MINIATURE MIXER-SETTLER EXPERIMENT

	Am		Pu	
	Concentration (g/l)	Calcine ^a Equivalent (nCi/g)	Concentration (g/l)	Calcine ^a Equivalent (nCi/g)
Feed	1.67×10^{-5}	~ 200	1.08×10^{-3}	~ 310
Mixer-Settler	1.7×10^{-8}	~ 0.2	3.45×10^{-7}	~ 0.10
Raffinate				

^a 1 l coprocessing raffinate calcines to ~ 250 g.

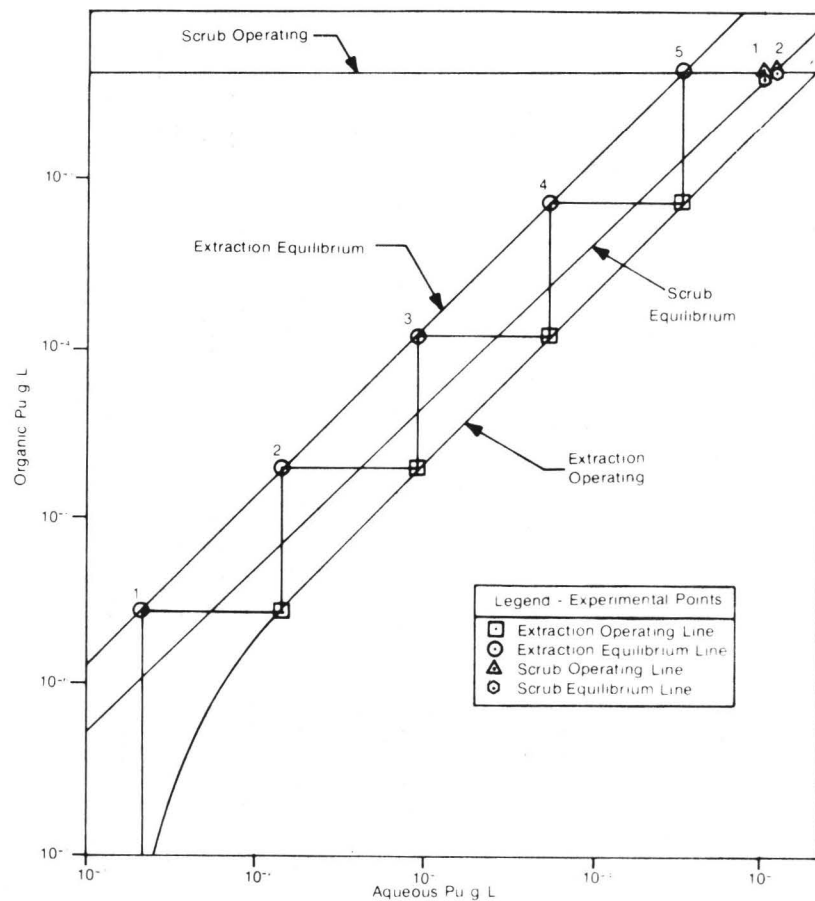


Fig. 3. Pu Operating Diagram: Batch Simulated Compound Column

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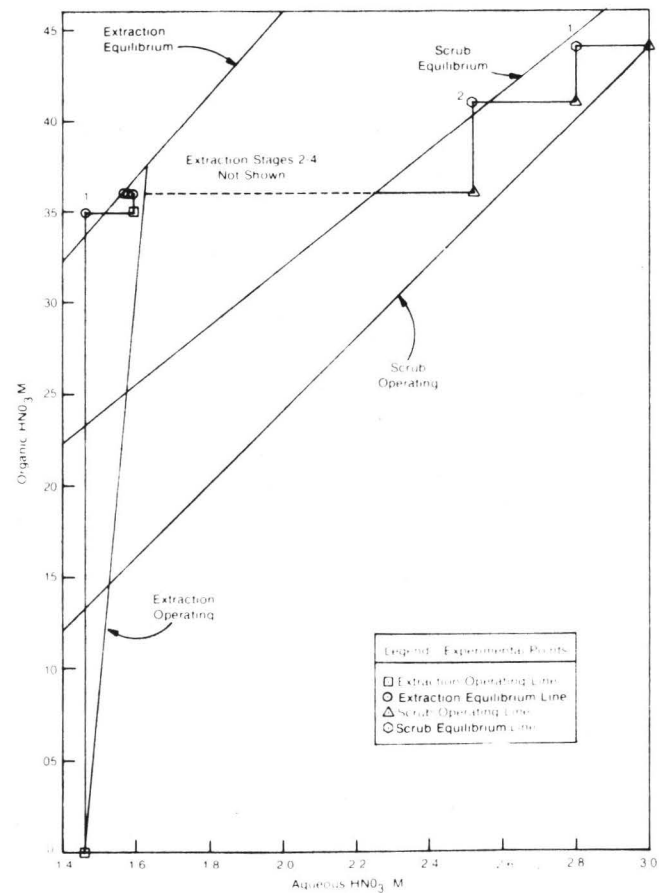


Fig. 4. HN03 Operating Diagram: Batch Simulated Compound Column

ACC-A-4035

PILOT PLANT STUDIES

The ICPP uses pulse sieve plate extraction columns for the recovery of U. Similar columns were used for pilot plant verification of the actinide removal process. Each of these columns is constructed of 5.1 cm (two inch) pyrex pipe and has stainless steel sieve plates spaced 5.1 cm apart. The plates have 0.3 cm diameter holes and have a free area of approximately 25 percent; they are wetted by the aqueous phase. The columns have samplers capable of separating individual aqueous and organic phases.

The hydraulics of this process in pulse columns have been acceptable and are described elsewhere.(4) Our pilot plant cannot be used for radioactive service. So, the use of actinide — or fission product — bearing streams was not possible. Instead, Ce(III) was chosen as the extractable species because it is a non-radioactive rare earth chemically similar to Am(III). The pilot plant results of the extraction of Ce from synthetic i.e., non-radioactive, coprocessing feeds and the subsequent stripping from the pregnant organic are presented in Table 3. From these tests, we have found that the Ce Height of a Transfer Unit (HTU) for extraction is reasonable, usually about 0.55 m. This is in the range of HTU's reported for other diffusion processes.(5) The variation of HTU with pulse amplitude and frequency is similar to that of PUREX processing.(6) We have also found that the number of scrub stages is relatively insensitive to feed location. There are usually two theoretical stages of scrubbing for Ce, and there is little Zr in the extract, indicating satisfactory column performance.

How applicable is this information to the extraction of actinides in pulse-columns in a plant scale actinide removal process? The concentration of actinides in the coprocessing feed is only about one percent of the Ce concentration used in these tests. Moreover, the presence of several actinides, though chemically similar to one another adds uncertainties. For example, hafnium and zirconium are also chemically similar, yet their separation can be made using TBP.(7) Therefore, chemical similarity does not ensure similar extraction behavior. To study the effects of solute upon extraction behavior, we extracted Ce, Th, and U from 1.5 M HNO_3 , both in simulated columns and in pulse columns. (A Th precipitate formed in the coprocessing feed preventing the use of this solution for the tests.) Ce, Th, and U are chemically similar metal solutes differing primarily in f orbital electrons. They do differ in valence, but so do the actinides in coprocessing feeds. For all tests, the solute feed concentration was 1.4×10^{-3} g moles/l. Simulated column tests proved that the extraction was not pinched, and therefore, similar. High distribution efficiencies of 41 and 64 for U and Th, respectively, meant that these solutes could not be analyzed after several contacts.

These same extractions were then performed in the pulse columns. Column separation efficiencies, expressed as HTU's, are presented in Table 4 for the overall extraction column, sections of the extraction column, and the concentrated end of the column through a midpoint. Data are shown for different pulsing frequencies. Sources of error in these calculations were: (1) Th and U values were below their detection limits in much of the column, (2) solute was sometimes present in the feed organic, and (3) mass transfer which occurred not only in the plate section but also in the upper disengaging head of the columns. In addition the data were screened using material

TABLE 3
OPERATING AND SEPARATION DATA FOR DHDECM⁵ EXTRACTION AND STRIPPING OF Ce

Column ¹ Section	Section Height (m)	Pulse Amplitude (Cm)	Pulse Frequency (CPM)	Percent of Flooding	Section ² Phase Ratio (A/O)	Volume Velocity (l/h·cm ²)	Stream Composition g Ce/l			HTU Column Section ⁴ (m)
							Feed ³	Raffinate	Extract	
Extraction	5.03	1.1	40	NM ⁵	2.18	3.25	0.23	0.0054	0.41	0.92
Extraction	3.78	1.1	40	NM	2.28	3.26	0.23	0.0127	0.45	0.90
Extraction	3.78	1.1	40	NM	2.12	3.08	0.40	0.01	0.81	0.68
Extraction	5.06	2.5	15	80	2.20	3.70	0.20	0.003	0.39	0.48
Extraction	5.06	2.5	20	80	2.20	3.55	0.21	0.001	0.43	0.59
Extraction	5.06	2.5	21.4	80	2.20	3.48	0.21	0.0003	0.45	0.47
Extraction	5.06	2.5	30	50	2.20	1.77	0.24	0.0006	0.51	0.51
Extraction	5.06	2.5	30	70	2.20	2.48	0.24	0.001	0.47	0.58
Extraction	5.06	2.5	30	80	2.20	2.83	0.21	0.001	0.45	0.58
Extraction	5.06	2.5	30	90	2.20	3.18	0.24	0.001	0.51	0.57
Extraction	5.06	2.5	40	80	2.20	1.98	0.20	0.0004	0.43	0.50
Strip	6.63	1.1	40	NM	1.71	2.81	0.39	0.22	0.0003	1.71
Strip	2.86	2.5	35	80	1.00	5.81	0.35	0.37	0.02	0.98
Strip	2.86	2.5	40	80	1.00	4.68	0.45	0.42	0.02	0.90
Strip	2.86	2.5	60	80	1.00	1.60	0.45	0.44	0.001	0.46

1. Extraction and scrub operated in compound column; total column height, including scrub section of 6.6 m
2. Scrub section phase ratio (A/O) of 0.2
3. Feed composition represents aqueous feed to extraction/scrub column and organic feed to strip column
4. Ce scrub HTU's typically were 4.9 m
5. Not Measured

TABLE 4
PULSE COLUMN SEPARATION EFFICIENCIES FOR EXTRACTION USING Ce, Th, & U

Operating Conditions, 2.5 Cm Pulse (cycles/min)	Solute	Height of a Transfer Unit, m					Feed Point Through Section 1	Feed Point Through Section 2
		Overall Column	Section 1, 0.64 m	Section 2, 0.64 m	Section 1-2, 1.28 m	Section 3, 0.94 m		
20	Ce	0.25	0.23	0.24	0.23	0.32	0.18	0.20
	Th	0.35	0.22	0.29	0.21	NM	0.17	0.21
	U	0.68	*	0.22	*	NM	0.15	0.18
30	Ce	0.23	0.15	0.17	0.18	0.16	0.12	0.16
	Th	0.32	0.17	0.35	0.23	NM	0.14	0.20
	U	0.42	0.18	*	*	NM	0.14	0.18
40	Ce	0.51	0.47	0.48	0.47	0.66	0.33	0.39
	Th	#	*	*	*	NM	0.12 [#]	0.20 [#]
	U	0.40	*	*	*	*	0.13	0.18
50	Ce	#	0.11	0.11	0.13	*	*	*
	Th	#	0.17	*	*	NM	*	*
	U	#	0.21	NM	*	NM	0.13 [#]	0.15 [#]

- # Column material balance did not close to within 10%
 * Section material balance did not close to within 25%
 NM Not measurable due to solute value below detection limit.

balances. Overall column analyses had to meet a ten percent material balance. The interstage analyses were rejected if they did not fall within a 25 percent material balance. Nevertheless, these data were grouped by solute for each operating condition. The four operating conditions were chosen solely to avoid the bias which might be associated with any particular one. ANOVA(8) tables were constructed to test the following null hypothesis: for each frequency, the HTU is different for the sample population for each of the solutes, Ce, Th, and U. In other words, if the null hypothesis is not satisfied, then the HTU is the same for all three solutes at a particular frequency. By this test, the HTU was found to be the same for the three solutes for 20, 30, and 50 CPM. In these tests, the F values chosen were for the five percent level of significance. Similar comparisons for the Height Equivalent to a Theoretical Stage (HETS) were not as conclusive. While the data are not overly forceful, it seems that the HTU is the better method of measuring column efficiency. The HTU appears to be valid for several solutes and over wide concentration ranges.

For plant operation, the pulse columns could probably be pulsed at 40 cycles per minute, 2.5 cm per pulse. At these operating conditions, the HTU should be no greater than 0.75 m even considering changes resulting from scale-up. (Sege(9) found that HTU increased by no more than 50% with an increase in column diameter of 167%.) Applying this to the feed described in Table 1, a 7.5 meter column (i.e., 10 transfer units) will deliver a raffinate which, when calcined, will contain less than 10 nCi of actinides per gram of waste.

SUMMARY AND RECOMMENDATIONS

Our pilot plant efforts have been largely directed to the performance of the extraction column. The raffinate from this column, an actinide-free stream, is the product of this process. While actual radioactive feeds have been used only in a limited number of tests, the analogies drawn from the simulated column and the solute comparison tests have shown us that the process will work in actual service. It also appears that the HTU is a good indicator of pulse column operation for several solutes through large concentration differences.

The hydraulics of the first strip have been proven in the pilot plant. The mass transfer of the strip operations has been proved in bench scale experiments but not in the pilot plant. These operations need to be further established. Nevertheless, it appears that the actinide removal process is feasible for ICPP feeds. Thus, the ICPP waste can be separated into two fractions, one of which is essentially nonradioactive within 500 years, and a much smaller fraction which may require geologic isolation.

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RECOVERY AND PURIFICATION OF AMERICIUM FROM MOLTEN SALT EXTRACTION RESIDUES

James D. Navratil, Larry L. Martella, and
Gary H. Thompson
Rockwell International
Rocky Flats Plant
P.O. Box 464
Golden, Colorado 80401

ABSTRACT

Americium recovery and purification development at Rocky Flats involves the testing of a combined anion exchange - bidentate organophosphorus liquid - liquid extraction or extraction chromatography process for separating americium from molten salt extraction residues. Laboratory-scale and preliminary pilot-plant results have shown that americium can be effectively recovered and purified from impurity elements such as aluminum, calcium, magnesium, plutonium, potassium, sodium, and zinc. The purified americium oxide product from the liquid - liquid extraction process contained greater than 95% AmO_2 with less than 1% of any individual impurity element.

INTRODUCTION

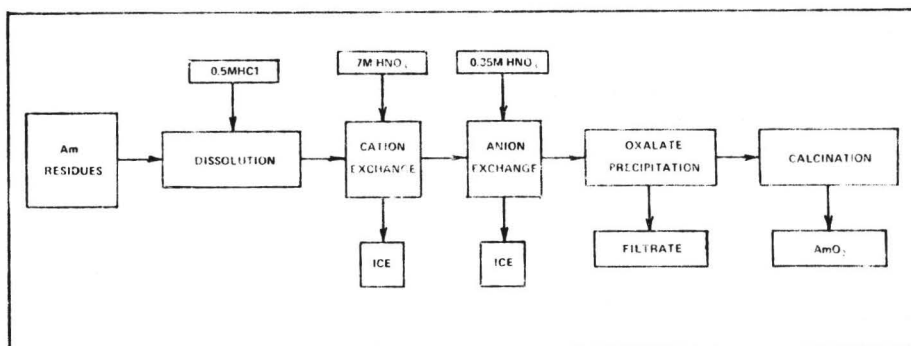
The Rocky Flats Plant (RFP) has a large facility to recover plutonium from miscellaneous scraps and residues. A by-product in the plutonium recovery stream is americium from the decay of plutonium-241. Currently a NaCl-KCl-MgCl_2 eutectic salt is used at Rocky Flats to separate americium from plutonium in a molten salt extraction (MSE) process (1).

As a consequence of experimental runs and changes in process salt mixtures, a variety of waste salts and alloys have been produced, and much of this material is in storage. These waste products contain varying quantities of aluminum, calcium, magnesium, sodium, potassium, and zinc, as well as plutonium and americium.

Although alloys produced during metallothermal reduction clean-up of waste salts are not being processed, processing of waste salts (except those containing aluminum and zinc) is being done by the RFP americium recovery process shown in Figure 1. The process includes (1) dilute hydrochloric acid dissolution of residues; (2) cation exchange to convert from the chloride to the nitrate system and to remove gross amounts of monovalent impurities; (3) anion exchange to remove plutonium; (4) oxalate precipitation; and (5) calcination at 600°C to yield AmO_2 . AmO_2 which meets specifications ($>95\%$ AmO_2 , $<1\%$ individual contaminant elements) is sent to the Department of Energy Isotope Pool.

FIG. 1

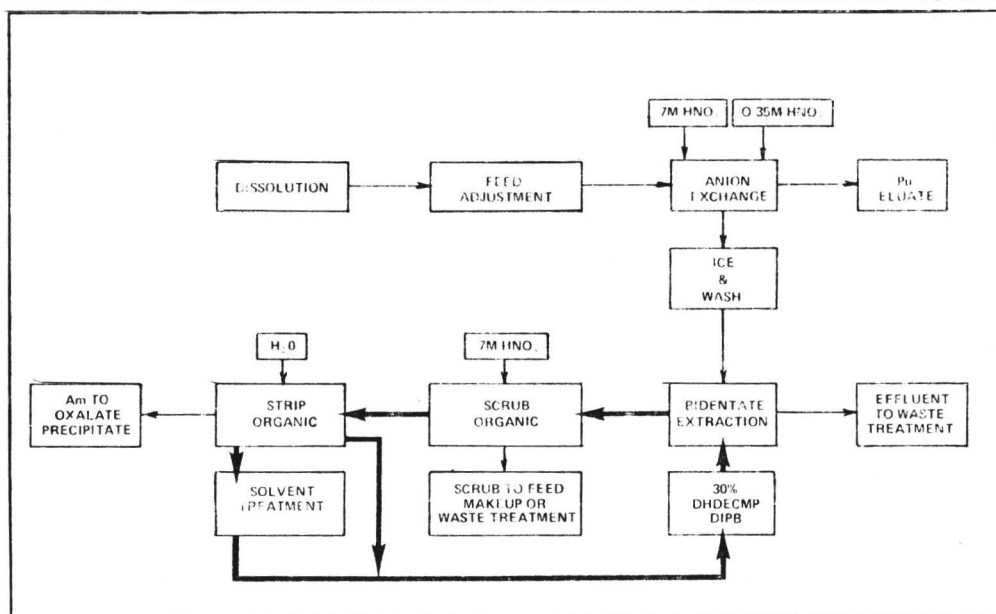
Rocky Flats Americium Recovery Process



Americium recovery development at Rocky Flats comprises work to improve the existing process as well as to introduce new methods, especially those that can partition americium from aluminum and zinc since the present cation exchange process cannot do this effectively. One new method is a combined anion exchange - bidentate organophosphorus extraction process. The conceptual flow sheet for the process is shown in Fig. 2. The bidentate, dihexyl-N, N-diethylcarbamoylmethylenephosphonate (DHDECMP), extracts actinides and lanthanides, but does not extract common RFP contaminants, e.g. aluminum and zinc. No lanthanides are used in process streams at RFP.

FIG. 2

Conceptual Flow Sheet For Processing Molten Salt Extraction Residues



The actinides are extracted from high acid (e.g. 7M HNO₃) solutions and can be back-extracted with dilute acid. The method is therefore easily used with the ion column effluent from the anion exchange plutonium recovery step.

The other new method fits the same flow sheet except that the extractant (DHDECMP) is absorbed on a non-ionic macroreticular support resin replacing the solvent extraction equipment with ion exchange columns.

This report describes attempts to improve the recovery of americium by the development of a process that will recover americium from residues containing aluminum as well as other common impurities. Results of laboratory and preliminary pilot-plant tests will be described.

EXPERIMENTAL

Materials

The alloy residues contain approximately 15% Al or Zn, 44% Mg, 29% Pu, 2% Am, and other impurities. The residues are dissolved by placing the alloy metal in 0.35M HNO_3 and slowly adding concentrated HNO_3 . Time is allowed between additions of concentrated HNO_3 for the dissolution reaction to subside. The solution is adjusted to 0.1M F^- with concentrated HF to remove any polymeric or residual plutonium. After filtration through Whatman 42 filter paper, the solution is adjusted to 7M HNO_3 .

Plutonium in this feed solution is removed by an anion exchange column process (Fig. 1). The anion exchange resin is Dowex 1-X4, 50 to 80 mesh nitrate form, obtained from BioRad Laboratories. Ferrous sulfamate is added to the solution to eliminate hexavalent plutonium, and the feed is passed through the column. The ion column effluent (ICE) contains the americium and impurities. Residual americium and impurities are washed from the column with 7M HNO_3 and the wash is combined with the ICE; this is the feed to the bidentate process. Plutonium is eluted with dilute nitric acid and returned to the production stream.

The DHDECMP for the liquid - liquid extractions was obtained from the Wateree Chemical Company, Lugoff, South Carolina, and was purified by an ion exchange method to approximately 67% pure; the method and extractant impurities have been described elsewhere (2,3). The DHDECMP for the chromatographic extraction tests was obtained from Bray Oil Company, Los Angeles, California. This material, 80% pure, was used without further purification. Diisopropylbenzene (DiPB) diluent was obtained from Pfaltz and Bauer, Inc. The solvent is 30% DHDECMP in DiPB.

The adsorbent is prepared by the following method. Amberlite XAD-4 resin is washed with acetone or methyl alcohol, then dried. The adsorbent is slurried in 50 vol% CCl_4 - 50 vol% DHDECMP. (This step is done in a beaker, as the adsorbent swells in this solvent and can pressurize and burst a column.) The swollen adsorbent is then poured into a column and the solvent mixture removed by vacuum. The column is filled with 80% DHDECMP and allowed to stand overnight. Excess 80% DHDECMP is removed by vacuum.

Liquid - Liquid Extraction

Americium in the combined wash and ICE was removed by liquid-liquid extraction in which 2.5 l of feed was extracted with 0.5 l of solvent (phase ratio, $r = 0.5$) with mixing for 15 minutes. This batch process was repeated with fresh batches of solvent until the americium concentration was $< 1.9 \times 10^{-2}$ g/l; three extractions were required.

Residual amounts of extracted impurities were removed from the extract by 7M HNO_3 scrubbing. Three to five extractions were made using an $r = 0.2$. The scrub raffinate was either sent to feed acid adjustment or discarded depending upon americium content. The americium was then stripped from the solvent with water (five to seven extractions) using an $r = 0.2$. The americium in the strip liquor was precipitated with oxalic acid, and the americium oxalate was calcined to AmO_2 .

Extraction Chromatography

In the lab scale extraction chromatography method, the DHDECMP-impregnated Amberlite XAD-4 was loaded into a column 1.8 cm dia. x 23.5 cm and conditioned with 7M HNO_3 . The americium feed was fed to the column at 1.5 ml/min until a total of 300 ml had been fed. The column was washed with 200 ml of 7M HNO_3 at 1.7 ml/min, then eluted with deionized water until elution was complete (determined radiometrically). Five to seven 50 ml fractions were required for elution. Samples were submitted for analysis.

In The Pilot Plant Tests

The dissolution feed (83 l) having a concentration of 15.7 g/l plutonium and 2.16 g/l americium was passed over 4 columns of anion exchange resin 15 cm x 122 cm containing Dowex 11 (20-50 mesh) and Dowex 1-X4 (50-80 mesh) resin individually. The effluents from this process became the americium feed after an evaporation step. The americium recovery was done with four columns in series. The first was a 10 cm dia. x 38 cm column containing Dowex 1-X4 (50-100 mesh) resin used as a polishing column for plutonium removal. The next two columns 10 cm dia. x 61 cm contained 3 litres each of XAD-4 resin with absorbed DHDECMP for americium recovery. The fourth column 10 cm dia. x 38 cm contained 2 litres of unconditioned XAD-4 resin for recovery of any solubilized DHDECMP from the previous columns.

The chromatographic procedure consists of (1) conditioning the columns with 7M HNO_3 , (2) passing the feed in 7M HNO_3 over the columns, (3) washing the impurities from the column with 7M HNO_3 and, (4) eluting the americium from the column with H_2O .

RESULTS AND DISCUSSION

Liquid - Liquid Extraction

Table I shows the average results of three laboratory runs of the solvent extraction step (after the plutonium was removed by anion exchange) using feeds from both the aluminum and zinc alloys and sodium/potassium residues. The major elements are shown before the solvent extraction step and in the final strip liquor. The data show that americium was effectively recovered and decontaminated from aluminum, magnesium, sodium, zinc, and other impurity elements in all runs.

Since aluminum residues are our major concern, pilot-plant testing was initiated on these residues. Results of the pilot-plant test of the liquid-liquid solvent extraction test are shown in Table II. Only 4 l of approximately 17 l of americium strip liquor were used in the precipitation step. Decontamination from Al and Mg was excellent with decontamination factors (DF) of 72 and 444, respectively. The corresponding DF for plutonium was 10. (DF is the ratio of impurity in the feed to impurity in the strip liquor).

TABLE I
RESULTS OF PROCESSING MSE RESIDUES

	<u>Major Elements mg</u>											
	<u>Am</u>	<u>Pu</u>	<u>Fe</u>	<u>Al</u>	<u>Mg</u>	<u>Na</u>	<u>K</u>	<u>Ca</u>	<u>Cl</u>	<u>F</u>	<u>Zn</u>	<u>Pb</u>
Al Feed	23	0.04	19	158	459	78	136	2	207	56	-	-
Strip Liquor	18	0.004	0.57	<0.1	<0.1	0.23	<.1	0.79	<0.1	7	-	-
Zn Feed	30	0.08	30	11	135	63	113	0.75	905	144	2940	9
Strip Liquor	24	0.04	6	<0.6	<0.3	<0.6	<0.3	<0.3	3	< 1	<0.3	<0.3
Na/K Feed	5.5	0.2	3	<2	120	800	1500	0.3	3500	6.3	<0.2	0.6
Strip Liquor	4.5	0.07	3	<2	<0.1	1	1	<0.1	3	0.2	<0.2	<0.3

TABLE II
RESULTS OF PILOT SCALE RECOVERY OF AMERICIUM FROM DISSOLVED Al-Mg ALLOY FROM
MSE PROCESS

	<u>Concentration g/l*</u>			
<u>Stream</u>	<u>Am</u>	<u>Pu</u>	<u>Al</u>	<u>Mg</u>
Feed	0.15	8.17×10^{-3}	0.385	1.02
Strip Liquor	0.14	7.5×10^{-4}	0.005	0.002

*Single Determination

Analysis of the final AmO₂ product is shown in Table III. Al and Mg were below the detectable limits for these elements. The product met specifications of > 95% AmO₂ with less than 0.5% Pu and less than 1% of any other single contaminant.

TABLE III
IMPURITIES IN AMERICIUM OXIDE PRODUCT*

	<u>Impurity Concentrations, µg/g**</u>				
<u>Plutonium</u>	<u>Aluminum</u>	<u>Magnesium</u>	<u>Iron</u>	<u>Lead</u>	<u>Potassium</u>
3240	<100	<50	524	645	120

* Specifications require > 95% AmO₂ with less than 1% of any individual impurity and less than 0.5% Pu.

** Single determination.

Extraction Chromatography

The results of the lab scale extraction chromatography tests are shown in Table IV. In spite of some analytical problems, it is evident that

americium was decontaminated from aluminum and magnesium.

Table VI shows analytical results of the americium feed after evaporation and the americium product. A flow rate of 10 l/hr. was maintained throughout the run. Only 15 litres of 7M HNO₃ was used for impurity removal. The results show more americium recovered than actually processed 35 grams recovered versus 33 actually loaded.

TABLE IV
RECOVERY AND PURIFICATION OF Am FROM Al-Mg
MSE RESIDUE BY EXTRACTION CHROMATOGRAPHY

<u>Test</u>	<u>Stream</u>	<u>Composition</u>			
		<u>Am,mg</u>	<u>Pu,mg</u>	<u>Al,mg</u>	<u>Mg,mg</u>
1	Feed	35	0.04	81	204
	Effluent	2	3×10^{-4}	89	200
	Wash*	4	+	+	+
	Product**	22	0.3	0.4	0.18
2	Feed	17	0.02	39	97
	Effluent	0.037	0.0015	25	65
	Wash*	+	+	+	+
	Product**	16	0.2	<0.2	0.2
3	Feed	29	0.04	68	170
	Effluent	0.4	0.003	57	+
	Wash*	3.5	0.0012	+	+
	Product**	25	0.2	<0.45	<0.23

* 7M HNO₃

** Strip

+ Not available

TABLE VPILOT PLANT RECOVERY OF ACTINIDES FROM Al-Mg ALLOY USING DHDECMP-LOADED AMBERLITE XAD-4 RESIN

<u>Composition</u>		
<u>Element</u>	<u>Feed, g</u>	<u>Product, g</u>
Am	33	35
Pu	5.5	0.24
Cu	139	1.0
Mg	312	3.2
Al	141	1.4

CONCLUSIONS AND FUTURE WORK

Laboratory results have shown that americium can be recovered and purified by liquid - liquid extraction well as chromatographic techniques using the bidentate DHDECMP.

Recovery and purification of americium was demonstrated using the liquid - liquid process on a pilot plant scale. The americium oxide product prepared from the strip liquor met specifications.

Pilot plant testing using the extraction chromatography technique was shown to be promising for future development. More testing will be conducted in the area of washing volumes and solubility of the organic after successive runs.

Pilot plant solvent extraction equipment is being installed at RFP. This system will be used for testing americium recovery using liquid - liquid extraction on a continuous basis. The two systems will be compared at a later date.

ACKNOWLEDGMENT

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THE EUROWATT PROCESSTreatment and Disposal of Spent Organic Solvent
from the Purex Process

H. Eschrich, L. Humblet, and J. van Geel

Eurochemic

MOL, Belgium

ABSTRACT

The Eurowatt process involves the quantitative extraction of tributyl phosphate (TBP), degradation products, and radionuclides from spent solvent mixtures by anhydrous phosphoric acid resulting in the recovery of a decontaminated diluent phase. The purified diluent can be re-used or disposed of by burning.

The radioactive TBP-phosphoric acid phase is heated to about 220 °C to decompose the organic compounds to volatile hydrocarbons and non-volatile inorganic phosphoric acids.

The inactive organic compounds are burned; the residual phosphoric acids, containing all the radionuclides, are conditioned for final storage by conversion into a phosphate glass or ceramic. Eurochemic's Eurowatt pilot installation is described and essential process data and results are given.

INTRODUCTION

Nuclear fuel reprocessing plants apply or will apply the Purex process, adapted to the different kinds of fuel, for the extractive separation and purification of uranium and plutonium from other actinides and the fission products. In the Purex process the extraction system diluted tributyl phosphate (TBP)-water-nitric acid is employed.

The extractant phase consists usually of a 30 vol.-% TBP solution in a saturated aliphatic hydrocarbon such as n-dodecane or refined kerosenes. During the performance of the various extraction cycles, especially in the first one, the TBP as well as its diluent are degraded by radiation and chemical reactions. Among the degradation products of TBP are dibutyl phosphate (DBP), monobutyl phosphate (MBP), long chain dialkyl phosphoric acids, and phosphoric acid; among the primary degradation products of the diluent are nitro-paraffins, aldehydes, ketones, carboxylic acids and organic nitrates some of which may form secondary products.

The degradation of the solvent mixture effects fission product retention (notably zirconium, niobium, ruthenium), plutonium and uranium losses, precipitates, build-up of crud at the interface, and a poor phase disengagement.

The solvent is therefore periodically cleaned by washing with alkaline and sometimes also acidic solutions or by passing it through a bed of a suitable organic or inorganic absorbent. If the applied clean-up procedure

fails to maintain the required quality of the solvent it has to be discarded and treated as radioactive waste. A Purex plant processing 1500 t uranium per year may produce up to some hundred cubic meter solvent wastes per year with a TBP content ranging from less than 1 vol.-% (diluent washes) up to 30 vol.-%. The spent 30 % TBP solvent may be estimated to contain $0.05 - 5 \text{ g Pu/m}^3$, $0.5 - 100 \text{ g U/m}^3$ and up to 50 Ci/m^3 fission products.

For the treatment of this type of waste either incineration or incorporation into a solid organic material (bitumen, polyethylene, polyvinyl chloride and similar matrices) have been applied or envisaged. However, both these treatment techniques suffer from several disadvantages. The incineration of TBP-containing waste solutions causes corrosion, pollution and off-gas purification problems and generates moreover relatively large volumes of secondary radioactive wastes in gaseous, liquid and solid form.

The incorporation into plastic materials is normally restricted to the TBP-fraction of the spent solvent. The amount of TBP in the final solidified product is limited to about 10 - 40 wt.-% causing a considerable volume increase of the radioactive waste to be handled and stored. Moreover, the solvent waste is not disposed of and remains an organic waste product with properties not entirely satisfactory for long-term storage.

The process developed at Eurochemic for the treatment and disposal of spent TBP-kerosene mixtures is judged to possess significant environmental, operational and economic advantages over the methods up to now applied or proposed. The various treatment steps and the installation used for this Eurochemic organic waste treatment (abbreviated to Eurowatt) process are described hereafter.

GENERAL PROCESS DESCRIPTION AND PRINCIPLES

The Eurowatt process comprises three main steps :

- the quantitative extractive separation of the spent solvent mixture by means of anhydrous phosphoric acid into its pure kerosene (diluent) component and a heavier TBP-phosphoric acid phase containing all degradation products, radionuclides, and other impurities;
- the thermal decomposition of TBP in the absence of air (pyrolysis), catalysed by the presence of phosphoric acid, into inactive volatile hydrocarbons and non-volatile inorganic phosphoric acids containing all radionuclides originally present in the solvent waste;
- the disposal of the inactive organic compounds from the pyrolysis step by burning or controlled release and the conditioning of the radioactive phosphoric acids for final storage by their conversion into a water-insoluble solid phosphate compound, glass, or ceramic.

The first process step is performed at room temperature by contacting the filtered solvent, which should be free from entrained aqueous solutions, with such an amount of anhydrous phosphoric acid that the TBP is quantitatively extracted from the solvent mixture into the phosphoric acid phase. This splitting of the TBP-diluent mixture is due to the phenomenon that mineral acids form polar adducts with TBP which may have a rather low solubility in unpolar diluents.

The solubility of TBP-acid adducts in aliphatic hydrocarbons decreases in the order $\text{HNO}_3 > \text{HCl} > \text{H}_3\text{PO}_4 > \text{H}_2\text{SO}_4 > \text{HClO}_4$.

Depending on the volume and concentration of the phosphoric acid contacted with a given TBP-diluent mixture, one, two, or three phases can be obtained [1]. The extraction of phosphoric acid and water by 100 % TBP has been thoroughly investigated by Higgins and Baldwin [2]. They found that at an equilibrium aqueous phosphoric acid concentration of 9 M the H_3PO_4 to TBP molar ratio is about one, at 13.6 M_a the ratio is 2 : 1; and at 16 M_a the ratio is 4 : 1; further increase of the equilibrium aqueous phosphoric acid concentration increases the distribution ratio rapidly until complete miscibility is reached when the 100 % TBP is contacted with anhydrous phosphoric acid.

The quantitative extractability of TBP from a kerosene solution by a sufficient amount of water-free phosphoric acid (preferably more than 3 moles H_3PO_4 per mole TBP) forms the basis of the Eurowatt process. The actinides, fission products, degradation products of the diluent and of the TBP, present in the spent solvent, are also quantitatively extracted into the newly formed TBP-phosphoric acid phase. The solubility of kerosene in this phase decreases with an increase of the acid concentration, however, is small anyway (< 1 vol.-%).

The diluent is separated from the heavier, highly viscous TBP-phosphoric acid phase and then washed with water to remove residual amounts of entrained phosphoric acids.

The extraction and separation of TBP from its diluent can be carried out batchwise or continuously using static mixers and static separators (coalescing filters), pulsed columns, mixer-settlers, single and multistage centrifugal extractors. As principally all these extraction units are suited for the TBP extraction and phase separation step the choice among them will depend on various factors of which the required through-put, the reliability, ease of maintenance, and the cost are the decisive ones.

The second process step (pyrolysis of TBP) consists in the complete dealkylation of TBP effected by its phosphoric acid catalysed decomposition at temperatures above 180 °C resulting in the formation of about twenty different condensable (at room temperature) hydrocarbons, water, non-condensable butenes (largest fraction of the hydrocarbons) and ortho-, pyro- and tri-phosphoric acid.

The pyrolysis is enhanced with increasing temperature and initial phosphoric acid concentration in the TBP phase; it can be carried out batchwise or continuously using preferably thin-film evaporators. The course of the TBP decomposition is characterized by three distinct reaction steps which take place successively at an increasing reaction rate and which formally correspond to the conversion of TBP to DBP, DBP to MBP, and MBP to H_3PO_4 under the liberation of the respective amount of butene, i.e. one third at each step. As the step attributed to the conversion of DBP into MBP is accompanied by strong foaming, the batchwise pyrolysis of a relatively large quantity of TBP can be troublesome.

To reduce the yield of phosphoric acid catalysed polymerization reactions, yielding condensable hydrocarbons and other compounds, the volatile pyrolysis products are removed from the pyrolyser by a stream of nitrogen.

The third step of the Eurowatt process involves the disposal of the products generated by the thermal destruction of TBP, in particular, the mixture of anhydrous phosphoric acids. This inorganic residue, containing the entire quantity of radionuclides originally present in the spent solvent, can be disposed of by using it as reagent in the solidification of intermediate-level or high-level waste solutions (e.g. bituminization, cementation, phosphate glass production) or by solidifying it using a MINERVA-type process as developed at Eurochemic [3].

The inactive, liquid and gaseous hydrocarbons are burned; alternatively, the filtered, non-condensable fraction (mainly butenes) can sufficiently be diluted by air prior to release. The other secondary waste streams, i.e. the sodium carbonate solution and the water washes of the inactive diluent fraction, are treated together with the low-level waste solutions of the reprocessing plant.

It has been shown that the basic principles involved in the Eurowatt process can also be applied to the treatment of other types of extractant-diluent systems (e.g. tri-alkyl amines and tri-alkyl phosphine oxides in kerosene).

IMPORTANT PROCESS DATA AND RESULTS

The normally envisaged aim of the Eurowatt process is the transformation of the TBP fraction of the primary solvent waste into a smaller volume of a stable, water-insoluble (inorganic) product suitable for safe long-term storage and the reuse of the decontaminated diluent.

The anhydrous phosphoric acid required for splitting quantitatively the solvent into its TBP and diluent components is generated by the process itself in the pyrolysis step. The pyrolysis of 1 m³ TBP produces about 0.2 m³ anhydrous phosphoric acids. A part of the acids is recycled, the rest is solidified. The repeated recycling of the radioactive phosphoric acids to effect the extraction of TBP and all impurities from the diluent does not lead to any recontamination of the diluent.

To avoid the formation of a third phase the water content within the extraction system must be maintained below 4 vol.-% of the TBP volume. The residual activity in the diluent phase is proportional to the residual TBP content which is a function of the phosphoric acid to TBP molar ratio and the temperature. Using a ratio of 3 : 1 the solubility of TBP in the kerosene phase amounts to less than 0.1 vol.-% at 20 °C.

In the standard flowsheet of the Eurowatt process a multistage extraction is applied and an acid to TBP molar ratio of 4.5 to improve the separation efficiency and to subsequently enhance the rate of the TBP pyrolysis.

The extraction of TBP from the kerosene into the phosphoric acid phase is fast (some seconds) provided a good dispersion is assured. Therefore a small vessel of some few liters capacity, equipped with an efficient stirrer, can be used as mixing unit and operated at a relatively high solvent through-put (> 100 l/h). For a clear-cut disengagement of equal volumes of the inactive light diluent from the active, highly viscous TBP/ H_3PO_4 phase a relatively long settling time is required (some hours). Fortunately, the settling of the heavy phase from the diluent phase can be fast (5 - 10 min.) and a complete disengagement of the diluent from the TBP/ H_3PO_4 phase is not absolutely necessary. If mixer-settlers are used a phase volume ratio of one in the mixing chamber should be envisaged to assure a high extraction efficiency.

The final volume obtained by mixing arbitrarily chosen volumes of 100 % TBP and 100 % H_3PO_4 are strictly additive.

A great number of extraction tests using different batches of spent solvents from the reprocessing plant have shown that the only radionuclides detectable in some few diluent fractions have been traces of ruthenium-106 and antimony-125. Coalescence tests and fission product and plutonium retention tests have shown that the recovered kerosene has the same or superior properties than fresh kerosene and can therefore be reused. Higgins and Baldwin [4, 5, 6, 7] found that the acid catalysed thermal decomposition of TBP leads to the formation of butenes, various liquid hydrocarbons, butanol, and - under certain conditions - to dibutyl ether and tetrabutyl pyrophosphate.

The inorganic liquid pyrolysis residue consists of a mixture of ortho-, pyro-, and tri-phosphoric acid, the fractional composition of which depends mainly on the reaction temperature and time. In the table below the times needed for quantitative TBP pyrolyses under various conditions are summarized.

TABLE

Time required for the complete thermal decomposition of TBP to hydrocarbons and phosphoric acids as a function of the temperature and the initial H_3PO_4 concentration

H_3PO_4 - TBP solution $\frac{\text{M}}{\text{M}} \text{H}_3\text{PO}_4$	Pyrolysis time [min.] at indicated temperature [°C]				
	180°	200°	220°	230°	250°
3.0	140	39	13	10	7.5
5.0	32.5	12	7	5.5	4.5
6.9	16	8	5	4	3.5
8.0	11.5	7	4.5	3.5	3.0
9.0	9	6	4	3.0	2.6
10.0	8.5	5.5	3.5	2.8	2.5
10.9	8	5.3	3.5	2.5	2.5
12.9	6.5	4.5	3.0	2.3	2.2

Beta-gamma emitting nuclides were not detectable in the off-gases after a phosphoric acid wash while less than 0.01 % of the beta-gamma activity of the spent solvent treated were found in the condensable pyrolysis gases. This condensate consists of a small fraction of water, liquid hydrocarbons, and other organic compounds containing up to about 1 % of the total phosphorus introduced into the pyrolyser. These phosphorus compounds are easily decomposed in contact with hot concentrated phosphoric acid. Therefore, a washing with phosphoric acid of the pyrolyser off-gas stream results in condensable and at room temperature non-condensable hydrocarbon fractions which are free from radioactive impurities.

EUROCHEMIC'S PILOT INSTALLATION

A pilot installation has been built at Eurochemic with the aims to dispose of the solvent inventory of the shut-down reprocessing plant and to demonstrate the safe operation and technical maturity of the Eurowatt process for the industrial scale application at a large reprocessing plant. The main components of the installation are schematically shown in figure 1 together with the flowsheet used for the treatment of 0.6 m³ of 30 % TBP-kerosene waste per day.

The solvent mixture is washed with a sodium carbonate solution in a single stage mixer-settler to remove residual nitric acid. The solvent is then filtered and fed to a four-stage mixer-settler where the TBP is extracted by anhydrous phosphoric acid in the first three stages while the diluent phase is washed with water in the fourth stage. Each mixer-settler is made of stainless steel AISI 304-L and has a mixer volume of 5.7 l and a settler volume of 31 l. A specially shaped turbine, driven by a pneumatic motor, mixes effectively the phases at 300 - 400 rpm without causing a too high degree of emulsification. The separated TBP-phosphoric acid phase is subsequently introduced into the top part of a wiped-film evaporator, shown in more detail in figure 2, to effect the pyrolysis of TBP. For this purpose the inside surface (1 m²) is kept at 200 - 220 °C by circulating a thermo-fluid (Texatherm 320) through the heating-jacket.

The parts of the pyrolyser coming in contact with the highly corrosive hot phosphoric acid are made of Hastelloy B 2 and graphite-loaded polytetrafluoroethylene; the other parts consist of stainless steel 304-L. The phosphoric acids leaving at the bottom outlet are cooled and then collected in a storage tank.

The pyrolysis gases are swept by nitrogen through a 5 l washing vessel (Hastelloy B 2) containing phosphoric acid kept at 200 - 220 °C by the circulating heating liquid. The off-gas stream passes then a condenser consisting of graphite and having a heat-exchange surface of 1.8 m². The condensate is collected in an aqueous organic phase separator whilst the non-condensed part of the gaseous stream passes a glass-fibre filter, acting as a demister. The organic gases passing the demister are diluted by air with the aid of a fan before they are introduced into the respective ventilation system of the plant.

The process and the installation described above have thoroughly been cold-tested; active operation will soon commence. The development of the Eurowatt process as well as the design, construction, and erection of the entire installation has been carried out by personnel of the Eurochemic Company.

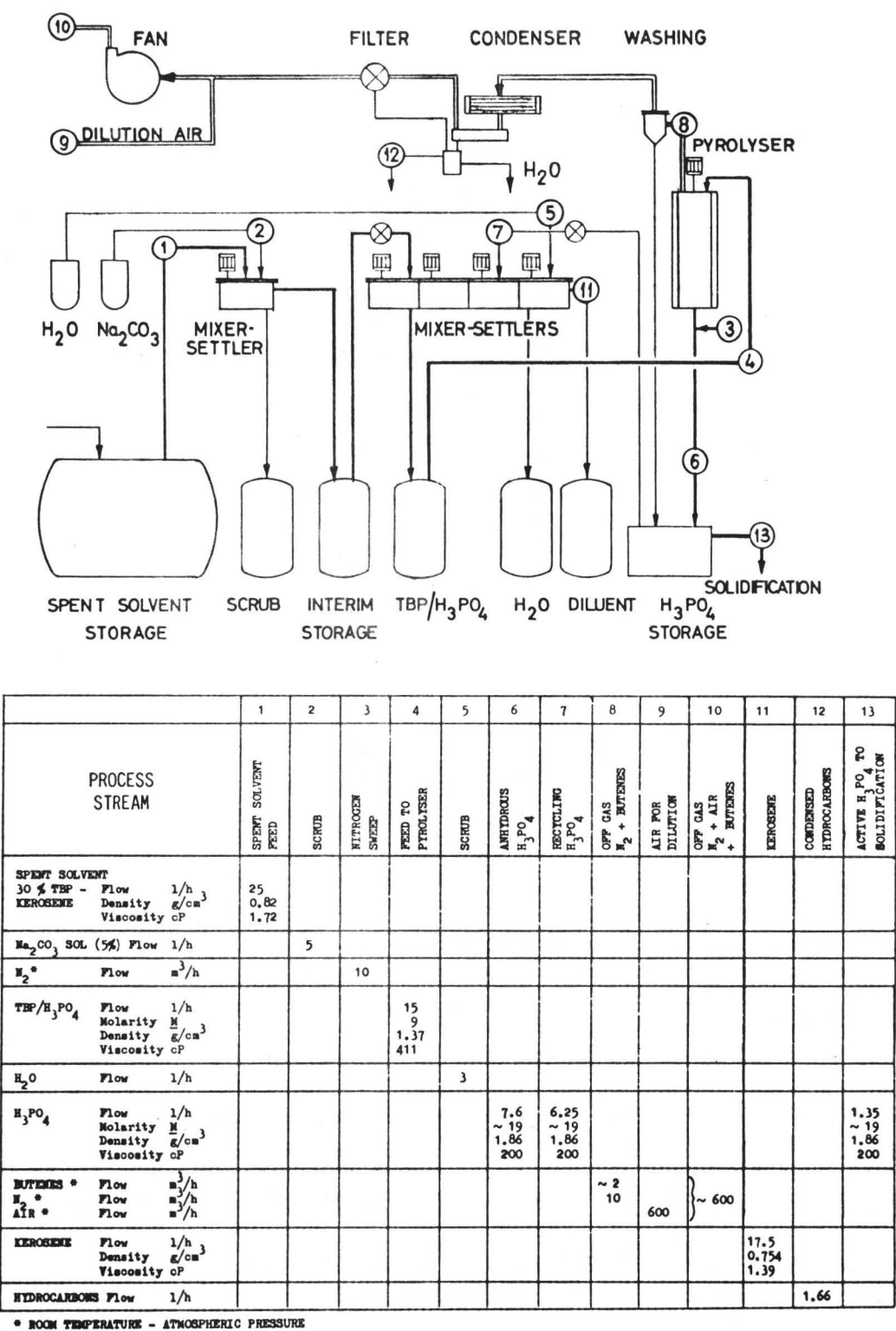


FIG. 1

Standard flowsheet for the treatment of spent 30 vol.-% tributyl phosphate-kerosene solvent.

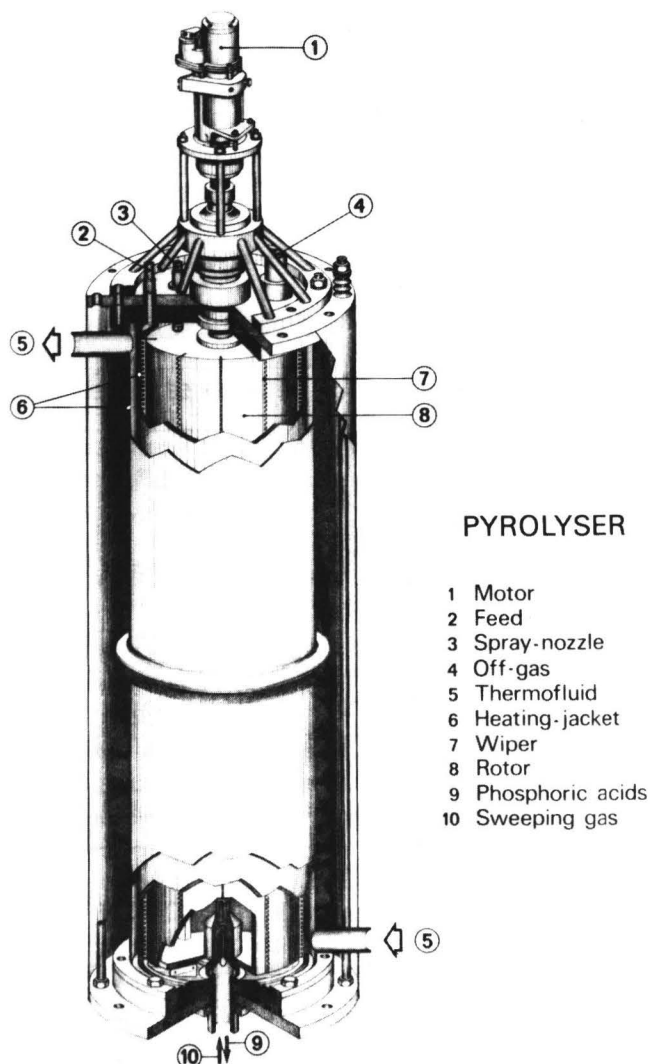


FIG. 2

Wiped-film evaporator used for the pyrolysis of TBP

ACKNOWLEDGEMENTS

The authors thank Dr. E. Detilleux, Manager of the Eurochemic Company, for his constant support of the Eurowatt Project, and also Dr. L. Salomon for his valuable contribution to the development of the Eurowatt process.

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DILUENT WASHING OF AQUEOUS PHASE USING CENTRIFUGAL CONTACTORS

M. Germain and P. Pluot

Commissariat à l'Energie Atomique DGR/SEP
Boîte Postale No.6
92260 FONTENAY AUX ROSES
France

The authors investigated the elimination of the extractant tributyl phosphate (TBP), dissolved or entrained in the aqueous phases of fuel reprocessing plants, by diluent washing of these aqueous phases.

Equilibrium and kinetics studies of TBP extraction served to establish flowsheets that were tested using a laboratory scale centrifugal contactor bank.

INTRODUCTION

In liquid-liquid extraction, the mutual solubilities of the two phases (aqueous and organic) are generally very low. However, in various industries, such as nuclear fuel reprocessing, it appears that traces of organic compounds in the aqueous phases must be eliminated completely. In the Purex process, the aqueous solutions are nitric acid solutions while the organic phase consists of 30 vol. % TBP in an inert diluent. The solubility of TBP in the aqueous phases, which is about 10^{-3} M, may, by chemical or radiolytic degradation, cause the formation of mono- and dibutyl phosphoric acids, whose presence is particularly undesirable in the purification cycles (loss of fissile materials, lower decontamination factors, risks of precipitation of insoluble salts, etc).

The two processes that have been investigated and that are used in nuclear plants involve steam stripping and diluent washing.

Diluent washing of the aqueous phases is effective in removing most of the TBP from the aqueous phases when carried out with mixer-settlers.

For nuclear safety reasons, however, ever-safe high throughput contactors must be employed. We investigated the possibility of using centrifugal contactors to achieve diluent washing of the aqueous phase.

EXPERIMENTAL

MATERIALS

Nitric acid and uranyl nitrate are pure products (RP) from Prolabo. The diluent is Hyfrane 120, a commercial diluent supplied from Hyfran SA; it is a mixture of branched paraffins with 12 carbons. Aqueous tributyl phosphate solutions were obtained either by solubilization of pure TBP in the aqueous phase, or by contacting the aqueous phase with 30 vol.% TBP-Hyfrane 120. In both cases the phases were allowed to settle for several hours or filtered on hydrophilic paper. TBP was purified before use by washing with caustic soda solution and water. ^{32}P -labelled TBP was supplied by the Amersham Radiochemical Centre.

EQUILIBRATION

Partition coefficients were determined by mixing the phases in thermostatically controlled cells, using a magnetic agitator for 15 minutes. TBP concentrations were varied by changing the aqueous TBP concentration or the phase volume ratio.

Transfer kinetics were measured using an EC8-1 laboratory scale centrifugal contactor (1) fed by pumps the flow rates of which were checked before and during the run.

Test runs were performed in a four-stage centrifugal contactor bank at $21 \pm 1^\circ\text{C}$. Aqueous flow rate was checked in line, while organic flow was provided by a syringe pump and checked at the bank outlet.

ANALYTICAL METHODS

Nitric acid and uranium were determined by titration with alkali and Ce^{4+} respectively. TBP was determined by gas-liquid chromatography or by liquid scintillation counting when using a ^{32}P -labelled phase.

RESULTS AND DISCUSSION

1 EQUILIBRIUM DATA

Preliminary studies showed that time to reach equilibrium is short (≤ 5 min) and increased slightly with decreasing aqueous TBP concentration. All our determinations were made after mixing for 15 minutes.

1.1 Effect of TBP concentration

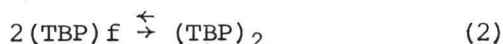
The partition of TBP between aqueous 2 M HNO_3 and Hyfrane 120 is shown in Figure 1. As stated previously (2 to 5), partition coefficients increase with aqueous TBP concentration (Figure 2) and this increase appears more pronounced when $(\text{TBP})_{\text{aq}} \geq 5 \cdot 10^{-5} \text{ M}$. Figure 1 shows that the slope of the curve lies between 1 (for $(\text{TBP})_{\text{aq}} < 10^{-5} \text{ M}$) and 2 (for $(\text{TBP})_{\text{aq}} > 10^{-4} \text{ M}$). The result is interpreted as the competition of two TBP extraction mechanisms:

- interaction with the diluent:



$$\text{where } K_1 = \frac{[\text{TBP}, D]}{[\text{TBP}]f \cdot [D]}$$

- dimerization reaction in the organic phase:



$$\text{where } K_2 = \frac{[(\text{TBP})_2]}{(\text{TBP})f^2}$$

The association of TBP in the organic phase was thoroughly investigated by Petkovic (6,7), who reported a self association constant of TBP in dodecane of 2.6 (8). The stoichiometries of these reactions show that the relative importance of dimerization increases with TBP concentration; if this reaction becomes predominant, then:

$$[\text{TBP}]_{\text{org}} = [\text{TBP}]f + [\text{TBP}, D] +$$

$$2[(\text{TBP})_2] \neq [\text{TBP}]f + 2[(\text{TBP})_2]$$

$$\text{with: } \text{TBP} \rightleftharpoons \text{TBP}f \quad (3)$$

$$\text{where } K = \frac{[\text{TBP}]f}{[\text{TBP}]a}$$

$$\text{as } D = \frac{[\text{TBP}]_{\text{org}}}{[\text{TBP}]a}$$

$$D \neq K + 2K_2K^2[\text{TBP}]a$$

Our experimental results are in good agreement with this equation when $[\text{TBP}]a \geq 5 \cdot 10^{-5} \text{ M}$.

1.2 Effect of temperature

A strong increase was observed in D_{TBP} with rising temperature (Table 1), resulting mainly from the lower solubility of TBP in the aqueous phase at higher temperature (9,10), as shown in Table 1, by the fact that the product of TBP by TBP solubility remains constant.

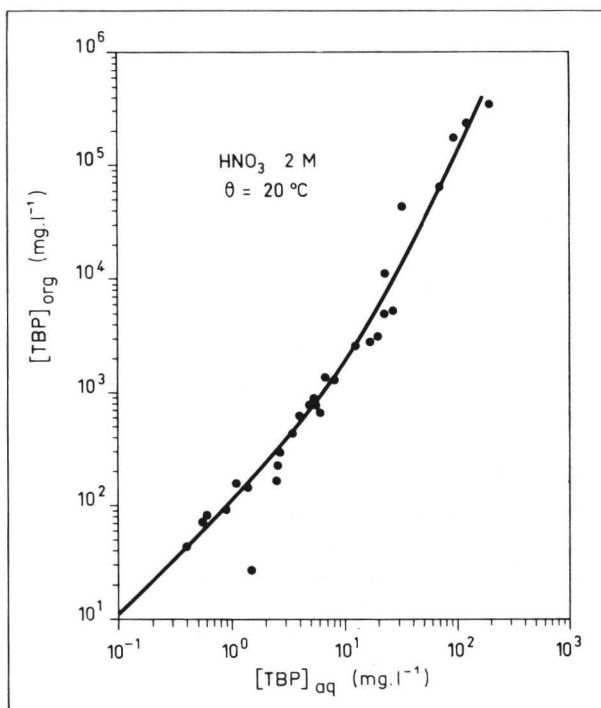


FIG.1

Partition of TBP between aqueous phases and Hyfrane 120

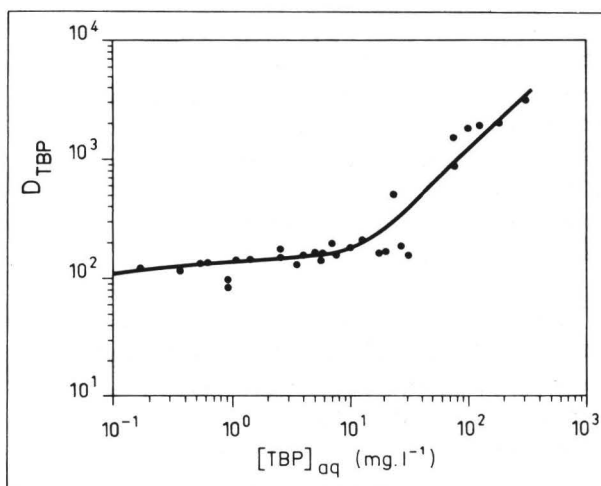


FIG.2

Variation of D_{TBP} with aqueous TBP concentration

1.3 Effect of aqueous phase composition

In nitric acid solutions, D_{TBP} appears to decrease between 0 and 2 M HNO_3 , then increases with higher HNO_3 concentration (Table 2). Michel (2) reported a continuous increase in D_{TBP} with rising HNO_3 concentration, in agreement with the lower solubility of TBP in this concentration range (4,10).

Our results suggest a more complex mechanism involving the complexation of TBP by nitric acid in aqueous solution.

In 0.5 M caustic soda solution, D_{TBP} increases with TBP concentration in a manner very similar to that in 2 M HNO_3 (Figure 3). D_{TBP} values are somewhat higher than those obtained in acid medium, especially at high TBP concentrations.

1.4 Effect of diluent branching

The influence of branching was investigated with two commercial products with an average of 12 carbons. Hyfrane 120 is the branched paraffinic diluent and Hyfrane 130 a mixture of n paraffins. In 2 M nitric acid solutions, D_{TBP} is practically unaffected by the type of diluent. Lower values of D_{TBP} were observed with the linear diluent for high TBP concentrations, and may result from a lower dimerization constant of TBP due to the lower polarizability of the linear diluent.

From the equilibrium study, we have shown that D_{TBP} values are very high ($D_{TBP} > 100$) and increase sharply with higher TBP concentration and temperature.

Table 1

Influence of temperature on partition coefficients of TBP				
Aqueous phase: 2 M HNO_3 90 mg · l ⁻¹ TBP				
Diluent: Hyfrane 120				
Volume ratio: $\sqrt{A}/\sqrt{O} = 10$				
3 °C	21	30	40	50
(TBP) _{aq} mg · l ⁻¹	4.3	3.5	3.2	3.4
D_{TBP}	157	215	270	287
solubility of TBP g · l ⁻¹	0.49	0.38	0.315	0.285
$D_{TBP} \times S_{TBP}$ g · l ⁻¹	76.9	81.7	85	81.8

Table 2

Influence of nitric acid concentration on D_{TBP}						
Aqueous phase: HNO_3 variable, 90 mg · l ⁻¹ TBP						
Diluent: Hyfrane 120						
Volume ratio: $\sqrt{A}/\sqrt{O} = 10$						
$\theta = 20$ °C						
HNO_3	0	0.05	0.5	1	2	4
(TBP) _{aq} mg · l ⁻¹	4.3	4.3	4.3	4.9	4.8	3.5
D_{TBP}	204	195	183	158	160	226

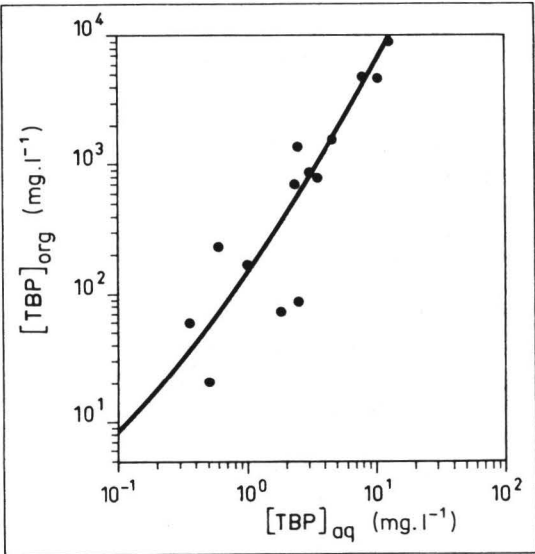


FIG.3

Partition of TBP between 0.5 M NaOH solutions and Hyfrane 120

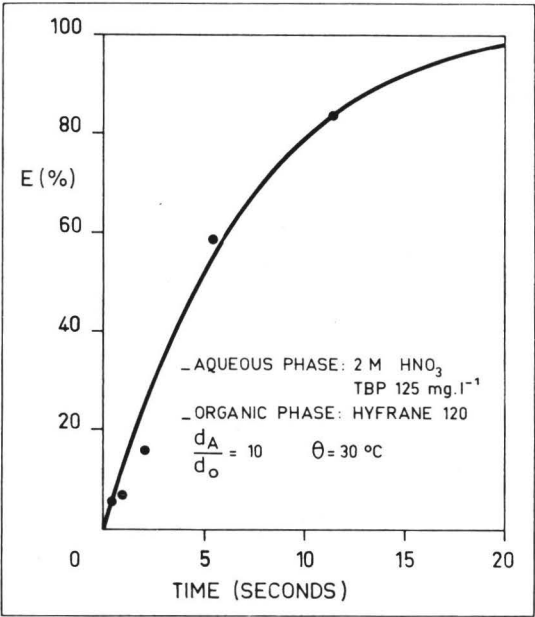


FIG.4

Evolution of Murphree's efficiency with time

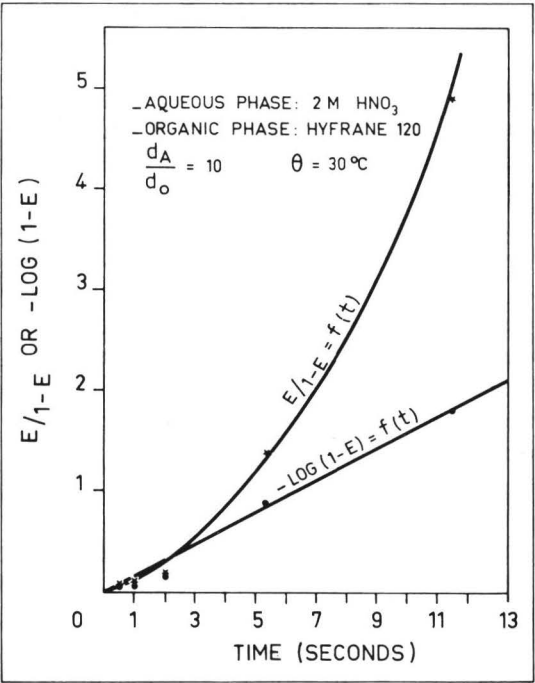


FIG.5

Variations of E/1-E and -log (1-E) with time of mixing

2 TRANSFER KINETICS

Centrifugal contactors are very short residence time contactors in which mixing of the two phases is achieved by creating a very fine emulsion for a few seconds and settling is achieved very rapidly under high centrifugal field.

We attempted to find the characteristic equation of our contactor in diluent washing conditions. Characteristic curves showing the dependence of Murphree's efficiency on mixing time can be seen in Figure 4, which shows that efficiency remains rather low. According to previous calculations (11), we plotted E/1-E and log (1-E) versus time (Figure 5), and it appears that log (1-E) is proportional to mixing time, indicating that the contactor behaves as a tubular reactor. Hence the characteristic equation is:

$$-\log (1-E) = \frac{(k \cdot a)}{\beta} \tau$$

- where:
- (k · a) apparent overall mass transfer coefficient,
 - β ratio of aqueous to total flow rate,
 - τ = v/(dA+do) mixing time in seconds,
 - v volume of mixing zone,
 - dA and do aqueous and organic flow rate.

These results show that our contactor in diluent washing conditions shows quite different behavior to most of the systems already studied, where the

characteristic equation was $E/(1-E) = \frac{(k \cdot a)}{\beta} \tau$ and extraction was very rapid.

The effect of flow rate is seen clearly in Figure 6, which shows that whatever the mixing time, E increases sharply with d_A/d_o . The same effect was observed for very low concentrations (curve 1 in Figure 6 is the same for initial TBP concentrations of 89 and 2.7 $\text{mg} \cdot \text{l}^{-1}$). Mean calculated values of $(k \cdot a)$ are respectively 0.058, 0.12 and 0.25 s^{-1} for d_A/d_o of 10, 50 and 100 in 2 M HNO_3 at 20 °C. We then plotted $\log (1-E)$ versus $1/d_o$, with all the experimental points (covering a wide range of concentrations and d_A/d_o), and obtained a curve showing that $\log (1-E)$ increases with $1/d_o$ (Figure 7). This increase results from longer residence time of the organic phase in the mixing zone, but is not proportional to time, as had been expected, and could result from a decrease of the retention of the organic phase with decreasing d_o . The overall effect is an increase in $-\log (1-E)$ with increasing residence time of the dispersed phase (organic).

The effect of TBP concentration on TBP extraction kinetics is well illustrated in Table 3, which shows that, within experimental errors (E is known within $\pm 15\%$), efficiency does not vary with aqueous TBP concentration.

The influence of temperature is shown in Table 4. While the values obtained did not enable us to calculate the activation energy of the transfer, they show that the effect of temperature is not very significant.

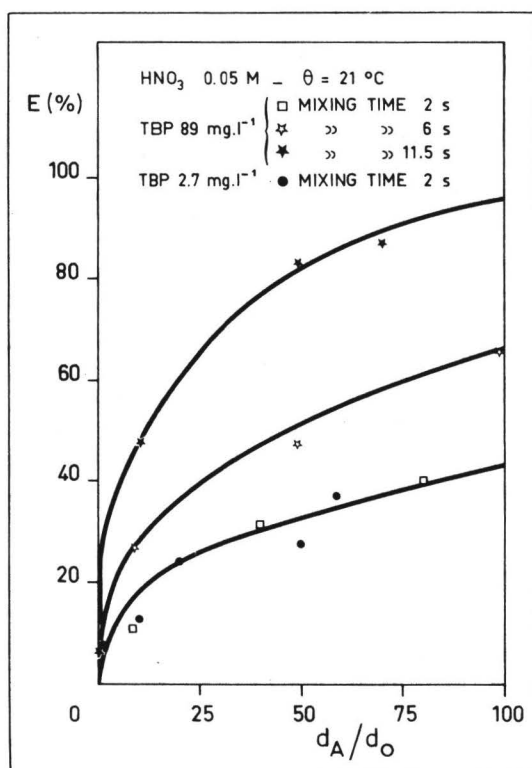


FIG.6

Variation of
Murphree's efficiency with flow ratio

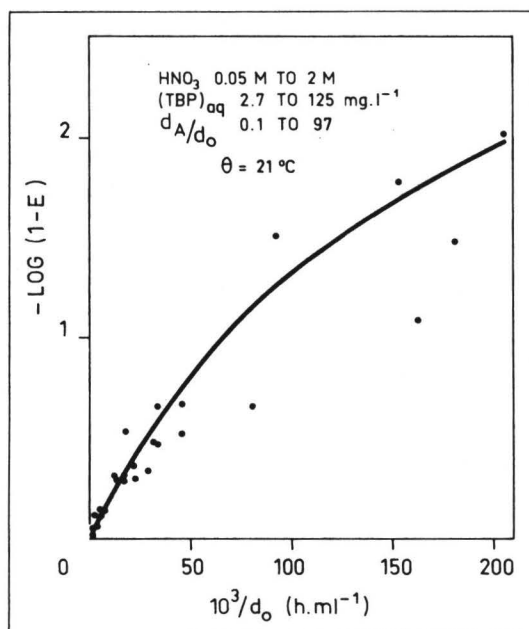


FIG.7

Variation of
 $-\log (1-E)$ with $1/d_o$

The effect of nitric acid concentration appears, within experimental errors, to be very limited (Table 5).

According to Fomin's classification (12), since the rate of TBP extraction is only slightly affected by changes in temperature and concentration, the system is a diffusion system. As efficiency increases with residence time of the organic phase, we can reasonably estimate that resistance to diffusion occurs mainly in the organic phase.

In practice, although the system is rather slow, high efficiencies can be obtained by ensuring sufficient residence time of the organic phase in the mixing zone, which can be achieved by a suitable combination of total flow rates and flow rate ratios.

3 TEST RUNS

Runs were performed on a four-stage centrifugal contactor bank. The aqueous phase composition was very similar to those found in uranium fuel reprocessing cycles:

HNO_3 0.07 M - UO_2^{++} 70 g · l⁻¹ -
TBP 200 mg · l⁻¹

Washing was investigated as a function of mixing time and flow rates. Mixing times of 2, 5 and 10 seconds per stage were considered. A typical concentration profile in the bank is shown in Figure 8, and most of the results are compiled in Table 6, which shows that D_{TBP} increases with mixing time as previously observed in single-stage kinetics studies. Consequently, residual TBP concentration decreases with longer mixing time.

With mixing time of 5 seconds, D_{TBP} rises from 30 to 200, as the flow ratio increases from 10 to 50. As a result of this increase, the final aqueous concentration is nearly independent of the flow rate.

Table 3
Influence of TBP concentration on Murphree's efficiency

Aqueous phase: 2 M HNO_3					
Diluent: Hyfrane 120					
$\theta = 20^\circ\text{C}$					
Flow rate ratio: $dA/dO = 10$					
(TBP) _{aq} mg · l ⁻¹	0.75	3.15	6.9	28.7	36
(TBP) _{org} mg · l ⁻¹	15	28.2	72.1	531	770
E* en %	11.8	8.4	9.1	13	12.6

*For valid comparison, efficiencies have been adjusted to the same mixing time (2 seconds)

Table 4

Variation of $[k \cdot a]$ with temperature

Aqueous phase: 2 M HNO_3 , 120 mg · l ⁻¹ TBP			
Organic phase: Hyfrane 120			
$dA/dO = 10$			
$\theta^\circ\text{C}$	21	30	40
$[k \cdot a] \text{ s}^{-1}$	0.084 ±0.02	0.12 ±0.03	0.09 ±0.02

Table 5

Influence of nitric acid concentration on efficiency

Aqueous phase:
variable HNO_3 , 80 mg · l⁻¹ TBP
Organic phase: Hyfrane 120
 $\theta = 21^\circ\text{C}$
 $\tau = 2$ seconds
 $dA/dO = 10$

$\text{H}^+ \text{ M}$	0	2	4
E %	9.8 ± 2	11 ± 2	9.9 ± 2

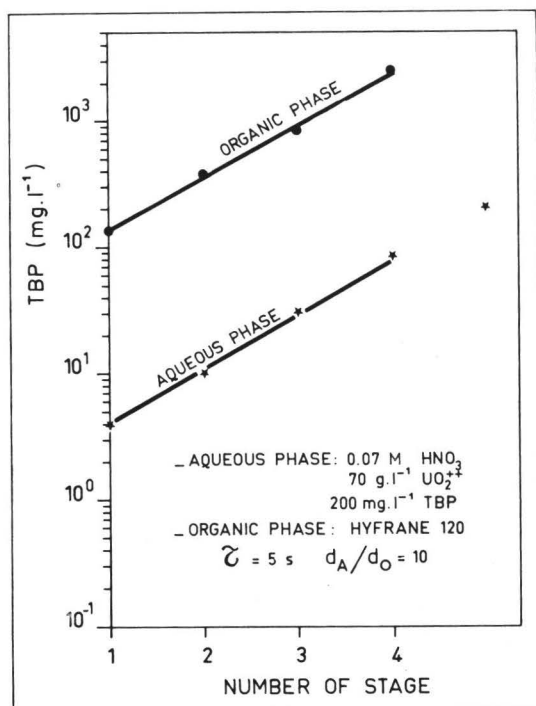


FIG.8

TBP concentration profiles
in the four-stage
centrifugal contactor bank

In Table 7 we have examined the variation of D_{TBP} with $1/d_o$ for the four runs. A linear increase is observed, as shown by the constancy of the ratio $D_{TBP}/10^3/d_o$ (2.5 ± 0.5).

These four runs provided positive confirmation of the results obtained with single-stage centrifugal contactors, especially concerning the influence of organic flow rate on TBP extraction efficiency.

CONCLUSIONS

In conclusion, although the kinetics of TBP transfer from aqueous phase to organic phase is rather slow, the use of centrifugal contactors appears feasible using high aqueous to organic flow rates, because of the very high TBP distribution coefficients.

Table 6

Effect of mixing time on
diluent washing with a
four-stage centrifugal
contactor bank

Aqueous phase:
0.07 M HNO_3 -
70 g · l⁻¹ UO_2^{++} - 200 mg · l⁻¹ TBP
Organic phase: Hyfrane 120
 $\theta = 21^\circ C$
 $dA/d_o = 10$

mixing time seconds	2	5	12
mean D_{TBP}	15	30	70
final aqueous TBP concentration mg · l ⁻¹	40	4	2.5

Table 7

Correlation between mean D_{TBP} and $1/d_o$

Aqueous phase:
0.07 HNO_3 70 g · l⁻¹ UO_2^{++}
200 mg · l⁻¹ TBP
Organic phase: Hyfrane 120
 $\theta = 21^\circ C$
 $dA + d_o$ and dA/d_o variable

$1/d_o \times 10^3$ h · ml ⁻¹	6.1	15.3	36.7	69.4
mean D_{TBP}	15	30	70	200
$D_{TBP}/10^3/d_o$	2.46	1.96	1.91	2.88

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ALKYLPYROCATECHOLS AS EXTRACTANTS FOR THE TRANSPLUTONIUM ELEMENTS ISOLATION FROM ALKALINE SOLUTIONS

B.F. Myasoedov, Z.K. Karalova,
L.M. Rodionova

Vernadsky Institute of Geochemistry
and Analytical Chemistry USSR, Academy of Sciences. Vorobjevskoe shosse 47a, Moscow 117334, U.S.S.R.

ABSTRACT 4(α,α -dioctylethyl)-pyrocatechol is an effective extractant for the extraction of both the tracer and the macroquantities of the transplutonium elements and rare earths from strongly alkaline solutions in the presence of aminopolyacetic acids. The conditions were found for both Am(III) and Eu(III) separation and many other elements by changing contact time as well as alkaline and extractant concentrations. The trivalent metals are extracted into organic phase as the species $\text{Na}_3(\text{MeDOP}_3)$.

Aliquate-336 can be successfully used for the isolation and concentration of transplutonium elements (TPE) from alkaline solutions as we have recently shown /1-4/. In this case the elements are extracted as ionic associates, the anionic part of which are hydroxocomplex of the metals (shown by NMR and I.R. spectroscopy). The complex forming agents α -oxycarbonic /1,2/ or aminopolyacetic acids are used in aqueous phase to keep the hydrolyzable elements as soluble form in alkaline solutions.

We have found that 4(α,α -dioctylethyl) pyrocatechol (DOP) is the more effective extractant for the extraction of TPE and rare earths from strongly alkaline solutions. Figure 1 shows the extraction of lanthanum by solutions of DOP and aliquate-336 in the presence of ethylenediaminetetracetic acid (EDTA) as a function of alkaline concentration. It is seen that substitution of aliquate by alkyldipyrrocatechol gives an enhancement of the lanthanum distribution coefficient by a factor of about 100 in 2 M NaOH. The americium extraction also increases with increasing NaOH concentration according to fig.2. The quantitative isolation of Am(III) (>99%) can be carried out by means of DOP from 1-10 M NaOH solutions.

In this case DOP provides a sufficiently full extraction of both the tracer and macroquantities of TPE and rare earths. Lanthanum in 10^{-1} M concentration in 2 M NaOH solution containing EDTA can be extracted over 90% by 0.3 M DOP-solution in toluene.

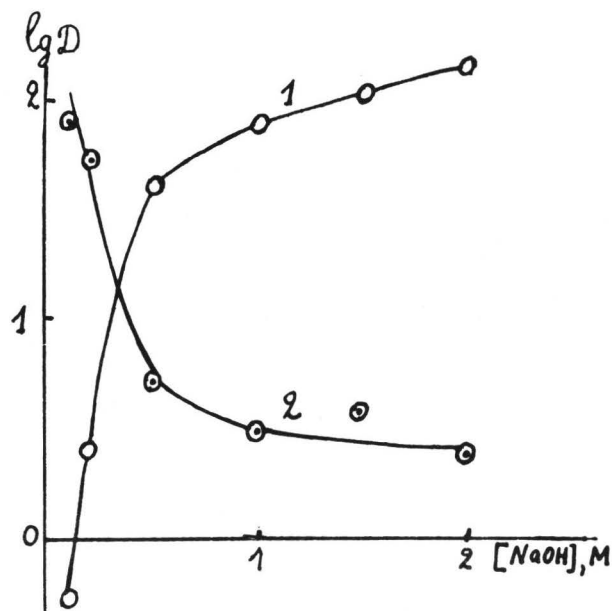


fig.1 NaOH-concentration dependence of extraction of lanthanum-140 in $2 \cdot 10^{-3}$ M EDTA solution by 0.04 M DOP solution in cyclohexane (curve 1) and by 0.02 M aliquate-336. OH solution in cyclohexane (curve 2).

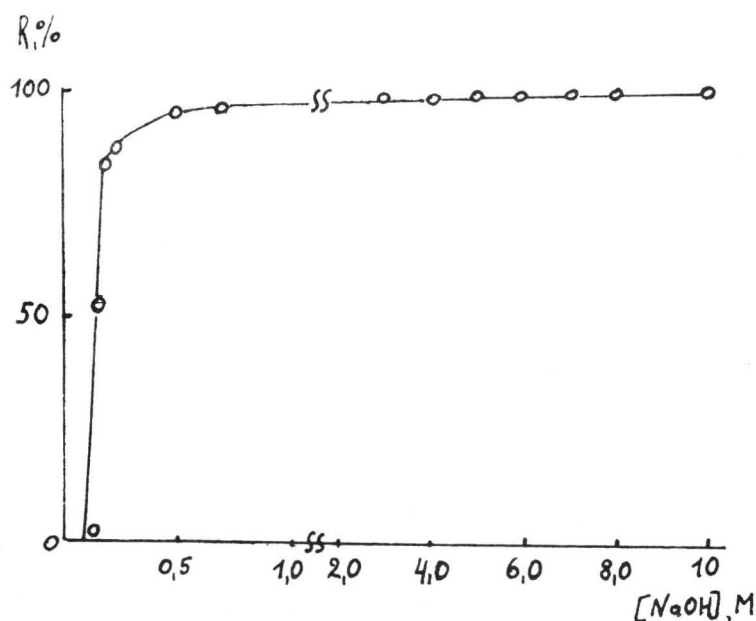


fig.2 NaOH-concentration dependence of extraction of americium in 0.025 M tartaric acid by 0.04 M DOP solution in toluene.

The extraction of TPE and rare earths by the DOP solution in toluene from alkaline diethyltriaminopentaacetic acid (DTPA) solutions was studied and it shows, that the distribution coefficients depend on many factors including kinetic ones. The extraction equilibria of these systems depend on contact time and complex-forming agent in aqueous phase. We believe that the stage limiting the extraction rate is the destruction of

DTPA-complexes with metals with the formation of inner-complex compound with extractant. The extraction of elements by DOP into organic phase occurs the slower the higher the stability of the complex compound in aqueous phase is. Indeed, about 98% of europium which forms a less stable complex with DTPA, can be extracted from 2 M NaOH by 0.04 M DOP solution in toluene for 10 minutes, but only 48% of americium.

Dependence extraction of macroquantities of europium on time at different DTPA concentration is shown in fig.3. It is

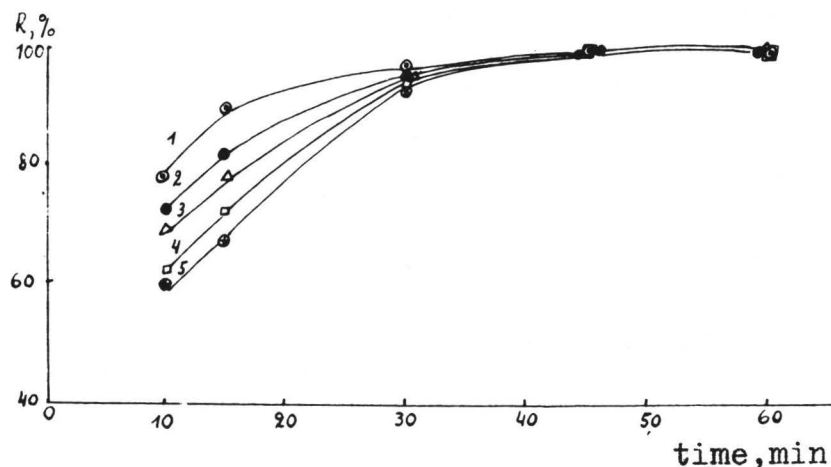


fig.3 Influence of contact time on the extraction of 1.10^{-4} M europium by 0.04 M DOP solution in toluene from 2 M NaOH in the presence of different DTPA concentration:

1 - $2.5 \cdot 10^{-4}$ M; 2 - $5 \cdot 10^{-4}$ M; 3 - $1 \cdot 10^{-3}$ M; 4 - $2 \cdot 10^{-3}$ M;
5 - $5 \cdot 10^{-3}$ M.

seen that the extraction rate of europium decreases significantly with increasing DTPA concentration. However the equilibrium is reached within 1 hour even if the amount of DTPA is 50-fold greater than that of the metal. The concentration of both metal and alkaline is less significant by DOP extraction. The extraction rate under otherwise identical conditions decreases with increasing metal concentration and increases with decreasing alkaline concentration. 0.04 DOP solution in toluene extracts 1.10^{-4} M europium concentration in

the presence of $5 \cdot 10^{-3}$ M DTPA, a change of NaOH concentration from 2 to 4 M and contact time within 15 minutes lead to an increase of the distribution coefficient from 2 to 100.

The influence of extractant and metal concentration on the TPE extraction from the alkaline solutions under equilibrium conditions was studied using europium. The organic phase at constant concentration of DOP in toluene (0.04 M/l) was contacted within 1 hour with 2 M NaOH solution contained different amount of metal. Europium is extracted with the large distribution coefficients about equal to $n \cdot 10^2$ in the range of concentration 10^{-4} - 10^{-3} M according to extraction isotherm which gives the distribution of metal equilibrium concentration in

organic and aqueous phases. The further increase of initial metal concentration leads to a decrease of metal extraction, the saturation of the organic phase is reached slowly and approaches a metal: extractant ratio 1:3. The same ratio value was confirmed by the molar ratio method. The extraction increases linearly with increasing extractant concentration in organic phase from $5 \cdot 10^{-3}$ M to $5 \cdot 10^{-2}$ M, and becomes stable as metal is connected with extractant to form complex compound; the point of intersection is found at metal to extractant ratio of 1:3. Sodium enters in the formation of the extracted compound that has been established with radioisotope ^{22}Na . Sodium passes into the extract at the concentration ratio sodium: extractant=1:1. The obtained data clearly prove that the trivalent metals are extracted into organic phase as the species $\text{Na}_3(\text{Me DOP}_3)$. It is most probably that the first stage of the extraction is the formation of pyrocatecholmetallic acid and then its Na-salt is formed. This is proved by decrease of the metal distribution coefficient after the preliminary treatment of the extractant by alkaline solution. The formed chelate is likewise coordinately saturated since its extraction does not depend on the nature of diluent.

The formation of the complex compounds with DOP is confirmed by IR-spectra. The IR-spectra of europium complex and those of DOP solution in toluene are given in fig.4. The ana-

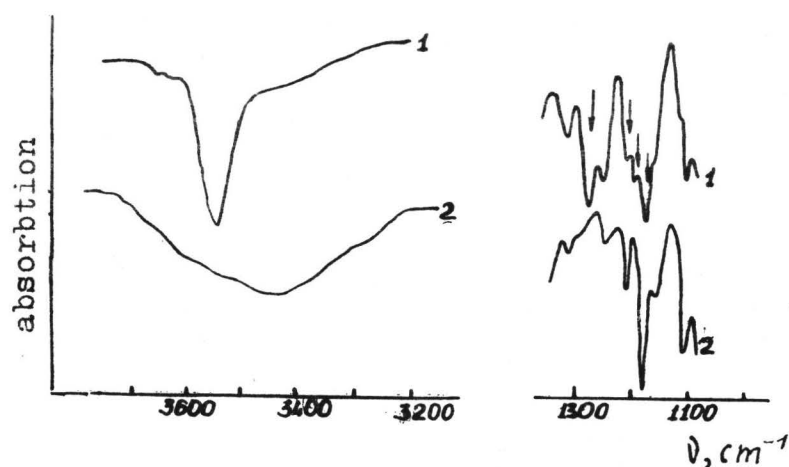


fig.4 IR-spectra of 4(α,α -dioctylethyl) pyrocatechol in toluene (curve 1) and organic phase saturated with lanthanum (curve 2).

lysis of these data shows that the spectrum of DOP complex with europium differs from the spectrum of alkylpyrocatechol itself. Firstly in the complex spectra the band 1200 cm^{-1} of phenolhydroxyl is missing. Secondly, the complex spectra lack characteristic band of OH-groups of alkylpyrocatechol in the range $3400\text{--}3550\text{ cm}^{-1}$ that proves that all OH-groups of o-diphenol are bound with metal in forming the complex compound. The blurred band at 3450 cm^{-1} in the complex spectra shows the formation of donor-acceptor bond with OH-groups.

We have studied the extraction of Th(IV), Pu(IV), Pa(V), U(VI), Fe(III), Zr(IV), Nb(V), Ru(III) and Cs(I) together with TPE and rare earths in the system alkaline-DTPA. The conditions were found for both Am(III) and Eu(III) separations and many other elements by changing contact time as well as alkaline and extractant concentrations. It is seen in fig.5 that

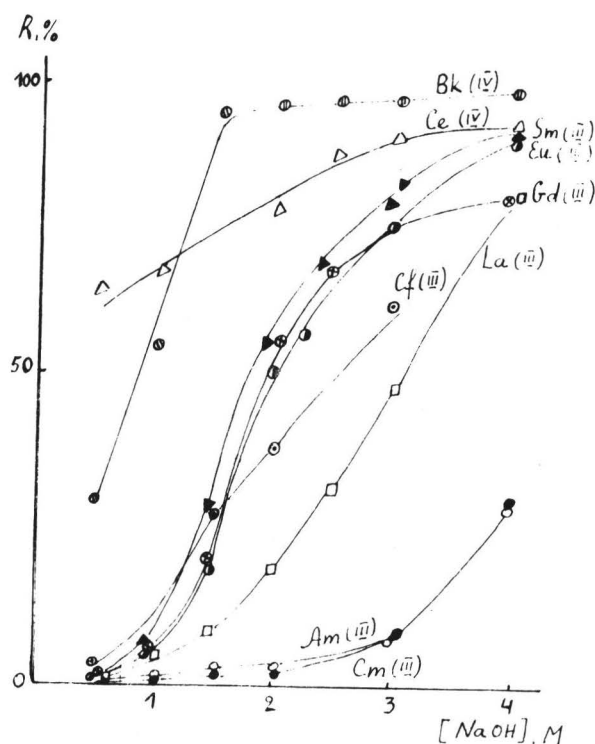


fig.5 Influence of NaOH concentration on the TPE and rare earths extraction from 10^{-4} M DTPA by 0.01 M DOP solution in toluene. Contact time is 10 minutes.

the increase of alkaline concentration in the initial solution influences ambiguously the extraction of the trivalent TPE and rare earths. The distribution coefficients of americium and curium grow slowly with increasing alkaline concentration whereas that of rare earths grows fast. The distribution coefficients of Eu(III) in 0.5-2 M NaOH grow by a factor of greater than 300 while that of Cm(III) only with one order. The features of the behaviour of Fe(III), that is extracted with very high distribution coefficients in all studying concentrations of NaOH, are worth noting in fig.6. The increase of the alkaline concentration has not the same influence on the extraction of tetravalent elements. The data in fig.6 show that the distribution coefficients of zirconium(IV) decrease with increasing those of plutonium(IV), pass through a maximum, and then decrease, but those of thorium(IV) after a maximum remain constant. In the case of the low alkaline concentrations the extraction grows in the sequence Zr Pu Th. On the contrary, in strongly alkaline media, Pu is extracted better than Zr. The tetravalent elements in the 0.5-2 M NaOH have much higher values for the distribution coefficients than

the trivalent Am and Cm. The extraction of the penta- and hexavalent elements occurs with lesser values of the distribution coefficients than of the tetravalent and practically is

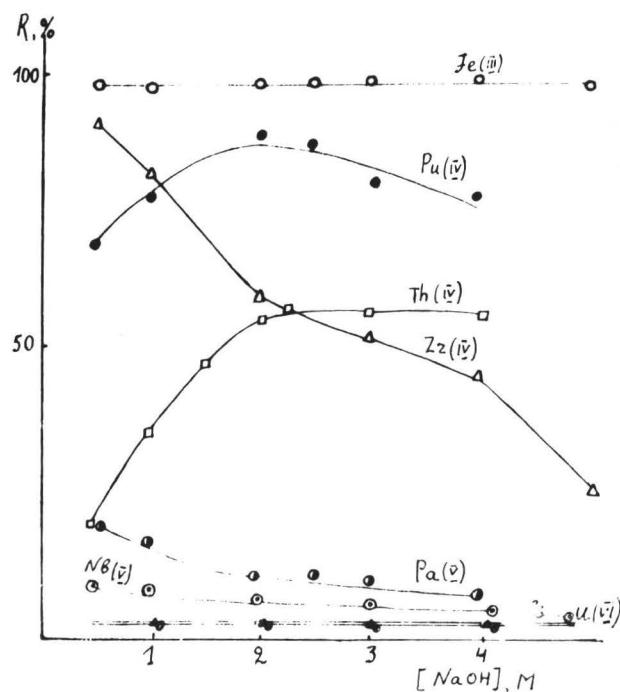


fig.6 Influence of NaOH concentration on the metal extractions from 10^{-4} M DTPA by 0.01 M DOP solution in toluene. Contact time is 10 minutes.

independent on the alkaline concentration. The difference in the extraction of Pa(V), Nb(V), U(VI) and Am(III) can be seen at the over 4 M alkaline concentration, i.e. in the conditions of the maximum extraction of TPE. The monovalent cesium, that is very slightly extracted at the studied alkaline concentrations, has the same behaviour. The distribution coefficient of cesium is 0.02 by the use of a 0.5-4 M NaOH solution. Those coefficients of the actinides in different oxidation states are changed in the sequence $Me(IV) > Me(III) > Me(V) > Me(VI)$. Thus the tetravalent actinides are extracted by the DOP-solution in toluene much better than the tri-, penta- and hexavalent ones. Therefore the degree of extraction of TPE and other metals from alkaline solutions by DOP are very different that creates the prerequisites for their separation. The extraction of americium and curium by DOP from alkaline solution containing DTPA is particularly selective. These elements practically are not extracted if the NaOH concentration is ≤ 3 M, but Ce(IV), Sm(III), Gd(III), Zr(IV), Fe(III), Th(IV) and Pu(IV) are extracted quantitatively into the organic phase in such conditions. From the strongly alkaline solutions (> 5 M NaOH) Am and Cm can be extracted quantitatively, but U(VI), Pa(V), Nb(V), Ru(III) and Cs(I) remain in aqueous phase. The greatest values of separation factors for the TPE and some other elements are given in table 1.

Table 1

Maximum separation factors for the TPE and other elements in system DOP-DTPA-NaOH

Pair of elements	Separation factors	Pair of elements	Separation factors
Ce(IV)-Am(III)	$> 3 \cdot 10^2$	Am(III)-U(VI)	$2 \cdot 10^3$
Sm(III)-Am(III)	40	Am(III)-Cs(I)	$2 \cdot 10^3$
Eu(III)-Am(III)	40	Bk(IV)-Am(III)	$4 \cdot 10^2$
Gd(III)-Am(III)	40	Bk(IV)-Cm(III)	$4 \cdot 10^2$
Fe(III)-Am(III)	$2 \cdot 10^4$	Bk(IV)-Cf(III)	20
Pu(IV)-Am(III)	$> 2 \cdot 10^2$	Bk(IV)-REE(III)	30
Zr(IV)-Am(III)	$10^3 - 10^2$	Fe(III)-Cf(III)	10^3
Th(IV)-Am(III)	10^2	Ce(IV)-Cf(III)	10^2
Am(III)-Pa(V)	10^2	Zr(IV)-Nb(V)	10^2

The data of table 1 show that it is possible to reach considerable separation factors for pairs: Fe(III)-Am(III) (20000); Ce(IV)-Am(III) (> 300); Am(III)-U(VI) and Am(III)-Cs(I) (2000); Bk(IV)-Am(III) and Bk(IV)-Cm(III) (400) in the system DOP-DTPA-NaOH. The trivalent TPE can be separated from some rare earths fission products. The optimum conditions for americium and europium separation are the following: 2 M alkaline concentration, 10^{-4} M DTPA, $1 \cdot 10^{-2}$ M DOP, the contact time is 10 minutes. About 97% of europium are extracted by the free-time extraction. The percentage of americium in aqueous phase is 90% and that of europium does not exceed 3%. The further quantitative extraction of americium from aqueous phase is reached by 0.04 M DOP solution in toluene within 45 min.

In conclusion it is necessary to note that the given examples, do not exhaust all possibilities for isolation and separation of TPE with the alkylpyrocatechols but the data cited give an idea on the wide capabilities of the extraction methods in strongly alkaline solutions.

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SEPARATION OF ACTINIDES FROM PUREX WASTE.

J.O.Liljenzin, I.Hagström, G.Persson and
I.Svantesson.

Department of Nuclear Chemistry, Chalmers
University of Technology

S-412 96 Göteborg, Sweden.

ABSTRACT

The CTH actinide separation process consists of three main circuits using the reagents: HDEHP to isolate U, Np and Pu, TBP to reduce acidity below 0.1 M and again HDEHP to isolate Am, Cm and higher actinides. The lanthanide - threevalent actinide separation utilises a modified type of the reversed TALSPEAK process. The process is briefly described and the mathematical models for the extraction of individual components, for extraction and strip circuits and for calculations on the complete flowsheet are described and discussed. Development of some essential auxiliary operations is described and results from mixer-settler tests of process performance is given. The calculated actinide recovery efficiencies are 99.99% U, 98.9% Np, >99.99% Pu, 99.8% Am and >99.9% Cm.

INTRODUCTION

At present, and probably for a long time to come, the PUREX process or variations thereof is the only method commercially used for reprocessing of spent nuclear fuel from power reactors. The normal PUREX process leaves a minor part of the uranium, plutonium and practically all the neptunium, americium, curium and higher actinides in the high-level liquid waste stream (HLLW).

An analysis of the dose to man from possible future releases of radionuclides from a deep repository in granite bedrock shows that uranium and neptunium isotopes together with their daughters, are the main contributors to the dose from the repository in some scenarios (1,2). The importance of the dose from Np-237 is further accentuated by new data on the effective dose equivalent per unit intake of this nuclide (3,4). The new data increase the dose by about a factor 100 and thus makes neptunium the all dominating hazard from the waste. Due to the long halflife of Np-237, 2.10⁶ years, the expected life of waste containers and waste forms plays a nonsignificant role in controlling the neptunium release, even if they are in the order of 100.000 years. It seems therefore much more effective to reduce the actinide content in the waste, especially neptunium, than to improve on containers and waste forms. To be meaningful, such a separation must offer other and better means of disposal or destruction of the separated actinides than planned for the bulk waste. Once the actinides are available in pure form, several options are open, e.g. transmutation in thermal or fast reactors, disposal in deep space or on other celestial bodies (5,6,7). A reduction of the actinide content in the waste by a factor of about 100 should be sufficient to reduce the long-time

dose to man to acceptable values (8).

PROCESS SELECTION

The main goal is an actinide removal efficiency of about 99% or better. It is further strongly desirable that the process should not introduce significant amounts of chemicals which would end up as indestructible products in the purified waste and contribute to the mass and volume of the solidified waste product. Because of the considerable radiation levels encountered, the process must be suited for remote operation. To avoid radiation degradation of reagents and criticality risks as much as possible, the process should not lead to any large accumulation of actinides in any part of the flowsheet, except as a final product. It was felt that on these grounds a solvent extraction process was preferable to other available methods, e.g. precipitation, ion exchange.

Using solvent extraction, several possible process alternatives exist. The selection among these must be based on several other criteria such as : availability and radiation resistance of reagents and diluents, extractive power for the actinides, effective ways of stripping, tolerable co-extraction of other elements present in the waste, sufficient loading capacity of the organic phase and means to clean and regenerate used reagent solutions.

On these grounds the use of bidentate extractants was ruled out due to low availability of reagents and possible stripping/regeneration difficulties. The use of TBP at high nitric acid concentrations was also ruled out due to the known difficulties encountered in obtaining an exhaustive plutonium extraction in the PUREX process. HDEHP (di-2-ethylhexyl phosphoric acid) was finally selected as the most promising candidate, although it will not extract all actinides at the same chemical conditions. To circumvent this restriction a three step process was developed, beginning with a HDEHP extraction at about 6 M nitric acid concentration followed by an acidity reduction step giving about 0.1 M acidity and finally a second HDEHP extraction. U, Np and Pu are removed by the first extraction and Am, Cm and higher actinides by the last extraction.

The necessary reduction in acidity can be obtained in several ways. Reaction of nitric acid with formaldehyde or formic acid during heating are wellknown procedures (9,10). However, preliminary tests showed a slow reaction rate below 1 M nitric acid concentration and the occurrence of precipitates when using simulated HLLW solutions. A more unconventional approach, extraction of nitric acid with TBP, was tested and found satisfactory (11).

Thus the framework of the CTH actinide separation process was set, but it remained to find actual operation conditions, treatment of waste and product streams etc. The current flowsheet is shown in Figure 1, where the three extraction cycles can be seen. The details of this flowsheet have been described and discussed elsewhere (12,13).

FLOWSHEET DESIGN AND OPTIMIZATION

The design and optimization of a flowsheet for any actinide separation process operating on HLLW must take into account the chemical and extractive behaviour of the actinides, fission products, corrosion products, acids and reagents used. To do this in a meaningful way is only possible with the aid of suitable computer programmes.

Extraction models. In the calculation of multi-element behaviour in countercurrent extraction and stripping circuits a simple, rapid and sufficiently accurate mathematical model for the extraction of each element is needed. The use of sophisticated chemical models leads often to equations, or systems of equations, solvable only by iterative techniques. Thus in general

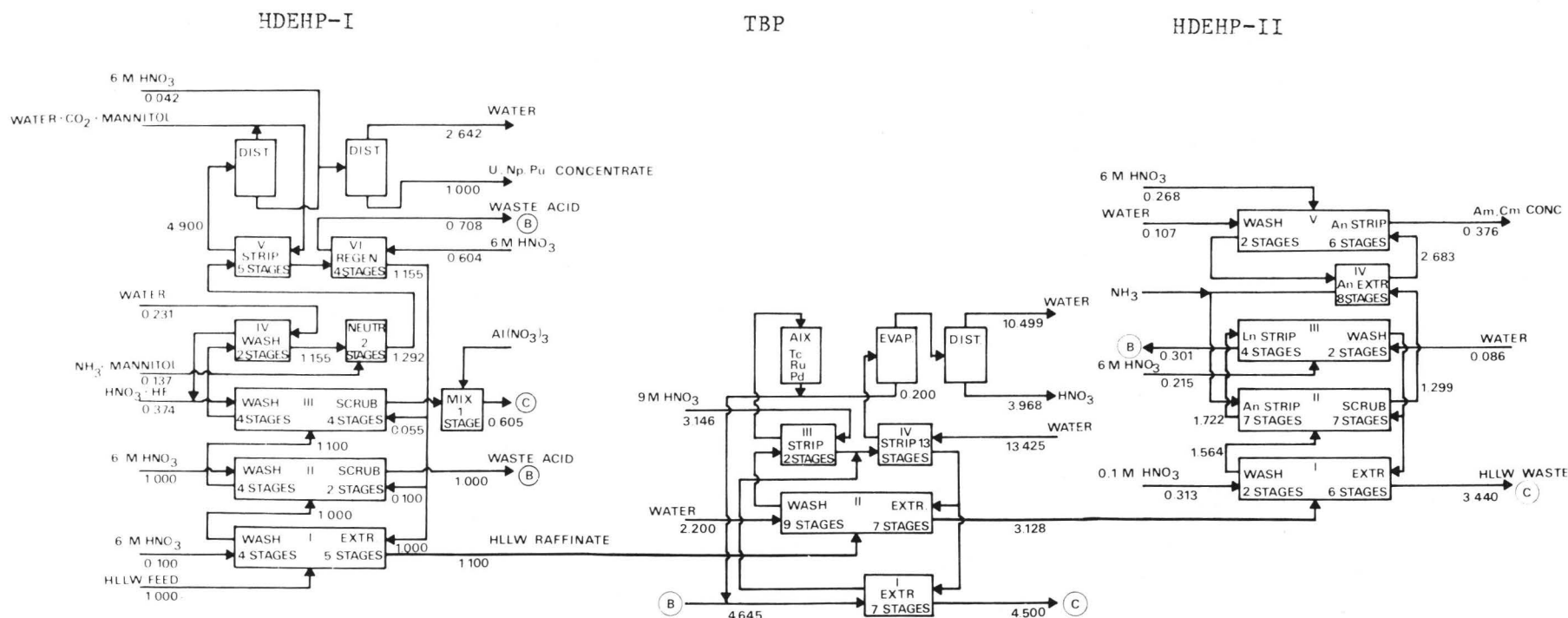


Figure 1. Flowsheet for the CTH actinide separation process. Numbers refer to the flowrates relative to the flowrate of the HLLW feed to the process. C denotes the final treatment of the purified waste, whether sorption on inorganic ion exchangers or vitrification.

chemical models lead to impractically long computation times when dealing with HLLW systems. Instead, the following empirical model was fitted to measured distribution data at 1 M HDEHP and at 50% TBP in kerosene (11,14).

$$D_M = \frac{k_0 + \sum_{i=1}^I k_i [\text{HNO}_3]^{l_i}}{1 + \sum_{i=1}^N m_i [\text{HNO}_3]^{n_i}} \quad (1)$$

where D_M is the distribution ratio of a given substance, M, at low loading by M and at a given nitric acid concentration, $[\text{HNO}_3]$, in the aqueous phase. The parameters k_i , l_i , m_i and n_i are adjusted to fit equation 1 to the available data. The limits I and N were chosen as low as possible without sacrificing a good description of available data.

In three special cases, stripping with hydrofluoric acid, ammonium carbonate and ammonium-DTPA-lactic acid mixtures, similar equations were used but with hydrofluoric acid, ammonium carbonate and ammonium ion concentrations respectively substituted for the nitric acid concentration in equation 1.

The extraction of nitric acid, especially in the TBP cycle, leads to changes in the phase volumes and thus of the flow ratio. Using the experimentally determined apparent molar volume, v , of nitric acid in each phase, the total phase volume, V , could be calculated from the following equation:

$$V = V^0 (1 + [\text{HNO}_3] v) \quad (2)$$

where V^0 is the phase volume in the absence of nitric acid and $[\text{HNO}_3]$ is the concentration of nitric acid in the phase considered. For the organic solutions a constant value of v , 0.0322, was used with sufficient accuracy, but for the aqueous phase v was computed from equation 3.

$$v = 0.02744 + 0.001439 [\text{HNO}_3]^{\frac{1}{2}} \quad (3)$$

Countercurrent extraction/strip of the controlling component. The calculation of extraction and strip effects in each countercurrent battery of mixer-settlers was begun with a calculation of the concentration in each stage of the controlling species, in most cases nitric acid, and the resulting organic to aqueous interstage flow ratios. In the case of nitric acid, the inflowing aqueous nitric acid concentration, x_{n+1} , to the n :th stage was computed iteratively from equation 4,

$$x_{n+1} = \frac{x_n A(x_n) + r |D(x_n) B(D(x_n)) - D(x_{n-1}) B(D(x_{n-1}))|}{A(x_{n+1})} \quad (4)$$

where x_n is the outgoing aqueous nitric acid concentration from the n :th stage, $D(x_n)$ is the D-value for nitric acid at concentration x_n in the aqueous phase obtained using equation 1 and the appropriate constants. The overall reduced flow ratio, r , is given by equation 5.

$$r = \frac{V_{\text{org.feed}} A(x_{\text{feed}})}{V_{\text{aq.feed}} B(y_{\text{feed}})} \quad (5)$$

where $V_{\text{org.feed}}$ and $V_{\text{aq.feed}}$ are the corresponding flow ratios into the battery. x_{feed} and y_{feed} are the nitric acid concentrations in the aqueous and organic feeds, respectively. The volume functions A and B for aqueous respectively organic phases are given by:

$$A(x) = 1 + x (0.02744 + 0.001439\sqrt{x}) \quad (6)$$

$$B(y) = 1 + 0.0322 y \quad (7)$$

which were obtained from equations 2 and 3 above. Equation 7 gives sufficient accuracy both for 1 M HDEHP and 50% TBP.

Equation 4 can be used recursively in an iterative manner to determine the nitric acid concentrations and flow ratios from known values of feed conditions and number of stages. Batteries with central feedpoints can also be treated by using an appropriate iterative method. Similar methods were used in the case of other controlling components, e.g. HF, $(\text{NH}_4)_2\text{CO}_3$, NH_4^+ .

Countercurrent extraction/strip of other components. In the CTH process both central aqueous and central organic feeds are used, as well as simple extraction or strip batteries. Having obtained the flow ratios and concentrations of the controlling species, by the method given above, it is a relatively straightforward process to calculate the behaviour of all other species as their D-values can be calculated from equation 1 for each stage in a battery. Due to the possible variation in interstage flow in a battery it is advantageous to base the calculations on mass flows (concentration times flow rate) rather than on concentrations. To illustrate this method we can start by introducing the extraction factor, P_n , for the n:th stage given by:

$$P_n = D_n r_n \quad (8)$$

where D_n and r_n are the distribution and phase flow ratios for the n:th stage within the battery. Stages are numbered from 1 at the aqueous effluent end to N before the feedpoint. The feedpoints are, for calculational purposes, at a hypothetical stage N+1. The remaining stages are then numbered up the aqueous stream from N+2 to M+N+1. Thus we have N stages down the aqueous stream from the feedpoint and M stages upstream. Introduce the following constants:

$$e_1 = \left(1 + \sum_{i=1}^N \prod_{k=i}^N P_k \right) \quad (9)$$

$$e_2 = \left(1 + \sum_{i=2}^N \prod_{k=i}^N P_k \right) \quad (10)$$

$$s_1 = \left(1 + \sum_{i=N+2}^{M+N+1} \prod_{k=i}^{M+N+1} P_k \right) \quad (11)$$

$$s_2 = \left(1 + \sum_{i=N+3}^{M+N+1} \prod_{k=i}^{M+N+1} P_k \right) \quad (12)$$

$$\varphi = \prod_{k=N+2}^{N+M+1} P_k \quad (13)$$

Then the aqueous effluent mass flow, X_p , can be shown to be given by the equation:

$$X_p = \frac{X_w + Y_w (e_2 \varphi + s_2) + Y_f s_1 + X_f s_2}{e_1 \varphi + s_2} \quad (15)$$

where X_w , Y_w , X_f and Y_f are the mass flows of the aqueous feed to the M+N+1:st stage, of the organic feed to the first stage, of the aqueous and of the organic feed to the central feedpoint, respectively. From a mass balance the organic effluent mass-flow, Y_p , is obtained as:

$$Y_p = X_f + Y_f + X_w + Y_w - X_p \quad (16)$$

The effluent concentrations can be obtained by dividing the outgoing mass flows by the effluent flow rates.

Process evaluations. The evaluation of the total flowsheet was divided into three nearly independent calculations, one for each of the three main cycles in Figure 1. The first cycle is completely independent of the following cycles. The second cycle is mainly dependent on the effluent from the first cycle and only to a minor extent on the effluents from the third cycle, if acid feedback is used. The last cycle is only dependent on the effluent from the second cycle.

Three separate, but very similar computer programmes were written, one for each cycle. In each programme a series of batteries was included. The flow between these batteries was set through a connection matrix.

The calculation was begun at the primary HLLW extraction battery and was first performed for the controlling species, and then for all other components. The calculation was forced to proceed from battery to battery throughout each part of the cycle and then to iterate from the beginning until no further changes occurred in any concentration. This gave all concentrations for the steady state operation of the cycle. The calculation was repeated in this way for each of the remaining cycles in turn. Typical calculation times on a Honeywell H-316 computer were a few hours, or less.

By changes in the connection matrices, stage numbers, flowrates and chemicals, various variations on the basic flowsheet could be studied. The most promising designs were then tested in mixer-settler experiments using simulated HLLW solutions. In general the analytical results agreed well with the calculated concentrations. Some deviations were, however, observed for a few elements where kinetic effects are very pronounced, e.g. iron and tin.

AUXILIARY OPERATIONS

Carbonate recovery. To recover the ammonium carbonate strip solution and to convert the U, Np, Pu, etc. carbonates to nitrates a distillation process was used. The pregnant strip solution is pumped to a measuring vessel from which it is fed batchwise to an evaporator of cyclone type. Here >95% of the ammonium carbonate and some water is distilled off. The distillate is collected and its pH adjusted with gaseous CO_2 to compensate for excess of ammonia, diluted with water, mannitol added and then fed back to the buffer tank for the strip solution. The concentrate, which is nearly neutral, is fed to a second evaporator where a measured amount of nitric acid is added and excess water distilled off to give a solution of fairly high concentration, but still avoiding the precipitation of nitrates. The further treatment of this product depends on its use.

Cesium sorption. Cesium can be recovered quantitatively from the actinide free HLLW solution leaving the process using small columns of mordenite,

a zeolite which is highly selective for cesium. Only very little sorption of other elements has been observed.

Ruthenium, palladium and technetium recovery. The noble elements Ru, Pd, and Tc can be recovered from the 2.6 M nitric acid effluent from the TBP(III) battery, see Figure 1, using anion exchange. At present we do not intend to strip these elements from the loaded columns, but prefer to replace the spent anion exchange resin.

Nitric acid recovery. The effluent from the TBP(IV) battery is a 3 M nitric acid with small amounts of radioactive isotopes. An evaporation to 1.4% of initial volume removes 93% of the nitric acid with the condensate. The residual concentrate is fed back to the extraction circuit. A pure 10 M nitric acid is then obtained from the condensate through fractional distillation. Part of this is reused in the process and part is a product from the process. These operations are wellknown and used, e.g. in the PUREX process.

PROCESS PERFORMANCE

The process has been extensively tested at low-activity levels using radioactive tracers and simulated HLLW solutions of two different compositions, one corresponding to the expected composition of PUREX waste and one corresponding to the composition of an old waste from processing of low burnup fuel. Data in Figure 1 refer to the "old waste" conditions. In both cases the process seems fairly easy to operate and control with only a few critical operations: neutralization of HDEHP in the first cycle and pH adjustment in the third cycle.

The calculated recovery factors are 99.99% U, 98.9% Np, >99.99% Pu, 99.8% Am and >99.9% Cm. These data agree, within analytical errors and experimental uncertainties, with those from tracer experiments and from the manual batch testing on a small sample of the "old waste" mentioned above. A small pilot test run on the "old waste" is planned to take place during the spring of 1980. This experiment will give a more accurate verification of the process performance at higher activity levels.

ACKNOWLEDGEMENT

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$^{99}\text{TcO}_4$ CYCLOHEXANONE SOLVENT EXTRACTION OF
FROM ALKALINE NUCLEAR WASTE SOLUTIONS

Wallace W. Schulz
Rockwell International
Rockwell Hanford Operations
Energy Systems Group
Richland, WA 99352
UNITED STATES

ABSTRACT

Cyclohexanone extracts pertechnetate ion with good efficiency and specificity from alkaline nitrate solutions. This fact provides the basis for countercurrent solvent extraction processes being developed for removal of long-lived ^{99}Tc from the water-soluble fraction of Hanford defense wastes. The current status of these studies including conceptual process flowsheets, distribution data, and mixer-settler process tests is summarized in this paper.

INTRODUCTION

Large volumes of high-level nuclear waste have accumulated at the U.S. Department of Energy Hanford Reservation as the result of fuel reprocessing operations performed between 1944 and 1972. Various alternative plans have been proposed for long-term management of the Hanford Defense high-level wastes (1,2,3). One of these alternative schemes (1) involves removal of most of the long-lived ($t_{1/2} > 10\text{y}$) radionuclides, and many of the shorter-lived ones as well, from these wastes. The objective of this radionuclide removal approach is to partition the water-soluble portion of the wastes into a small volume of highly radioactive waste requiring further immobilization for long-term disposal and a large volume of very low-level waste which can be safely stored or disposed of by inexpensive means. Cost data (1) indicate potential economic benefits may result from a reduction in the volume of high-level waste requiring immobilization and high integrity containers and storage facilities.

The water-soluble fraction ($\sim 10^8$ kg) of the Hanford Defense wastes comprises both solid salt cake ($95\,000\text{ m}^3$) and residual liquid ($45\,000\text{ m}^3$). Inert sodium salts- NaNO_3 , NaOH , NaAl(OH)_4 , NaNO_2 , Na_2CO_3 , Na_2CrO_4 , Na_2SO_4 , and Na_3PO_4 - make up over 99% of the mass of this material. Many short and long-lived (e.g. ^{106}Ru , ^{60}Co , ^{147}Pm , ^{137}Cs , ^{90}Sr , ^{99}Tc , etc.) radionuclides are present in the salt cake and residual liquid. Although from an activity standpoint, ^{137}Cs and ^{90}Sr ($\sim 10^7$ Ci) are the principal radionuclides, the

water-soluble fraction is estimated to contain about 1800 kg (3.1×10^4 Ci) of ^{99}Tc ($t_{1/2} = 2.1 \times 10^5 \text{y}$). This amount of ^{99}Tc is that calculated (1) to be present in the existing water-soluble plus water-insoluble Hanford Defense wastes. The calculated inventory of other radionuclides in these wastes is listed in References 1 and 3.

For removal of $^{99}\text{TcO}_4^-$ from highly alkaline nuclear waste solutions we are currently developing continuous countercurrent solvent extraction processes which employ cyclohexanone as the pertechnetate ion extractant. This paper summarizes the current status of development and demonstration of these new solvent extraction processes. Technology for strong base anion exchange recovery of $^{99}\text{TcO}_4^-$ from alkaline solutions is well known (4,5). The principal disadvantage to this recovery method is that large volumes of 6 M HNO_3 are required to elute ^{99}Tc from the resin. Treatment of the acid eluate to concentrate the ^{99}Tc and recover HNO_3 for reuse requires complex and expensive capital equipment.

REAGENTS FOR SOLVENT EXTRACTION OF PERTECHNETATE ION

Various organic compounds are known to extract pertechnetate ion from strong alkaline solutions. The list of usable reagents includes pyridine; (4, 6-11) methylpyridine derivatives including 2-methylpyridine, (9,10) 3-methylpyridine, (9) 4-methylpyridine, (9) 2-4-dimethylpyridine, (9,10,12) and 2-methyl-5-ethylpyridine; (10) quinoline; (10) quaternary ammonium compounds; (4,13) methylethylketone; (14,15) acetone; (16) and cyclohexanone (8,11).

Cyclohexanone is currently considered to be the most suitable extractant for use in removal of ^{99}Tc from Hanford salt cake solutions and residual liquids. Cyclohexanone is commercially available in large quantities ($\sim \$1.00/\text{kg}$), and its physical and chemical properties (e.g., aqueous phase solubility, radiolytic and chemical stability, mass transfer kinetics, etc.) are satisfactory and superior to those of other candidate ketones such as acetone or methylethylketone. Distribution coefficients of TcO_4^- between aqueous alkaline nitrate feed stock and cyclohexanone are high enough (e.g. 5-10) to permit satisfactory countercurrent engineering-scale extraction of ^{99}Tc . Cyclohexanone is nearly specific for TcO_4^- and provide excellent decontamination from both inert and radioactive contaminants. Most important, technetium can be removed from cyclohexanone extracts by simple stripping with water.

TECHNETIUM CYCLOHEXANONE SOLVENT EXTRACTION PROCESSES

Two approaches to cyclohexanone solvent extraction of $^{99}\text{TcO}_4^-$ from alkaline Hanford defense waste solutions are presently under consideration. One (Fig. 1) involves countercurrent extraction of the $^{99}\text{TcO}_4^-$ into an equal (perhaps double) volume of cyclohexanone followed by stripping of the technetium into water. Anticipating results discussed in detail later, cyclohexanone extracts TcO_4^- from alkaline waste solutions with good efficiency and selectivity.

Technetium preferentially transfers to the aqueous phase when the cyclohexanone extract is contacted with water. Water stripping operations are complicated, however, by the formation, under some conditions, of stable emulsions from which aqueous and organic phases disengage only slowly. (It is not known if such emulsions form under agitation conditions typical of plant-scale pulse columns.) Stable cyclohexanone - water emulsions form apparently as the

result of the partial solubility of cyclohexanone in water and because of the lack of any dissolved electrolyte. Phase disengaging times of cyclohexanone - water mixtures are substantially decreased by addition of small amounts of finely divided talc (magnesium silicate). Formation of intractable emulsions can also be avoided by use of dilute sodium salicylate solutions to strip ⁹⁹Tc from cyclohexanone extracts.

Cyclohexanone is significantly soluble (60-80 g/L at 25°C) in water and also dissolves, but to a lesser extent, in extraction column aqueous raffinate. Dissolved cyclohexanone in strip and raffinate solutions can be recovered (and recycled) by simple thermal concentration of such solutions. Technetium recovered by cyclohexanone extraction will be combined with other radionuclides recovered by the Hanford Radionuclide Removal Process and with sludge for eventual drying and immobilization. Behavior of ⁹⁹Tc in the drying and immobilization steps was not studied in this investigation.

Hydroxide-form, macroreticular strong base anion exchange resins such as, for example, Amberlyst A-26 or A-27 (Rohm and Haas Co.), strongly sorb TcO_4^- from cyclohexanone solutions. One volume of resin will sorb essentially all the technetium from 150-200 volumes of cyclohexanone extract containing 10-100 $\mu Ci/L$ ⁹⁹Tc. This resin sorption technique provides a straightforward way of stripping (and concentrating) technetium from cyclohexanone solutions and completely eliminates any need to cope with aqueous-organic phase disengaging difficulties. Resin stripping of technetium is particularly attractive when used with a "spin" type extraction column. In this scheme (Fig. 2), the cyclohexanone is recycled to the extraction column to concentrate technetium from say 5-10 $\mu Ci/L$ to about 100 $\mu Ci/L$. Ten to 20-fold concentration of the ⁹⁹Tc prior to stripping significantly reduces resin requirements.

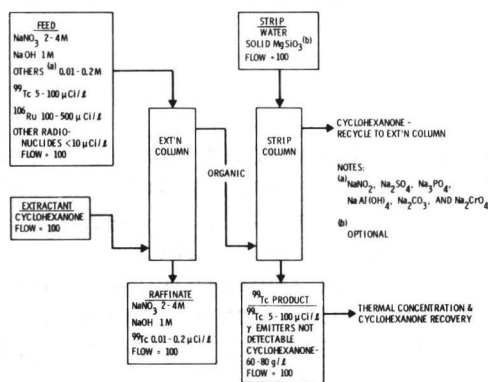


FIG. 1
Cyclohexanone Technetium Extraction-Strip Process

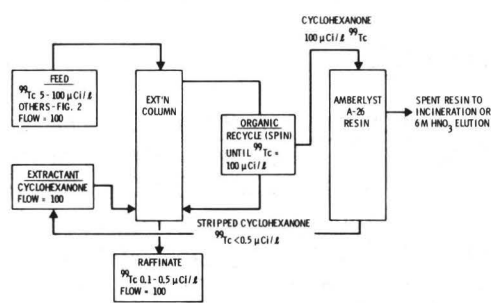


FIG. 2
"Spin" Type Cyclohexanone-Resin Stripping Technetium Recovery Process

Macroreticular anion exchange resin beds loaded with technetium can be eluted with 6 M HNO_3 and also with a few column volumes of a 30 vol% quaternary ammonium compound dissolved in kerosene. Technetium-loaded resin beds can, of course, be directly incinerated without elution; the economic practicability of such resin treatment has not yet been determined. Spent quaternary ammonium compound-kerosene elution solution can also be incinerated.

Miniature mixer-settler tests with both synthetic and actual waste solutions have adequately demonstrated the simple (Fig. 1) cyclohexanone extraction column approach. Mixer-settler runs to study suitable conditions for operation of a "spin-type" (Fig. 2) extraction column have not yet been made.

EXPERIMENTAL

MATERIALS

A few extraction experiments were performed using cyclohexanone supplied by the Ashland Chemical Co. and by the Amsco Division of Union Oil Company (>99.7% and >99.7% cyclohexanone, respectively). Reagent grade cyclohexanone supplied by Matheson, Coleman, and Bell was used in all other tests.

Amberlyst A-26 resin is a strong-base macroreticular anion exchanger made by Rohm and Haas Co. Beds of Cl-form 14-50 mesh (U.S. Standard Screen Series) resin were converted to OH-form material by down flow of excess volumes of 1-4 M NaOH. Some important physical and chemical properties of A-26 resin are listed in Reference 17.

^{99}Tc in the form of a solution of NH_4TcO_4 in pH 7 water was obtained from the ICN Chemical and Radioisotope Division, Irvine, California. ^{95}Tc was procured from New England Nuclear Corp. as a solution of NaTcO_4 in pH 4 water.

Actual waste solutions were used in two mixer-settler tests of the cyclohexanone ^{99}Tc extraction process. Compositions of these two solutions before and after removal of ^{137}Cs and ^{90}Sr and other >2+ radionuclides are given in References 3 and 18, respectively.

PROCEDURES

Distribution Ratios. The distribution of pertechnetate ion, either $^{99}\text{TcO}_4^-$ or $^{95}\text{TcO}_4^-$, between cyclohexanone and various aqueous solutions was measured at both 25 and 50°C. Phases were contacted 10 minutes by mechanical stirring and separated by centrifugation. Cyclohexanone solutions were contacted twice with equal volumes of aqueous phases not containing technetium and then finally, with an equal volume of aqueous phase containing either ^{99}Tc or ^{95}Tc . The technetium distribution ratio (D_{Tc}) was calculated from analysis of aqueous and organic phases from the last contact.

A-26 Resin Sorption of Tc From Cyclohexanone

Glass columns (1.05 cm ID) containing 5.0 mL of Amberlyst A-26 resin, supported by a stainless steel screen, were used to study sorption of Tc from cyclohexanone solutions. Prior to use, resin beds were converted to the OH form by downflow of excess 4 M NaOH; subsequently, resin beds were classified by upflow of water and then washed free of water with pure cyclohexanone. Cyclohexanone solutions containing 10-200 $\mu\text{Ci/L}$ ^{99}Tc were prepared by batch

equilibration with 5 M NaNO_3 - 1 M NaOH - ^{99}Tc solutions. Columns were operated at $\sim 25^\circ\text{C}$ with downflow of cyclohexanone at the rate of 1 or 2 column volumes (CV) per hour. Resin bed performance was determined from measurements of the volume and ^{99}Tc content of the effluent stream.

Mixer-Settler Runs

Extraction column tests of the simple extraction-strip flowsheet were made in a 12-stage all-stainless steel mixer settler. This unit was a Hanford designed version of a type developed earlier by Coplan *et al.* (19). The mixer-settler was operated with the particular aqueous feed and cyclohexanone solutions required until steady-state conditions were reached. Aqueous and organic streams were metered to the mixer-settler by means of FMI (Fluid Metering Instrument Co.) pumps. Samples of the effluent streams were taken hourly and analyzed to determine when steady-state was attained. Technetium losses were computed from analysis of the steady-state effluent streams.

ANALYTICAL

^{99}Tc in aqueous solutions was initially determined by a solvent extraction procedure in which TcO_4^- is quantitatively extracted, in the presence of tetrapropyl ammonium hydroxide, into a mixture of chloroform and methylisobutylketone. An aliquot of the final organic extract was mounted on a planchet, dried, and beta counted. Initially also, ^{99}Tc in cyclohexanone solutions was determined by beta counting of mounted and dried aliquots. Later in the program ^{99}Tc in both aqueous and cyclohexanone sample was determined by liquid scintillation counting methods.

Standard gamma energy pulse height methods employing a lithium-drifted germanium $\text{Ge}(\text{Li})$ detector were used to determine the concentrations of ^{95}Tc and other gamma emitting radionuclides in aqueous and organic phases.

RESULTS AND DISCUSSION

TECHNETIUM EXTRACTION BEHAVIOR

Liquid-liquid extraction of the pertechnetate ion from aqueous media by undiluted cyclohexanone depends, as the data plotted in Figures 3 and 4 illustrate, upon technetium concentration and the type and concentration of aqueous phase salting agent. Technetium distribution ratios (D_{Tc}) decrease with increasing technetium concentration (Fig. 3). Lavrukhina and Pozdnyakov (11) report that D_{Tc} for extraction of technetium from acid media by ketone-type extractants falls off when the technetium concentration exceeds 10^{-3} M. The same authors also cite data for decreases in D_{Tc} for pyridine extraction of technetium from Na_2CO_3 - NaOH media as the technetium concentration increases from 0.008 to 0.16 M.

Experiments to determine the extraction mechanism and organic species involved in cyclohexanone extraction of TcO_4^- have not been performed. Lavrukhina and Pozdnyakov (11) state that polar, strongly basic solvents such as ketones extract pertechnetate from alkaline media as the ion associate $\text{S}_z\text{Me}^{x+}(\text{H}_2\text{O})_n\text{S}_m(\text{OH}_2)_y\text{S}_j(\text{TcO}_4)_x$ where S is the solvent molecule and Me^{x+} is the inorganic cation. On the other hand, for cyclohexanone extraction of ReO_4^- from NaOH solutions Jordanov, Pavlova, and Boikova (20) postulate the formation of a single solvate of the type $\text{NaReO}_4 \cdot 10$ cyclohexanone. Whatever the

exact organic entity involved, Lavrukhina and Pozdnyakov (11) ascribe decreases in D_{Tc} with increasing technetium concentration to the limited solubility of technetium solvates or ion associates in the particular solvent involved.

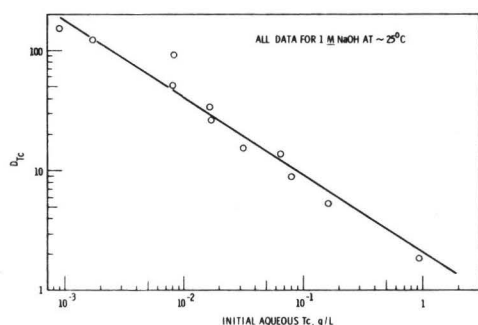


FIG. 3
Cyclohexanone Extraction of ^{99}Tc :
Variation of D_{Tc} with Tc Concentration

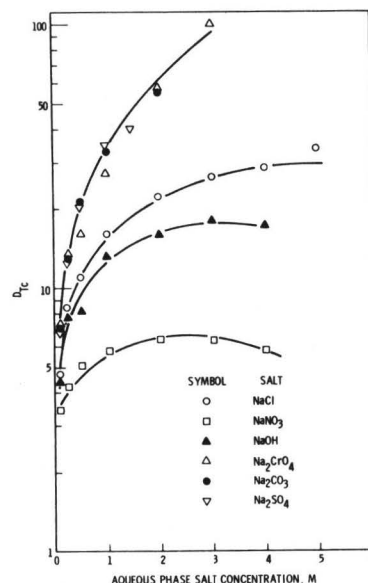


FIG. 4
Cyclohexanone Extraction of ^{99}Tc :
Variation of D_{Tc} with Salting

Extraction of technetium(VII) ion associates by polar solvents is strongly dependent upon the type and concentration of aqueous phase salting agent. As evidenced in Figure 4, 2:1 electrolytes are much more efficient than 1:1 salts in enhancing cyclohexanone extraction of technetium. All three 2:1 salts tested (Na_2CrO_4 , Na_2SO_4 , and Na_2CO_3) are about equally effective salting agents. Of the 1:1 electrolytes, however, $NaNO_3$ is noticeably inferior to either $NaOH$ or $NaCl$ in promoting transfer of technetium to the cyclohexanone phase. Other workers have also commented about the depressant effect of nitrate ion on extraction of pertechnetate ion by various ketones and other organic reagents. The relative order of salting strengths observed in these tests was $CrO_4^{2-} = SO_4^{2-} = CO_3^{2-} > Cl^- > OH^- > NO_3^-$. This order differs only slightly from the general order listed by Lavrukhina and Pozdnyakov.

Alkaline feeds to the cyclohexanone extraction process discussed here are essentially 4-5 M $NaNO_3$ solution containing, typically, 1-2 M $NaOH$ and smaller concentration of Na_2CrO_4 , $NaAl(OH)_4$, $NaNO_2$, and Na_2CO_3 . Technetium concentrations range from 3 to 200 $\mu Ci/L$. Under these conditions D_{Tc} values range from 5-10, which are sufficiently high to permit satisfactory countercurrent extraction recovery. Empirical extraction rate measurements indicate ^{99}Tc transfers rapidly from aqueous waste solutions to the cyclohexanone extractant.

TECHNETIUM STRIPPING TESTS

Stripping With Aqueous Solutions

Water was the most effective of several aqueous solutions tested (Table 1) for stripping $^{99}\text{TcO}_4$ from cyclohexanone solutions. In agreement with temperature effects noted in ^{99}Tc extraction studies, water strips removed technetium slightly more efficiently at 50°C than at 25°C . Kinetic data indicate technetium transfers to the water phase very rapidly at both 25 and 50°C . Water stripping of technetium at both 25 and 50°C seems to be dependent on the initial concentration of technetium in the cyclohexanone phase; this concentration effect may be more apparent than real, however, reflecting both experimental and analytical errors. Of the other agents studied, dilute HNO_3 and Na_2CO_3 solutions were completely ineffective for stripping technetium. Dilute sodium salicylate solution, although not as effective as water, do strip technetium from cyclohexanone. Concentrated sodium salicylate solutions have been reported (4) to elute technetium from strong base anion exchange resins.

TABLE 1. Batch Stripping of ^{99}Tc from Cyclohexanone Solutions

Conditions: Three Equal-Volume Batch Strips

Aqueous Strip Solution	Temp. $^\circ\text{C}$	Initial Organic ^{99}Tc $\mu\text{Ci/L}$	D_{Tc}			% Tc Not Stripped
			Strip 1	Strip 2	Strip 3	
Water	25	150-240	1.15	0.290	0.890	3.3
Water	25	14	3.16	0.659	1.36	16.1
Water	50	150-240	0.898	0.244	0.339	1.7
Water	50	14	1.61	0.647	1.39	10.4
0.1 M Sodium Salicylate	25	114	1.95	1.88	1.73	17.2
0.25 M Sodium Salicylate	25	114	1.46	0.729		15.1
0.01 M HNO_3	25	14	24.8	22.1	27.2	>99.
0.01 M Na_2CO_3	25	14	2.94	4.76	6.04	62.5

Intimately-mixed water-cyclohexanone systems, such as produced by mechanical stirring, disengage very slowly and, in some cases, thick white scums form at the phase boundary. These problems are slightly less prevalent at 50°C than at 25°C . Such phenomena obviously constitute a major disadvantage to use of water to strip technetium from cyclohexanone extracts. Scum formation and other undesirable phenomena which characterize emulsified water-cyclohexanone mixtures are believed to be associated in part with the appreciable solubility (70-80 g/L) of cyclohexanone in water and in part with the absence of dissolved electrolytes. In the latter connection, emulsified mixtures of cyclohexanone and dilute (>0.01 M) electrolyte solutions separate cleanly and rapidly without formation of interfacial scums.

Several remedies are available to eliminate, or reduce the severity of, phase disengaging difficulties with cyclohexanone-water systems. One alternative discussed in detail later, which totally eliminates the problem is to use strong base macroreticular anion exchange resin to strip ^{99}Tc . Small concentrations (e.g., 20-40 mg/L) of finely-divided talc (MgSiO_3) promote coalescence and disengaging of cyclohexanone-water emulsions.

Phase disengaging problems can also be avoided by using 0.25 M sodium salicylate rather than water to strip technetium from cyclohexanone. Technetium-containing sodium salicylate solutions can likely be thermally concentrated and taken to dryness without difficulty. The salicylate fraction of the dried solid will decompose during any high temperature immobilization process while sodium is one of the primary inert constituents of the radioactive sludge with which the dried solids would be combined prior to immobilization. Sodium salicylate solutions are not as effective as water in stripping technetium, however. Their use would require more efficient or larger (more stages) solvent extraction contactors.

Sorption on Amberlyst A-26 Resin

Strong base macroreticular anion exchange resins such as Amberlyst A-26 efficiently sorb TcO_4^- from cyclohexanone solutions (Table 2). Such resin treatment neatly avoid the phase disengaging properties encountered in water stripping operations. Because of their built-in large pore structure, macroreticular resins do not present significant hydraulic resistance to passage of organic solutions. Technetium loads smoothly on to A-26 resin to yield cyclohexanone entirely suitable for recycle to the extraction contactor.

TABLE 2. Amberlyst A-26 Resin Sorption of Tc from Cyclohexanone

Experimental Conditions: As Stated Under Procedures

Run 1(a,b)		Run 2(c)		Run 3(d)	
Column Volumes	Effluent ^{99}Tc $\mu\text{Ci/L}$	Column Volumes	Effluent ^{99}Tc $\mu\text{Ci/L}$	Column Volumes	Effluent ^{99}Tc $\mu\text{Ci/L}$
16	<0.0224	33.6	<0.117	34.4	0.0310
94.7	<0.0184	108	<0.0268	80.0	0.0282
121	<0.0396	130	<0.0198	94.4	0.0443
149	<0.0396	169	<0.0184	120	0.574
156	0.0494	250	<0.0222	144	1.78
186	0.720	291	<0.0180		
214	5.52	317	<0.0328		
294	73.7	415	6.10		

(a) Feed contained 115 $\mu\text{Ci/L}$ ^{99}Tc ; 1 CV/hr.

(b) Data are average of duplicate runs.

(c) Feed contained 9.2 $\mu\text{Ci/L}$ ^{99}Tc ; 1 CV/hr.

(d) Feed contained 100 $\mu\text{Ci/L}$ ^{99}Tc ; 2 CV/hr.

Sufficient data to completely quantify the Tc-cyclohexanone-A-26 resin system have not yet been obtained. Available results indicate almost complete resin uptake of Tc up to a very sharp breakthrough point. For initial ^{99}Tc concentrations in the range 10-100 $\mu\text{Ci/L}$ a single bed of A-26 resin will remove 99% of the technetium from 180-300 column volumes of cyclohexanone feed. Kinetic factors are also involved since ^{99}Tc sorption efficiency drops off with increasing flow rate.

MIXER-SETTLER FLOWSHEET TESTS

Results (Table 3) of mixer-settler runs with both synthetic and actual waste solutions illustrate that countercurrent cyclohexanone solvent extraction removal of ⁹⁹Tc to very low levels can be accomplished by proper specification of extraction stages and phase flow ratios. Organic extracts from tests with actual waste solution contained no detectable gamma emitters. The cyclohexanone extract from the run with actual salt cake solution contained 4.86 x 10⁻³ M sodium, <1.15 x 10⁻⁵ M chromium, and <2.22 x 10⁻⁴ M aluminum corresponding to decontamination factors of 1030, >21 and >630, respectively.

TABLE 3. Typical Results of Mixer-Settler Tests of Cyclohexanone ⁹⁹Tc Extraction Process

Waste Type	⁹⁹ Tc μCi/L	Mixer- Settler Stages	Flow Ratios Aq:Org	Steady-State Aqueous Raffinate ⁹⁹ Tc	
				%	μCi/L
Synthetic ^(a)	228	8	1:1	2.0	4.55
Synthetic ^(a)	234	12	1:2	0.70	1.64
Actual Salt Cake Solution ^(b,c)	12.7	12	1:1	0.33	0.0425
Actual Residual Liquid ^(b,d)	4.8	12	1:1	0.80	0.0387

- (a) 5 M NaNO₃ - 1 M NaOH.
- (b) After removal of ¹³⁷Cs and ⁹⁰Sr.
- (c) Feed contained 284 μCi/L ¹⁰⁶Ru; 3.0 μCi/L ¹⁵⁵Eu, 1.3 μCi/L ¹⁵⁴Eu, 1.2 μCi/L ¹²⁵Sb and 1.4 μCi/L ⁶⁰Co; all other gamma emitters below detection limit.
- (d) Ozonated, 5-fold diluted residual liquid. Feed to mixer-settler contained 650 μCi/L ¹⁰⁶Ru, 117 μCi/L ¹²⁵Sb, 21 μCi/L ⁶⁰Co, 5.5 μCi/L ¹⁵⁵Eu, 0.54 μCi/L ⁹⁰Sr, and <0.1 μCi/L ¹³⁷Cs.

CONCLUSIONS

The ⁹⁹Tc cyclohexanone solvent extraction process is still in the bench-scale development stage. But, even at this stage, the process appears well suited for engineering-scale removal of ⁹⁹Tc from alkaline Hanford waste solutions. The most pressing process development need is to resolve the phase disengaging problems encountered during water stripping operations. Stripping tests in pulse columns and/or centrifugal contactors are particularly needed to determine the magnitude of the phase disengaging problem in engineering-scale equipment and to find suitable remedies.

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EXTRACTION SEPARATION OF RARE EARTH ELEMENTS, SCANDIUM
AND THORIUM WITH MONO (2-ETHYL HEXYL) 2-ETHYL HEXYL
PHOSPHONATE (HEH(EHP))

Li Deqian, Wan Xiong, Lin Daozhi,
Xie Yanfeng, Lin Suxian, Wang
Zhonghuai, Li Han, and Ji Enyui

Changchun Institute of Applied Chemistry,
Chinese Academy of Sciences
Changchun, Jilin, China

ABSTRACT—The HEH(EHP) system has been systematically studied for the extraction of heavy rare earths. It has the advantage of easier stripping, no emulsion formation, in comparison with the wellknown HDEHP. In this article a part of the results -- dissociation, distribution, dimerization constants and solubility of HEH(EHP) in H_2O --mineral acids-- n-heptane system; extraction of mineral acids. Sc, Th and rare earths with HEH(EHP); mathematical model of Nd, Sm and their mixtures; group division of rare earths and Sm-Gd separation, as well as group division of rare earths (Nd-Sm) in HCl solution by ammoniated HEH(EHP) are included.

INTRODUCTION

Di(2-ethyl hexyl) phosphoric acid (HDEHP) has been widely used in the extraction technology(1-5) of rare earths since the publication of Peppard et al.(6) Although it is an efficient extractant for the separation of rare earths, the difficulties in back-extraction have limited its utilization in extraction separation of heavy rare earths and group division of mixtures containing large amounts of heavy rare earths.

HEH(EHP) is an extractant of acidic phosphoric type, analogous to HDEHP. In virtue of the existence of the bond between carbon and phosphorus atoms in the molecule, the extractability by HEH(EHP) of heavy rare earths or high valent elements is smaller than that of HDEHP.(7-9) The former has the advantage of easier back extraction, as well as the fact that no emulsion is formed.

Few articles have been published on the extraction of rare earths with HEH(EHP). Peppard et al. investigated the extraction of Pm, actinide series and thorium from mineral acid solutions.(7-8,10)

We have systematically studied the extraction separation of rare earths, Sc and Th by HEH(EHP) in order to evaluate the extraction characteristics of HEH(EHP). Part of the recent research work is included in the present article.

EXTRACTION OF RARE EARTHS Sc AND Th FROM AQUEOUS MINERAL ACIDS BY HEH(EHP)

Extraction from Nitrate or Chloride Aqueous Solutions

In the extraction of rare earths Sc and Th from nitrate or chloride aqueous solutions with HEH(EHP), the extraction curves are very similar for various acid concentrations of the solution. If $\lg D$ is plotted as a function of atomic number of the rare earths Z (Fig.1), a typical tetrad effect is found in both systems. The mean separation factor (β_z^{2H}) is 2.4 for the nitrate system and 2.2 for the chloride system. Within the experimental region of concentrations of nitric acid β_{La}^{Pr} is found to be 4-5, β_{Nd}^{Sm} 3.4-6.4, β_{Sm}^{Gd} 2.2-4.8, β_{Gd}^{Tb} 3.6-4.2, β_{Ho}^{Er} 2-2.4, β_{Tm}^{Yb} 2.5-2.8, and β_{Er}^{Tm} 2.3-3.6 etc. Y lies between Ho and Er. All these separation factors give the possibility of division of the rare earths into several groups or the separation between heavy lanthanides by extraction with HEH(EHP). The comparison of the extraction efficiency of Ce(IV), Sc, Th and Lu(III) at various concentrations of nitric acid is given in Table 1.

Table 1. Extraction Coefficient of Ce(IV), Sc, Th and Lu(III) from Various Initial Concentrations of Nitric Acid.

Initial Concen- tration of Nitric Acid, <u>M</u>	Extraction Coefficient (%)			
	Ce(IV)	Sc	Th	Lu(III)
0.57	-	100	-	98.2
1.00	92.7	-	99.3	-
1.15	-	100	-	85.8
1.43	-	100	-	79.0
2.00	91.3	100	98.9	59.3
2.50	-	100	-	47.4
3.00	88.9	-	99.2	-
4.00	86.9	-	99.4	-
5.00	84.1	-	99.0	-

It is shown in Table 1 that the extraction coefficient of the above elements decreases in the following order: Sc Th Ce(IV) Lu(III). The extraction coefficients of these elements differ so widely that it is possible to separate Sc, Th and Ce(IV) from the trivalent rare earths. Ce can be separated from Sc and Th by reduction stripping.

Extraction from Sulfuric Acid Solutions

The extraction curves of rare earths Sc and Th for

aqueous solutions with various acidities are plotted in Fig. 2. It is evident that the extraction coefficient of the trivalent rare earths decreases with the increase of the initial aqueous concentration of sulphuric acid. The lower the acidity of the aqueous solution, the faster the extraction coefficient decreases. The extraction coefficient of Ce(IV) and Th also

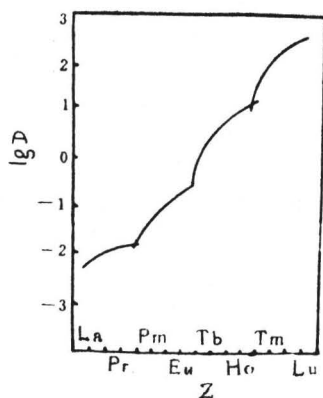


Fig. 1

The dependence of $\lg D$ on the atomic number Z of rare earths

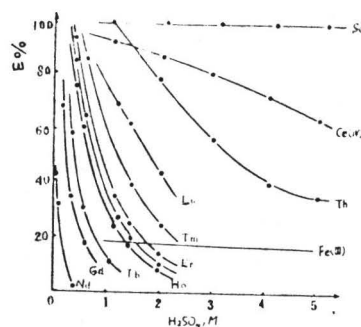


Fig. 2

The influence of the initial aqueous H_2SO_4 concentration on the extraction of rare earths(III), Ce(IV), Sc, Th and Fe(III)

decreases with the increase of the concentration of sulphuric acid, although much slower. The extraction coefficient of Ce(IV) is greater than that of Th at a concentration of sulphuric acid greater than 1.5. However, within the experimental range of acidities the extraction coefficient of Sc exceeds 98%. The order of extraction coefficients of the above elements with HEH(EHP) is as follows :

$Sc > Ce(IV) > Th > RE(III)$. The great difference between the extraction coefficients of these elements makes it possible to separate Sc, Th, Ce(IV) from rare earth elements (III). The extracted Ce(IV) in the organic phase can be separated from Sc and Th by reduction stripping. The extraction coefficient of Th drops to only 35% when the acidity exceeds 5N, therefore it is possible to separate it from Sc by stripping at high acidity. It is interesting to note the extraction behaviour of Fe(III) from sulphuric acid solutions. Within the range of 1-5N H_2SO_4 , the extraction coefficient of Fe(III) is about 20% and is independent of the acidity of the aqueous solution. This makes it possible to strip Fe(III) from HEH(EHP) with H_2SO_4 .

$\beta_z^{2H}(H_2SO_4)$ for rare earth elements is equal to 2.0, this shows that the separation of these elements with HEH(EHP) in sulphuric acid solutions is more difficult than in nitric acid solutions. The order of separation efficiency is as follow: $HNO_3 > HCl > H_2SO_4$.

EXTRACTION MECHANISM AND MATHEMATICAL MODEL

The Distribution and Solubility of HEH(EHP) in Water-Mineral Acid--n-Heptane System at 25°C

For further understanding of the reaction occurred in the extraction system with HEH(EHP) and the calculation of extraction constant, we have investigated the physico-chemical properties -- dissociation constant, distribution constant, dimerization constant and solubility of HEH(EHP) in the given system.

In Fig. 3 the solubility of HEH(EHP) in mineral acid aqueous solutions at 25°C is plotted as a function of the concentration of the mineral acid. It can be accounted for the depression of the dissociation at low acidity but increase of accociation between HEH(EHP) with mineral acid forming molecular compound at high acidity. The solubility of HEH(EHP) in water is 3.1×10^{-4} M at 25°C.

Correlating the hydrogen ion concentration in the aqueous solution and the distribution data of HEH(EHP) in n-heptane--0.1N (Na,H) X, we determined the dissociation constants of HEH(EHP) in HNO_3 , H_2SO_4 and HCl solutions graphically. pK_a in all cases are 2.34. The value of pK_a of HEH(EHP) is greater than that of HDEHP(1.3) and 2-ethyl hexyl phenyl phosphonic acid (HEH(ϕ P))(1.70). This shows good agreement with the lower acidity and lower extractability of HEH(EHP) in comparison with the other two extractants.

Having studied the distribution of HEH(EHP) in the range of low concentration, we obtained the distribution constant $\lg K_d$ and dimerization constant $\lg K_2$ graphically. They are 2.50 and 2.22 respectively.

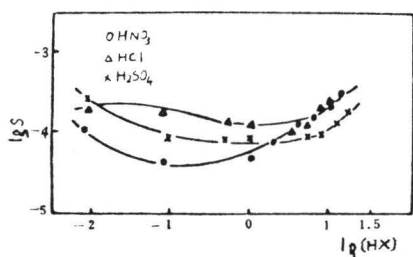


Fig. 3

The Solubility of HEH(EHP) in aqueous mineral acid solutions at 25°C.

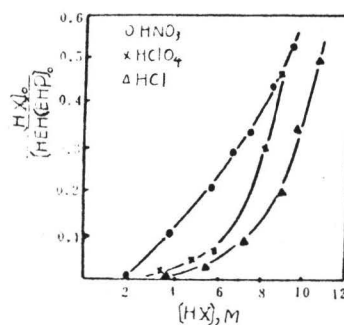


Fig. 4

Distribution Curves of extraction of HNO_3 , HClO_4 and HCl with HEH(EHP).

The Extraction of Mineral Acids with HEH(EHP)

In the investigation of extraction of Yb(III) from solutions of high-acid concentration with HEH(EHP), we observed that there exists the combination with $\text{P}=\text{O} \dots \text{HNO}_3$ type. Thus we studied the extraction behaviour of HEH(EHP) in detail.

The distribution curves of HNO_3 , HClO_4 and HCl extracted

with HEH(EHP) are shown in Fig. 4. The extractability of HEH(EHP) increases with the increase in equilibrium concentration of aqueous mineral acid solution. The extraction coefficient of mineral acids with HEH(EHP) is as follow:
 $\text{HNO}_3 > \text{HClO}_4 > \text{HCl}$

The composition of the extracted complex in the extraction of mineral acids by HEH(EHP) determined graphically is: $\text{HNO}_3 \cdot \text{HEH(EHP)}$, (6.4-8.0M HNO_3); $\text{HClO}_4 \cdot \text{HEH(EHP)}$, (7.8M HClO_4) and $\text{HCl} \cdot \text{HEH(EHP)}$, (8.4M HCl) respectively.

The distribution curves of HNO_3 are plotted in Fig. 5 in which the order of extractability is Di(2-ethyl hexyl) phosphonic acid(H(DEHP)) $>$ HEH(EHP) $>$ $\text{HEH}(\phi\text{P})$ $>$ HDEHP .

Similarly the composition of the extracted complex in the extraction of HNO_3 with H(DEHP) , $\text{HEH}(\phi\text{P})$ and HDEHP , is :

$\text{HNO}_3 \cdot \text{H(DEHP)}$, (6.4M HNO_3); $\text{HNO}_3 \cdot \text{HEH}(\phi\text{P})$, (6.4M HNO_3);
 $\text{HNO}_3 \cdot \text{HDEHP}$ (8.0M HNO_3).

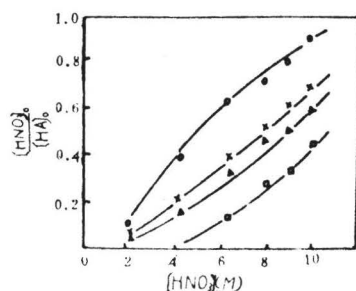
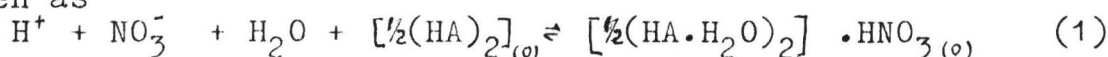


Fig. 5

Distribution curves of extraction of HNO_3 with several dialkyl phosphonates
 O - H(DEHP) , X - HEH(EHP) , Δ - $\text{HEH}(\phi\text{P})$, $\square$ - HDEHP

According to the composition of the extracted complex and the extraction of water, the reaction of extraction can be written as



$$\bar{K} = \frac{y}{[\text{H}^+][\text{NO}_3^-] \gamma_{\pm}^2 a_{\text{H}_2\text{O}} (s-y)} \quad (2)$$

where $y = \{[\frac{1}{2}(\text{HA} \cdot \text{H}_2\text{O})_2] \cdot \text{HNO}_3\}_{(o)} = [\text{HNO}_3]_{(o)}$

s -- the initial concentration of the extractant(HA)

Y -- Average activity coefficient of the ions

$a_{\text{H}_2\text{O}}$ -- activity of water

(o) -- represent the organic phase

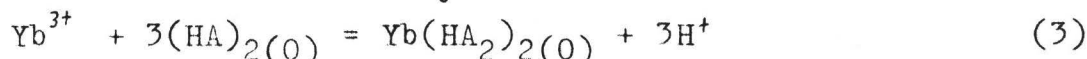
$\bar{K}$ -- apparent equilibrium constant

According to equation (2) we calculated the $\bar{K}$ values of extraction of HNO_3 with HA: $\bar{K}_{\text{H(DEHP)}}$ (1.2×10^{-2}); $\bar{K}_{\text{HEH(EHP)}}$ (4.1×10^{-3}); $\bar{K}_{\text{HEH}(\phi\text{P})}$ (2.9×10^{-3}); $\bar{K}_{\text{HDEHP}}$ (1.2×10^{-3}).

Mechanism of Extraction of Rare Earths(III) with HEH(EHP)

1. Mechanism of extraction of Yb(III) from dilute nitric acid solution with HEH(EHP).

The reaction in extraction of Yb(III) from dilute nitric acid solution with HEH(EHP) - kerosine and the composition of the extracted complex is studied by several methods, the results indicate that this reaction is a cation exchange mechanism. The composition of the extracted complex is $\text{Yb}(\text{HA}_2)_3$. The reaction of extraction may be written as



2. Mechanism of extraction of Nd(III), Sm(III) from HCl solution with ammoniated HEH(EHP).

Since ammoniated HEH(EHP) can improve the separation effect in the group division of Nd-Sm we determined the separation factor in the extraction of Nd(III) and Sm(III) with ammoniated HEH(EHP). When the initial concentration of hydrogen ion in both cases equals 0.25N HCl, $\beta_{\text{Nd}}^{\text{Sm}}$ [ammoniated HEH(EHP)] equals 16, $\beta_{\text{Nd}}^{\text{Sm}}$ [HEH(EHP)] equals 8.8

Lg D against lg (H^+) is plotted in Fig. 6. The absolute value of the slopes of these straight lines decreases with the increase in ammoniation

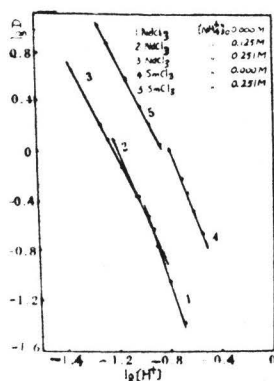


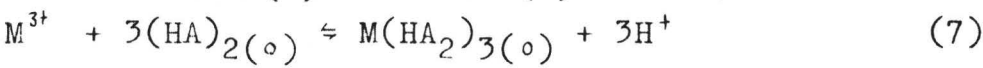
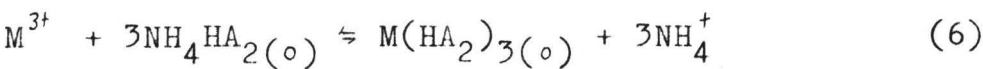
Fig. 6

Relation of lg D and lg(H^+) with the degree of ammoniation.

From the experimental results we assume that the reaction of the extracted complex and extraction can be written as ammoniation:

$$\text{NH}_4\text{OH} + (\text{HA})_2(\text{O}) \rightleftharpoons \text{NH}_4 \cdot \text{HA}_2(\text{O}) + \text{H}_2\text{O} \quad (4)$$

Extraction: $\text{NH}_4 \cdot \text{HA}_2(\text{O}) + \text{H}^+ \rightleftharpoons (\text{HA})_2(\text{O}) + \text{NH}_4^+ \quad (5)$



When the phase ratio is 1:1, we obtain from (4)-(7) the following equation:

$$C_{H^+} = 3C_{M^{3+}(o)} - (C_{NH_4^+(o)} - C_{H^+(i)}) \quad (8)$$

Where $C_{H^+(i)}$, C_{H^+} represent the initial and equilibrium concentration of the aqueous phase respectively, while $C_{M^{3+}(o)}$, $C_{NH_4^+}$ represent the equilibrium concentration of the rare earths and the initial concentration of ammonium ion in the organic phase respectively.

C_{H^+} calculated according to equation (8) agrees with the experimental result.

The Infra-red spectrum of the organic phase is shown in Fig. 7

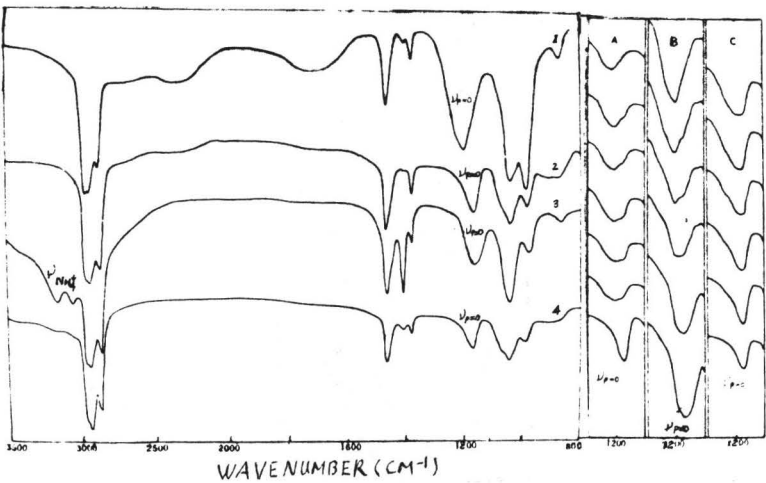


Fig. 7

Infra-red spectrum of the extracted organic phase.

- 1. -- HEH(EHP) -- kerosine;
- 2. -- HEH(EHP) -- kerosine -- Sm(III);
- 3. -- ammoniated HEH(EHP) -- kerosine;
- 4. -- ammoniated HEH(EHP) -- kerosine -- Sm(III);
- A -- Displacement of $\nu_{p=0}$ in HEH(EHP) at various Sm (III) concentration;
- B -- Displacement of $\nu_{p=0}$ in HEH(EHP) at various degree of ammoniation;
- C -- Displacement of $\nu_{p=0}$ in ammoniated HEH(EHP) at various Sm(III) concentrations.

After the extraction of rare earths $\nu_{\rho=0}$ is removed from 1205 cm^{-1} to 1175 cm^{-1} and the absorption peak of the vibration of OH^- at 2380–2300 cm^{-1} and 1770–1680 cm^{-1} is remarkably decreased. Therefore the reaction between rare earths and HEH(EHP) proceeds according to (7). After the ammoniation of HEH(EHP) the absorption peak of ammonium ion appears at 3060 cm^{-1} and 3180 cm^{-1} , at the same time the absorption peak is removed forward 1175 cm^{-1} and the absorption peak of $\nu_{\rho=0}$ is remarkably weakened. Thus we can assume that the reaction of ammoniation proceeds according to equation (4). After the extraction of rare earths the absorption of ammonium ion has disappeared. The change of $\nu_{\rho=0}$ and ν_{OH^-} is exactly the same case of HEH(EHP) . Evidently the reaction proceeds according to (6) with the formation of the same extracted complex as in HEH(EHP) .

3. Mechanism of extraction of rare earths(III) from concentrated mineral acids with HEH(EHP)

Taking Yb(III) as an example, we have studied the extraction behaviour of trivalent rare earths from concentrated HNO_3 , HClO_4 and HCl solutions with HEH(EHP) . The distribution ratio D of Yb(III) against the concentration of the mineral acids is plotted in Fig. 8. The order of extraction efficiency from concentrated mineral acid solutions is as follows :

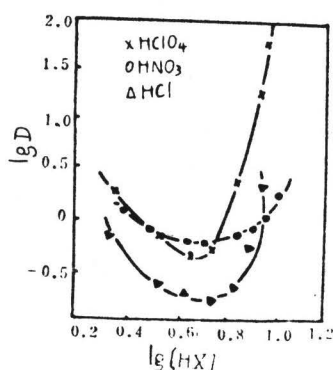
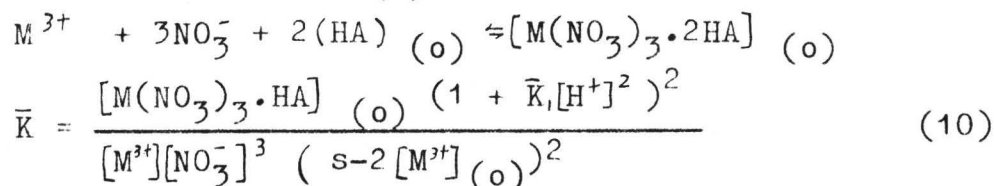
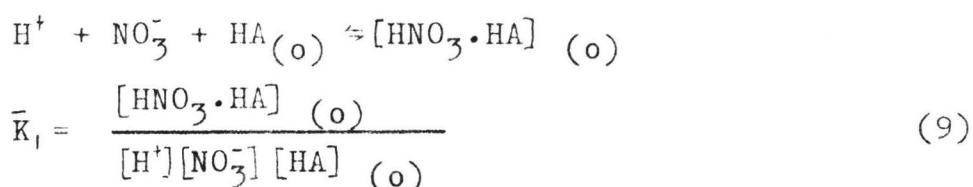
$$\text{Yb(ClO}_4)_3 > \text{YbCl}_3 > \text{Yb(NO}_3)_3.$$


Fig. 8

Relation between $\lg D$ and $\lg (Hx)$

The composition of the extracted complex in the extraction of Yb(III) from concentrated HNO_3 and HCl solutions with HEH(EHP) are determined by investigation of the relationship of D_{Yb} to (H^+) , (NO_3^-) , (HClO_4) and of $\lg D$ to $\lg S$. They are $\text{Yb(NO}_3)_3 \cdot 2\text{HEH(EHP)}$ and $\text{H}_i\text{Yb(ClO}_4)_{i+3} \cdot 2\text{HEH(EHP)}$, where $i = 1, 2, \dots$

The apparent equilibrium constant K is calculated according to the following equations:



where S -- the initial concentration of HEH(EHP)
 $[M^{3+}]$, $[M^{3+}]_{(o)}$ -- equilibrium concentration of the metal
 ion in the aqueous and organic phases respectively.

Here we obtain $\bar{K}_{Yb} = 7.3 \times 10^{-3}$, $\bar{K}_{Tb} = 1.8 \times 10^{-3}$, $\beta_{Tb}^{Yb} = \frac{\bar{K}_{Yb}}{\bar{K}_{Tb}} = 4.1$

Mathematical Model

We have found that at definite range of acidity and metal ion concentrations, the extraction of single lanthanide with HEH(EHP)-n-heptane, as other extractants, can be expressed by a simple unified linear relation

$$\frac{1}{D} = a_0 + a_1 C_a \quad (11)$$

D -- distribution ratio, C_a -- metal ion concentration in equilibrium aqueous phase, a_0 , a_1 are coefficients correlated to initial acidity. Then equation (11) can be written as

$$\frac{1}{D} = b_0 e^{b_1(H^+)} + b_2 e^{b_3(H^+)} C_a \quad (12)$$

In the range of acidity 0.01-0.25M and initial metal ion concentrations 0.02-0.30M, the mean relative errors (M.R.E.) of experimental and calculated value with equation (12) for Nd(III), Sm(III) extracted with 1.0M HEH(EHP) -HCl are the following:

HCl, M		0.01	0.05	0.10	0.15	0.20	0.25
M.R.E. %	Nd	4.73	3.86	1.70	5.28	5.18	-
	Sm	3.30	1.35	2.45	3.89	1.58	3.55

For binary system, the extraction of Nd-Sm with HEH(EHP) at total metal ion concentration 0.20M and various acidity (0.01-0.10M) can be correlated in a unified form as

$$C_{a,M} = a_0 \times M^{a_1} \quad (13)$$

C_a , M -- metal ion concentration in equilibrium aqueous phase,
 x_M -- initial mole fraction.

The mean relative errors of experimental and calculated values with equation (13) are less than 0.3%.

GROUP DIVISION OF RARE EARTHS AND Sm-Gd SEPARATION

By the study of fundamental properties of lanthanides extracted with HEH(EHP), the separation of lanthanides with HEH(EHP) were carried out. For the mixed lanthanides, 4 groups abundance of La-Nd; Sm-Gd; Tb-Er; Tm-Lu divided with HEH(EHP) were gained. By the use of synthetic pure Sm_2O_3 - Gd_2O_3 , Sm-Gd was separated, satisfactory results were obtained for both.

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EXTRACTION OF FISSION TECHNETIUM AND PALLADIUM
- LABORATORY SEARCH FOR A TECHNOLOGICAL
FLOWSHEET

F.Macášek, V.Mikulaj, R.Kopunec,
M.Koreňovská, P.Rajec, P.Tarapčík
Department of Nuclear Chemistry,
Comenius University
816 31 Bratislava, Czechoslovakia

ABSTRACT - Non-flammable solvents for the technetium and palladium isolation from waste nitric acid solutions were investigated. The tri-n-octylamine (TOA)/CCl₄ system was the most promising, but attention was paid also to TOA/CCl₄-chlorinated biphenyls, TOA/1,2,4-trichlorobenzene (TCB), tri-n-octylphosphine oxide (TOPO)/CCl₄ and TOPO/TCB systems. Possibility of thiourea complexes of technetium and palladium extraction with nitrobenzene solutions of bis(1,2-dicarbollyl)cobalt(III) (DCC) is demonstrated.

INTRODUCTION

Interest in technetium and palladium as the fission products and rare metals is due to their high fission yield and value (1). Isolation of technetium from waste solutions of fission products has already been considered, using amine extraction (2,3), and the use of carbon tetrachloride, as a non-flammable diluent, was investigated (4). Despite the difference in the chemistry of Tc(VII) and Pd(II), there are some features which cause the need to consider their mutual recovery in solvent extraction with neutral and basic extractants from nitric acid solutions (5). From our previous papers (4,5) it is known that the tri-n-octylamine (TOA)/CCl₄ systems, in spite of several advantages, exhibit some peculiarities. Products originally present or arising in TOA/CCl₄ mixtures, whether by standing or irradiating, may exert⁴ an influence on extraction equilibria. This occurs particularly in a difficult stripping of technetium at trace concentrations and an enhanced extraction of palladium at low concentrations. Hence, an attempt was made to answer the following questions :

- 1) Would another chlorinated diluent be better ?
- 2) Would a neutral extraction agent be more convenient ?
- 3) Can another composition of solvent be applied to technetium and palladium recovery from acid solutions ?

Now we would like to give partial answers to these questions. For experimental details see papers (4,5).

CHLORINATED DILUENTS FOR TOA

Because of the instability of trialkylamines solutions in carbon tetrachloride, they are supposed to be inconvenient in nuclear applications (6). In solutions of lower trialkylamines, the formation of trialkylamonium chlorides (7), N-trichloromethyl- (8) and N-dichloromethylenederivatives (9) was observed due to photochemical dissociation of CCl_4 and formation of charge-transfer complexes.

By means of GC/MS system we analyzed a several months old solution of TOA (Rhône-Poulenc), which originally contained only 2-3 % of tri-n-butylamine and traces of tri-n-nonylamine and two other low-weight amines. The sample was neutralized by washing with 10 % Na_2CO_3 and analysed (Fig.1). Besides the

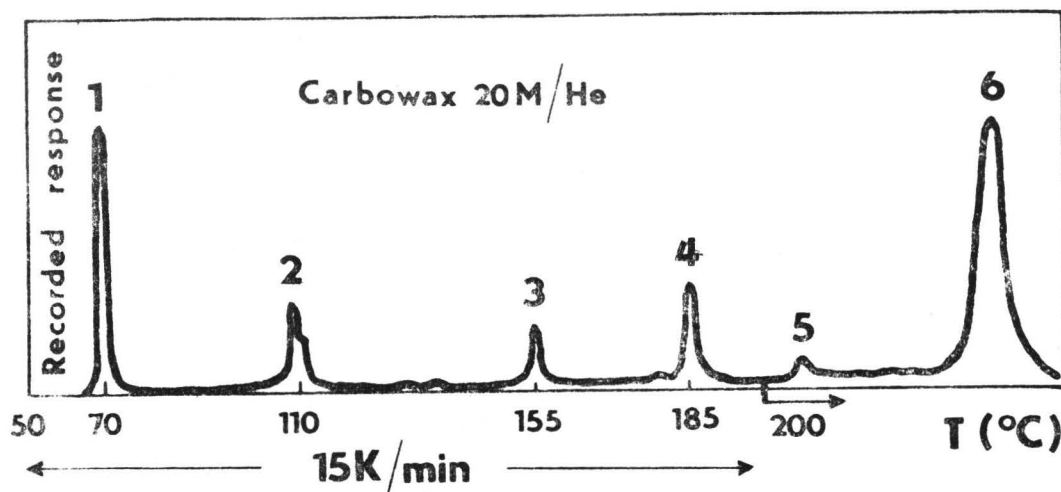


FIG.1

Gas chromatogram for TOA products arising in CCl_4 solutions

peaks of diluent and CHCl_3 (peak 1), the gas chromatogram exhibited five main components. Since the mass spectra of these components were not found among the investigated compounds (10), their identification was difficult. First of all, the peak 6 had to be interpreted as an enamine, confirming its formation from TOA according to reaction (6) :



The difference between mass-spectra of original TOA and its enamine consisted not only in different mass of dominating ions, i.e. $(C_8H_{17})_2CH_2=\overset{+}{N}$ and $(C_8H_{17})_2CH=\overset{+}{N}$ respectively, but also in lower abundance of $(C_8H_{17})NCH_3^+$ and $C_8H_{16}^+$ ions in the spectrum of peak 6. Other peaks (3-5) exhibit the ions typical for amines (11) and together with fragmentations of alkyls and retention times they were considered to belong to: chlorinated dialkylamine (presence of isotope doublet $C_8H_{15}(CCl)N^+$)- peak 3, dioctylamine - peak 4 and alkylodioctylamine - peak 5, respectively. The mass-spectrum of peak 2 is similar to the tabulated one for octylaldehyde. However, this spectrum would not be at variance with the spectrum of propylallylamine in its unresolved mixture with dipropylamine (10) - see the chromatogram. Further, no primary amines with a characteristic fragment $CH_2=NH_2^+$ were found.

Thus, the corresponding enamine and dialkylamines are the major amine products of thermal and photochemical degradation of TOA in CCl_4 . This decomposition, indicated by HCl evolution (4), is strongly suppressed in trialkylamonium salt solutions. Hence, in our case, the freshly prepared solutions of TOA, and presaturated with HNO_3 were used. Considering that the dialkylamines are also the major products of radiolysis in hydrocarbons (12) there appears no practical difference in the use of CCl_4 as the diluent. Nevertheless, the use of chlorinated aromates or dienes should be considered. Following Schulz et al. (13) we tried to use 1,2,4-trichlorobenzene (TCB), and also partially to replace CCl_4 by a commercial mixture of chlorinated biphenyls (Delor 103, 60 % of trichlorobiphenyl).

The extraction properties of the solvents for TcO_4^- extraction were compared, considering exchange reactions



(R = extraction agent, TOA particularly). If $\bar{K}_{np}$ is an effective constant of this reaction (involving organic phase activity coefficients), the distribution ratio of technetium

will be

$$D = \frac{\sum [(R)_n (HNO_3)_{p-1} (HTcO_4)]_{org}}{[TcO_4^-]} = K \frac{a_H (\gamma_{\pm})_{Tc} \bar{c}_{HNO_3}}{a_{HNO_3}} \quad (2)$$

where $K = \sum_{n,p} \bar{K}_{np} [(R)_n (HNO_3)_p]_{org} / \sum_{n,p} p [(R)_n (HNO_3)_p]_{org}$,

$\bar{c}_{HNO_3}$ is the concentration of HNO_3 in organic phase and a 's are the ionic activities (14). $(\gamma_{\pm})_{Tc}$ are the activity coefficients of TcO_4^- in nitric acid solutions taken as mean ionic coefficients of HNO_3 or from $TlTcO_4$ solubility data (15). The solvents investigated exhibited a decrease of K value with increasing HNO_3 concentration, probably due to higher average p values, but the effective exchange constants did not differ substantially. The highly reliable correlation was achieved by linear approximation corrected by coefficient b :

$$\log (D/a_H \gamma_{\pm Tc}) = \log K + b \log (\bar{c}_{HNO_3} / a_{HNO_3}) \quad (3)$$

which is valid in a wide interval (0.1- 6 M) of equilibrium concentrations of HNO_3 in aqueous phase (Table 1).

TABLE 1

The effective exchange constants for Eq.(1) in different diluents of TOA (10 % v/v), $T = 25^\circ C$

Diluent	$(\gamma_{\pm})_{Tc} = (\gamma_{\pm})_{HNO_3}$		$(\gamma_{\pm})_{Tc} = (\gamma_{\pm})_{TlTcO_4 (HNO_3)}$	
	log K	b	log K	b
CCl_4	2.31 ± 0.08	1.38 ± 0.05	2.56 ± 0.04	1.19 ± 0.02
CCl_4 -Delor (50% w/w)	2.30 ± 0.04	1.41 ± 0.02	2.55 ± 0.05	1.21 ± 0.03
TCB	2.04 ± 0.05	1.25 ± 0.03	2.26 ± 0.02	1.04 ± 0.01

The data approach those obtained with TLA/xylene ($\log K = 2.20$) (16) and TOA/sintin/octanol ($\log K = 2.62$) (17) systems at a constant ionic strength.

Because the viscosity of CCl_4 -Delor mixtures at $40^\circ C$ increases rapidly above 2 cP ($2 \cdot 10^{-3} \text{ kg.m}^{-1} \cdot \text{s}^{-1}$) with the

Delor content above 50 % w/w, their use appears dubious. Though the radiation yield of HCl in this diluent, contacted with water phase, is 3 times smaller than for pure carbon tetrachloride (8×10^{-3} M HCl after 10 kGy dose), its protective influence disappears when TOA.HNO₃ is present (Table 2).

TABLE 2

Concentration of HCl (mol.dm⁻³) in (1) TOA and (2) TOA.HNO₃ solution after irradiation (⁶⁰Co source) under aqueous phase layer ; 10 % TOA v/v

Solvent	Radiation dose (kGy)			
	1	10	100	1000
(1) in CCl ₄	0.080	0.200	0.340	0.700
(2) in CCl ₄	0.015	0.045	0.220	0.800
(1) in CCl ₄ ⁺ Delor	-	0.190	-	-
(2) "	-	-	0.160	-
(1) in TCB	0.002	0.014	0.076	0.495
(2) in TCB	0.003	0.016	0.077	0.570

Unfortunately, the same happens in TCB solutions which, however, are quite stable at a long-time storage, as expected. At higher radiation doses, the separation of organic phase with TCB deteriorates and even solid radiolysis products appear in the case of neutral amine solutions.

Concerning the extraction of palladium, high distribution ratios can generally be achieved also with TOA/CCl₄ solvent (Fig.2). The [Pd(NO₃)₄](TOAH)₂ and [Pd(NO₃)₃TOA](TOAH) complexes are the probable species extracted from nitric acid solutions. While for technetium a difficult stripping from TOA extracts by ammonia solutions is typical, for palladium, an increased extraction from acid solutions in concentrations of metals of the same order (10^{-3} - 5×10^{-4} M) occurs (Fig.3). Supposing that an impurity, e.g. a quaternary ammonium salt, is responsible for such behaviour of technetium and palladium, we were not successful in finding out the agent which, at concentration of 10^{-3} M, would provide the extraction occurring with 0.23 M TOA. Neither the content of secondary amines nor

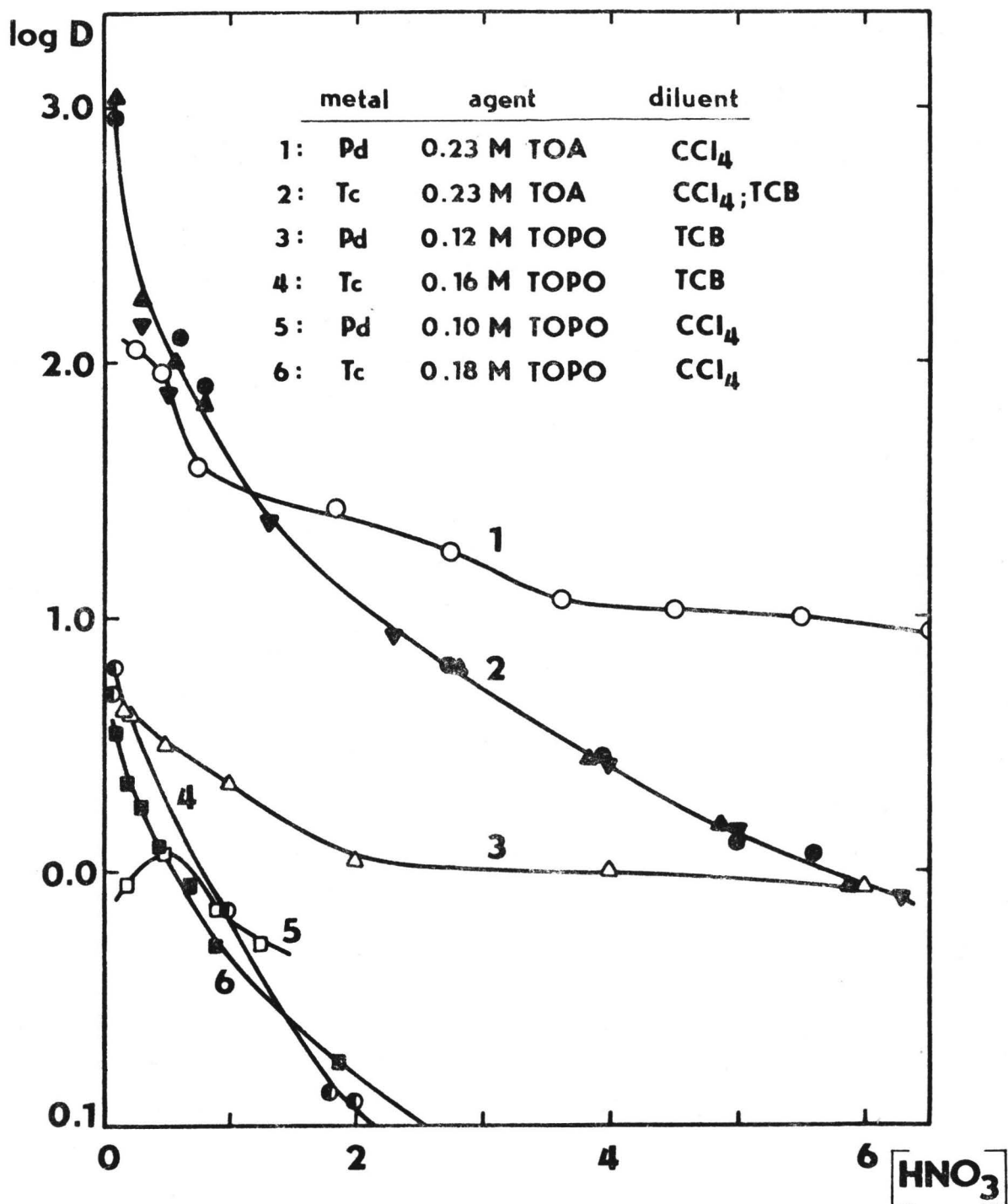


FIG.2

Distribution ratios of $^{99\text{m}}\text{TcO}_4^-$ and Pd^{2+} as a function of equilibrium nitric acid concentration (mol.dm^{-3}) in aqueous phase

Curve 2 : ● CCl_4 , ▲ CCl_4 -Delor 103 (50 % w/w), ▼ TCB

Palladium concentrations in initial aqueous phase :

○ 0.008 g.dm^{-3} , □ 0.04 g.dm^{-3} , △ 0.03 g.dm^{-3}

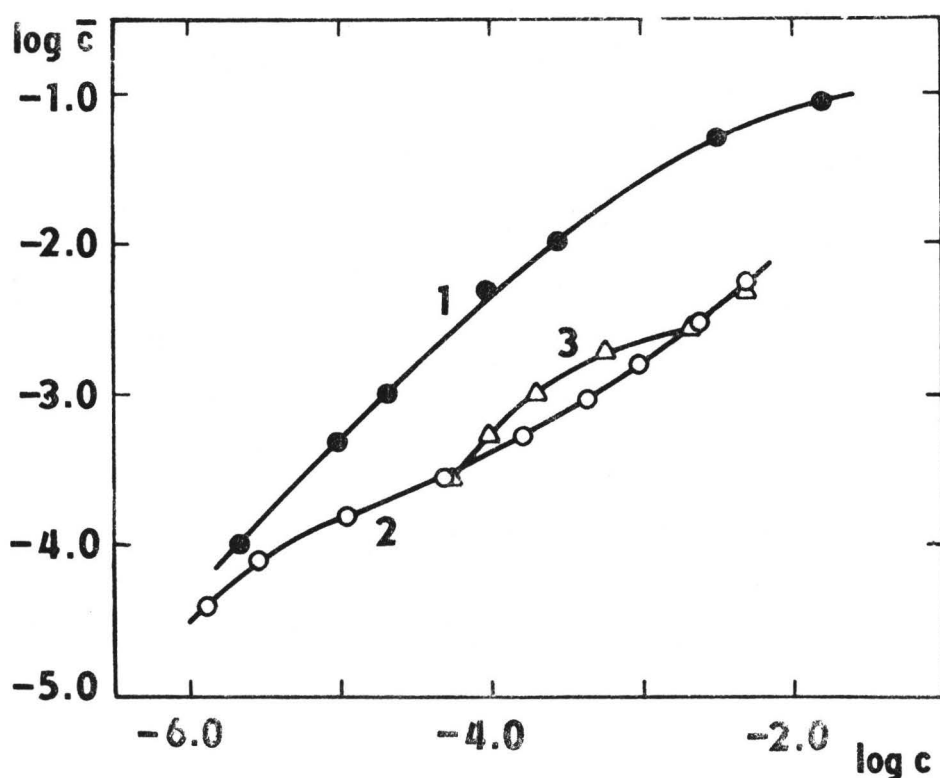


FIG.3

Extraction isotherms of TcO_4^- and Pd^{2+} for 0.23 M TOA/ CCl_4 - $\text{HNO}_3(\text{HCl})$ systems : 1 - Tc from 1 M HNO_3 , 2 - Pd from 1 M HNO_3 , 3 - Pd from 1 M HNO_3 - 0.0075 M HCl

that of quaternary ammonium salts, detected spectrophotometrically at concentrations above 10^{-5} M (18), was crucial in this respect.

Chloride and nitrite ions enhance the extraction of palladium (5) and the Cl:Pd molar ratio 5:1 in HNO_3 solutions is sufficient to maintain $D(\text{Pd})=4$. A possible flowsheet ensuing from supposition of this ratio at 1 M HNO_3 and real extraction isotherm of technetium, was considered for Tc and Pd recovery (Fig.4). Its evaluation (19) was performed by iterative method in order to ensure technetium preconcentration and decontamination from other fission products (FP). The feeding was supposed to be 5×10^{-4} M Tc and Pd solution in 1 M HNO_3 . The scheme would provide 95 % yield of technetium and 88 % of palladium recovery with decontamination factor 2×10^2 (in respect to Zr), technetium being purified more effectively and concentrated 500 times due to the arrangement of scrubbing and stripping sections.

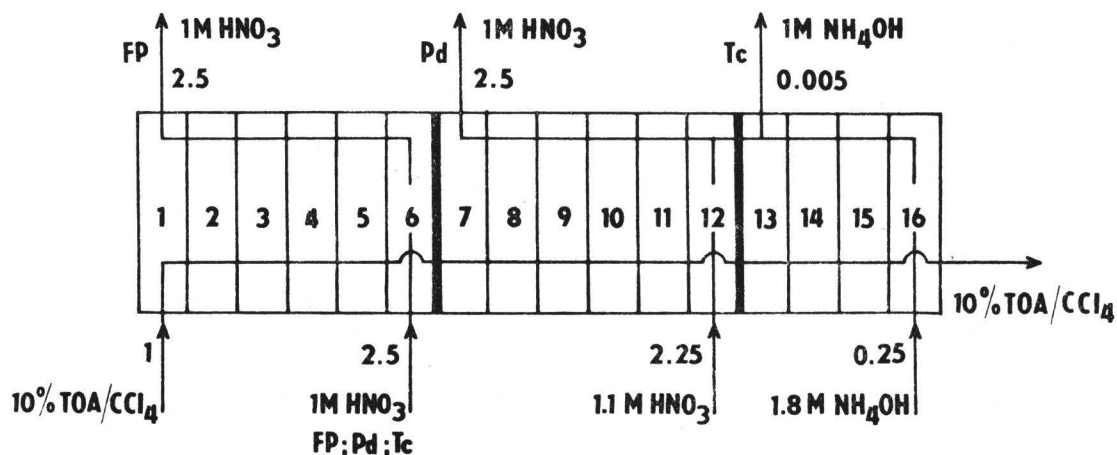


FIG.4

A possible flowsheet of technetium and palladium recovery from waste nitric acid solutions of fission products (FP) (the flow ratio of the aqueous phase to solvent is indicated at arrows)

TOPO AS THE EXTRACTANT

Relatively high distribution ratios were reported for the extraction with TOPO from nitric acid solutions both for technetium, using cyclohexane (20) and decane (21) as diluents, and palladium into toluene (22).

The original samples of TOPO (Lachema Brno) required purification. Non-purified solutions of TOPO in CCl_4 exhibited HCl formation up to $1/3$ of TOPO concentration already after several hours of standing. Their clean separation from alcalic emulsions was extremely difficult and water was extracted in a greater extent by TOPO concentrations above 0.1 M. After purification of the solutions by passing through a Al_2O_3 column, these phenomena disappeared.

Nevertheless, CCl_4 was not found to be a convenient diluent for TOPO. The effective exchange constant for technetium - eq.(2) - decreases rapidly with HNO_3 concentration. For a sufficient Tc extraction from 1 M HNO_3 the solutions of 0.5 M TOPO should be applied, with TCB diluent too (Fig.2). The extraction of palladium is basically the same and the distribution is strongly dependent on palladium concentrations. Much better results ($D \approx 20$ at 1 M HNO_3) were found with 0.1 M TOPO/benzene as the solvent, and shifting to 1,2,4-trichloro-

benzene diluent the yield of palladium extraction remained sufficient up to 2.5 M HNO_3 concentrations (Fig.2).

NITROBENZENE SOLUTIONS OF BIS(1,2-DICARBOLLYL)COBALT(III)

Nitrobenzene solutions of DCC were proposed for extraction of cesium (23) and of alkaline earths in presence of polyethyleneglycols (PEG) (24). Extremely high extraction yields of technetium reduced and complexed with thiourea in nitric acid medium were reported (25).

Palladium is extracted with nitrobenzene alone from 0.5 M HNO_3 in some extent ($D=0.19$), and with DCC solutions and PEG additions the extraction can be increased. Distribution ratio $D=2.8$ had been achieved by concentration of 0.04 M DCC in nitrobenzene and 2×10^{-3} M Pd with 1 % PEG 300 in aqueous phase. Presence of thiourea in concentration as low as 10^{-3} M increases the extraction of Pd with DCC solutions to the same extent and 0.01 M tu can be considered to ensure high extraction yields even from 1 M HNO_3 . From the extracts of thiourea complexes, technetium can be stripped with 5 M HNO_3 or 0.1 M NaOH and palladium with 20 % solutions of NH_4SCN or NH_4Cl or with concentrated hydrochloric acid.

From the viewpoint of organic solvent, the extraction system can be modified by additives of halogenderivatives (CHBr_3 , CHCl_3 , CCl_4 or TCB). The halogenderivatives of DCC, prepared beforehand or arising in the course of organic phase irradiation, could ensure the same extraction condition as DCC/nitrobenzene system (26). The mixture of thiourea and nitric acid solution, however, does not seem to be perspective in technological nuclear applications.

ACKNOWLEDGMENTS

The authors wish to express gratitude to Ing.A.Švec for valuable help with extraction flowsheet calculations and Mrs.Eva Roncová for skilled technical assistance.

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A COMPARISON IN THE PERCENT LOADING CAPACITY OF THE ELEMENTS U(VI), Mo(VI), Zr(IV) and Sr(II) BY TRIOCTYL AMINE (TOA) AND ITS RADIO - LYTIC PRODUCTS DIOCTYL AMINE (DOA) AND PRIMARY OCTYL AMINE (POA).

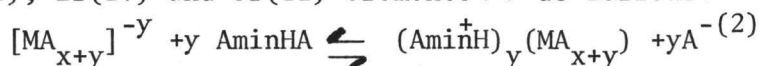
Amer M.AL-ANI , Fatma M.MASOUD

Dept. of Chem., Nuclear Research Center

Baghdad - IRAQ

ABSTRACT

High molecular wt. amines salts, soluble in organic diluents and immiscible with aqueous solutions are used for the extraction of U(VI), Mo(VI), Zr(IV) and Sr(II) elements(1) as follows:



The stability of $\text{AminH}^+ : \text{MA}^{-(3)}$ increases with the increase of the electron donating capacity of the anion amine salt, i.e in the order TOA>DOA>POA; this was proved by our results after estimating %E (the percent of the conc. extracted to the organic layer, out of the total conc. present originally in the aqueous layer) of the previous mentioned elements from HNO_3 solutions 1-6M, using 10% TOA, DOA and POA/xylene respectively. DOA and POA were selected for comparison with TOA, as they are expected to be the first radiolytic products of TOA irradiation.(4) The failure of Sr to be extracted by these amines may be due to its poor ability to form ionic species under these conditions. The very little capacity of POA to extract elements may be due to the association by bonding of the salt anions.

The similarity in the behavior of Zr(IV) toward both TOA and DOA, as shown from its extraction percents gives the important result: that the comparison of zirconium number before and after TOA irradiation, as most authors do,(5) is not enough to prove the resistance of this amine against irradiation and some other methods must be applied as well. This is not the case with U, as %E by DOA is much lower than with TOA. With Mo, the extraction percent by TOA is not much higher than that by DOA.

Table of maximum %E by 10% Amine/xylene

Element	[HNO ₃]	TOA	DOA	POA
U(VI)	5M	53.52	7.14	0.71
Mo(VI)	3M	20.00	12.00	0
Zr(IV)	1M	12.50	13.75	0
Sr(II)	1-6M	0	0	0

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VALENCE CONTROL IN THE SEPARATION OF ACTINIDESBY LIQUID-LIQUID EXTRACTION

Yu-Keung Sze and Joseph A. Gosselin

Chemical Technology Branch
Atomic Energy of Canada Limited
Whiteshell Nuclear Research Establishment
Pinawa, Manitoba, Canada
ROE 1L0

In the separation of actinides by liquid-liquid extraction, chemical reactions leading to valence changes in one or both phases may become important as a result of species redistribution. This phenomenon can lead to insufficient separation. In a recent attempt in our laboratory to extract Th(IV) and U(VI) from aqueous solution containing Pu(III), Th(IV) and U(VI) in 0.3 mol/L hydroxylamine nitrate (HAN), 0.1 mol/L hydrazine nitrate and 1.5 mol/L HNO_3 using laboratory-scale mixer/settlers, it was found that a large fraction of the Pu was also extracted into the organic phase (30% TBP in an inert diluent). We have studied the organic phase by UV/visible spectroscopy and found that oxidation of Pu(III) to the much more extractable Pu(IV) occurred in this phase. The oxidation was accelerated by HNO_2 which was generated in the reaction. This reaction occurred because extracted HNO_3 acted as an oxidant on the small amount of Pu(III) extracted into the organic phase whereas the reductant, HAN, and the HNO_2 scavenger, hydrazine, were virtually inextractable.

To remedy this situation, it is necessary to use chemicals which have one or both of these functions:

1. They must react with HNO_2 in the organic phase faster than HNO_2 is produced, and
2. They must reduce Pu(IV) rapidly in either or both phases.

The reductants should be free from the disadvantages of traditional Pu reducing agents, such as introduction of a metal impurity into the system and incomplete reduction at moderately high concentrations of HNO_3 . We have tested a large number of chemicals under conditions similar to those of the organic phase of a settler. The following are some of the more important observations:

1. Acetaldoxime, butyraldoxime, methylethylketoxime, phenylhydrazine, N-phenylbenzylamine and p-nitroaniline were very effective reactants with HNO_2 . Oxidation of Pu(III) in the organic phase was completely inhibited by these chemicals during the observation period (at least 70 minutes) which was much longer than the average residence time of the organic phase in the settlers.
2. N,N-diethylhydroxylamine and phenylhydrazine were very powerful reducing agents in comparison to HAN. These two chemicals reduced Pu(VI) and Pu(IV) rapidly and completely, even when the nitric acid concentration was 3.0 mol/L.
3. A mixer/settler run using acetaldoxime as HNO_2 scavenger and N,N-diethylhydroxylamine as Pu reductant indicated the Pu loss to the organic stream was below 0.03%. The decontamination factors of Th and U from Pu were satisfactory. Both acetaldoxime and N,N-diethylhydroxylamine were completely decomposable in hot concentrated HNO_3 .

SYNERGISTIC EXTRACTION OF URANIUM BY A MIXTURE OF SULPHOXIDES AND SOME ACIDS

Yu.G.Kuvatov, Yu.I.Murinov,
Yu.E.Nikitin, A.M.Rozen,
B.F.Myasoedov
Institute of Chemistry of the
Baschkirian Branch of the USSR
Ufa, USSR

Extraction of uranium by sulphoxides was investigated previously. Good extractants of uranium from nitric acid media, sulphoxides are inferior for extraction from hydrochloric acid solutions and failed to extract from sulfuric acid solutions.

Synergism is known to highly increase extractibility. The paper presented describes extraction of uranium by the synergistic systems: sulphoxide-uranyl-picrolonic acid, sulphoxide-uranyl-HDEHP, sulphoxide-uranyl-pentachlorodienoic acid.

On studying extraction of uranium by these mixtures a considerable synergistic effect has been established. To understand the mechanism, the dependence of the extraction on different parameters has been studied, with dihexyl sulphoxide (DHSO) as a model. The composition of the extracted complex has been determined by the isomolar series and equilibrium shift methods as well as by the pH dependence of the extraction in the aqueous phase and is found to correspond to the formula $UO_2A_2 \cdot 2S$ where A is the anion of organic acid, S is a sulphoxide molecule. Extraction of UO_2SO_4 and UO_2Cl_2 , respectively labelled by ^{35}S and ^{36}Cl , confirms these data. The activities in the two cases completely remain in the aqueous phase, with complete extraction of uranyl which forms an organic phase.

The general equation describing the extraction equilibrium is:



The formation of the mixed complex in the organic phase is verified by the spectral data. In IR spectra a low frequency shift of $65-70\text{ cm}^{-1}$ of the valence vibration band of the sulphoxide SO group molecule is observed.

EXTRACTION OF TRIVALENT ACTINIDES
AND LANTHANIDES BY LONG CHAIN
AMINES FROM CONCENTRATED CHLORIDE
SOLUTIONS

P. K. Khopkar and Jagdish N. Mathur

Radiochemistry Division, Bhabha Atomic
 Research Centre

Trombay, Bombay-400 085, India

These studies are concerned with the extraction of Am(III) and Eu(III) by some primary, secondary, tertiary and quaternary amines and Pu(III), Cm(III), Cf(III) and Tm(III) by some tertiary and quaternary amines in xylene medium from concentrated lithium chloride solutions (~ 12 M) of low acidity; the subject is of interest in the separation of trivalent actinides from lanthanides. In the case of the primary amine (primine-JMT) and the secondary amine (amberlite IA-1) negligible extraction of both Am(III) and Eu(III) was observed. With the tertiary and quaternary amines studied the separation factors of trivalent actinides with respect to Eu(III) and Tm(III) follow the order $\text{Pu} > \text{Am} > \text{Cm} < \text{Cf}$ which is explained by the participation of '5f' orbitals in the metal ligand bond formation of the trivalent actinides. It has been observed that in general the separation factor ($K_{\text{DAn}}/K_{\text{DEu}}$ or K_{DTm}) of trivalent actinides (Pu, Am, Cm, Cf) with respect to Eu(III) or Tm(III) was substantially lower (at least 20 times) with quaternary amines as compared to that with tertiary amines. The higher separation factors of trivalent actinides with respect to Eu(III) or Tm(III) when extracted by tertiary amines have been attributed to the stabilization of higher chloro-complexes (probably hexachloro) of trivalent Pu, Am, Cm and Cf presumably through hydrogen bonding with the tertiary amines, whereas such a bonding is not possible in the case of quaternary amines. This view is further substantiated from the study of absorption spectra of Am(III) and Nd(III) in the aqueous solutions as well as when these metal ions are extracted from lithium chloride into tertiary and quaternary amines. The extinction coefficient of Am(III) and Nd(III) extracted into tertiary amines were found to be remarkably lower as compared to that when extracted into the quaternary amines; the extinction coefficient of Am(III) corresponds to that of the known octahedral AmCl_6^{3-} species. It was observed that the plutonium extracted from 12M LiCl containing 0.02M ascorbic acid at tracer concentrations is always present as Pu(III). Experiments performed under identical conditions with macro concentrations of plutonium indicated the presence of only Pu(IV) (PuCl_6^{2-}) as observed in the absorption spectral studies of plutonium extracted both by tertiary and quaternary amines even when holding reductants are present in both phases.

NN-DI-ALKYL ALIPHATIC AMIDES AS EXTRACTANTS OF ACTINIDES:
EXTRACTION OF U AND Pu WITH NN-DI-n-BUTYLOCTANAMIDE (DBOA)

G.GROSSI, G.M.GASPARINI and W.DEMBINSKI
 Comitato Nazionale per l'Energia Nucleare
 C.S.N. della Casaccia
 Laboratorio Ricerche Ritattamento
 00100 ROMA C.P. 2400 ITALY

Following our research on the disubstituted alkyl amides as extractants of actinides and fission products(I), this paper shows the results obtained with the NN-Di-Butyloctanamide (DBOA) in mesitylene as extractant.

DBOA, the less expensive compound of this series, is very soluble in the usual organic diluents and does not give third phases or precipitates into a wide range of U and HNO_3 concentrations ($\text{U}=350 \text{ g/l}$, $\text{HNO}_3 \text{ } 6\text{M}$, DBOA 1.5 M).

The radiation stability of DBOA is elevated and the degradation products do not interfere during the process.

With this compound we have determined:

- The extraction equilibria of HNO_3
- The U loading capacity at different amide concentrations.
- The U extraction at different HNO_3 and total U concentrations (FIG I).
- The U extraction and stripping kinetics.
- The extraction of Pu III, Pu IV and Pu VI at different HNO_3 concentrations.
- The influence of the total U conc. and DBOA conc. on the extraction coefficients of Pu IV.

The results obtained show that DBOA may be proposed as alternative of TBP in conventional reprocessing schemes and in co-processing applications.

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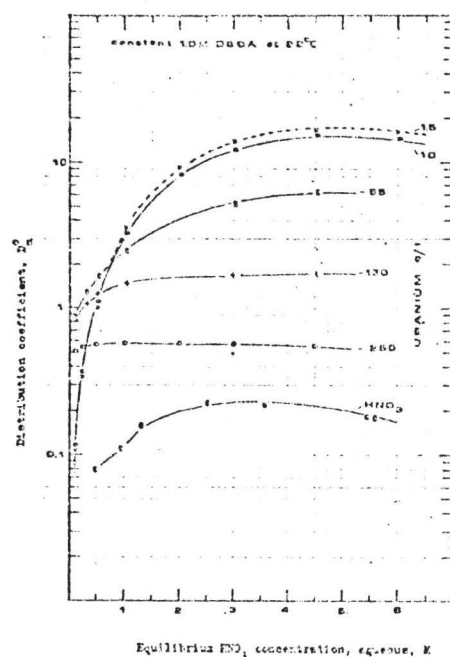


Fig. 1 Distribution coefficient as a function of HNO_3 aqueous concentration for different initial concentration of uranyl nitrate; 1.0 M DBOA in mesitylene

OXIDATION OF U(IV) IN A LIQUID-LIQUID DISPERSION AND SEPARATE LIQUID PHASES

Z. Kolarik

Institute of Hot Chemistry
Nuclear Research Centre

75 Karlsruhe 1, P. O. Box 3640
Federal Republic of Germany

The oxidation of U(IV) by nitric acid and air oxygen was studied in a liquid-liquid dispersion, consisting of a 30% solution of tributyl phosphate in dodecane and an aqueous solution of $\leq 0.8M$ nitric acid + $\leq 0.1M$ hydrazinium nitrate + $\leq 0.08M$ U(IV), and in the separate phases of the dispersion. The amount of oxidized U(IV) was measured under the exclusion of light as a function of the time at different starting concentrations of nitric acid and U(IV) in the absence of foreign metal species and also in the presence of $0.001M$ Pu(III) or Fe(II).

The oxidation of U(IV) by nitric acid in the absence of air is extremely slow. The oxidation by the air oxygen in the separate organic phase is a rather slow first order reaction with respect to U(IV); the rate constant, 0.023 h^{-1} , does not depend on the starting concentration of nitric acid. At higher starting concentrations of U(IV), namely $\geq 0.03M$, there is a strong tendency to an autocatalytic acceleration of the oxidation which can be ascribed to the formation of nitrous acid.

The oxidation of U(IV) by air oxygen in the separate aqueous phase and the dispersion is rather fast and its rate decreases with increasing concentration of nitric acid. Two hydrogen ions are released in the oxidation of one U(IV) ion. There is no significant consumption of hydrazine during the oxidation and the rate is suppressed in the presence of Pu(III) and Fe(II).

The apparent reaction orders of the oxidation of U(IV) by the air oxygen in the separate aqueous phase and the dispersion were sought by a least square treatment of the results. The reaction order with respect to U(IV) is zero. The order with respect to nitric acid can be expressed by the dependency of the oxidation rate constant k on the nitric acid concentration C as

$$k = a(C^b + cC^d)^{-1}$$

with the parameters a , b , c and d . At higher concentrations of nitric acid the first term in the brackets is negligible in comparison with the second term, both in the absence and presence of Pu(III), and the parameter d approaches fairly well the expected value of two. In the presence of Pu(III) the values of a , b and c and, consequently, the shape and position of the $\log k$ vs. $\log C$ plot are markedly changed. The nonlinear course of the $\log k = f(\log C)$ dependency is ascribed to the hydrolysis of U(IV).

MULTI-STAGE EXTRACTORS AND THEIR USE FOR SEPARATION
OF RARE EARTH AND TRANSPLUTONIUM ELEMENTS IN
ANALYTICAL AND PREPARATIVE RADIOCHEMISTRY

G.V.Korpusov, Yu.S.Krylov,
A.T.Filyanin

Institute of Physical Chemistry,
USSR Academy of Sciences

Moscow, USSR.

In the main tri-valent state rare-earth and transplutonium elements are similar in their chemical properties and in any extraction system the separation coefficients of two bordering elements do not exceed 2-8. For this reason any extraction separation of these elements can be conducted only as a multi-stage process on multi-stage extractors. In industry counter-current methods of separation are mainly used, but in preparative and analytical practice fraction methods and corresponding extractors are taken into account. Semicounter-current method of extraction is one of such methods. Naturally, it is difficult to construct mechanical extractors with an effective volume of the stage less than 1-3 ml.

Semicounter-current method of separation is analogous with the chromatographic one, but allows the higher rates on centrifugal extractors and rule out the use of a solid phase.

Semicounter-current methods permit obtaining of pure preparations of elements and enrichment of impurities to analyze highly pure substances. They can be also used instead of extraction chromatography.

The efficiency of semicounter-current process of separation was proved correct by the experiments on centrifugal 10-, 25-, 50 stage extractors and the examples of promethium-147 extraction americium, curium, berkelium and californium separation and rare earth elements gradient separation.

Multi-stage countercurrent laboratory centrifugal extractors can be successfully used for different fraction processes of separation.

Among the known fraction countercurrent extraction methods of wide use is Kreig's distribution method. It is, however, low yielding and its separation cycle is rather long.

In preparative practice this separation process can be considerably improved. Some more efficient modifications of countercurrent fractionation of multi-component mixtures are suggested, e.g. three fraction and multi-fraction processes with the use of centrifugal multi-stage extractors.

THE RADIATION STABILITY OF BENZYL-DIBUTYLAMINE AND BENZYL-DIMETHYLDODECYLAMMONIUM NITRATE BY THE EXTRACTION LANTHANIDES FROM THE PRODUCTS OF NUCLEAR FISSION.

Jedinakova Věra^a, Teply Jiri^b, Novak Jaromir^a, Cech Roman^c.

^aInstitute of Chemical Technology,
Prague.

^bInstitute of Nuclear Research, Rez

^cComenius University, Bratislava,
Czechoslovakia.

The change in the extraction capacity of these agents and its solutions in aromatic solvents in the extraction of Eu(III) and Am(III) was investigated in dependence on the absorbed dose of ionizing radiation. In the extraction of Eu from aqueous solutions at 7 M NO_3^- after a dose of 100 kGy, D_{Eu} dropped from 17.4 (before irradiation) to 15.9, which represents only 8.6 %. For americium, the greatest reduction in the distribution ratios under identical conditions (from 79.4 to 66) was found at 6.5 M NO_3^- , amounting 16.9 %.

The chromatography of $\text{BDBuN-C}_6\text{H}_6\text{-HNO}_3$ solutions irradiated by a dose of 160 kGy, together with mass - and NMR spectra identified altogether 24 degradation products. Due to the effect of nuclear ionizing radiation, secondary amines are formed in the organic phase, representing the main portion. Diphenyl and a number of alkyl-diphenyls are formed due to the degradation of benzene and the effect of nitric acid and its degradation products. The identification of the degradation products in an irradiated solution of BDMLNNO_3 provided a total of 18 substances. The mass drop in BDMLNNO_3 is a markedly lower than in the case of BDBuN .

PROPERTIES OF DIALKYLDITHIOPHOSPHORIC ACIDSAS ACTINIDE EXTRACTANTS

R. FITOUSSI, C. MUSIKAS

Division de Chimie - CEN - FAR

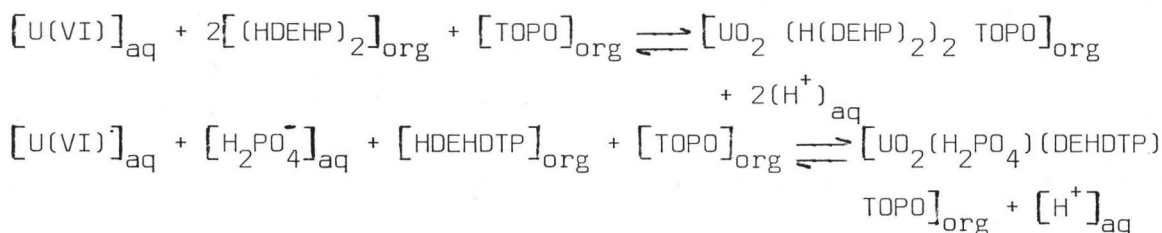
FONTENAY-AUX-ROSES - 92260 (FRANCE)

I. ACTINIDE AQUEOUS COMPLEXES WITH DIALKYLDITHIOPHOSPHATES

Aqueous actinide dialkyldithiophosphate complexes are weaker than dialphosphate (1). In some instances, in spite of this lower chemical affinity the sulfur donors extract actinide better than their oxygen donors homologues.

II. U(VI) EXTRACTION BY DI-2-ETHYLHEXYLDITHIOPHOSPHORIC ACID (HDEHDP)

As an example for HDEHDP and HDEHP two extractants which differ only by the nature of the donor(S vs O) the extraction from concentrated phosphoric acid occurs according to the mechanisms



These differences are the consequences of :

- The weaker ability of SH group to give hydrogen bonds (HDEHDP is monomeric in hydrocarbons, HDEHP is dimeric ,HDEHDP is not bonded to TOPO contrary to HDEHP)
- The weaker S to metal bond which allows a H_2PO_4^- ion to enter the U(VI) coordination sphere in the organic phase.

III. Np(IV) EXTRACTION BY DIALKYLDITHIOPHOSPHORIC ACIDS

The weak S to metal bond has for consequences a great variety of extraction mechanisms which are dependent of the aqueous phases composition. For example species such as $\text{Np}(\text{DEHDP})\text{Cl}_3$, $\text{Np}(\text{DEHDP})_2\text{Cl}_2$ are observed in the organic phases when Np(IV) is extracted respectively from concentrated and diluted solutions of hydrochloric acid.

IV. EXTRACTION OF Np(V) BY DIALKYLDITHIOPHOSPHORIC ACIDS

Np(V) is extracted by synergistic mixtures of HDEHDP and a neutral oxygen donor like TBP or TOPO but Np(V) is reduced into Np(IV) with the time.

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RESEARCH FOR NEW LIGANDS FOR TRIVALENT ACTINIDE -
LANTHANIDE GROUP SEPARATION BY SOLVENT EXTRACTION

G. LE MAROIS, C. MUSIKAS

Div. de Chimie - CEN - FAR

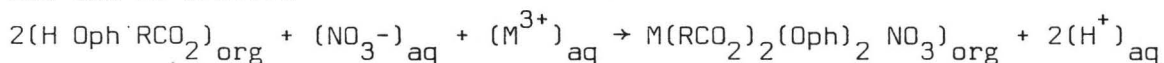
FONTENAY-AUX-ROSES (92260) FRANCE

Nitrogen ligands form more stable aqueous complexes with 5f trivalent ions than with 4f ions (1) (2). We investigated the influence of three cationic exchanger on the Am(III) - Eu(III) separation factors by solvent extraction using orthophénanthroline (Oph).

- Extraction coefficients of Am(III) - Eu(III) into 0.25 M Oph and 0.25 M nonanoïc acid in nitrobenzene are contained Table I.

HNO ₃	pH	Log D _{Am}	Log D _{Eu}	D _{Am} /D _{Eu}
0.0037	5.08	1.71	0.45	18.3
0.0057	4.89	1.36	0.15	16.6
0.0077	4.75	1.00	- 0.22	17.1
0.0097	4.64	0.86	- 0.40	18.5

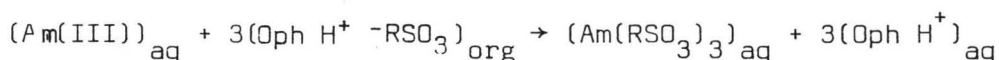
The extraction mechanism found out by distribution curves slope analysis can be written



- Extraction coefficients of Am(III) - Eu(III) in Oph and dibutylphosphoric acid mixtures are shown table II

HNO ₃	HDBP	Oph	pH	Log D _{Am}	Log D _{Eu}	D _{Am} /D _{Eu}
0.1	0.1	0	1.0	- 0.77	0.7	0.034
0.1	0.1	0.05	2.12	2.65	3.25	0.251
0.1	0.1	0.5	4.04	3.14	2.95	1.55
0.1	0.001	0.5	4.16	- 0.48	- 1.17	4.90

- Sulfonic acids with long organic chains do not extract selectively Am³⁺ because the extraction mechanism is :



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Physical Chemistry

Session 15

Co-chairmen : Y. Marcus (The Hebrew University of Jerusalem, Israel)
H.M.N.H. Irving (University of Cape Town, Rondebosch, South Africa)

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- 80-208 Effect of diluent on extraction (physico-chemical principles).
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ANION EXCHANGE EXTRACTION, HYDRATION AND SOLVATION
OF ANIONS IN NON-AQUEOUS SOLUTIONS.

I.M. Ivanov, V.P. Zaitsev

Institute of Inorganic Chemistry
Siberian Branch of the Academy of
Sciences of the USSR, 630090,
Novosibirsk, USSR.

ABSTRACT. The results of thermodynamic and near infrared spectra investigation of the hydration and solvation of quaternary alkylammonium salts in non-aqueous solutions are discussed.

Two types of water exist in the organic phase. The first is the water in the hydration sphere which shows a sharp band at 5250 and 4800 cm^{-1} ; the second is the water solubilized in the micelles which shows a broad band at 5150 cm^{-1} .

For the processes of exchange of stable anions in systems with salts of quaternary ammonium bases (QAB)



the change of standard free energy, G_{ex}° , of the reaction (1) and the free energy of transfer of the anions, $\Delta G_{\text{tr}}^{\circ}$, are determined mainly by the difference of free energies of hydration, ΔG_h^x , and solvation, ΔG_s^x , of ions. With the respect to standard ion A^- , the free energy of exchange is equal to

$$\Delta G_{\text{ex}}^{\circ} = (\Delta G_h^x - \Delta G_s^x) - C_1 \text{ or } \Delta G_{\text{ex}}^{\circ} = (1 - K_G) G_h^x - C_1 \quad (2)$$

where $K_G = \Delta G_s^x / \Delta G_h^x$ is a coefficient of resolution of the X^- ions for their transport from water to non-aqueous solvents; C_1 is a constant.

The change of standard free energy of ions on their transfer from a reference solvent into another one

$$\Delta G_{\text{tr}}^{\circ} = \Delta G_h^x - \Delta G_s^x = \Delta G_{\text{ex}}^{\circ} + C_1 \quad (3)$$

may be calculated for "dry" systems (hypothetical extraction systems where the equilibrium between the solvents does not

take place) by measuring the solubility products, K_s , of salts with a common cation but different anions or it may be determined directly for real extraction systems [1] from data on the interphase exchange of anions.

For stable inorganic anions the value of ΔG_{tr}^0 is observed to increase in the series $ClO_4^- < I^- < NO_3^- < Br^- < Cl^- < F^- < OH^-$ in accordance with the increase of their free energy and enthalpy of hydration or proton affinity. All the exchange reactions of anions for dry systems are well described by the linear equation (2). The coefficient of re-solvation, K_G , is not dependent on the properties of the anion, but is determined only by the solvent nature (Fig. 1a).

The coefficient K_G calculated from the values of ΔG_{tr}^0 [2] by means of equations (2) and (3) shows the linear correlation with the parameter E_t , defining the solvating properties of the solvent [3]. Water is characterized by the maximum value of E_t , that's why the inequality $\Delta G_h^x > \Delta G_s^x$ is correct for all the extraction systems.

In the real extraction systems, for example with distribution of the salts of tetraoctylammonium bases between water and toluene, a significant coextraction of water with anion takes place. It has been established that the larger is the hydration energy of an anion in water the larger is the quantity of coextracted water [4]. In fact, in aqueous solution saturated with water the anion is partly solvated by water and partly by molecules of the solvent and this leads to the general increase of solvation energy of the anions $\Delta G_{s(h)}^0$. The difference of chemical potential of anion is a "dry" solvent, μ_s^0 , and in a solvent saturated with water, $\mu_{s(h)}^0$, may be determined by investigating the processes of hydration in non-aqueous solutions.

A quantity of coextracted water depends on the nature of the anion and the properties of the solvent. For the salts of the tetraoctylammonium ion (TOA), which have a symmetrical cation, the hydration numbers $\bar{h} = (C_{H_2O}^{tot} - C_{H_2O}^{in}) / C_{QAB}$ (where $C_{H_2O}^{tot}$ = total concentration of water in non-aqueous solution, $C_{H_2O}^{in}$ = solubility of water in pure solvent) are not dependent on the salt concentration in the range of 0 - 0.2 M. For the salts of the dimethylbenzyldecylammonium ion (DMBDA), which have unsymmetrical cations, the hydration numbers $\bar{h}$ increase with increase in the total concentration of salts (Fig. 2). However, in the range of low salt concentrations (up to 0.02 M), the solubility of water does not depend on the structure of the cation. For TOA salts, only the anionic part has been assumed to be hydrated. The high solubility of water does not depend on the structure of the cation. For TOA salts only the anionic part has been assumed to be hydrated. The high solubility of water in the presence of the DMBDA salts is connected with the appearance of micelles which contain the solubilized water.

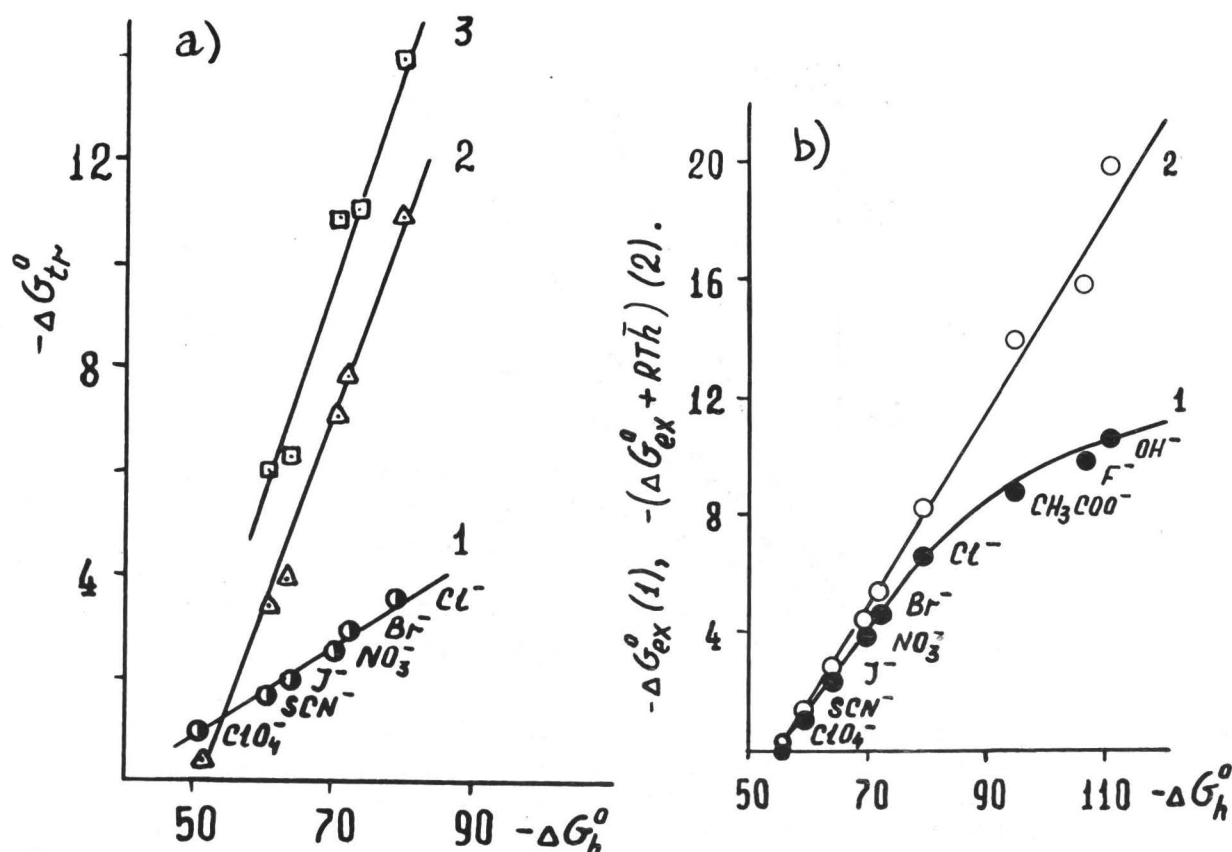


Fig. 1. The change of the free energy ΔG_{tr}^0 (ΔG_{ex}^0) with the transfer of the anion from water into non-aqueous solvents vs. the free energy of hydration of the anion in water ΔG_h^0 .

a) "Dry" system : 1 - methanol, 2 - dimethylsulphoxide, 3 - dimethylacetamide. b) Extraction systems (solvent - toluene) : 1 - eq. 2, 2 - eq. 6.

The difference in nature of the water molecules coextracted with the salts of TOA and DMBDA determines the difference in shapes of the absorption bands of water due to the $(\nu_2 + \nu_3)$ combination modes (Fig. 3).

In the infrared spectra of water in water saturated solutions of TOA salts in benzene, one easily observes the narrow absorption band of "free" water ($\nu_{OH} + \nu_2^-$) [5] at 5250 cm^{-1} and the weak broad band of water molecules bound with anion by hydrogen bonds. The position of the first band does not depend on the nature of the anion and on the properties of the solvent. It has been found that the relative intensity $I/\bar{h}$ increases in the row $Cl^- < Br^- < I^-$ where I = the intensity of the absorption band at 5250 cm^{-1} , $\bar{h}$ = the hydration number of the anion in the non-aqueous solvent. This fact can be interpreted as due to the decrease of stability of water bonding in the hydration sphere of an anion.

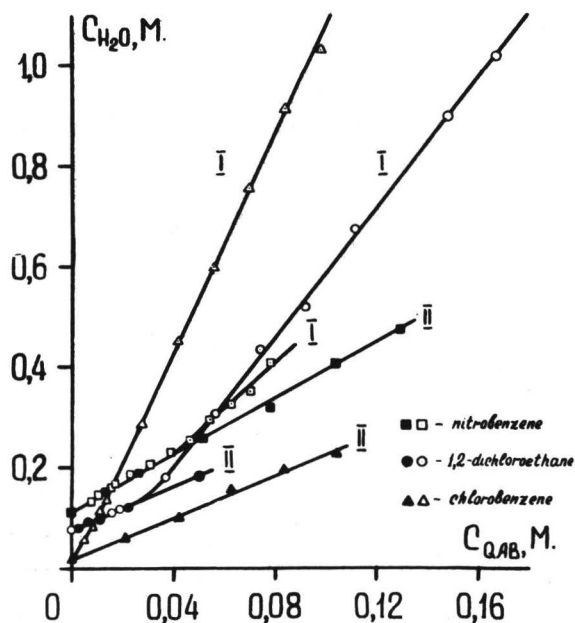


Fig. 2. Solubility of water vs. the concentration of quaternary ammonium salts, QAB, in non-aqueous solvent. 1 - dimethyldodecylbenzylammonium chloride, 2 - tetraoctylammonium chloride.

In the spectra of DMBDA salts, besides the two bands mentioned above, the broad symmetrical band which is also present in the spectrum of pure water appears at 5180 cm^{-1} . We suppose that DMBDA forms in the solution spherical micelles which contain "pure" water. On introducing an aliphatic alcohol into the solution, the micelles are broken down and the band at 5180 cm^{-1} disappears. In contrast to this, polymerization of the salts with symmetrical cations takes place and leads to the formation of linear or planar polymeric molecules. The hydration spheres of the anions in these systems are only slightly distorted by the presence of neighbouring cations. For example, the value of $\bar{h}$ (hydration number) does not depend on the degree of aggregation or dissociation of tetraoctylammonium (TOA) salts in nitrobenzene. For the salts having Cl^- , Br^- , NO_3^- , SCN^- as anion, the intense "free" water band at 5250 cm^{-1} and the weak broader band at 5250 cm^{-1} due to the hydrogen-bonded OH are observed in all the solvents where h does not exceed 4-6. This fact shows that the main part of the water is located in the first hydration sphere of the anion where the separate molecules of water are not bonded with each other by hydrogen bonds but interact with the anion and the solvent only (Fig. 4). For the tetraoctylammonium salts featuring an anion with a high value of the hydration number $\bar{h}$ ($\text{F}^- = 10$, $\text{OH}^- = 16$, $\text{SO}_4^{2-} = 14$, $\text{CO}_3^{2-} = 22$), a group of bands appears between the two bands mentioned above. We suppose that the appearance of these bands is due to the formation of the secondary hydration sphere of the anion (Fig. 4a).

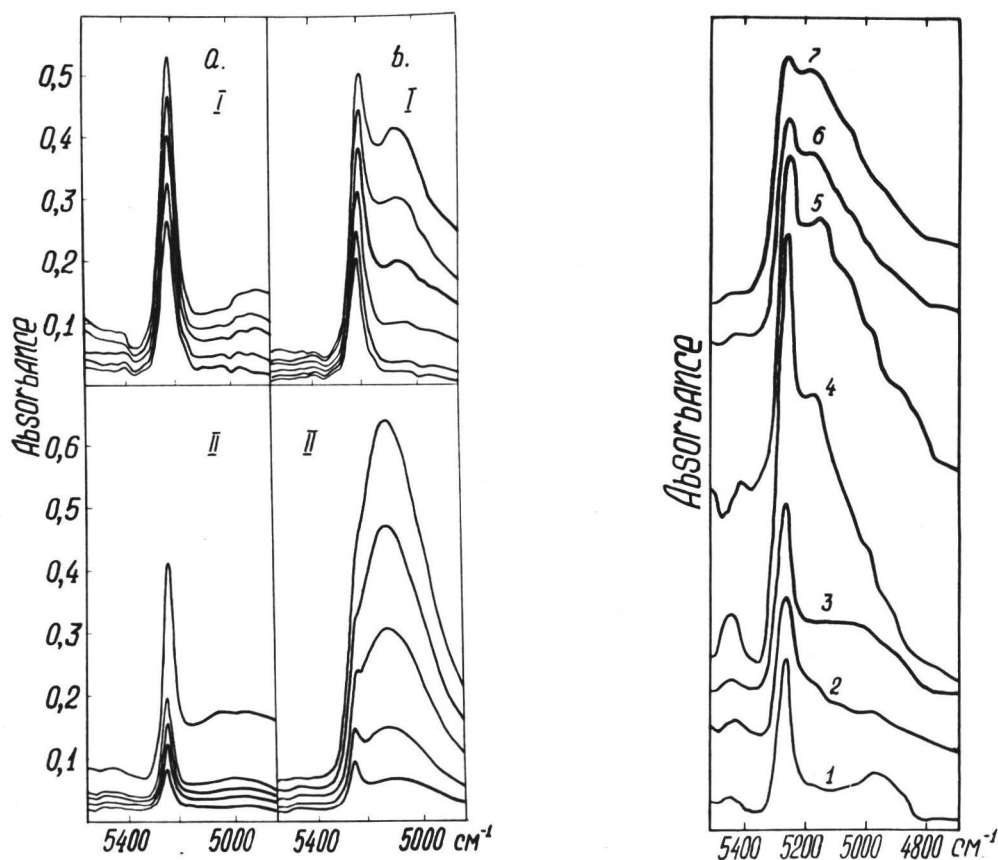


Fig. 3. IR - spectra of H_2O for different concentrations of hydrated quaternary ammonium salts, QAB, in dichlorethane (I) and chlorobenzene (II) : a) tetraoctylammonium chloride, b) dimethylbenzylammonium chloride.

Fig. 4. IR - spectra of H_2O associated to various tetraoctylammonium salts in benzene : 1 - NO_3^- ; 2 - $\text{Fe}(\text{CN})_6^{3-}$; 3 - Cl^- ; 4 - $\text{Fe}(\text{CN})_6^{4-}$; 5 - SO_4^{2-} ; 6 - F^- ; 7 - OH^- .

On introducing an aliphatic alcohol into the solution at first the substitution of water in the secondary sphere and then in the primary coordination sphere of the anion takes place. But the complete substitution of water does not take place even at a high concentration of alcohol. Phenol is more effective. At low concentrations, practically complete substitution of water from the first sphere occurs. The electron donor solvents, such as tributylphosphate, don't exert a visible influence on the composition of the first hydration sphere of an anion. The complex anion $\text{Fe}(\text{CN})_6^{3-}$ in benzene solutions contains water only in the primary sphere. The ion $\text{Fe}(\text{CN})_6^{4-}$ is far more strongly hydrated (Fig. 4).

Salt hydration in non-aqueous solvent saturated with water can be described as a process of complexing with

$$\bar{h} = \frac{\beta_1 a_w + 2\beta_2 a_w^2 + \dots}{1 + \beta_1 a_w + \beta_2 a_w^2 + \dots} = \frac{F}{\phi}$$

where β_n - the stability constant of hydrate $X^-(H_2O)_n$; a_w - water activity in the system. The difference between the standard chemical potential of the anion in "dry" solvent and in solvent saturated with water is given by

$$\Delta\mu^0 = \mu_s^0 - \mu_{s(h^-)}^0 = -RT \ln \phi \quad (5)$$

For the dilute solution of a quaternary ammonium salts QAB equation $\Delta\mu = RT.h.a_w$ may be used [6], where $h = \bar{h}/a_w$. With allowance for the energy of hydration of anion the whole expression for G_{ex}^0 takes the form

$$\Delta G_{ex}^0 = (1 - K_g) \Delta G_h^0 - RT.h.a_w - C_1 \quad (6)$$

Equation (6) rather better than eq. (2) described the experimental data for reactions of extraction exchange of stable monocharged anions (Fig. 1b).

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THREE-DIMENSIONAL SOLUBILITY PARAMETERS FOR THE CORRELATION AND
PREDICTION OF LIQUID-LIQUID PARTITION CONSTANTS OF METAL CHELATE
COMPLEXES

Stig Wingefors, Jan-Olov Liljenzin and
Elisabeth Saalman

Department of Nuclear Chemistry
Chalmers University of Technology

412 96 Göteborg, Sweden

ABSTRACT

A new form of the three-dimensional solubility parameter concept is proposed for correlation of liquid-liquid partition constants. The model accounts for the dispersion, polar, induced polar and weak hydrogen bonding energies for solvents and liquid mixtures. The different partial contributions to the total solubility parameters of solutes like metal β -diketonates are estimated by non-linear least squares analysis of partition data.

INTRODUCTION

The three-dimensional nature of the solubility parameter was discussed by Small as early as 1953 (1), and since then many alternative subdivisions of the total cohesion energy have appeared in the literature (2,3). Today the model that is most widely accepted in the field of paint and polymer technology is that developed by Hansen (4-6), who proved the versatility of his model by extensive experimental work, and also found a satisfactory agreement between experimentally and theoretically derived polar and hydrogen bonding contributions for a vast number of organic solvents (6). In other fields of applied research the work of Prausnitz *et al.* (7-9) should be mentioned in the first place. Even if these workers only employed two solubility parameters corresponding to the non-polar (dispersion) and polar parts of the cohesion energy, they developed the fundamental principles for estimation of dispersion solubility parameters through the homomorph concept. Later Hansen extended their model to hydrogen bonded liquids.

According to Hansen (4) the total cohesion energy density of a molecular liquid can be divided into three parts,

$$-\frac{u_c}{v} = \delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (1)$$

where δ ($\text{J}^{1/2} \text{cm}^{3/2}$; units are omitted below) is the total (ordinary) solubility parameter, v = liquid molal volume (cm^3) and δ_d , δ_p and δ_h the solubility

parameters describing the dispersion, polar and hydrogen bonding characteristics of the liquid, respectively. The total molar cohesion energy, $-u_c$, is given here with a minus sign, because of its property of a potential energy function, which is = 0 for an ideal gas (10). Hansen's approach (3,4) to the prediction of polymer solubility in the formulation of solvents for film forming resins has been shown to be very useful, but nevertheless it is of rather qualitative nature. A good solvent or solvent mixture for a polymer should have a set of three-dimensional solubility parameters falling in the vicinity of the corresponding set of the polymer in the $\delta_d - \delta_p - \delta_h$ space. This is reasonable when compared with the Scatchard-Hildebrand equation for excess energy of mixing for binary mixtures,

$$\underline{u}^E = (\underline{x}_1 \underline{v}_1 + \underline{x}_2 \underline{v}_2) (\underline{\delta}_1 - \underline{\delta}_2)^2 \underline{\phi}_1 \underline{\phi}_2 \quad (2)$$

where $\underline{x}$ and $\underline{\phi}$ denote the mole and volume fractions of each component respectively. Minimum excess mixing energy and, consequently, maximum solubility is found for $\underline{\delta}_1 = \underline{\delta}_2$. In Hansen's method this reasoning is used for each of the three forms of interactions separately.

There are some problems and ambiguities connected with this approach. First, Hansen's model does not take into account the asymmetry of molecular interactions. This is most apparent in the handling of hydrogen bonding, where in each pair of interacting molecules, one must be a proton donor and the other a proton acceptor (1). Solvents which are proton acceptors (or electron donors) with a small tendency to participate in hydrogen bonding in the pure liquids (e.g., ethers and ketones) are consequently ascribed relatively high values of δ_h , even when this δ_h is effective only in mixtures with proton donors. In fact Hansen's δ_h gives a reasonable estimate of hydrogen bonding in the pure liquids only for alcohols, which have strong donor as well as acceptor properties. Secondly, the δ_p -term in Eq. (1) is actually the sum of contributions from polar-polar and polar-induced polar interactions, and the latter is also asymmetric in behaviour. It is interesting to note that the inductive part of the cohesion energy of polar liquids has been shown (11) to be larger than expected from the simple Debye formula (12). One may not, therefore, a priori ignore this influence in strongly asymmetric mixtures, as was formerly common practice. These shortcomings of the original three-dimensional solubility parameter concept have to be overcome before Eq. (2) can be applied to liquid mixtures, in a way more in line with the form proposed for regular solutions where the dispersion forces are predominating.

This paper deals primarily with the correlation between organic solvent solubility parameters and the partition constants of metal chelate complexes; the development in this field is covered in the comprehensive review by Irving (13).

A MODEL FOR THE TOTAL MOLAR EXCESS ENERGY OF MIXING

Contributions from dispersion forces are to be dealt with as in the original form of the Scatchard-Hildebrand equation (10). However, different Greek letters will be used for the three-dimensional solubility parameters; therefore $\underline{\lambda}$ is used here instead of δ_d (cf. also refs. 7-9). The dispersion part of the excess mixing energy is then given by

$$\underline{u}^E(\text{disp.}) = (\underline{x}_A \underline{v}_A - \underline{x}_S \underline{v}_S) (\underline{\lambda}_A - \underline{\lambda}_S)^2 \underline{\phi}_A \underline{\phi}_S \quad (3)$$

where the indices A and S denote the two components of the mixture; S stands for the organic solvent.

Contributions from forces between permanent dipoles (orientation forces) are as symmetric in behaviour as the dispersion forces. Using τ for the polar solubility parameter (cf. refs. 7-9), the orientation part of the excess mixing energy is

$$\underline{u}^E(\text{orient.}) = (\underline{x}_A \underline{v}_A + \underline{x}_S \underline{v}_S)(\tau_A - \tau_S)^2 \underline{\phi}_A \underline{\phi}_S \quad (4)$$

Contributions from forces between permanent dipoles and induced dipoles (induction forces) have to be considered in more detail. From the common simplified expression for the London dispersion energy, the Keesom formula for orientation energy and the Debye formula for induction energy (12), it follows that the induction contribution to the cohesion energy of a liquid is given by $\underline{k}_I \lambda \tau$. The induction factor $\underline{k}_I$ is thereby obtained as

$$\underline{k}_I = (8kT/\underline{U}_e)^{1/2} \quad (5)$$

where k is Boltzmann's constant and $\underline{U}_e$ is the electronic oscillation potential. This approach was also used by Gardon (14), who actually never calculated τ , but gave values of "fractional polarity" ($= \tau^2 / \delta^2$) as a measure of solvent polar properties. Gardon used $\underline{k}_I = 0.142$, which is obtained from Eq. (5) at 25°C with $\underline{U}_e = 10$ eV as a mean value for most organic compounds; it was then assumed that $\underline{U}_e$ equals the first ionization potential of the molecules. Unfortunately, the formulas used for derivation of Eq. (5) are highly approximative, even for quite simple molecules in the gas phase, and their application to large molecules in a condensed state is suspect. However, for the moment we will assume that $\underline{k}_I$ is approximatively constant and treat it as an adjustable parameter. In the derivation of the induction force contribution to the excess energy of mixing, it is assumed that the induction energy density between two different molecules is given by the sum of the two unsymmetric interaction terms. Otherwise the derivation is the same as for the originally described dispersion force field (10). The resulting contribution from induction energy is then

$$\underline{u}^E(\text{ind.}) = (\underline{x}_A \underline{v}_A + \underline{x}_S \underline{v}_S) \underline{k}_I (\lambda_A - \lambda_S)(\tau_A - \tau_S) \underline{\phi}_A \underline{\phi}_S \quad (6)$$

Contributions from hydrogen bonding must reflect the unsymmetric nature of this interaction. Several proposals have been made. For instance, one might treat the donor and acceptor properties as specific interaction potentials on an arbitrary scale without any thermodynamic possibility of giving the absolute values (cf. electrode potentials). In such a case one must choose a reference relation, e.g., that $\delta_h = \sigma_a \sigma_b$, where $\sigma_a = \sigma_b$ for alcohols (15). The problem with this approach is evidently that σ_a and σ_b for all other solvents have to be determined from experimental data, and this is not very promising, due to the highly non-ideal behaviour of mixtures with alcohols. On the other hand, when one is content to take only weak hydrogen bonding into account, another approach might prove fruitful. Assuming that proton acceptor and electron donor properties run in parallel, it would be plausible that for weak hydrogen bonding (without severe structuring and loss of entropy like in water and alcohol) δ_h is proportional to τ , or $\delta_h = \sigma \cdot \tau$, where σ incorporates a universal conversion factor (such as $\underline{k}_I$), as well as the more obscurely defined proton donor property. It then follows (in full analogy

with the treatment of the induction contribution) that the contribution to the excess energy of mixing from hydrogen bonding is given by

$$\underline{u}^E(\text{h.b.}) = (\underline{x}_A \underline{v}_A + \underline{x}_S \underline{v}_S)(\underline{\sigma}_A - \underline{\sigma}_S)(\underline{\tau}_A - \underline{\tau}_S)\underline{\phi}_A \underline{\phi}_S \quad (7)$$

In order to simplify the expressions we shall introduce the following abbreviations: $(\underline{\lambda}_A - \underline{\lambda}_S) = \underline{\Delta \lambda}$; $(\underline{\tau}_A - \underline{\tau}_S) = \underline{\Delta \tau}$ and $(\underline{\sigma}_A - \underline{\sigma}_S) = \underline{\Delta \sigma}$. By summation of Eqs. (3), (4), (6) and (7) the total molar excess energy of mixing is obtained as

$$\underline{u}^E = (\underline{x}_A \underline{v}_A + \underline{x}_S \underline{v}_S)(\underline{\Delta \lambda}^2 + \underline{\Delta \tau}^2 + \underline{k}_T \underline{\Delta \lambda} \underline{\Delta \tau} + \underline{\Delta \sigma} \underline{\Delta \tau})\underline{\phi}_A \underline{\phi}_S \quad (8)$$

Since the last parenthesis in this expression is assumed to be a constant, independent of composition, it may be denoted by $\underline{\Delta(A,S)}$. When $\underline{\tau}_A = \underline{\tau}_S = \underline{\sigma}_A = \underline{\sigma}_S = 0$, Eq. (8) reduces to Eq. (2).

APPLICATION OF THE MODEL TO AQUEOUS-ORGANIC PARTITION OF METAL CHELATE COMPLEXES

Let $\underline{K}_D$ denote the partition constant in the molarity scale of a solute that is distributed between an aqueous and an organic phase. The solute (A) may be a neutral metal chelate complex with the same composition in both phases. For small concentrations of A, the partition constant in the mole fraction scale is given by $\underline{K}_{Dx} = \underline{K}_D (\underline{v}_S / \underline{v}'_W)$ where $\underline{v}'_W$ is the "effective" molal volume of water in the aqueous phase. $\underline{v}'_W$ might be different from the real molal volume of water due to the presence of electrolytes and clustering of water molecules.

When the pure liquid at the actual temperature and pressure is chosen as standard state for A in both phases, $\underline{K}_{Dx} = \underline{\omega}_Y / \underline{\omega}_{\bar{Y}}$, where $\underline{\omega}_Y$ and $\underline{\omega}_{\bar{Y}}$ are the activity coefficients at infinite dilution in the aqueous and organic phases respectively. The activity coefficient in the organic phase is given by (9)

$$\underline{RT} \ln \underline{Y}_A = \left(\frac{\partial \underline{G}^E}{\partial \underline{n}_A} \right)_{\underline{n}_S, \underline{P}, \underline{T}} \quad (9)$$

where $\underline{G}^E$ is the total excess (Gibbs') free energy for a mixture of $\underline{n}_A$ moles of A and $\underline{n}_S$ moles of S. Following Scatchard (10), we now assume that the volume change on mixing is negligible and thus that Gibbs' free energy of mixing at constant $\underline{P}$, $\underline{T}$ might be replaced by Helmholtz free energy of mixing at constant $\underline{P}$, $\underline{V}$. Thus, with an ideal (regular) entropy of mixing ($\underline{S}^E = 0$) we have $\underline{G}^E = (\underline{n}_A + \underline{n}_S)\underline{u}^E$. Insertion of this expression into Eq. (9) gives

$$\underline{RT} \ln \underline{Y}_A = \underline{v}_A \underline{\Delta(A,S)} \underline{\phi}_S^2 \quad (10)$$

The final equation for the partition constant at infinite dilution in the molarity scale is then given by

$$\underline{RT} \ln (\underline{K}_{DA} \underline{v}_S) = \underline{RT} \ln (\underline{\omega}_{Y_A} \underline{v}'_W) - \underline{v}_A \underline{\Delta(A,S)} \quad (11)$$

For organic solvents with small aqueous solubility, the first right hand term of Eq. (11) is a constant independent of the composition of the organic

phase. With this term and the solubility parameters of the distributed solute as adjustable parameters, Eq. (11) can be used for correlation of partition data. For this purpose, values of solvent molal volumes and the three-dimensional solubility parameters λ_s , τ_s and σ_s are needed, as well as the molal volume of the extracted complex. The latter quantity might be estimated from partial molar volumes or solid state density (16); values of v_s are easily attainable from reference sources (17,18).

EVALUATION OF THE THREE-DIMENSIONAL SOLUBILITY PARAMETERS

The total solubility parameter is divided according to

$$\underline{\delta}^2 = \underline{\lambda}^2 + \underline{\tau}^2 + \underline{k_I} \underline{\lambda} \underline{\tau} + \underline{\sigma} \underline{\tau} \quad (12)$$

The sum of the two middle terms in this expression equals Hansen's $\underline{\delta}_p^2$ for non-hydrogen bonded liquids (cf. Eq. 14). Before any attempt to use Eq. (12) for evaluation of the partial solubility parameters it must be ascertained that the solvent in question is sufficiently immiscible with water. Even an equilibrium water content of a few % (by weight) in the organic phase makes it questionable whether this phase really is described by pure organic solvent properties. The division of the total solubility parameter may then proceed according to the following scheme, cf. Table 1.

$\underline{\lambda}$ is obtained from the homomorph concept as described by Blanks and Prausnitz (8) and Hansen (4). Ambiguities in the choice of a suitable homomorph for branched aliphatic solvents may later be overcome by a recently developed correlation between $\underline{\lambda}$ and refractive index (19).

For non-hydrogen bonded polar solvents, $\underline{\delta}_p$ is either determined from the difference

$$\underline{\delta}_p^2 = \underline{\delta}^2 - \underline{\lambda}^2 \quad (13)$$

or calculated from the dielectric constant, refractive index and dipole moment, as described by Hansen (6). The latter alternative is preferable for slightly polar solvents with $\underline{\tau} < 2$. For hydrogen bonded solvents this is as yet the only way. Subsequently $\underline{\tau}$ is obtained as a solution to the equation

$$\underline{\tau}^2 + \underline{k_I} \underline{\lambda} \underline{\tau} - \underline{\delta}_p^2 = 0 \quad (14)$$

where $\underline{k_I}$ must be assumed to be known.

In order to eliminate the problems with Hansen's hydrogen bonding parameter, as mentioned in the introduction, one has to decide (or define) what solvents actually are hydrogen bonded in pure form. The only solvents of this kind that are of interest in the present application, and that also fulfill the requirement of aqueous immiscibility, are the halogenated hydrocarbons with a hydrogen in α -position to a halogen atom. The most typical example of such a solvent is chloroform. $\underline{\sigma}$ is thereby obtained from the relation

$$\underline{\sigma} = (\underline{\delta}^2 - \underline{\lambda}^2 - \underline{\delta}_p^2)^{-1} \underline{\tau} \quad (15)$$

TABLE 1.

Molar volumes ($\underline{v}_S$, cm³) and solubility parameters (unit: J^{1/2} cm^{3/2}) for organic solvents employed for the correlation. The values of $\underline{\tau}_S$ and $\underline{\sigma}_S$ given in the last two columns are calculated with $\underline{k}_I = 0.73$. See text for further details and data sources.

Solvent	$\underline{v}_S$	$\underline{\delta}_S$	$\underline{\lambda}_S$	$\underline{\delta}_p^2$	$\underline{\sigma}_S \underline{\tau}_S$	$\underline{\tau}_S$	$\underline{\sigma}_S$
n-Hexane	131.6	14.88	14.88	0.0	0.0	0.0	0.0
Di-n-butyl ether	170.4	15.88	15.22	20.4	0.0	1.6	0.0
Cyclohexane	108.8	16.76	16.76	0.0	0.0	0.0	0.0
Carbontetrachloride	97.1	17.50	17.50	0.0	0.0	0.0	0.0
Methylisobutyl ketone	125.8	17.56	15.37	72.1	0.0	4.6	0.0
Toluene	106.9	18.27	18.21	1.7	0.0	0.1	0.0
Benzene	89.4	18.74	18.74	0.0	0.0	0.0	0.0
Chloroform	80.7	18.74	17.70	9.5	28.7	0.7	41.1
Benzonitrile	103.1	22.69	19.81	122.7	0.0	6.0	0.0

TEST OF THE MODEL

In order to test the model, liquid-liquid partition data for three metal bis(acetylacetonate) complexes, Be(AA)₂ (26), Cu(AA)₂ and Zn(AA)₂ (27) were used, cf. Table 2. The three-dimensional solubility parameters $\underline{\lambda}_A$, $\underline{\tau}_A$, $\underline{\sigma}_A$ and the aqueous phase term $RT \ln(\underline{y}_A \underline{v}_W) = \underline{w}_A$ in Eq. (11) were treated as adjustable parameters. The calculations were first done by linear least squares fitting with an assumed constant value of $\underline{k}_I = 0.142$. However, a negative $\underline{\sigma}$ for Cu(AA)₂ was found by this procedure - a result that indicated that another value of $\underline{k}_I$ should be chosen. Details of these preliminary calculations have been described elsewhere (20).

The subsequent non-linear least squares fitting was performed for the three complexes at the same time and now $\underline{k}_I$ was also adjusted. The total solubility parameters of solvents from Hoy (21) were used as input data; $\underline{\lambda}_S$ and $\underline{\delta}_{pS}$ were those given by Hansen (6). However, in all cases where Hansen had used a non-zero value for $\underline{\delta}_{hS}$, except for chloroform, his $\underline{\delta}_h^2$ was included in $\underline{\delta}_{pS}^2$, see Table 1. The molar volumes of the metal complexes were estimated from solid densities and partial molar volumes (16) to be 167, 166 and 175 cm for the Zn, Cu and Be complexes, respectively.

The minimization was actually performed with respect to the square root of the adjustable parameters, in order to secure a minimum with a set of physically meaningful (positive) parameters. The result is shown in Tables 2 and 3, where the results from using the original SH equation are also given for comparison. $\underline{k}_I$ was determined to 0.73.

DISCUSSION

The overall fit of data is better in the proposed model than in the original SH equation. However, the real improvement might lie more in the possibilities offered by the physical interpretation of the new parameters. At the moment, the only parameter that can be tested against other evidence is $\underline{k}_I$. It has been found that the induction contribution ($-\underline{u}_I$) to the total molar cohesion energy for polar liquids is appreciably larger than obtained when $\underline{k}_I = 0.142$. For 2-alkanones Meyer *et al.* (11) found $-\underline{u}_I$ to be at least 4.5 kJmole⁻¹. With $\underline{k}_I = 0.142$ ca 2 kJmole⁻¹ is obtained whereas $\underline{k}_I = 0.73$,

according to the present calculation, gives $-u_1 \approx 6 \text{ kJmole}^{-1}$, cf. Table 4. This might speak in favour of the new model. An extension of the model should incorporate the variation of k_T with dielectric constant (ϵ) of the organic phase, or in fact the pure organic solvent, since we are as yet only interested in dilute solutions. The dependency of k_T on ϵ may approximatively be derived from the classical theories of electric polarization (22). However, for the solvents employed in this work, the expected change in k_T does not seem particularly important.

TABLE 2.
Experimental values of $\log K_{DA}$ for $\text{Be}(\text{AA})_2$, $\text{Cu}(\text{AA})_2$ and $\text{Zn}(\text{AA})_2$ together with the difference between experimental and calculated values $\Delta \log K_{DA} = \log K_{DA}(\text{exp.}) - \log K_{DA}(\text{calc.})$ according to the new model (this work) and the original Scatchard-Hildebrand equation (SH).

Complex	Organic solvent	$\log K_{DA}$	$\Delta \log K_{DA}(\text{this work})$	$\Delta \log K_{DA}(\text{SH})$
$\text{Be}(\text{AA})_2$	n-Hexane	0.64	-0.07	+0.04
	Cyclohexane	0.87	+0.57	+0.71
	Carbontetrachloride	1.90	-0.16	-0.01
	Methylisobutyl ketone	1.75	-0.15	+0.04
	Toluene	2.01	-0.07	+0.07
	Benzene	2.35	-0.23	-0.05
	Chloroform	3.50	0.0	-1.13
	Benzoenitrile	2.33	+0.11	+0.41
$\text{Cu}(\text{AA})_2$	n-Hexane	-0.60	-0.08	-0.19
	Cyclohexane	-0.04	+0.31	+0.37
	Carbontetrachloride	0.85	-0.24	-0.02
	Methylisobutyl ketone	0.61	0.00	+0.14
	Toluene	0.85	0.00	+0.33
	Benzene	1.04	+0.01	+0.44
	Chloroform	2.54	0.0	+1.02
$\text{Zn}(\text{AA})_2$	n-Hexane	-1.57	+0.03	-0.08
	Di-n-butyl ether	-1.05	+0.04	-0.12
	Cyclohexane	-1.16	+0.33	+0.51
	Carbontetrachloride	-0.39	-0.20	+0.03
	Methylisobutyl ketone	-0.15	-0.15	-0.31
	Toluene	-0.37	-0.07	+0.18
	Benzene	-0.21	-0.09	+0.22
	Chloroform	0.83	0.0	-0.78
	Benzoenitrile	0.21	+0.11	+0.19

TABLE 3.
Three-dimensional solubility parameters and aqueous phase interaction constants for metal β -diketonates obtained from non-linear least square analysis of partition data. The last two columns show the result when only the total solubility parameters are used. Solubility parameters are given in $\text{J}^{1/2} \text{cm}^{3/2}$ and ${}^\circ W_A$ in kJmole^{-1} .

Metal complex (A)	λ_A	I_A	σ_A	δ_A	${}^\circ W_A$	$\delta_A(\text{SH})$	${}^\circ W_A(\text{SH})$
$\text{Be}(\text{AA})_2$	21.9	1.8	1.7	22.8	26.9	22.9	27.1
$\text{Cu}(\text{AA})_2$	23.1	2.0	2.1	24.0	22.8	26.7	29.9
$\text{Zn}(\text{AA})_2$	21.0	1.6	5.0	21.8	12.4	22.7	13.8

TABLE 4.

Comparison of the contribution to the molar cohesion energy from induction forces ($-\underline{u}_I$) for some ketones.

Ketone	δ $\text{J}^{1/2}\text{cm}^{-3/2}$	λ $\text{J}^{1/2}\text{cm}^{-3/2}$	$\underline{v}$ cm^3	$-\underline{u}_I$ ($k_I=0.142$) kJmole^{-1}	$-\underline{u}_I$ ($k_I=0.73$) kJmole^{-1}
Diethyl ketone	18.53	15.67	106.4	2.1	6.9
Methyl-n-propyl ketone	18.39	15.79	107.5	2.0	6.5
Di-isobutyl ketone	16.49	15.89	177.4	1.3	3.1
Methyl-isobutyl ketone	17.55	15.32	125.8	2.1	6.5

From Table 2 it is evident that the data for cyclohexane curiously enough is fitted less well than for the other solvents. It should be noted that in comparison with its high melting point (6.5°C), cyclohexane has a very low heat of fusion (2.7 kJmole^{-1}); cf. benzene, m.p. 5.5°C , heat of fusion 9.8 kJmole^{-1} . This might mean a more ordered liquid structure for cyclohexane than for other solvents. The bad fit should then reflect the inability of the SH model to take into account excess entropy.

On the other hand, no influence of the variation in solvent molar volume could be noted, cf. Fig. 1. Formerly it was common practice (13) to include a Flory-Huggins excess entropy (12) term in the correlation of partition data according to the solubility parameter concept. Hildebrand has shown (23) that this approach is, in fact, only necessary when polymeric chains are present in the system; for large bulky molecules the SH excess energy term is sufficient to describe non-ideal behaviour for non-associating liquid mixtures. Evidently this also holds for metal chelate complexes.

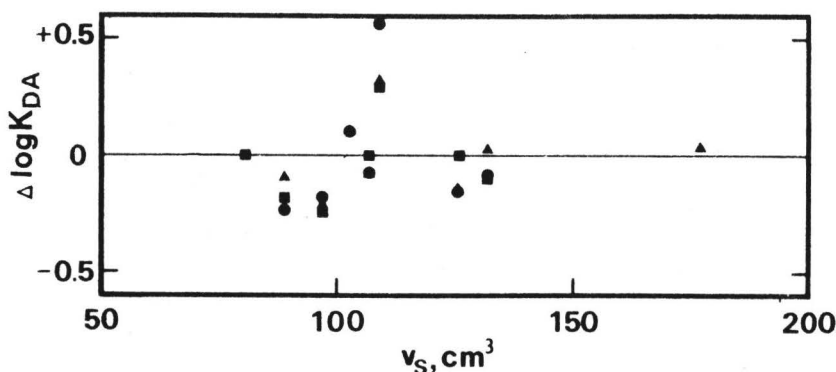


FIG. 1

The difference between experimental and calculated values of $\log K_{DA}$ as a function of solvent molar volume. $\text{Be}(\text{AA})_2$ ●; $\text{Cu}(\text{AA})_2$ ■; $\text{Zn}(\text{AA})_2$ ▲.

It might well be a fortuitous coincidence, but it is interesting to note, that aqueous solubility data for $\text{Be}(\text{AA})_2$ (16) provide an experimental value of the constant term ${}^\infty W_A = 26.9 \text{ kJmole}^{-1}$, which is exactly the value obtained when the new model is used. However, the comparison is not conclusive, since the solubility value also incorporates the free energy of fusion for $\text{Be}(\text{AA})_2$ at the actual temperature. Solubility data for the other two complexes in the actual ionic medium are not yet available.

The obtained values of λ_A , τ_A and σ_A for the different complexes are

difficult to comment on in the light of the data available. λ_A should in the first place be determined by the polarisability, which in turn increases with the aromatic character of the chelate rings. In view of the different molecular structures, ($\text{Be}(\text{AA})_2$ regular tetrahedron, $\text{Cu}(\text{AA})_2$ square planar and $\text{Zn}(\text{AA})_2$ distorted tetrahedron), it is quite reasonable to find the highest λ_A for $\text{Cu}(\text{AA})_2$, where the easily polarisable π -electrons of the rings are less shielded than in the tetrahedric structure. The small values of τ_A are perhaps not so significant, but it should be recognized that even highly symmetric metal complexes are polar in nature (24). It is also reasonable that τ_A is about the same for all three complexes, owing to the presence of the same number and type of polar groups. The zinc value of σ_A is much higher than for the other complexes. According to our model, this should in the first place be possible when an acidic hydrogen is present in the molecule. Other evidence, such as the low value of ${}^\infty W_A$ and thermodynamic data (25), indicates that the zinc complex is hydrated, at least in the aqueous phase. Thus $\sigma_A = 5$ for zinc seems to imply that this hydrated complex also exists in the organic phase. This conclusion is an illustration of the possibilities offered by the new model. The small but non-zero values of σ_A for Be and Cu are more difficult to connect with the chemical constitution of the complexes. However, a residual coordination capability on the metal atom might always lead to $\sigma_A > 0$, even if this capability does not lead to otherwise observable specific solvation.

The assumption of a direct coupling of σ and τ is what makes the present model of practical value. On the other hand, it turns out that it is only possible to estimate separate values of σ_A and τ_A , when a proton donor such as chloroform is present among the tested solvents. Thus, too much weight is given the chloroform data, and in further work along these lines other solvents of this kind will have to be included. It is also clear that, in order to test the model thoroughly, as wide a range of solvents as possible with respect to polarity and polarisability should be employed.

The values of the solvent solubility parameters have a great influence on the results, and the λ_s values are especially critical. The values of λ_s used in this study were primarily obtained from Hansen's tables. However, it is important to find better ways of estimating λ_s . We have, therefore, investigated other methods for that purpose and these will be described in a series of subsequent papers.

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ANION SOLVATION FREE ENERGIES FROM DISTRIBUTION EQUILIBRIA

Y. Marcus, E. Pross and J. Hormadaly

Department of Inorganic and Analytical
Chemistry, The Hebrew University

Jerusalem, Israel

ABSTRACT

The solvation Gibbs free energies of anions are key items for understanding solvent extraction equilibria. Transfer Gibbs free energies, $\Delta G_t^\circ(X^-, W \rightarrow S)$, based on the tetraphenylarsonium tetraphenylborate assumption, represent them adequately. Data for these for 11 anions X^- and 15 solvents S are tabulated, and expressed parametrically as $\Delta G_t^\circ(X^-, W \rightarrow S) = a(X^-) + b(X^-)[E_T(W) - E_T(S)]$ in terms of the solvent polarity index E_T . A distribution method, based on the sequestration of potassium ions by crown ethers, is shown to provide experimental data for anion transfer between water and immiscible solvents, relevant to solvent extraction. The equation used is $\Delta G_t^\circ(X^-, W \rightarrow S) = -RT \ln K_{\text{distr}}(X^-, S/W) + p(1/\epsilon_S) + q$, where K is the equilibrium constant for the ion-pair extraction of KCw^+X^- (Cw is the crown ether), ϵ_S the dielectric constant, p an independently known constant, and q must be obtained by calibration with a solvent with known $\Delta G_t^\circ(X^-, W \rightarrow S)$.

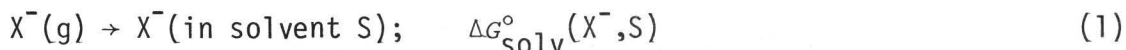
INTRODUCTION

The role of the solvent in solvent extraction equilibria has been the subject of many investigations. Much attention has focused on the solvation of the metal cations in the organic phase (1). If a chelating agent is absent, or if it does not neutralize the charge on the cation completely, anions must be coextracted. It is then necessary to provide for the solvation requirements of these anions. On the other hand, the anions, either simple or complex, may be the primary subjects of our interest. They may then be extracted as ion pairs with suitable organic-soluble cations (2). Even in low dielectric constant solvents, the ion-pairs formed are solvated, including their anion end.

A different source of interest in the solvation of anions arises from the effect the solvent has on their reactivity. This effect is manifested both in equilibria, such as in complexation equilibria in nonaqueous or mixed media, of interest to the coordination chemist (3), and in reaction kinetics, such as in nucleophilic substitution reactions of interest to the organic chemist (4).

There are two main measures for estimating the solvation of ions. One is the solvation number, or in mixed solvents also the solvent sorting around the ion. This measure is complicated by the vague definition of the portion

of the solvent which may be said to belong to the solvation sphere of an ion. The other measure for the solvation of ions is the standard molar Gibbs free energy of solvation (and its components, the enthalpy and entropy changes for solvation, which will not be discussed here). This quantity is clearly defined as pertaining to the reaction



where, for our purpose, the temperature must be specified, and atmospheric pressure is implied. It is more convenient to consider this quantity relative to the solvation in a reference solvent, commonly chosen as water. Thus the quantity of interest is the standard molar Gibbs free energy of transfer of the anion X^- from water to the solvent S .



Gibbs free energies of transfer of electrolytes are measurable (5), but individual ionic transfer Gibbs free energies, necessitate an extrathermodynamic assumption. There are good reasons (5,6) for accepting the tetraphenylarsonium tetraphenylborate (TPA TPB) assumption:

$$\Delta G_t^\circ(Ph_4As^+, W \rightarrow S) = \Delta G_t^\circ(BPh_4^-, W \rightarrow S) \quad (3)$$

The standard molar Gibbs free energy of transfer of an anion X^- is then obtained from the measured ΔG_t° of electrolytes:

$$\Delta G_t^\circ(X^-, W \rightarrow S) = \Delta G_t^\circ(Ph_4AsX, W \rightarrow S) - (1/2)\Delta G_t^\circ(Ph_4AsBPh_4, W \rightarrow S) \quad (4)$$

ANION TRANSFER GIBBS FREE ENERGIES

Transfer Gibbs free energies of electrolytes are generally based on solubility measurements. For the estimation of $\Delta G_t^\circ(X^-, W \rightarrow S)$ at least four solubility measurements are required:

- a) the solubility $s(Ph_4AsBPh_4, W)$, of the reference electrolyte in water
- b) the solubility $s(Ph_4AsBPh_4, S)$, of the reference electrolyte in the solvent
- c) the solubility $s(Ph_4AsX, W)$, of the X-salt in water
- d) the solubility $s(Ph_4AsX, S)$, of the X-salt in the solvent.

It is assumed here that these solubilities are sufficiently low, so that activity coefficient corrections are unnecessary, or at least can be adequately estimated from theory. Then

$$\Delta G_t^\circ(X^-, W \rightarrow S) = RT[2\ln s(Ph_4AsX, S) - 2\ln s(Ph_4AsX, W) + \ln s(Ph_4AsBPh_4, W) - \ln s(Ph_4AsBPh_4, S)] \quad (5)$$

If the solvent S is reasonably water-immiscible, distribution ratio determinations may replace solubility measurements, i.e.

- e) the distribution $D(Ph_4AsBPh_4, S/W)$ of the reference electrolyte
- f) the distribution $D(Ph_4AsX, S/W)$ of the X-salt.

Two distribution measurements should then suffice:

$$\Delta G_t^\circ(X^-, W \rightarrow S) = RT[2 \ln D(\text{Ph}_4\text{As}X, S/W) - \ln D(\text{Ph}_4\text{AsBPh}_4, S/W)] \quad (6)$$

The results of measurements that have been made on the transfer of anions from water into many solvents are summarized in Table 1.

TABLE 1

Standard molar transfer Gibbs free energies of anions, $\Delta G_t^\circ(X^-, W \rightarrow S)/\text{kJ mol}^{-1}$, at 25°C, on the molar scale (adapted from (5)).

	Cl^-	Br^-	I^-	I_3^-	N_3^-	SCN^-	ClO_4^-	NO_3^-	CH_3CO_2^-	Pic^{-j}	BPh_4^-
methanol	13	11	7	-13		6	6		16	-5	-24
ethanol	20	18	12		17		10	14		0	-21
TFE ^a	-11	-9	-9								
EG ^b	8	6	3							-7	-21
acetone	56	41	25		43		14				-32
PC ^c	40	30	14		29	7	-8				-36
formamide	14	11	7	-7	11	7	-12				-24
DMF ^d	49	36	21	-24	36	18	4		69	-7	-38
DMA ^e	56	44	22	-30	46	21	-3		75		-38
NMPy ^f	51	37	20		46	18	-12				-39
acetonitrile	42	31	17	-15	37	14	2	21	61	-4	-33
nitromethane	39	30	19		37	15	-5				
DMSO ^g	40	28	11	-36	30	10	-1		54		-37
TMS ^h	47	35	21		41	22	-1				-36
HMPT ⁱ	58	46	30		51	20	-7				-39

^atrifluoroethanol, ^bethylene glycol, ^cpropylene carbonate, ^ddimethyl formamide, ^edimethylacetamide, ^fN-methylpyrrolidone, ^gdimethylsulfoxide, ^htetramethylenesulfone, at 30°C, ⁱhexamethylphosphoric triamide, ^jpicrate.

For those solvents and ions where sufficient information exists, it was found that a correlation with a suitable polarity scale of the solvent (4) can be written (7,8):

$$\Delta G_t^\circ(X^-, W \rightarrow S) = a(X^-) + b(X^-)[E_T(W) - E_T(S)] \quad (7)$$

where E_T is the transition energy in kJ mol^{-1} of the betaine dye triphenyl-

pyridinium-N-(diphenylphenoxide) (4). For six of the anions in Table 1 could statistically highly significant correlations be made according to eq. (7), and the parameters a and b for each anion are shown in Table 2. These can be used for the prediction of $\Delta G_t^\circ(X^-, W \rightarrow S)$ for many more solvents S , for which E_T values are known, as was done (9) for chloride anions. The addition of other terms to eq. (7), such as a dependence on the donor numbers of the solvents, which is important for the cations (7), was found (8) not to give a statistically significant improvement for the anions.

TABLE 2

Correlation of $\Delta G_t^\circ(X^-, W \rightarrow S)/\text{kJ mol}^{-1}$ with $E_T/\text{kJ mol}^{-1}$ for anions according to eq. (7). Accuracy of the values: $\Delta G_t^\circ \leq \pm 4 \text{ kJ mol}^{-1}$; $E_T \leq \pm 0.5 \text{ kJ mol}^{-1}$.

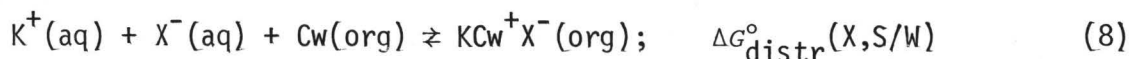
anion	n	a	b	σ	r
chloride	13	-9.8 ± 3.3	$+0.724 \pm 0.046$	3.3	0.979
bromide	13	-5.7 ± 3.3	$+0.526 \pm 0.046$	3.4	0.960
iodide	13	-1.8 ± 3.5	$+0.279 \pm 0.049$	3.6	0.864
thiocyanate	11	-2.1 ± 4.2	$+0.240 \pm 0.058$	3.9	0.811
azide	12	-8.7 ± 4.9	$+0.607 \pm 0.066$	4.1	0.946
BPh_4^-	12	-14.8 ± 3.2	-0.265 ± 0.045	3.2	0.883

n = number of solvents; a and b are shown with their standard deviations; σ = std. dev. of the correlation; r = correlation coefficient.

A NEW DISTRIBUTION METHOD

If an electrolyte can be transferred from water to a solvent in such a manner that only the anion "sees" the solvent, but the cation is completely shielded from it, the resultant measured ΔG_t° will differ from that of the anion by a constant only. This idea has been applied in a somewhat different manner by Villiermaux and Delpuech (10) and by Lejaille (11). However our proposal (9) yields directly $\Delta G_t^\circ(X^-, W \rightarrow S)$ values from simple distribution measurements, provided the solvent S is reasonably immiscible with water.

Potassium cations are very effectively solvated by water-insoluble crown ethers (such as dibenzo-18-crown-6, DBC, Cw) and extracted by them. For solvents of not too high dielectric constant, the distribution equilibrium



can be observed. If sufficiently low concentrations are employed, so that no solute-solute interactions need be taken into consideration, and for equal phase volumes,

$$\Delta G_{\text{distr}}^\circ = -RT \ln [D(1 + D)^2 / c_{\text{KX}}^\circ (c_{\text{Cw}}^\circ (1 + D) - c_{\text{KX}}^\circ D)] \quad (9)$$

where D is the distribution ratio of KX , and c° are the initial concentra-

tions. It has been found (12), for instance, that for m-cresol, the order of $\Delta G_{\text{distr}}^{\circ}/\text{kJ mol}^{-1}$ is SO_4^{2-} (-10.62), Cl^- (-13.04), Br^- (-13.48), I^- (-14.47), NO_3^- (-14.95), CH_3CO_2^- (-15.82) and F^- (-17.25).

Reaction (8) can be considered to occur in several steps, as follows.



The bar over a symbol designates the species as a solute in a hypothetical state of being only as much solvated as it is in the ion-paired complex $\text{KCw}^+\text{X}^-(\text{org})$. Some of these steps are completely independent of the solvent (steps (10) and (13)), and others only mildly dependent on it (steps (12), (15) and (17)), in a mutually compensating manner. Still other steps depend on the solvent through ϵ_S , the dielectric constant, from the modified Born (step (11)) and Bjerrum (step (16)) equations. Rearranging eqs. (8) and (10) to (17) yields

$$\Delta G_t^{\circ}(\text{X}^-, \text{W} \rightarrow \text{S}) = \Delta G_{\text{distr}}^{\circ}(\text{X}, \text{S}/\text{W}) + p(1/\epsilon_S) + q \quad (18)$$

The l.h.s. describes reaction step (14). The first term on the r.h.s. is known experimentally, through eq. (9), the second one can be written as

$$p(1/\epsilon_S) = -138.9[1/2(0.133 + \Delta) - 1/(0.133 + r_{\text{X}^-})]/\epsilon_S \quad (19)$$

where Δ , in nm, is an adjustable parameter of the modified Born equation, and r_{X^-} , again in nm, is the crystalline radius of the anion. The value of Δ applicable in water, 0.080 nm, was found (9) to give a reasonable correlation for solvents of known $\Delta G_{\text{distr}}^{\circ}$ and ΔG_t° for the particular case of the chloride anion, Fig. 1, with $p = 116$ and $q = 29 \pm 3 \text{ kJ mol}^{-1}$.

Fig. 2 shows the contributions of the various reaction steps to $\Delta G_t^{\circ}(\text{Cl}^-, \text{W} \rightarrow \text{S})$ for two solvents A and B. The experimentally determined quantities, $\Delta G_{\text{distr}}^{\circ}$, are shown by heavy black arrows, and the desired quantities, ΔG_t° by outlined arrows. Steps which should be independent of the solvent are shown by continuous lines, steps calculatable from eq. (19) by dashed lines. Finally, steps which involve transitions from partly desolvated to fully solvated species or vice versa are depicted by dotted lines, whose vectorial sums cancel out for each solvent.

Some tests of the validity of this approach are suggested. The linearity of ΔG_t° with $\Delta G_{\text{distr}}^{\circ}$ should hold irrespective of the nature of the cation. For instance, sodium ions could replace potassium ions, with only changes in the numerical values of the parameters. A different crown ether, e.g., dicyclohexo-18-crown-6, DCC, could be used instead of the dibenzo-

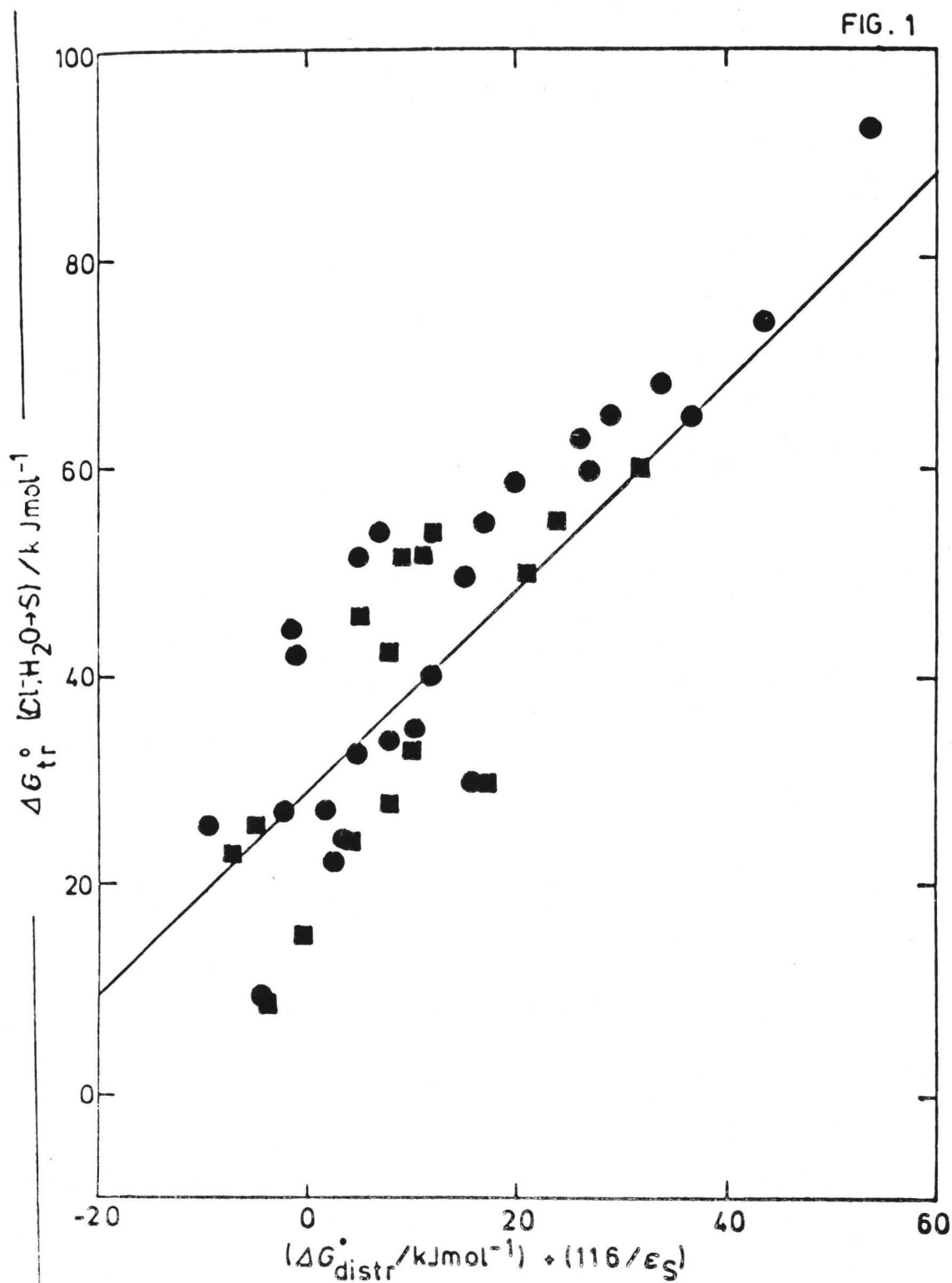


FIG. 1

The Gibbs free energy of transfer of chloride ions from water to solvents plotted against the free energy of distribution of KCl between crown ether (squares: DBC, circles: DCC) solutions in them and water, corrected for the $(1/\epsilon_S)$ term.

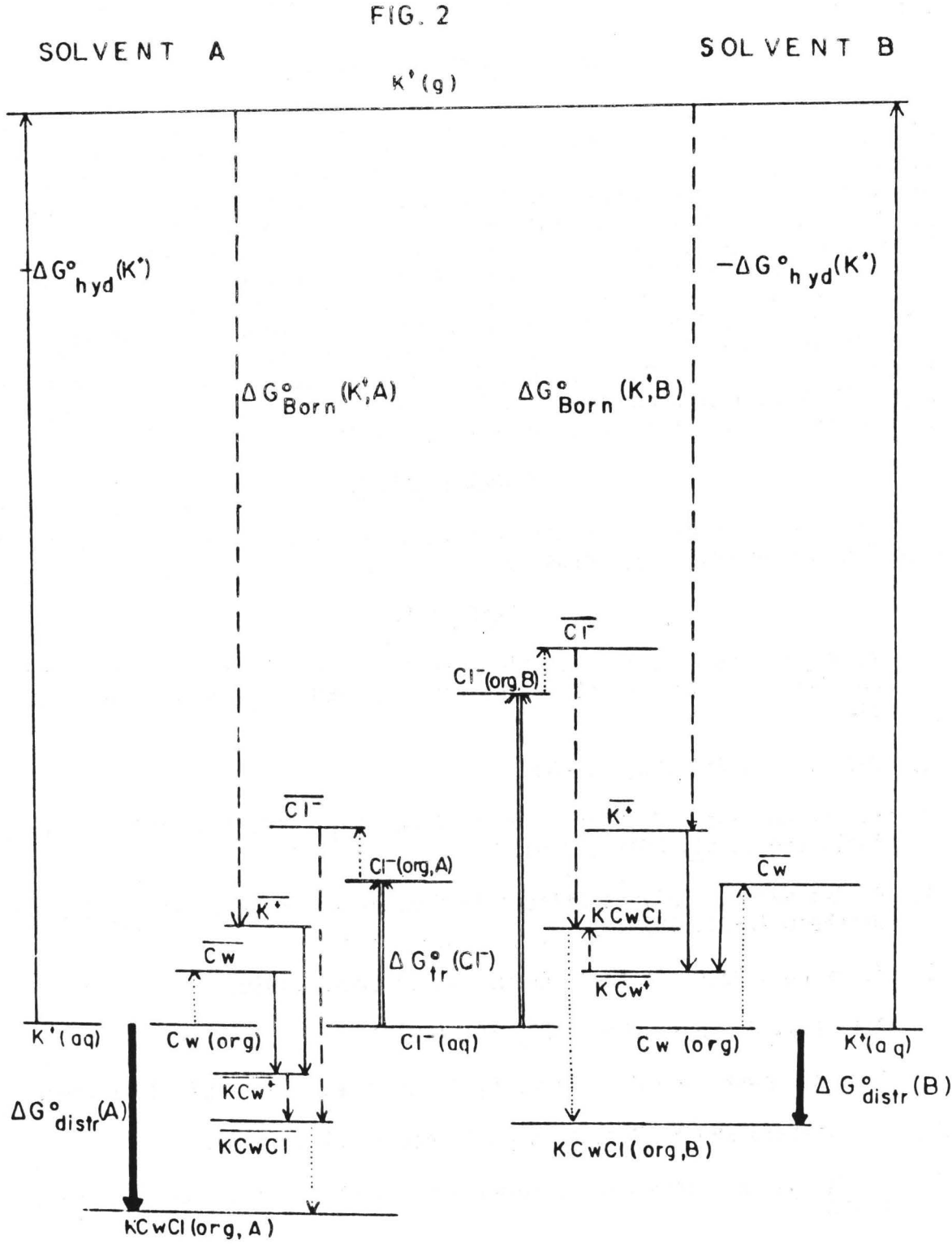


FIG. 2

Gibbs free energy level diagram for the distribution of KCl between solutions of Cw in solvents A and B and water.

derivative, DBC. This has, indeed, been done (9), with satisfactory results. (Fig. 1).

SUMMARY: PROPOSED PROCEDURE

For a water-immiscible solvent S, $\Delta G_t^\circ(X^-, W \rightarrow S)$ can be determined from the distribution of the salt MX between its dilute aqueous solution and that of a water-insoluble crown ether Cw in S. The cation M^+ and crown ether Cw must be chosen so that they give effective mutual solvation and a distribution ratio that can be measured accurately. Potassium as M^+ and DBC as Cw are known to work well, but alternatives, such as Cs^+ with dibenzo-30-crown-10 could conceivably be even better. From the distribution ratio D , $\Delta G_{distr}^\circ(X^-, S/W)$ is calculated according to eq. (9), and $\Delta G_t^\circ(X^-, W \rightarrow S)$ from eq. (18). The parameters p and q must be obtained from solvents for which $\Delta G_t^\circ(X^-, W \rightarrow S)$ is already known. The slope of the $(1/\epsilon_s)$ term, however, can be obtained independently, so that eqs. (9), (18) and (19) give a quantity which differs from $\Delta G_t^\circ(X^-, W \rightarrow S)$ only by a constant, q , independent of the solvent. A calibration with a single solvent should, therefore, suffice.

ACKNOWLEDGEMENT

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CALCULATION OF THE ACTIVITY COEFFICIENTS IN
THE EXTRACTION BY TERTIARY AMINE SALTS

Ochkin A.V., Lazarevich V.E.,
 Sergievsky V.V.
 Mendeleev Institute of Chemical
 Technology
 Moscow, USSR

"ABSTRACT"

The determination of the activity coefficients of alkylammonium salts and of metal complexes formed in the organic phase is considered. The activity coefficients of trilaurylammonium nitrate complexes with cerium or europium nitrates are calculated. The effect of tetradecanol on activities of trilaurylammonium chloride is described quantitatively.

Metal extraction by salts of tertiary amines can be represented by the equation



with the equilibrium constant

$$K = \frac{[(R_3NH)_n MA_{m+n}] \cdot \gamma_3}{[M^{+m}] \cdot [A]^{-m} \gamma_{\pm}^{m+n} [R_3NHA]^m \gamma_2^m} \quad (2)$$

where $\gamma_{\pm}$ is the average ionic activity coefficient in the aqueous phase, γ_i is the activity coefficient in the organic phase, the subscripts 1, 2 and 3 refer to solvent, alkylammonium salt and the metal complex respectively. Due to the association and the hydration of alkylammonium salts in the organic phase the activity coefficients γ_2 and γ_3 are not equal to one, but depend on component concentrations and are usually unknown. Moreover high-molecular alcohols are sometimes added to the organic phase to avoid third-phase formation and they affect the equilibrium. Therefore it is scarcely surprising that no value of K has been found before. Here we report some methods to determine γ_2 and γ_3 .

When microconcentrations of metal are used the values in the eq. (2) are equal to those of the binary system ($m_3 = 0$).

Then γ_2 can be determined by integrating the Gibbs-Duhem equation

$$\frac{10^3}{M_1} \frac{\partial \ln a_1}{\partial m_2} dm_2 + m_2 \frac{\partial \ln a_2}{\partial m_2} dm_2 = 0 \quad (3)$$

The dependence of $\ln a_1$ on m_2 has been studied by ebulliometry. Experimental data have been treated through the equation (4)

$$\frac{m_2^2}{\ln f_1} = 1 + Bm_2 \quad (4)$$

where f_1 is the mole activity coefficient of solvent. Substituting (4) into (3) and integrating we find

$$\ln \gamma_2 = - \frac{10^3}{M_1 B} \cdot \left[\ln(1 + \frac{B}{A} m_2) + \frac{Bm_2}{A + Bm_2} \right] \quad (5)$$

The values of A and B for trilaurylammonium nitrate are given in Table 1.

Table 1.

COEFFICIENTS A AND B IN THE EQUATIONS (4) AND (5)
FOR TRILAURYLAMMONIUM NITRATE SOLUTIONS

Solvent	t°C	A	ΔA	B	ΔB
CCl ₄	45	0,0200	0,0012	14,38	0,16
Benzene	51	1,16	0,11	27,1	4,7

In order to determine γ_3 we can use the Gibbs-Duhem equation in the form

$$\frac{10^3}{M_1} \frac{\partial \ln a_1}{\partial m_2} dm_2 + m_2 \frac{\partial \ln a_2}{\partial m_2} dm_2 + m_3 \frac{\partial \ln a_3}{\partial m_2} dm_2 = 0 \quad (6)$$

After integration we get

$$\ln \frac{a_3^*}{a_3} = - \frac{10^3}{M_1 m_3} \int_0^{m_2^*} \frac{\partial \ln a_1}{\partial m_2} dm_2 - \frac{1}{m_3} \int_0^{m_2^*} m_2 \frac{\partial \ln a_2}{\partial m_2} dm_2 \quad (7)$$

where a_3^* and a_3 are the activities of metal complex at $m_2 = m_2^*$ and $m_2 = 0$ respectively. When rare earth nitrates are extracted by tertiary amine salts the distribution ratio does not depend on metal concentration [2]. Then

$$\left(\frac{\partial \ln a_2}{\partial m_2} \right)_{m_3}$$

may be taken from binary solutions ($m_3 = 0$).

$$\int_0^{m_2^*} m_2^2 \frac{\partial \ln a_2}{\partial m_2} dm_2 = - \frac{10^3}{M_1} \int_0^{m_2^*} \frac{\partial \ln a_1^0}{\partial m_2} dm_2 \quad (8)$$

where a_1^0 is the solvent activity in the binary solutions ($m_3=0$). Substituting (8) into (7) we get

$$\ln \frac{a_3^*}{a_3} = \frac{10^3}{M_1 m_3} \int_0^{m_2^*} \frac{\partial (\ln a_1^0 - \ln a_1)}{\partial m_2} dm_2 \quad (9)$$

The activity coefficient γ_3 can be found as

$$\ln \gamma_3 = \lim_{m_3 \rightarrow 0} \ln \frac{a_3^*}{a_3} \quad (10)$$

Solutions of trilaurylammonium nitrate in carbon tetrachloride or benzene containing cerium or europium nitrates have been investigated by an ebulliometric method. The dependence of $\ln a_1$ on m_2 at $m_3 = \text{constant}$ was linear

$$\ln a_1 = \ln a_1^0 - b m_2 \quad (11)$$

where a_1^0 is the solvent activity at $m_2 = 0$. Therefore the activity coefficients γ_3 calculated from equation (10) do not depend on the composition assumed for the complex. The values γ_2 and γ_3 are presented in Table 2.

Table 2.

THE ACTIVITY COEFFICIENTS OF TRILAURYLAMMONIUM NITRATE γ_2 AND ITS COMPLEX WITH NITRATE OF CERIUM OR EUROPIUM γ_3 IN CCl_4 AND BENZENE.

$10^3 m_2$	$-\log \gamma_2$	$-\log \gamma_3$	
		cerium	europium
CCl ₄ at 45°C			
0,3	0,074	0,043	0,074
0,5	0,112	0,061	0,109
1,0	0,188	0,096	0,19
2,0	0,291	0,139	0,30
3,0	0,360	0,143	0,35
4,0	0,412	0,143	0,36
5,0	0,453	0,143	0,36
Benzene at 51°C			
1,0	0,0093	0,036	0,045
2,0	0,0184	0,065	0,082
3,0	0,0274	0,092	0,117
5,0	0,0442	0,137	0,178

$10^3 m_2$	$-\log \gamma_2$	$-\log \gamma_3$	
		cerium	europium
8,0	0,0641	0,185	0,247
10,0	0,0822	0,203	0,278
15,0	0,115	0,203	0,304
20,0	0,144	0,203	0,304

The knowledge of γ_3 makes it possible to determine the stoichiometric coefficient n in the equation (1). In fact the distribution ration D can be expressed at a constant composition of the aqueous phase as

$$\log D = \text{const} + \log \frac{m_2^n \gamma_2^n}{\gamma_3} \quad (12)$$

or eliminating the constant as

$$\log D - \log D_{m_s} = \log \frac{m_2^n \gamma_2^n}{\gamma_3} - \log \left(\frac{m_2^n \gamma_2^n}{\gamma_3} \right)_{m_s} \quad (13)$$

where m_s is the value of m_2 choosen as the standard. The left hand side of equation (13) depends on m_2 whereas the right hand side depends on both m_2 and n . Using the values of γ_2 and γ_3 from Table 2 we calculated $\log m_2^n \gamma_2^n / \gamma_3$ at $n = 2$ and $n = 3$ as a function of $\log m_2$. These curves are given in Fig. 1 and 2. It is seen that the experimental distribution ratios fall on the computed curves at $n = 3$ for carbon tetrachloride and at $n = 2$ for benzene.

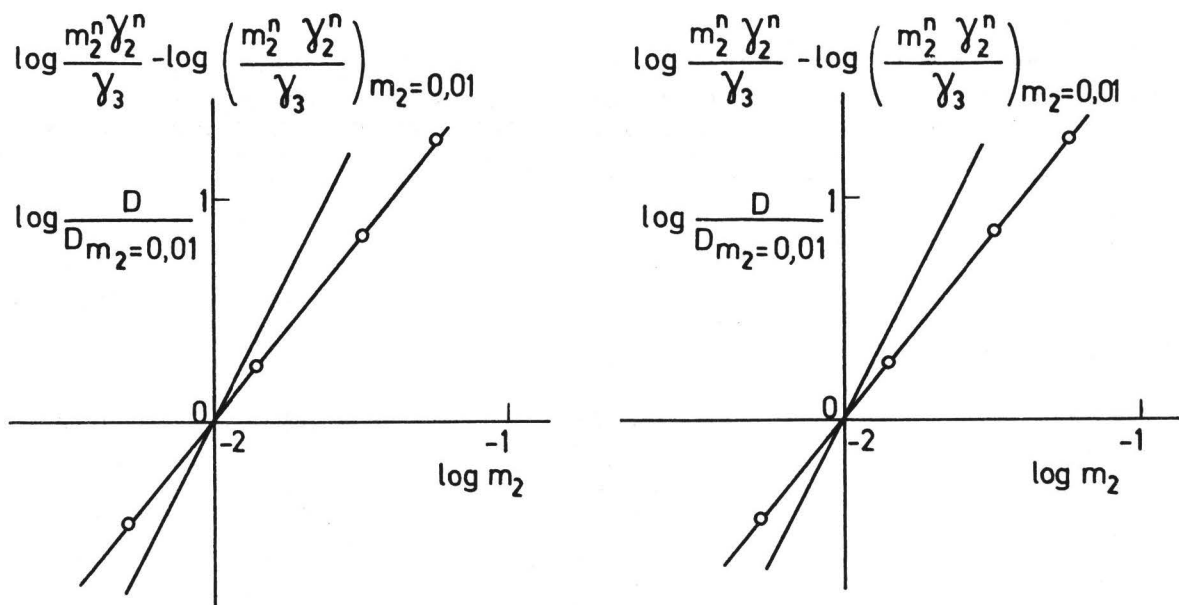


FIGURE 1

The plots of $\log m_2^n \gamma_2^n / \gamma_3$ and $\log D$ versus $\log m_2$ for the cerium complex (a) and the europium complex (b) with trilaurylammonium nitrate in benzene 1. $n = 3$, 2. $n = 2$.

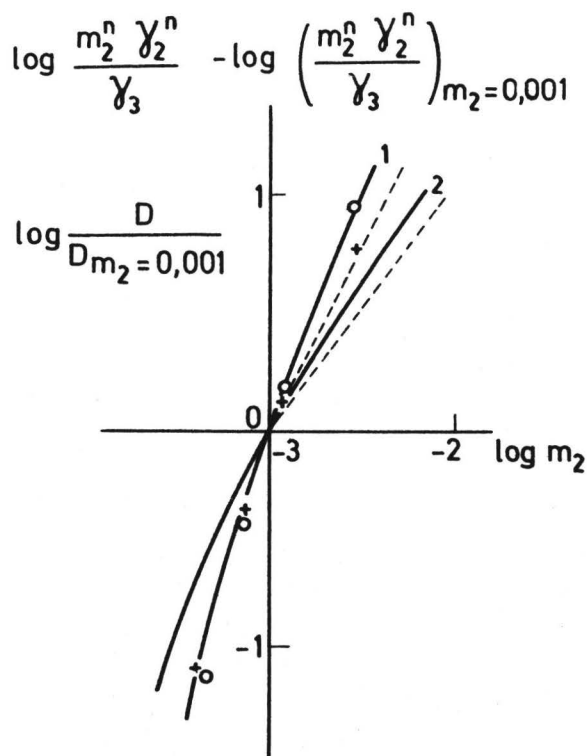


FIGURE 2

The plots of $\log \frac{m_2^n \gamma_2^n}{\gamma_3}$ and $\log D$ on $\log m_2$ for metal complexes with trilaurylammonium nitrate in CCl_4 . 1. $n = 3$, 2. $n = 2$.

————— computed curve and 0 = $\log D$ for europium
 ----- computed curve and + = $\log D$ for cerium

The addition of high molecular alcohols to amine extraction systems results in decreasing the distribution coefficients of metals due to decreasing the activity coefficients of alkylammonium salts. As a matter of fact the solvation by alcohols is similar to the hydration of alkylammonium salts. Therefore it is reasonable in these systems to use the equation found previously for their hydration, viz. :

$$m_4 = a_4 (1 + km_2) \quad (14)$$

where the subscript 4 refers to the alcohol. Since

$$\left(\frac{\partial \ln a_4}{\partial m_2} \right)_{m_4} = \left(\frac{\partial \ln a_2}{\partial m_4} \right)_{m_2} \quad (15)$$

we find, after integration

$$\ln \frac{a_2}{a_2^0} = - \frac{K}{1 + Km_2} \cdot m_4 \quad (16)$$

where a_2° is the activity of ammonium salt in binary solutions ($m_4 = 0$).

In order to determine $\ln a_1$ we use the Gibbs-Duhem equation in the form

$$\frac{10^3}{M_1} \frac{\partial \ln a_1}{\partial m_4} dm_4 + m_2 \frac{\partial \ln a_2}{\partial m_4} dm_4 + m_4 \frac{\partial \ln a_4}{\partial m_4} dm_4 = 0 \quad (17)$$

Substituting (14) and (16) into (17) and integrating we find

$$\ln \frac{a_1}{a_1^\circ} = - \frac{1}{1 + km_2} \cdot \frac{M_1}{10^3} m_4 \quad (18)$$

The system CCl_4 -trilaurylammonium chloride-tetradecanol is used to test equation (18). The experimental values of $\ln a_1$ depend linearly on m_4 in accordance with equation (18). The coefficients $1/(1 + km_2) \cdot M_1/10^3$ for various m_2 given in Table 3 are used to calculate the values of $k = 15,83 \pm 0,79$ at 45°C and $k = 8,95 \pm 0,97$ at 76°C .

Table 3

THE COEFFICIENTS $\frac{1}{1 + km_2} \cdot \frac{M_1}{10^3}$ IN THE EQUATION (18)
THE SYSTEM $\text{CCl}_4 - (\text{C}_{12}\text{H}_{25})_3\text{NHCl} - \text{C}_{14}\text{H}_{29}\text{OH}$ [3]

76°C		45°C	
$10^3 m^2$	$\frac{1}{1 + km_2} \cdot \frac{M_1}{10^3}$	$10^3 m^2$	$\frac{1}{1 + km_2} \cdot \frac{M_1}{10^3}$
0	0,1538	0	0,1538
5,62	0,1431	9,66	0,1366
6,91	0,1385	12,53	0,1366
7,18	0,1484	16,18	0,1221
10,40	0,1449	18,94	0,1146
12,76	0,1314	22,25	0,1188
13,41	0,1365	26,07	0,1073
13,61	0,1438		
14,80	0,1403		
21,18	0,1350		
26,38	0,1187		

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ENHANCEMENT OF RATE OF METAL CHELATE EXTRACTION INTO
POLAR ORGANIC SOLVENTS WHEN ION-PAIR EXTRACTION OCCURS.

Tatsuya SEKINE

Department of Chemistry,
Science University of Tokyo,
Kagarazaka, Shinjukuku, Tokyo,
162 JAPAN.

ABSTRACT. The rate of solvent extraction of Be(II), Ga(III), Fe(III), and Cr(III) in aqueous perchlorate solutions with β -diketones(HA) is measured. When the diluent is nonpolar, the rate is dependent on the concentration of metal ion, β -diketone, and hydrogen ion and the controlling reaction is assumed to be association of hydrolyzed metal ion with HA or A^- in the aqueous phase. When the diluent is 4-methyl-2-pentanone or 4-methyl-2-pentanol, the rate is higher and dependent not only on these but also on perchlorate. This is explained by that an extraction of the metal takes place first and the controlling reaction, complex formation of the extracted metal species with HA or A^- , occurs in the organic phase.

The rate of solvent extraction of metal ions in aqueous solutions with chelating acid extractants is often controlled by complex formation in the aqueous phase as is recognized from the dependence of the rate on the concentration of metal ion, the chelating extractant, and very often on that of the hydrogen ion in the aqueous phase when the two phases are agitated so vigorously that no increase in the rate occur by an increase in the agitation speed and thus the effect of the material transport is eliminated.

The solvent extraction of metal ions with chelating extractants usually proceeds rapidly but there are some which are extracted with these extractants only slowly. Chromium(III), iron(III), and beryllium(II) are examples of such metal ions and the slow extractions are explained in terms of their inertness in the complex formation in the aqueous phase.

In the course of a series of kinetic studies on the metal extraction with β -diketones [1-6], it has been observed that when the organic diluent is polar, the rate is also dependent on the presence of perchlorate in the aqueous phase.

This dependence of the rate of metal chelate extraction on the concentration of "inert" perchlorate was found to be explained in terms of a mechanism that the metal ions are first extracted as ion-pairs with the perchlorate ions and then the final uncharged metal chelate complex with the extractant is formed in the organic phase.

EXPERIMENTAL

The experiments were carried out at 25°C. The organic phase was a diluent containing a β -diketone. The aqueous phase was a constant ionic medium containing the metal ion and sodium perchlorate, and in some cases, a part of the perchlorate was replaced by chloride or nitrate. It was buffered at a definite hydrogen ion concentration.

The two phases were placed in a glass tube and agitated so vigorously that no increase in the rate of extraction was observed on a further increase in the agitation speed. After a certain interval, the two phases were centrifuged off and a portion was taken from the organic phase. The metal concentration in this organic phase was measured by radiometry, absorptiometry, or by atomic absorption and that in the aqueous phase was calculated from the initial aqueous concentration and this organic concentration.

METHOD OF CALCULATION

The rate of solvent extraction of a metal ion M^{m+} can generally be written as;

$$v = -d[M^{m+}]/dt = k_0[M^{m+}][B]^b[C]^c[D]^d \dots \dots \dots (1)$$

where B, C, D, ... are certain components in the two phases. When the concentrations other than that of the metal ions are kept constant, the following equation is obtained from Eq.(1);

$$-d[M^{m+}]/dt = q[M^{m+}] \quad (2)$$

$$-\log [M^{m+}] = q't + C_0 \quad (3)$$

where $q = k_0[B]^b[C]^c[D]^d \dots \dots \dots$ and $q' = q \times \log e$.

When only the concentration of a certain component, for example, B is changed and the others are fixed at $[C_1]$, $[D_1]$,, then

$$\log q_B = \log k_b + b \log [B] \quad (4)$$

where $q_B = k_0[B]^b[C_1]^c[D_1]^d \dots$ and $k_b = k_0[C_1]^c[D_1]^d \dots$

Thus if a series of measurements of the rate at several concentrations of B is made, the dependence "b" can be determined from the slope of the $\log q_B$ vs $\log [B]$ plot. By the same way, the values c, d, ... can also be determined and then the value of the rate constant in Eq.(1) can be calculated. When there are more than one extraction mechanisms and consequently more than one dependences on a certain component are found, Eq.(4) is written as

$$\log q_B = \log k_b + \log \sum k_n [B]^n \quad (5)$$

then, for example, the following equation is obtained;

$$\log q_B = \log k_b + \log (1 + k_1[B] + k_2[B]^2) \quad (5')$$

In such cases, the values k_b , as well as k_1 and k_2 can be obtained from the $\log q_B$ vs $\log [B]$ plot by a curve-fitting method [1] or by other calculation methods.

This kind of treatment is possible only for the data from the early stage of the extraction where the back-extraction from the organic to the aqueous phase is negligible. Only such data are employed for the arithmetical treatment in this paper.

RESULTS

An agitation speed where no increase in the rate by an increase in the speed was found in each system studied. The determination of the rate was always carried out under such conditions. In general, this does not mean that the effects of the material transport are completely eliminated [7,8]. However, since the rate of complex formation is never high in the extraction systems studied, such effects should only be slight.

DEPENDENCE OF THE RATE ON THE METAL ION AND EXTRACTANT CONCENTRATION.

In all the cases, the rate of extraction was first order with respect to the concentration of metal ion in the aqueous phase. The plot of $\log [M]$ vs time was a straight line when the concentrations of the other components were kept constant. Figure 1 gives an example of the plot of the decrease in the aqueous metal concentration as a function of the two-phase agitation time. These observations indicate that the rate is first order with respect to the metal ions as is seen from Eq. (3).

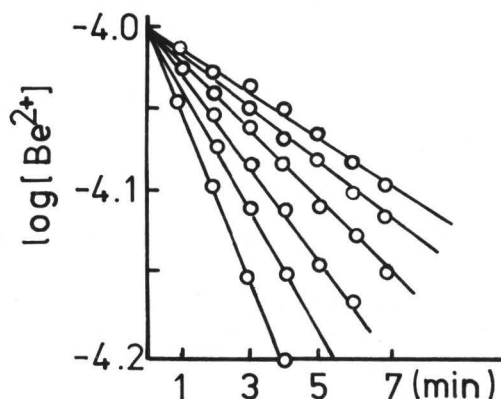


FIG. 1
Decrease in Be^{2+} conc. in aq. phase
as a function of agitation time
when $[\text{HA}]_{\text{org}}$ is 0.15, 0.12, 0.1,
0.08, 0.06, and 0.05 mol dm^{-3} .
Org. phase ; TTA-CCl_4 . Aq. phase ;
0.1 mol dm^{-3} NaClO_4 at pH 3.0.
The slope gives q' in Eq. (3). [1]

Equations (3) and (4) indicate that plotting the slope vs the extractant concentration should give the dependence of the rate on the extractant. The rate in the systems in this paper was always found to be first order with respect to the chelating extractant. Figure 2 gives such a plot obtained from the data in Fig. 1. The slope of the plot in Fig. 2 is unity and thus the rate is first order with respect to the concentration of β -diketone.

DEPENDENCE OF THE RATE ON HYDROGEN ION CONCENTRATION.

By the similar way, the dependence of the rate on the concentration of hydrogen ion in the aqueous phase was measured. Several dependences, e.g., zero, first, and second order were found with respect to hydrogen ion in the systems in this paper.

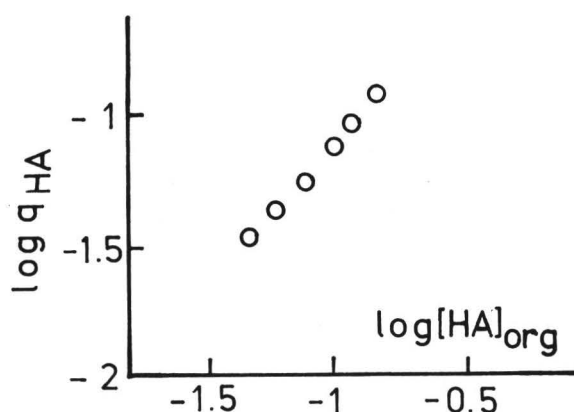


FIG. 2
Dependence of Be^{2+} extraction rate on $[\text{HA}]_{\text{org}}$. $\log q_{\text{HA}}$ obtained from FIG. 1 is plotted as a function of $\log [\text{HA}]_{\text{org}}$. From the slope +1, the first order dependence of the rate on $[\text{HA}]_{\text{org}}$ is concluded.[1]

EFFECT OF COEXISTING SALTS IN THE AQUEOUS PHASE

When the diluent was nonpolar, the effect of the concentration of the background perchlorate on the rate was not large. A small change in the rate by a change in the perchlorate concentration was assumed to be due to changes in the activity coefficients of the solutes.

When the diluent was 4-methyl-2-pentanone or 4-methyl-2-pentanol, on the other hand, a marked dependence of the rate on the perchlorate was observed. As is discussed later, this was concluded to be due to an extraction of ion-pairs with perchlorate. Figure 3 gives an example of such dependence of the rate on the perchlorate in the aqueous phase.

Replacement of the perchlorate with chloride enhanced the rate of extraction of iron(III) with TTA into carbon tetrachloride[2] and this was assumed to be caused by formation of chloride complex which was kinetically more active than hexahydrated Fe^{3+} . On the other hand, replacement of perchlorate by chloride or nitrate decreased the rate of extraction of beryllium(II) with TTA into 4-methyl-2-pentanone. This was assumed to be an impairment of the extraction of beryllium(II) perchlorate by the decrease in its concentration.

The dependences of the rate on the components in the system observed in the systems studied are summarized in Table I.

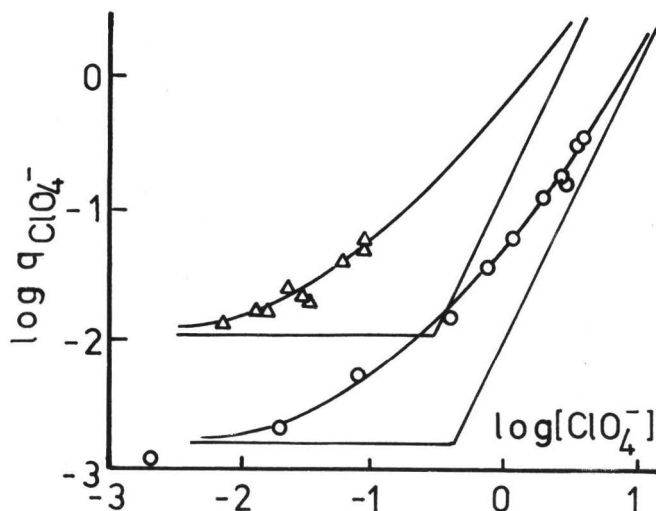


FIG. 3
Dependence of Be^{2+} -TTA extraction on $[\text{ClO}_4^-]$ in 4-methyl-2-pentanone-aq. $\text{Na}(\text{Cl}, \text{ClO}_4)$ at 4 (circles) and 0.1 (triangles) mol dm^{-3} . The slope of the asymptotes is 0 and +2. From the parameters of the fitted curves, the values of constants in TABLE I are obtained.[1]

TABLE I Summary of Results

Metal	Solvent	Equation
Be^{2+}	TTA- CCl_4	$v = k_0[\text{Be}^{2+}][\text{HA}]_{\text{org}}[\text{H}^+]^{-1}$
	TTA-MIBK*	$v = k_0[\text{Be}^{2+}][\text{HA}]_{\text{org}}[\text{H}^+]^{-1}(1 + k_{s1}[\text{ClO}_4^-] + k_{s2}[\text{ClO}_4^-]^2)$
	$\log k_0/(\text{s}^{-1})$	CCl_4 : $-5.0(0.1\text{M } c^{\dagger}); -6.0(4\text{M } c^{\dagger})$ MIBK*: $-5.8(0.1\text{M } c-c^{\dagger}); -6.6(4\text{M } c-c^{\dagger})$
	$\log k_{s1}/(\text{M}^{-1})$	MIBK*: $1.6(0.1\text{M } c-c^{\dagger}); 1.3(4\text{M } c-c^{\dagger})$
	$\log k_{s2}/(\text{M}^{-2})$	MIBK*: $1.0(0.1\text{M } c-c^{\dagger}); 0.8(4\text{M } c-c^{\dagger})$
Ga^{3+}	TTA- CHCl_3	$v = k_0[\text{Ga}^{3+}][\text{HA}]_{\text{org}}[\text{H}^+]^{-2}$
	$\log k_0/(\text{M s}^{-1})$	: $-6.0(0.1\text{M } c^{\dagger})$
Fe^{3+}	TTA- CCl_4 , TTA- CHCl_3	$v = k'_0[\text{Fe}^{3+}][\text{HA}]_{\text{org}}(1 + k_{\text{Hl}}[\text{H}^+]^{-1})$
	TTA-MIBK*	$v = k'_0[\text{Fe}^{3+}][\text{HA}]_{\text{org}}(1 + k_{\text{Hl}}[\text{H}^+]^{-1}) \times (1 + k_{s3}[\text{ClO}_4^-]^3)$
	$\log k'_0/(\text{M}^{-1}\text{s}^{-1})$	$-3.1(\text{CCl}_4); -3.7(\text{CHCl}_3); -3.6(\text{MIBK}^*)$
	$\log k_{\text{Hl}}/(\text{M})$	$-0.3(\text{CCl}_4); -0.3(\text{CHCl}_3); -0.4(\text{MIBK}^*)$
	$\log k_{s3}/(\text{M}^{-3})$	-1.1 (aq. phase $4\text{M } c^{\dagger}$ except k_{s3})
Cr^{3+}	Acetylacetone-MIBK*, Acetylacetone-MIBC**	$v = k''_0[\text{Cr}^{3+}][\text{HA}]_{\text{org}}[\text{H}^+]^{-1}[\text{ClO}_4^-]^2$
	$\log k''_0/(\text{M}^{-2}\text{s}^{-1})$	$-8.5(\text{MIBK}^*); -7.9(\text{MIBC}^{**})$ (aq. phase NaClO_4)

Be^{2+} : ref. 1, Ga^{3+} : ref. 3, Fe^{3+} : ref. 2,4, Cr^{3+} : ref. 6.

$\text{M} = \text{mol dm}^{-3}$. $c^{\dagger} = \text{NaClO}_4$, $c-c^{\dagger} = \text{Na}(\text{Cl}, \text{ClO}_4)$

MIBK* = 4-methyl-2-pentanone, MIBC** = 4-methyl-2-pentanol.

DISCUSSION

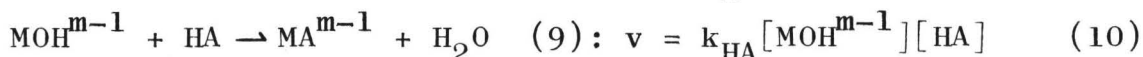
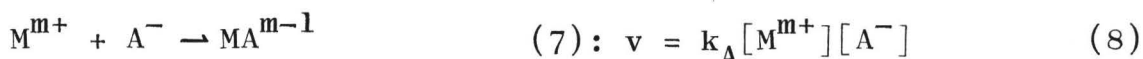
EXTRACTION INTO NONPOLAR SOLVENT

Since the extraction of species other than the uncharged chelate should be very poor into a nonpolar solvent and since the rate of extraction of the uncharged chelate in the aqueous phase into the organic phase should be much higher than that of the complex formation in the aqueous phase in these systems, the controlling reaction should be the complex formation in the aqueous phase when the solvent is nonpolar.

The rate of extraction of Be^{2+} and Fe^{3+} with a β -diketone is written as;

$$v = -d[\text{M}^{m+}]/dt = k_0[\text{M}^{m+}][\text{HA}]_{\text{org}}[\text{H}^+]^{-1} \quad (6)$$

There is an ambiguity in interpreting the proton dependence : the rate given by Eq.(6) can be explained by both of the following controlling reactions.



Equation(8) can be rewritten as follows.

$$[\text{A}^-] = \kappa_a \kappa_D^{-1} [\text{HA}]_{\text{org}} [\text{H}^+]^{-1} \quad (11)$$

where $\kappa_a = [\text{H}^+][\text{A}^-]/[\text{HA}]$ and $\kappa_D = [\text{HA}]_{\text{org}}/[\text{HA}]$ and thus

$$v = k_A[\text{M}^{m+}] \times \kappa_a \kappa_D^{-1} [\text{HA}]_{\text{org}} [\text{H}^+]^{-1} \quad (12)$$

The rate constant k_0 in Eq.(6) can be written as $k_0 = k_A \kappa_a \kappa_D^{-1}$. Equation 10 can be rewritten as follows.

$$[\text{MOH}^{m-1}] = \kappa_h [\text{M}^{m+}][\text{H}^+]^{-1} \quad (13)$$

where $\kappa_h = [\text{MOH}^{m-1}][\text{H}^+]/[\text{M}^{m+}]$ and thus

$$v = \kappa_{\text{HA}} [\text{M}^{m+}][\text{H}^+]^{-1} \times \kappa_D^{-1} [\text{HA}]_{\text{org}} \times \kappa_h \quad (14)$$

The rate constant in Eq.(6) can be rewritten as $k_0 = \kappa_{\text{HA}} \kappa_h \kappa_D^{-1}$.

No direct and definite conclusion may be drawn only from the results of such types of kinetic experiments as in the present paper. However, the assumption that the reaction between the hydrolyzed metal ion and undissociated β -diketone is the controlling reaction seems to explain the experimental findings most reasonably.

TABLE II gives the rate constant for the extraction of Fe^{3+} from 4 mol dm^{-3} aqueous perchlorate solutions into carbon tetrachloride with six β -diketones[5]. As is seen, the difference among the apparent rate constant k_0 defined by Eq.(6) is very large and this indicates that the rate of Fe^{3+} extraction from a certain aqueous solutions with these β -diketones is quite different. The differences among the values k_A are even larger than those among k_0 . This indicates that if the controlling reaction were to be complex formation between the hydrated Fe^{3+} and the β -diketonate anion, the reactivity of the iron(III) is very much different when the ligand is different; the reactivity of iron(III) with hexafluoroacetylacetonate ion is six to seven order higher than that with benzoylacetonate ion. It is not easy to find an explanation for such a large difference in the reactivity.

On the other hand, differences among the values of κ_{HA} are

TABLE II Rate constants for the extraction of iron(III) with six β -diketones[5]. Org.phase: CCl_4 , aq.phase: 4 mol dm^{-3} NaClO_4 , temperature: 25°C.

β -diketone	$\log k_0$	$\log k_A$	$\log k_{HA}$	$\log k_{HA}(\text{enol})$
Acetylacetone	ca.0*	--	--	--
Benzoylacetone	-2.5	8.3	3.1	ca.4
Trifluoroacetylacetone	-1.6	4.7	1.5	3.3
TTA	-3.6	5.0	1.1	2.9
Benzoyltrifluoroacetone	-3.9	5.1	1.9	3.7
Hexafluoroacetylacetone	-1.4	1.6	0.2	--

Units: $k_0 \text{ s}^{-1}$; k_A, k_{HA} , and $k_{HA}(\text{enol}) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

* The rate of acetylacetone extraction was too high to be determined.

not large. Thus the rates of the reactions between the FeOH^{2+} species and the different β -diketones in the undissociated form are rather similar. When the correction is made for the keto-enol equilibria of the β -diketones the agreement of the values is better still. For these reasons, it may be concluded that the controlling reaction of the iron(III) extraction into the non-polar solvent is that given by Eq.(9) where HA is in the enol form. The higher reactivity of the FeOH^{2+} species was also found in the extraction of iron(III) perchlorate with trioctylphosphine oxide(TOPO)[9]; the rate was given by $v = k_0[\text{Fe}^{3+}] \times [\text{TOPO}]_{\text{org}}[\text{H}^+]^{-1}$. There is no ambiguity in the role of the proton in the extraction with TOPO and this finding should support the above interpretation of extraction by a β -diketone.

In the extraction of iron(III) by TTA into carbon tetrachloride, another mechanism being dependent only on the β -diketone and independent of the hydrogen ion was found. This was also reported about iron(III) extraction with TTA[10] and β -isopropyltropone[11]. The controlling reaction in these extractions is;



Although only TTA extraction was kinetically studied with beryllium(II)[1], it may also be assumed that the controlling reaction of the TTA extraction of this metal ion into nonpolar solvent should be the association of hydrolyzed metal ion with the undissociated enol form TTA in the aqueous phase.

The rate of solvent extraction of gallium(III) with TTA into chloroform was first order with respect to the β -diketone and inverse second order with respect to hydrogen ion[3]. The controlling reaction of this extraction was assumed to be the association between the GaOH^{2+} and β -diketonate anion.

EXTRACTION INTO POLAR SOLVENTS

Solvent extraction of metal ions with chelating extractants into 4-methyl-2-pentanone is sometimes very effective

because of synergistic enhancement of the extraction due to solvation (or adduct formation) of this solvent on the uncharged chelate in the organic phase. Since the distribution coefficient of several chelating extractants in 4-methyl-2-pentanone-aqueous solution system is higher in nonpolar diluent-aqueous solutions systems due to stronger interactions between the diluent and the solute molecules in the former, the concentration of the extractant in the aqueous phase should be lower in the former system. Thus when the extractant concentration in the organic phase is similar, the rate of chelate formation in the aqueous phase is higher in 4-methyl-2-pentanone-aqueous solution system. This was actually observed in the TTA extraction of beryllium(II) in aqueous chloride solutions(see TABLE I). [1] However, as is seen from TABLE I, the rate of this extraction into 4-methyl-2-pentanone is dependent on the perchlorate in the aqueous phase and it is higher when the diluent is non-polar.

The enhancement of the rate of extraction when the solvent is polar was also observed in the extraction of iron(III) with TTA into 4-methyl-2-pentanone. The rate of this extraction is given by a combination of four equations. Two of them show that the controlling reactions are similar to those in the non-polar solvent-aqueous solutions systems but the other two show that the rate is third order with respect to perchlorate.

The extraction of chromium(III) with acetylacetone is also a good example. As is well known, the extraction of hydrated Cr^{3+} with β -diketones into nonpolar solvent is extremely slow at room temperature; the extraction is negligible even after two phase agitation for several hours.

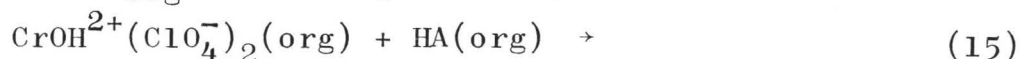
The extraction of chromium(III) with acetylacetone was, however, to some extent achieved even at room temperature in the absence of any other effective complexing reagent when 4-methyl-2-pentanone or 4-methyl-2-pentanol was used as the diluent and the aqueous phase contained perchlorate; the rate in these systems was dependent on the perchlorate concentration.

The complex formation of these metal ions with perchlorate ions in the aqueous phase should be, if any, only slight. The only extraction mechanism which explains the observations reasonably is that the metal ions are first extracted as ion-pairs with perchlorate ions and then the complex formation takes place in the organic phase.

The rate of the extraction of chromium(III) as perchlorate in these systems is high and the ion-pair extraction should reach equilibrium in a short time. This was observed when the two phases were agitated in the absence of the chelating extractant; the distribution ratio of the metal ion reached a constant value within a very short time. The chemical form of the dominant extracted species was $\text{Cr}(\text{ClO}_4)_3$ when the pH was lower than 4 and the extraction of hydrolyzed species was very poor.

However, from the charge balance, it is assumed that the controlling reaction of the extraction whose rate is given by

$v = k_0[\text{Cr}^{3+}][\text{HA}]_{\text{org}}[\text{H}^+]^{-1}[\text{ClO}_4^-]^2$ should be;

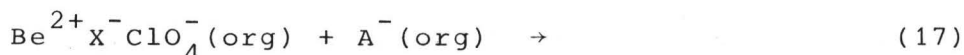
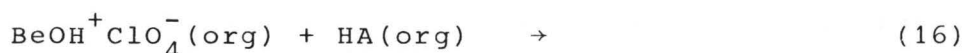


Reaction with dissociated β -diketonate anion A^- does not seem to be possible because the charged $Cr^{3+}(ClO_4^-)_2$ species can not be extracted into the organic phase.

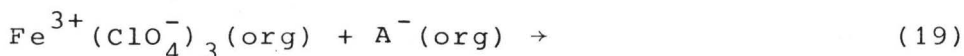
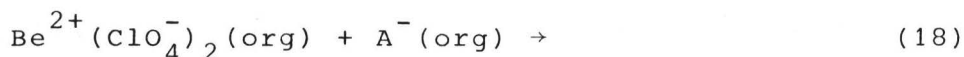
The controlling reaction of the extraction whose rate is given by $v = k_0 [Fe^{3+}] [HA]_{org} \times k_{s3} [ClO_4^-]^3$ should be ;



In the extraction of beryllium(II) a reaction was found whose rate was given by $v = k_0 [Be^{2+}] [HA]_{org} [H^+]^{-1} \times k_{s1} [ClO_4^-]$. Since the aqueous phase was 4 mol dm^{-3} $Na(X, ClO_4)$ (where X^- is Cl^- or NO_3^-), either or both of the following two controlling reactions are possible ;



For the reactions given by $v = k_0 [Be^{2+}] [HA]_{org} [H^+]^{-1} \times k_{s2} [ClO_4^-]^2$ and $v = k_0 [Fe^{3+}] [HA]_{org} [H^+]^{-1} \times k_{s3} [ClO_4^-]^3$, the following reactions seem to be possible ;



However, if hydrolysis of the extracted metal species occurs in the 4-methyl-2-pentanone phase and the rate of the reaction of the hydrolyzed species with the undissociated form TTA is high, the same is also possible in the organic phase as was already considered in Eqs.(7) and (9) for the reaction in the aqueous phase.

Such an enhancement of the rate of metal chelate extraction when the organic solvent is polar and when anions are large enough to allow an extraction of ion-pairs with the metal ion has been reported in other system [12-16]. In these papers, a similar mechanism viz. that chelate formation in the organic phase follows metal extraction as ion-pairs, was suggested also.

One of the explanations for the above findings may be that the rate constant for complex formation of the metal ions with the β -diketone (in the undissociated and/or dissociated form) is greater in the organic phase than in the aqueous phase and thus the extraction proceeds mainly through this route.

Another explanation may be that although no marked difference is present in the rate constant, effective collisions of the metal ion and the β -diketone occur more frequently in the organic phase because these chelating extractants are "organophilic" and the concentrations of the reacting species are higher in the organic phase.

The knowledge about the equilibrium and kinetics of metal

species in organic solvents is much more limited than that in aqueous solutions. It does not seem to be easy to know whether the extracted metal ion in the ion-pairs is still hydrated in the polar solvent or whether the water molecules are replaced by the diluent molecules. Only a little is known about the hydrolysis of the metal ion, acid dissociation of the weak acid, and the stability constants of metal complexes in the organic phase. For these reasons, basic studies for such equilibria will be indispensable in order to learn the reasons for the observations in the present paper.

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KINETICS FOR ION-PAIR EXTRACTION OF QUATERNARY AMMONIUM IONS.

T. Nordgren and A.K. Kolstad

Department of Analytical Pharmaceutical
Chemistry, University of Uppsala,
Biomedical Center, Box 574,
S-751 23 UPPSALA, SWEDEN

ABSTRACT

The transfer rate of ion pairs to and from an organic phase has been studied by a drop technique. An evaluation of rate constants for different stages of the transfer procedure has been made, based on the assumption of steady state at the liquid-liquid interface.

Ion-pair extraction constants calculated from the found rate constants show good agreement with extraction constants obtained under equilibrium conditions.

Comparisons of transfer rates at low and high degrees of ion-pair formation in the organic phase indicate that an ion-pair extraction comprises a fast transfer of two separate ions to the organic phase followed by a slower ion-pair formation.

In analytical chemistry, a highly important task is the determination of trace amounts of substances in complex materials, e.g. of biological origin. This often requires an isolation of the substrate before the final quantitation and this often includes techniques based on liquid-liquid partition designed as batch extraction or chromatography.

During the last thirty years a series of studies have been carried out to increase the knowledge of the mechanisms that are involved in the transfer of a substrate in a two-phase system.

Most of the investigations have dealt with the extraction of metal ions which can be extracted to an organic phase as uncharged complexes with anionic extracting agents. The studies have indicated that a lot of factors influence the transfer rate. The properties of the organic phase [1] and the resolution of the ions in the organic phase [2] influence the extraction rate. The diffusion rate in the aqueous phase is also important [3,4] especially when a powerful extracting agent is used. Several examples of slow extractions have been reported [5-7] and it has, in some cases, been possible to increase the rate by adding a competing anion [6,7].

Transfer rate studies of processes involving organic substrates are fewer. Most investigations have so far been made on unionized organic acids and amines.

An ionizable organic compound can be extracted in ionized form as ion pair with an equivalent amount of an ion of opposite charge, the counter

ion [8]. This technique, ion-pair extraction, is especially useful for hydrophilic protolytes and aprotic ions. It can be adapted to substrates of widely different kinds by a proper choice of nature and concentration of the counter ion. Ion-pair extraction has been utilized in chromatographic isolations as well as in quantitative determinations using photometric, fluorimetric or titrimetric techniques, e.g. [9-12].

Slow equilibration in ion-pair extraction has been observed in a few cases, e.g. [10] but so far only a few investigations have been made on the transfer mechanism. The properties of the organic phase [13] and the hydrophobicity of the ion pair [14] have been shown to influence the transfer rate.

The further development of separation techniques based on liquid-liquid partition will require an improved knowledge of transfer mechanisms and the factors that influence the transfer rates. Low extraction rates may, in batch extraction, lead to incomplete equilibration and in liquid-liquid chromatography to a decrease of the separation efficiency [15].

The aim of this investigation was to study the factors that affect the transfer rate by the extraction of ion pairs and to obtain a better knowledge of the mechanism.

EXPERIMENTAL

Chemicals and reagents

N,N-dimethylprotriptyline was synthesized according to [16]. The aliphatic ammonium ions were used as bromides, hydrogen sulfates or as hydroxides. Picric acid 0,05 M, pH 6.5, was prepared as described in [10]. All other substances were of analytical grade.

Transfer rate measurements

The transfer rate from a continuous phase to a falling or rising drop was measured using experimental equipment, essentially as described by Nitsch [17].

The continuous phase was applied in a thermostated column (length 60 cm) with a volume of 120 cm³, provided with a glass capillary at one end and a drop receiver at the other. The capillary which was connected to the reservoir of the disperse phase, had a ground tip and an internal diameter of 2.0 mm. The receiver had an internal diameter of 4 mm.

The column was kept in a vertical position. The disperse phase emerged from the capillary, passed through the continuous phase and was collected in the receiver which was connected to the outlet. The flow rate of the dispersed phase was regulated by the level of the reservoir.

The distance between the tip of the capillary and the receiver could be varied by using capillaries of different lengths. The time for free fall or rise of a drop was measured by a stopwatch. The standard deviation of the mean time was 0.03 sec. Contact times < 3 s were not used.

The drop size was obtained from the number of drops and the volume of the liquid passed. The area of the drop was calculated from the drop volume, assuming the drops to be spheres.

Chloroform or methylene chloride, equilibrated with water, were used as organic phase. The aqueous phase had an ionic strength of 0.1. Phosphate buffer, pH 6.5, was used for adjustment of the ionic strength when necessary. The experimental temperature was 25.0°C.

The concentration of the substrate was measured photometrically or fluorimetrically in both dispersed and continuous phases. Alkylammonium ions were determined by the picrate method [10].

RESULTS AND DISCUSSION

Measurement of transfer rate

The kinetic studies were performed with one continuous, donating phase and one dispersed, receiving phase which in the form of drops falls or rises through the donating phase. The observed transfer rate, v ($\text{mol} \times \text{cm}^{-2} \times \text{s}^{-1}$), of a compound from the continuous to the receiving phase is defined:

$$v = \frac{dq}{A \times dt} \quad (1)$$

where q is the number of moles and A is the interfacial area, i.e. the area of the drop.

If the drops are assumed to be spheres, the observed transfer rate is:

$$v = \frac{r \times dC}{3000 \times dt} \quad (2)$$

r is the drop radius and C the concentration of the transferred substance in moles per liter of the receiving phase. The radius (in cm) is calculated by:

$$r = \left(\frac{V_{fr} \times 3}{4 \times \pi \times t_{fr} \times d} \right)^{1/3} \quad (3)$$

where t_{fr} is the time in seconds to collect a volume $V_{fr} \text{ cm}^3$ of the dispersed phase at a drop speed of d drops per second.

All experiments were performed under such conditions that the concentrations of the actual species in the donating phase were almost constant during the time of the experiment.

Errors due to distribution effects during the formation and coalescence of the drop were found to be insignificant by the contact times used.

Extraction with high degree of ion-pair formation in the organic phase

An ion-pair extraction is usually performed under such conditions that the degree of ion-pair formation in the organic phase is high. The evaluation of rate constants under these conditions was based on the model given in FIG.1.

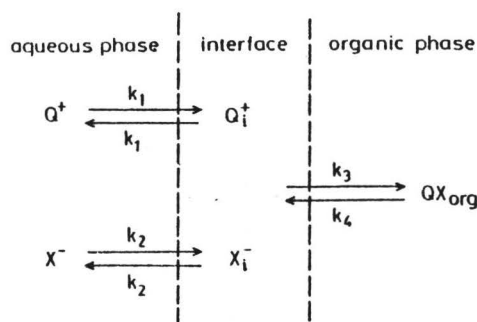


FIG.1

Model for the ion-pair extraction process.

The model takes into consideration two steps: one includes transport of the ions between the bulk of the aqueous phase and the interface (rate constants: k_1 and k_2) and the other interfacial transport, ion-pair formation or dissociation and transport between the interface and the bulk of the organic phase (rate constants: k_3 and k_4). All rate constants have been evaluated from transfer rates obtained by the extraction from the aqueous or the organic phase to the dispersed receiving phase.

The rate by which the substrates enter the interfacial region is given by the following equations.

$$\frac{dq_{Q^+}_i}{A \times dt} = k_1 \times [Q^+] - k_1 \times [Q^+]_i - k_3 \times [Q^+]_i \times [X^-]_i + k_4 \times [QX]_{org} \quad (4)$$

$$\frac{dq_{X^-}_i}{A \times dt} = k_2 \times [X^-] - k_2 \times [X^-]_i - k_3 \times [Q^+]_i \times [X^-]_i + k_4 \times [QX]_{org} \quad (5)$$

The application of the model was based on a steady state approximation for the amount of the substrates at the interface, supported by the assumption that they represent a very small fraction of the total amounts of Q^+ and X^- in the system. This gives

$$\frac{dq_i}{A \times dt} = 0 \quad (6)$$

The studies of transfer from the aqueous to the organic phase were performed with Q^+ and X^- in the continuous aqueous phase and with pure organic phase as the receiving dispersed phase. The observed transfer rate of QX to the organic phase, v_{QX} , is given by

$$v_{QX} = \frac{r \times d[QX]_{org}}{3000 \times dt} = k_3 \times [Q^+]_i \times [X^-]_i - k_4 \times [QX]_{org} \quad (7)$$

The relation between the ion-pair extraction constant K_{ex} and the transfer rate constants, k_3 and k_4 , can be obtained from eq. (7) by introducing equilibrium conditions. This gives

$$[QX]_{org} \times [Q^+]^{-1} \times [X^-]^{-1} = K_{ex} = k_3/k_4 \quad (8)$$

The studies were in most cases performed with a large excess of one of the ions in the aqueous donating phase giving $[Q^+]_i = [Q^+]$ or $[X^-]_i = [X^-]$. Equations that enable a computation of the rate constants can then be obtained by combination of eqs. (4) or (5) with eqs. (6-8). This gives after integration

$$[Q^+] \gg [X^-]. \quad Z^{-1} = k_4^{-1} + K_{ex} \times k_2^{-1} \times [Q^+] \quad (9)$$

$$[X^-] \gg [Q^+]. \quad Z^{-1} = k_4^{-1} + K_{ex} \times k_1^{-1} \times [X^-] \quad (10)$$

$$\text{where } Z = \frac{2.3 \times r}{3000 \times t} \times \log \frac{K_{ex} \times [Q^+] \times [X^-]}{K_{ex} \times [Q^+] \times [X^-] - [QX]_{org}} \quad (11)$$

Eqs. (9) and (10) enable a computation of the rate constants k_1 , k_2 and k_4 by use of slope analysis. An example is given in FIG. 2 which shows the graphical evaluation of k_1 and k_4 for the extraction of tetrapropylammonium as perchlorate ion pair to chloroform.

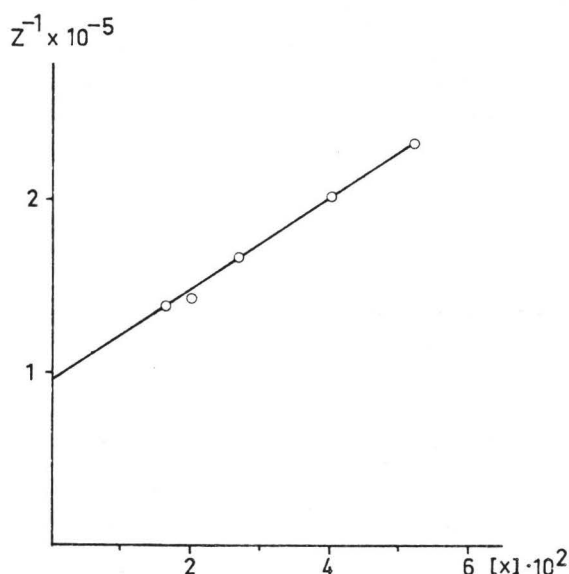


FIG. 2

Graphical computation of k_1 and k_4 for tetrapropylammonium perchlorate.

The studies of the transfer from the organic to the aqueous phase were performed with QX in the continuous organic phase. The receiving dispersed phase was an aqueous buffer which, in most of the experiments initially contained a large excess of Q^+ or X^- (i.e. $[Q^+]_i = [Q^+]$ or $[X^-]_i = [X^-]$).

The observed transfer rate of Q^+ and X^- to the aqueous phase is given by

$$v_{Q^+} = \frac{r \times d[Q^+]}{3000 \times dt} = k_1 \times [Q^+]_i - k_1 \times [Q^+] \quad (12)$$

$$v_{X^-} = \frac{r \times d[X^-]}{3000 \times dt} = k_2 \times [X^-]_i - k_2 \times [X^-] \quad (13)$$

Equations that enable a computation of the rate constants can be obtained by combination of eqs. (5) and (13) or (4) and (12) with eqs. (6) and (8). This gives after integration

$$[Q^+] \gg [X^-]. \quad U^{-1} = k_2^{-1} + k_3^{-1} \times [Q^+]^{-1} \quad (14)$$

$$[X^-] \gg [Q^+]. \quad U^{-1} = k_1^{-1} + k_3^{-1} \times [X^-]^{-1} \quad (15)$$

$$\text{where } U = \frac{2.3 \times r}{3000 \times t} \times \log \frac{[QX]_{org}}{[QX]_{org} - K_{ex} \times [Q^+] \times [X^-]} \quad (16)$$

Eqs. (14) and (15) enable the determination of k_1 , k_2 and k_3 by slope analysis.

When the ion pair is highly hydrophobic the transfer rate measurements were made with equal concentration of the ions in the aqueous phase and the rate constants were evaluated according to [18].

The rate constants found for transport between the bulk of the aqueous phase and the interface (k_1 and k_2) are of similar magnitude for all ions with a mean value of $10^{-5.2}$ ($\text{cm} \times \text{s}^{-1} \times 10^3$). The constants have the same value whether the aqueous phase constitutes the donating or the receiving phase (Tables 1 and 2).

Table 1

Extraction of quaternary ammonium ions: transport and transfer rate constants.

Organic phase: chloroform

Ion pair	$-\log k_1$	$-\log k_2$	$-\log k_3$	$-\log k_4$	$\log k_3/k_4$	$\log K_{ex}$
TEA-Pi	-	5.22	3.47	4.65	1.18	1.32
TPrA-BNS	5.09	5.09	3.95	5.10	1.15	1.24
TPrA-I	5.18	-	4.38	4.89	0.51	0.8
TPrA-ClO ₄	5.23	-	3.81	4.97	1.16	1.3
MPT-Br	5.67	-	4.23	5.22	0.99	1.01
TPrA-Pi	5.05	4.86	1.10	4.55	3.45	3.64
MPT-Pi	5.2	5.2	0.6	6.3	5.7	5.5
TBA-Pi	5.0	5.0	0.1	6.2	6.1	5.91
TPeA-Pi	5.1	5.1	-0.5	8	8.5	8.1

Pi = picrate, BNS = naphthalene-2-sulfonate, TEA = tetraethylammonium, TPrA = tetrapropylammonium, TBA = tetrabutylammonium, TPeA = tetrapentylammonium, MPT = N,N-dimethylprotriptyline.

Table 2

Extraction of N,N-dimethylprotriptyline (MPT) as bromide ion pair: transport and transfer rate constants.
Organic phase: methylene chloride

Direction of transfer	$-\log k_1$	$-\log k_3$	$-\log k_4$	$\log k_3/k_4$	$\log K_{\text{ex}}$
Aqueous to organic	5.51	-	5.22	1.12	1.20
Organic to aqueous	5.52	4.10	-		

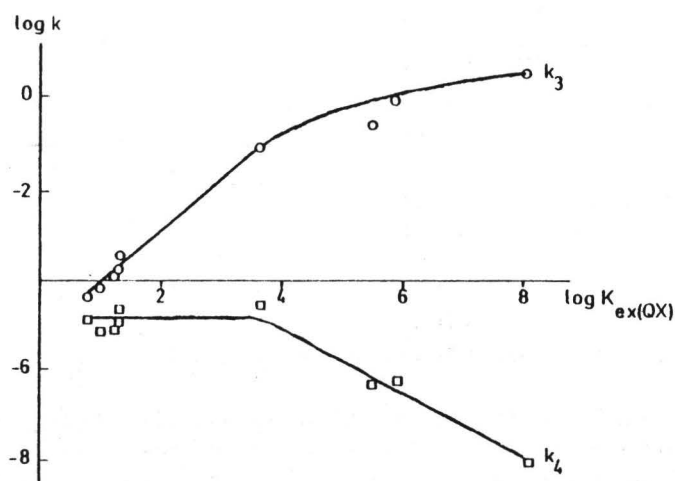


FIG. 3

Relation between transfer rate and extraction constant.

○ k_3 ($\text{cm}^4 \times \text{s}^{-1} \times \text{mole}^{-1} \times 10^6$)

□ k_4 ($\text{cm} \times \text{s}^{-1} \times 10^3$)

The transfer rate constants (k_3 and k_4) are highly dependent on the hydrophobicity of the ion pair. This is illustrated in FIG. 3 which shows the relation between the rate constants and the ion-pair extraction constant with chloroform as the organic phase. $\log k_3$ increases rectilinearly with $\log K_{\text{ex}}(\text{QX})$ up to a value of the ion-pair extraction constant of about 10^4 . Above this level the increase of $\log k_3$ is lower. k_4 is almost constant when $\log K_{\text{ex}}(\text{QX}) < 4$ and decreases when the ion-pair extraction constant is higher. Similar observations have been made by Lippold et al [14].

The experimental transfer rate constants, k_3 and k_4 , were tested by a comparison with the ion-pair extraction constant, determined under equilibrium conditions, using equation (8).

Good agreement was found in all cases (Tables 1 and 2) which supports the validity of the experimental rate constants.

Extraction with low degree of ion-pair formation in the organic phase

The degree of ion-pair formation in the organic phase decreases with decreasing concentration of the ion pair in the organic phase [10]. At a concentration level where the ion-pair formation is insignificant the extraction process can be described as an extraction of two separate ions. A model is given in FIG. 4. The main difference from the model in FIG. 1 (e.g. ion-pair extraction) is that the transfer rate constants (k_5 and k_{-5}) are unaffected by ion-pair formation and dissociation.

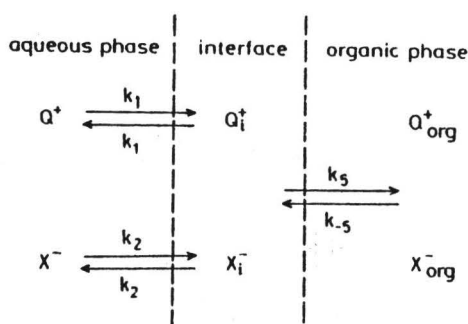


FIG. 4
Model for the ion extraction process

The application of the model is based on a steady state assumption for the amount of substrate at the interface. Equations that enable a computation of the rate constants can be obtained by the same principles that were used for an ion-pair extraction. The following equations are obtained when the anion is present in large excess in the aqueous phase [19].

Transfer of Q^+ to the organic phase

$$([Q^+] \times [X^-])^{\frac{1}{2}} \times T^{-1} = (k_5 \times k_{-5})^{-\frac{1}{2}} + K_{ie}^{\frac{1}{2}} \times k_{-1}^{-1} \times [X^-] \quad (17)$$

$$\text{where } T = \frac{2.3 \times r}{6000 \times t} \log \frac{(K_{ie} \times [Q^+] \times [X^-])^{\frac{1}{2}}}{(K_{ie} \times [Q^+] \times [X^-])^{\frac{1}{2}} - [Q^+]_{org}} \quad (18)$$

Transfer of Q^+ from the organic phase

$$S^{-1} = k_{-1}^{-1} + k_5^{-1} \times [X^-]^{-1} \quad (19)$$

$$\text{where } S = \frac{2.3 \times r}{3000 \times t} \log \frac{[Q^+]_{org}^2}{[Q^+]_{org}^2 - K_{ie} \times [Q^+] \times [X^-]} \quad (20)$$

K_{ie} is the equilibrium constant for the ion extraction process i.e.
 $K_{ie} = [Q^+]_{org} \times [X^-]_{org} \times [Q^+]^{-1} \times [X^-]^{-1}$. Eqs. (17) and (19) enable a computation of the rate constants by slope analysis.

The studies were performed with N,N-dimethylprotriptyline (MPT) as cation and bromide as counter ion with methylene chloride as the organic phase. MPT can be determined by fluorimetry down to concentrations of about 10^{-8} mol/ which in the organic phase give a degree of ion-pair formation of only a few per cent.

The value of the constant for transport of the cation (i.e. MPT) in the aqueous phase, k_1 was found to be independent of the direction of transfer (Table 3) and in good agreement with values obtained at a high degree of ion-pair formation (Table 2).

Table 3

Rate constants for the extraction of MPT with bromide at low degree of ion-pair formation in the organic phase.

Organic phase: methylene chloride

Direction of transfer	$-\log k_1$
Aqueous to organic	5.32
Organic to aqueous	5.39

The transfer rate constants (k_5 and k_{-5}) could not be evaluated since the ion extraction was so fast that the transfer rate was controlled by the transport of the cation in the aqueous phase.

Influence of ion-pair formation on the transfer rate

The influence of ion-pair formation on the extraction process can be illustrated by a comparison of transfer rates, from the aqueous to the organic phase, at a low degree of ion-pair formation (i.e. ion extraction) with calculated transfer rates obtained by use of rate constants valid at a high degree of ion-pair formation (Table 2). The comparison showed considerable differences, the rates by an ion extraction being about 100 times higher than by an ion-pair extraction.

The validity of the assumption that the difference in transfer rates was due to the differences in the degree of ion-pair formation was tested by addition of an excess of bromide to the organic phase which increased the degree of ion-pair formation of MPT-bromide from less than 15% to 98%. The transfer rate constants (Table 4) were in good agreement with results obtained at such high concentrations of MPT-bromide that the degree of ion-pair formation is high (Table 2).

Table 4

Rate constants for extraction of MPT with bromide: excess of bromide in the organic phase.

Organic phase: tetrahexylammoniumbromide (10^{-4} M) in methylene chloride.

Direction of transfer	$-\log k_3$	$-\log k_4$
Aqueous to organic	-	5.13
Organic to aqueous	4.03	-

The fact that the transfer rate to the organic phase is considerably higher at a low degree of ion-pair formation than at a high, indicates that an ion-pair extraction process comprises a fast transfer of the ions to the organic phase and a slower ion-pair formation in the organic phase. The process can be described by the model given in FIG. 5. The ion extraction is so fast that equilibrium can be assumed between the ions in the interfacial region at a high degree of ion-pair formation in the organic phase.

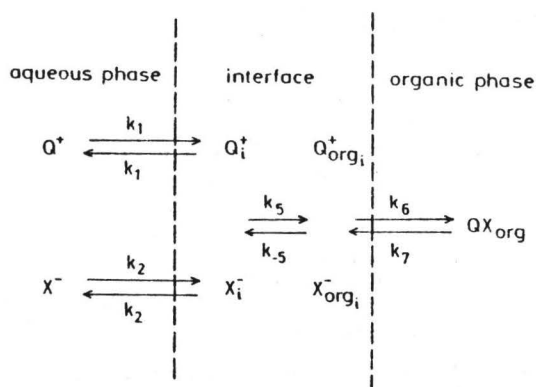


FIG. 5

Model for the ion extraction process with ion-pair formation in the organic phase

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KINETICS OF EXTRACTION OF ZINC BY DI (2-ETHYLHEXYL) PHOSPHORIC ACID
IN N-HEPTANE

L.A. Ajawin, E.S. Pérez de Ortiz and H.
Sawistowski
Department of Chemical Engineering
Imperial College of Science and Technology

London SW7, England

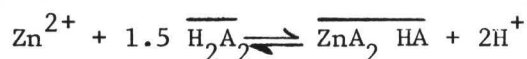
ABSTRACT

The rate of zinc extraction by di (2-ethylhexyl) phosphoric acid in n-heptane from dilute sulphuric acid solutions has been investigated in a stirred transfer cell with a well defined interfacial area. The measurements were carried out at a temperature of 25°C and an ionic strength of 1.0 kmol m⁻³. By varying the interfacial area and phase volumes it was found that the controlling reaction occurred at the interface. The results indicate that the overall reaction is first order with respect to zinc, first order with respect to HDEHP and inverse first order with respect to the hydrogen ion concentration. The rate constant of this reaction is estimated to be 5.1 x 10⁻⁶ s⁻¹.

INTRODUCTION

The extraction of zinc from dilute solutions is currently attracting considerable attention. Two commercial solvent extraction plants for zinc are at present in operation and both use di (2-ethylhexyl) phosphoric acid (HDEHP or HA) as the extractant in the extraction stage. The first plant (1) has been in operation in Sweden since 1975. In this plant zinc is extracted from weakly acidic effluent from the manufacture of rayon. In the second plant, which is in Bilbao in Spain, the feed is the effluent from chloride roasting of pyrites cinder. This plant has been in operation since 1976 (2).

HDEHP is known to have high selectivity for the extraction of zinc with respect to a number of metals, notably copper, cobalt, nickel, manganese, cadmium, calcium and lead. Some equilibrium studies of the extraction of zinc by HDEHP have been reported in the literature (1, 3-7) but almost none of significance has been carried out using the industrially important aqueous sulphate solutions. The stoichiometry of the system under study has been shown (8) to be



with an equilibrium constant equal to 2.60 x 10⁻³ kmol^{1/2} m^{-3/2} at 25°C and an ionic strength of one. In this equation H₂A₂ denotes HDEHP which is known to be dimeric in n-heptane (9-17) and the bars indicate species in the organic phase.

On the other hand kinetic studies on the system are lacking. A knowledge of extraction rates is of vital importance in any rational design of industrial solvent extraction equipment. The purpose of this work is, therefore, to carry out a systematic study of the kinetics of the extraction of zinc from dilute sulphuric acid solutions using HDEHP in n-heptane as the extractant. The measurements were carried out using a stirred cell with a definite interfacial area.

EXPERIMENTAL

(a) Reagents

The HDEHP was obtained from BDH and was purified by either the method of Partridge and Jensen (18) or the method of Sato (19).

n-Heptane of knock-testing quality was supplied by Esso, BP and Shell companies and was used without further purification. The organic phase separated at the end of a run was distilled in a glass column to regenerate the n-heptane. The product obtained in the boiling range 97-99°C gave the required purity as was evident from refractive index measurements.

All other chemicals were of AnalaR grade and were used without further purification.

Zinc solutions were prepared by dissolving in distilled water the calculated quantities of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and were standardized by titration with sodium ethylene-diamine-tetra-acetate solution using Eriochrome black T as indicator (20).

The pH was adjusted by H_2SO_4 and the ionic strength by both H_2SO_4 and Na_2SO_4 .

(b) Analysis

The concentration of zinc in aqueous solutions was determined using an atomic absorption spectrophotometer at the wavelength of 213.9 nm.

(c) The experimental procedure

The kinetics of the extraction process was investigated in a specially designed stirred cell of constant interfacial area. It is a modified version of the Nitsch cell (21) in which the interface is protected by a metal gauze. All the components of the cell are separate pieces which can be dismantled easily. A schematic diagram of the cell is shown in Fig. 1.

The cell was assembled and brought to the desired operating temperature. The zinc solution, at the same temperature, was introduced into the cell via a funnel connected with a long flexible PVC tubing, the tip of which rested on the upper wire mesh to avoid wetting the upper part of the cell. n-Heptane saturated with water, at the same temperature, was charged into the cell and the motors were run for about five minutes during which the speed was adjusted to the desired value. The motors were stopped. A specific volume of a concentrated solution of HDEHP in n-heptane was injected into the organic phase - after having removed an equal volume of n-heptane from the cell - great care being taken not to disturb the interface. The stopwatch was started simultaneously. The motors were started again and the course of the reaction was followed by taking samples from the selected phase by means of a hypodermic syringe and analysing them for the concentration of zinc. At the end of the run the solutions were drained off and the cell was dismantled and cleaned.

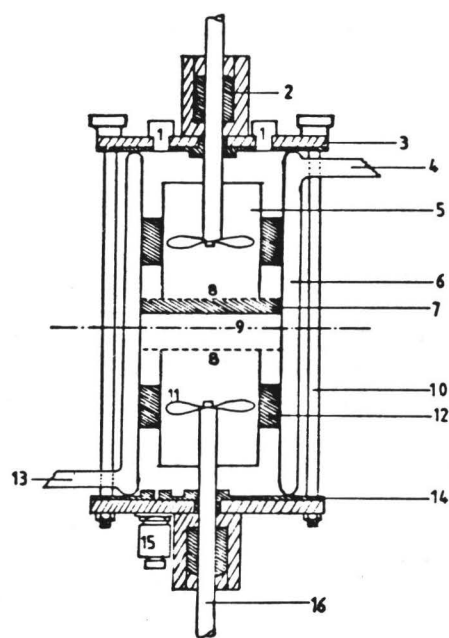


FIG. 1
The quiescent interface cell.

1. Sampling port.
2. PTFE gland.
3. Upper flange.
4. Water outlet.
5. Cylindrical glass baffle (draft tube).
6. Water jacket.
7. PTFE ring.
8. Stainless steel gauze.
9. Interface.
10. Tie rod.
11. Stirrer blades.
12. PTFE baffle support.
13. Water inlet.
14. Flange cover (PTFE).
15. Drain valve.
16. Stirrer shaft.

Scale
20 mm.

Amongst the possibilities, the above method of starting the experiment was found to give the best results and, as it can be seen from Fig. 2, the concentration-time plots showed that the initial conditions correspond fairly well to zero time.

In most experiments the volumes of the aqueous and the organic phase were 370 and 380 cm³ respectively. The stirring speed was always equal in both phases.

When the course of the reaction was followed by drawing samples from the organic phase, the samples were stripped by a molar solution of H₂SO₄ before analysis. The total amount of the samples drawn during a run did not exceed 6% of the phase from which they were removed.

All the experiments were carried out at 25°C and an ionic strength of 1.0 kmol m⁻³.

OPERATION UNDER CHEMICAL CONTROL

In liquid-liquid mass transfer with chemical reaction the overall extraction rate, in general, depends on both the rate of diffusive mass transfer of the species and the rate of chemical reaction. In order to investigate the dependence of the reaction rate on concentrations of the species involved, it is necessary to operate the cell under conditions of chemical control. This is the case where the specific rate of diffusive mass transfer is far higher than the specific rate of the chemical reaction and hence the overall rate of extraction is chemically controlled. Under these conditions it is possible to delineate the rate-determining step(s) in the overall reaction in a straightforward manner. To avoid any complications that might be introduced by the reverse reaction only the initial reaction rates were considered.

The apparent initial rate of reaction, r_z ,

$$r_z = \left(\frac{dC_{zo}}{dt} \right)_{t=0} = - \left(\frac{dC_{za}}{dt} \right)_{t=0} \quad (1)$$

can be represented by

$$r_z = k_I C_Z^\alpha C_{OI}^\beta C_H^\gamma \quad (2)$$

from which

$$\log r_z = \log k_I + \alpha \log C_Z + \beta \log C_{OI} - \gamma \text{ pH} \quad (3)$$

where C_{Za} and C_{Zo} are the zinc concentrations in the aqueous and the organic phase, respectively, at any time; C_H , C_{OI} and C_Z are the hydrogen ion, HDEHP and total zinc concentrations respectively; k_I is the forward reaction rate constant and α , β and γ are constants.

The flux of zinc across the interface, R , is r_z/a where a is the relevant specific interfacial area.

Each of the constants α , β and γ can be determined from the rate measurements when two of the concentrations in equation (2) are kept at certain values. Hence, if the concentrations of zinc and HDEHP are kept constant, equation (3) reduces to

$$\log r_z = k' - \gamma \text{ pH} \quad (4a)$$

while at constant pH and C_Z it becomes

$$\log r_z = k'' + \beta \log C_{OI} \quad (4b)$$

and when pH and C_{OI} are kept constant the equation can be written as

$$\log r_z = k''' + \alpha \log C_Z \quad (4c)$$

The definitions of the constants k' , k'' and k''' follow from equations (3) and (4). Therefore, the relevant plots of equation (4) should enable the determination of the constants α , β , γ and k_I .

Equations (4) are the basis of the approach to the study of the extraction under the conditions of chemical control.

Under chemical control it is also possible to distinguish whether the reaction takes place in the bulk or at the interface between the phases. In interfacial reactions the reaction flux is independent of phase volumes whereas in volume reactions, under similar conditions, it depends on phase volumes. Also the rate of reaction is proportional to the specific interfacial area if the reaction is interfacial but independent of it if the reaction was taking place in a bulk phase.

RESULTS AND DISCUSSION

One characteristic of chemical control is that the rate of reaction, under otherwise similar conditions, does not depend on the stirring speed of the phases and hence varying the stirring speed should enable the determination of that region, i.e. the "plateau region". As the rate increases with increasing C_Z , C_{OI} and the pH, great care must be exercised in the choice of conditions under which to carry out this search. In this study only those values of these variables the combination of which was expected to give the highest extraction rate were chosen. This was to ensure that once the regime of chemical control has been established under those conditions, any subsequent experiment should be conducted within it.

A preliminary series of qualitative and quantitative experiments was performed to establish the range of stirring speeds within which the cell could be operated. The lowest speed at which the aqueous phase was instantaneously and uniformly mixed was determined by injecting a dye into that phase. If the mixing appeared to be instantaneous a run was made, the course of which was followed by taking samples alternately at two different vertical positions within one phase. A plot of the concentration vs. time of the results thus obtained should fall on a smooth monotonic curve if mixing is uniform. The maximum speed attainable is judged simply by the observation of the interface.

The lowest speed chosen was 150 rpm. At this speed the dye experiment showed the mixing was not instantaneous and therefore this speed was no longer considered. At 200 rpm the dye experiment was positive so a run was made under the chosen conditions. The concentration-time plot, as can be seen in Fig. 2, gave points which fall on a reasonable straight line.

At 450 rpm the interface was somewhat perturbed and therefore all the experiments to establish the plateau region were carried out in the range 200-400 rpm.

All the experiments were such that the total concentration of zinc was much lower than either the HDEHP concentration or the concentration of the hydrogen ion.

In all the runs the plots of zinc concentration against time was linear over the sampling period and therefore the initial rate of reaction, r_z , was calculated from the slope of the straight line. Fig. 2 is typical of such plots. In addition, in all the experiments the variation in the initial concentration of zinc, and hence C_{OI} and the pH, was kept as low as possible.

(a) Dependence of the rate on the stirring speed

Initial series of experiments was carried out to establish the region of chemical control. This involved the measurements of the rate of extraction at different stirring speeds under the conditions referred to earlier. The starting C_z and C_{OI} values were 10^{-3} and 0.05 kmol m^{-3} respectively. However, it was not until both C_z and C_{OI} dropped considerably that the rate became independent of stirring. These conditions are plotted in Fig. 3. Hence, at speeds in excess of 280 rpm the rate is chemically controlled. All the subsequent experiments were, therefore, carried out at 300 rpm.

(b) The site of the Reaction

Under the conditions of chemical control as above, the rate was measured at different interfacial areas. The interface was reduced by insertion into the cell of suitably designed rings of different inside diameters. The results obtained are plotted in Fig. 4. A straight line was obtained which passes through the origin. This shows that the rate is proportional to the specific interfacial area and, additionally, that the geometric interfacial area is identical with the area available for reaction.

The volume of one phase was varied by increasing or decreasing the volume of the other phase. Fig. 5 is a plot of the mass flux vs. the volume of the aqueous phase. It is clear that the flux is independent of the phase volumes.

These two sets of results taken together indicate that the controlling reaction occurred at the interface.

(c) The Dependence of the Rate on pH, C_{OI} and C_Z

Runs at $C_Z = 10^{-4}$ and $C_{OI} = 10^{-2}$ kmol m⁻³ were carried out to investigate the dependence of the rate on the initial value of pH. The results are given in Fig. 6. The slopes of the straight lines are unity.

It was observed that under such low concentrations of zinc and HDEHP the pH did not change noticeably after the reaction has reached equilibrium. Some runs were repeated to establish the reproducibility of the results. The average error was about 2% which is quite satisfactory.

Next, the extraction rate was measured at $C_Z = 10^{-4}$ kmol m⁻³ and pH of 2.98 at different HDEHP concentrations. The results are shown in Fig. 7. The slope of the straight line is unity.

It was not possible to measure rates at HDEHP concentrations less than 2×10^{-3} kmol m⁻³ as it was very difficult, due to the very low concentrations, to follow the course of the reaction.

The linear plots of concentration against time during a run were indicative that the reaction was first order with respect to zinc. However, it was necessary to confirm this by actual measurements. This is indeed the case as Fig. 8 shows. The results were obtained at $C_{OI} = 10^{-2}$ kmol m⁻³ and pH of 2.98 at different values of zinc concentration.

The three values of k_I obtained from these results - according to equations (4) - were in very good agreement. The average value is 5.09×10^{-6} s⁻¹.

CONCLUSIONS

The rate equation of chemical change in the extraction of zinc by di (2-ethylhexyl) phosphoric acid in n-heptane was found to be first order with respect to zinc, first order with respect to HDEHP and inverse first order with respect to the hydrogen ion concentration. The reaction rate constant was found to be 5.1×10^{-6} s⁻¹ at 25°C at an ionic strength of 1.0 kmol m⁻³. Evidence produced by the effect on the reaction rate of the variation of the interfacial area and phase volumes indicates that the controlling reaction occurred at the interface.

ACKNOWLEDGEMENT

The authors wish to thank BP, Esso and Shell for the donation of chemicals and the University of Khartoum, Sudan, for provision of a scholarship to Mr L.A. Ajawin.

SYMBOLS USED

a	specific interfacial area
C_H	hydrogen ion concentration in the bulk aqueous phase
C_{OI}	HDEHP concentration in the organic phase (on the basis of the molar mass of the monomer)
C_Z	total zinc concentration
C_{Za}	zinc concentration in the aqueous phase at time t
C_{Zo}	zinc concentration in the organic phase at time t
k_I	concentration-based forward reaction rate constant in equation (2)
k', k'', k'''	constants in equations (4)
R	molar flux
r	reaction rate of zinc
t	time; α, β, γ constants in equation (2).

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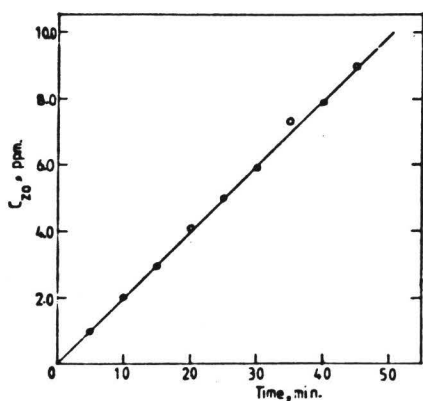


FIG. 2
Change in the concentration of zinc in the organic phase with time. Stirring speed = 200 rpm, $C_{OI} = 0.05$, $C_Z = 10^{-3}$ kmol m^{-3} , pH 2.95.

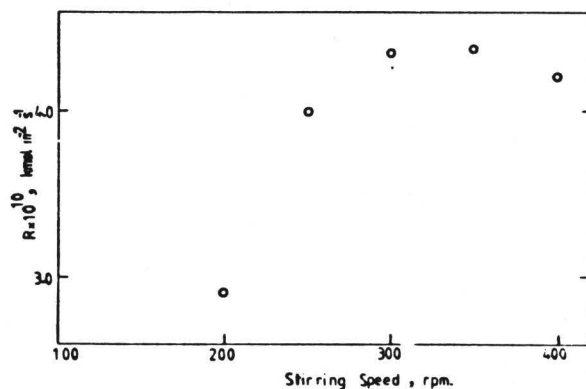


FIG. 3
Effect of the stirring speed on the rate of extraction. $C_{OI} = 10^{-2}$, $C_Z = 10^{-4}$ kmol m^{-3} , pH 2.94.

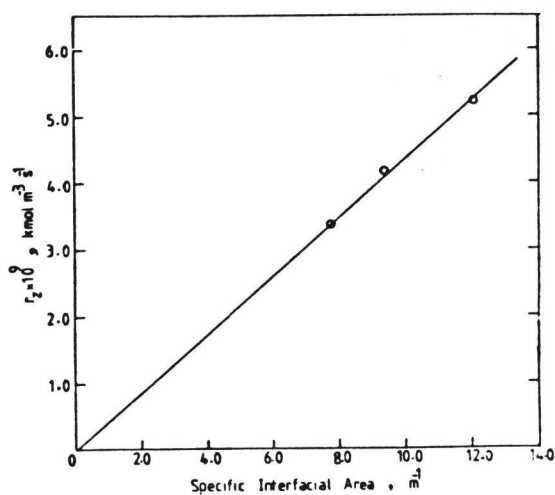


FIG. 4
The dependence of the extraction rate, r_z , of zinc on the specific interfacial area of the aqueous phase. $C_{OI} = 10^{-2}$, $C_Z = 10^{-4}$ kmol m^{-3} , pH 2.93.

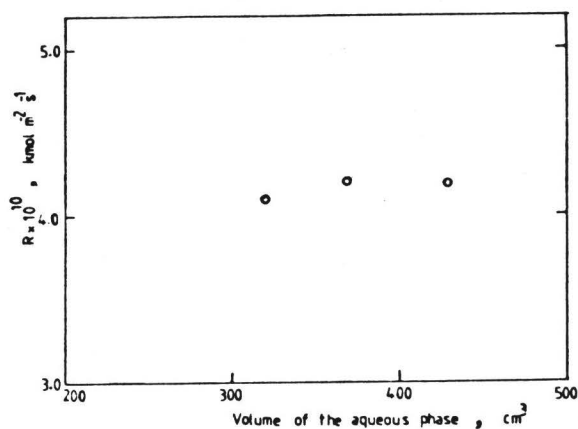


FIG. 5
The dependence of the flux, R , on the volume of the aqueous phase. $C_{OI} = 10^{-2}$, $C_Z = 10^{-4}$ kmol m^{-3} , pH 2.98.

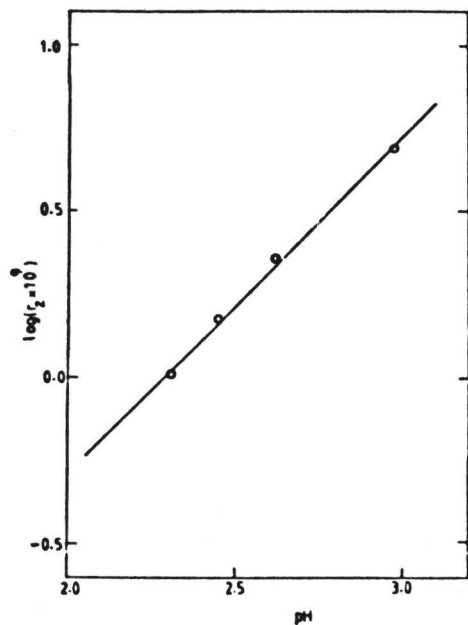


FIG. 6
The extraction rate, r_z , of zinc as a function of pH. $C_{OI} = 10^{-2}$, $C_z = 10^{-4}$ kmol m⁻³.

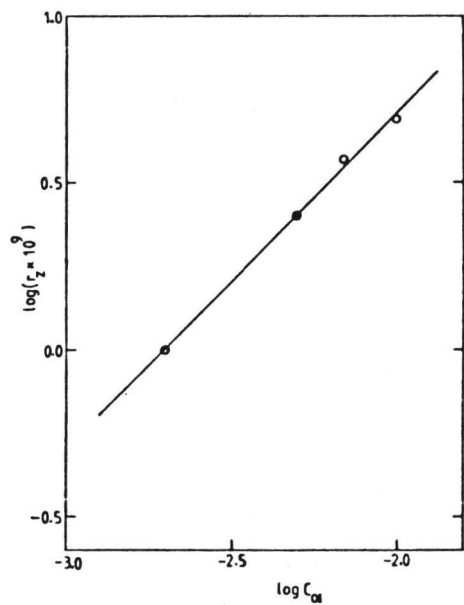


FIG. 7
The extraction rate, r_z , of zinc as a function of C_{OI} . pH 2.98, $C_z = 10^{-4}$ kmol m⁻³.

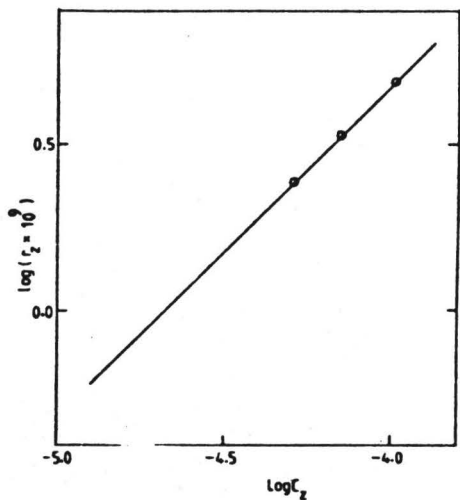


FIG. 8
The extraction rate, r_z , of zinc as a function of C_z . pH 2.98, $C_{OI} = 10^{-2}$ kmol m⁻³.

KINETICS OF EXTRACTION OF ZINC BY DI (2-ETHYLHEXYL) PHOSPHORIC ACID
IN N-HEPTANE

L.A. Ajawin, E.S. Pérez de Ortiz and H.
Sawistowski
Department of Chemical Engineering
Imperial College of Science and Technology

London SW7, England

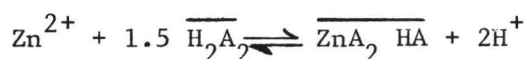
ABSTRACT

The rate of zinc extraction by di (2-ethylhexyl) phosphoric acid in n-heptane from dilute sulphuric acid solutions has been investigated in a stirred transfer cell with a well defined interfacial area. The measurements were carried out at a temperature of 25°C and an ionic strength of 1.0 kmol m⁻³. By varying the interfacial area and phase volumes it was found that the controlling reaction occurred at the interface. The results indicate that the overall reaction is first order with respect to zinc, first order with respect to HDEHP and inverse first order with respect to the hydrogen ion concentration. The rate constant of this reaction is estimated to be 5.1 x 10⁻⁶ s⁻¹.

INTRODUCTION

The extraction of zinc from dilute solutions is currently attracting considerable attention. Two commercial solvent extraction plants for zinc are at present in operation and both use di (2-ethylhexyl) phosphoric acid (HDEHP or HA) as the extractant in the extraction stage. The first plant (1) has been in operation in Sweden since 1975. In this plant zinc is extracted from weakly acidic effluent from the manufacture of rayon. In the second plant, which is in Bilbao in Spain, the feed is the effluent from chloride roasting of pyrites cinder. This plant has been in operation since 1976 (2).

HDEHP is known to have high selectivity for the extraction of zinc with respect to a number of metals, notably copper, cobalt, nickel, manganese, cadmium, calcium and lead. Some equilibrium studies of the extraction of zinc by HDEHP have been reported in the literature (1, 3-7) but almost none of significance has been carried out using the industrially important aqueous sulphate solutions. The stoichiometry of the system under study has been shown (8) to be



with an equilibrium constant equal to 2.60 x 10⁻³ kmol^{1/2} m^{-3/2} at 25°C and an ionic strength of one. In this equation H₂A₂ denotes HDEHP which is known to be dimeric in n-heptane (9-17) and the bars indicate species in the organic phase.

On the other hand kinetic studies on the system are lacking. A knowledge of extraction rates is of vital importance in any rational design of industrial solvent extraction equipment. The purpose of this work is, therefore, to carry out a systematic study of the kinetics of the extraction of zinc from dilute sulphuric acid solutions using HDEHP in n-heptane as the extractant. The measurements were carried out using a stirred cell with a definite interfacial area.

EXPERIMENTAL

(a) Reagents

The HDEHP was obtained from BDH and was purified by either the method of Partridge and Jensen (18) or the method of Sato (19).

n-Heptane of knock-testing quality was supplied by Esso, BP and Shell companies and was used without further purification. The organic phase separated at the end of a run was distilled in a glass column to regenerate the n-heptane. The product obtained in the boiling range 97-99°C gave the required purity as was evident from refractive index measurements.

All other chemicals were of AnalaR grade and were used without further purification.

Zinc solutions were prepared by dissolving in distilled water the calculated quantities of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and were standardized by titration with sodium ethylene-diamine-tetra-acetate solution using Eriochrome black T as indicator (20).

The pH was adjusted by H_2SO_4 and the ionic strength by both H_2SO_4 and Na_2SO_4 .

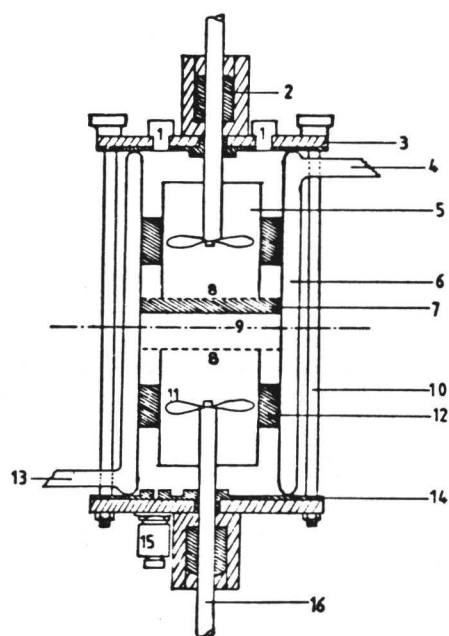
(b) Analysis

The concentration of zinc in aqueous solutions was determined using an atomic absorption spectrophotometer at the wavelength of 213.9 nm.

(c) The experimental procedure

The kinetics of the extraction process was investigated in a specially designed stirred cell of constant interfacial area. It is a modified version of the Nitsch cell (21) in which the interface is protected by a metal gauze. All the components of the cell are separate pieces which can be dismantled easily. A schematic diagram of the cell is shown in Fig. 1.

The cell was assembled and brought to the desired operating temperature. The zinc solution, at the same temperature, was introduced into the cell via a funnel connected with a long flexible PVC tubing, the tip of which rested on the upper wire mesh to avoid wetting the upper part of the cell. n-Heptane saturated with water, at the same temperature, was charged into the cell and the motors were run for about five minutes during which the speed was adjusted to the desired value. The motors were stopped. A specific volume of a concentrated solution of HDEHP in n-heptane was injected into the organic phase - after having removed an equal volume of n-heptane from the cell - great care being taken not to disturb the interface. The stopwatch was started simultaneously. The motors were started again and the course of the reaction was followed by taking samples from the selected phase by means of a hypodermic syringe and analysing them for the concentration of zinc. At the end of the run the solutions were drained off and the cell was dismantled and cleaned.



Scale
20 mm.

FIG. 1
The quiescent interface cell.

1. Sampling port.
2. PTFE gland.
3. Upper flange.
4. Water outlet.
5. Cylindrical glass baffle (draft tube).
6. Water jacket.
7. PTFE ring.
8. Stainless steel gauze.
9. Interface.
10. Tie rod.
11. Stirrer blades.
12. PTFE baffle support.
13. Water inlet.
14. Flange cover (PTFE).
15. Drain valve.
16. Stirrer shaft.

Amongst the possibilities, the above method of starting the experiment was found to give the best results and, as it can be seen from Fig. 2, the concentration-time plots showed that the initial conditions correspond fairly well to zero time.

In most experiments the volumes of the aqueous and the organic phase were 370 and 380 cm³ respectively. The stirring speed was always equal in both phases.

When the course of the reaction was followed by drawing samples from the organic phase, the samples were stripped by a molar solution of H₂SO₄ before analysis. The total amount of the samples drawn during a run did not exceed 6% of the phase from which they were removed.

All the experiments were carried out at 25°C and an ionic strength of 1.0 kmol m⁻³.

OPERATION UNDER CHEMICAL CONTROL

In liquid-liquid mass transfer with chemical reaction the overall extraction rate, in general, depends on both the rate of diffusive mass transfer of the species and the rate of chemical reaction. In order to investigate the dependence of the reaction rate on concentrations of the species involved, it is necessary to operate the cell under conditions of chemical control. This is the case where the specific rate of diffusive mass transfer is far higher than the specific rate of the chemical reaction and hence the overall rate of extraction is chemically controlled. Under these conditions it is possible to delineate the rate-determining step(s) in the overall reaction in a straightforward manner. To avoid any complications that might be introduced by the reverse reaction only the initial reaction rates were considered.

The apparent initial rate of reaction, r_z ,

$$r_z = \left(\frac{dC_{zo}}{dt} \right)_{t=0} = - \left(\frac{dC_{za}}{dt} \right)_{t=0} \quad (1)$$

can be represented by

$$r_z = k_I C_Z^\alpha C_{OI}^\beta C_H^\gamma \quad (2)$$

from which

$$\log r_z = \log k_I + \alpha \log C_Z + \beta \log C_{OI} - \gamma \text{ pH} \quad (3)$$

where C_{Za} and C_{Zo} are the zinc concentrations in the aqueous and the organic phase, respectively, at any time; C_H , C_{OI} and C_Z are the hydrogen ion, HDEHP and total zinc concentrations respectively; k_I is the forward reaction rate constant and α , β and γ are constants.

The flux of zinc across the interface, R , is r_z/a where a is the relevant specific interfacial area.

Each of the constants α , β and γ can be determined from the rate measurements when two of the concentrations in equation (2) are kept at certain values. Hence, if the concentrations of zinc and HDEHP are kept constant, equation (3) reduces to

$$\log r_z = k' - \gamma \text{ pH} \quad (4a)$$

while at constant pH and C_Z it becomes

$$\log r_z = k'' + \beta \log C_{OI} \quad (4b)$$

and when pH and C_{OI} are kept constant the equation can be written as

$$\log r_z = k''' + \alpha \log C_Z \quad (4c)$$

The definitions of the constants k' , k'' and k''' follow from equations (3) and (4). Therefore, the relevant plots of equation (4) should enable the determination of the constants α , β , γ and k_I .

Equations (4) are the basis of the approach to the study of the extraction under the conditions of chemical control.

Under chemical control it is also possible to distinguish whether the reaction takes place in the bulk or at the interface between the phases. In interfacial reactions the reaction flux is independent of phase volumes whereas in volume reactions, under similar conditions, it depends on phase volumes. Also the rate of reaction is proportional to the specific interfacial area if the reaction is interfacial but independent of it if the reaction was taking place in a bulk phase.

RESULTS AND DISCUSSION

One characteristic of chemical control is that the rate of reaction, under otherwise similar conditions, does not depend on the stirring speed of the phases and hence varying the stirring speed should enable the determination of that region, i.e. the "plateau region". As the rate increases with increasing C_Z , C_{OI} and the pH, great care must be exercised in the choice of conditions under which to carry out this search. In this study only those values of these variables the combination of which was expected to give the highest extraction rate were chosen. This was to ensure that once the regime of chemical control has been established under those conditions, any subsequent experiment should be conducted within it.

A preliminary series of qualitative and quantitative experiments was performed to establish the range of stirring speeds within which the cell could be operated. The lowest speed at which the aqueous phase was instantaneously and uniformly mixed was determined by injecting a dye into that phase. If the mixing appeared to be instantaneous a run was made, the course of which was followed by taking samples alternately at two different vertical positions within one phase. A plot of the concentration vs. time of the results thus obtained should fall on a smooth monotonic curve if mixing is uniform. The maximum speed attainable is judged simply by the observation of the interface.

The lowest speed chosen was 150 rpm. At this speed the dye experiment showed the mixing was not instantaneous and therefore this speed was no longer considered. At 200 rpm the dye experiment was positive so a run was made under the chosen conditions. The concentration-time plot, as can be seen in Fig. 2, gave points which fall on a reasonable straight line.

At 450 rpm the interface was somewhat perturbed and therefore all the experiments to establish the plateau region were carried out in the range 200-400 rpm.

All the experiments were such that the total concentration of zinc was much lower than either the HDEHP concentration or the concentration of the hydrogen ion.

In all the runs the plots of zinc concentration against time was linear over the sampling period and therefore the initial rate of reaction, r_z , was calculated from the slope of the straight line. Fig. 2 is typical of such plots. In addition, in all the experiments the variation in the initial concentration of zinc, and hence C_{OI} and the pH, was kept as low as possible.

(a) Dependence of the rate on the stirring speed

Initial series of experiments was carried out to establish the region of chemical control. This involved the measurements of the rate of extraction at different stirring speeds under the conditions referred to earlier. The starting C_z and C_{OI} values were 10^{-3} and 0.05 kmol m^{-3} respectively. However, it was not until both C_z and C_{OI} dropped considerably that the rate became independent of stirring. These conditions are plotted in Fig. 3. Hence, at speeds in excess of 280 rpm the rate is chemically controlled. All the subsequent experiments were, therefore, carried out at 300 rpm.

(b) The site of the Reaction

Under the conditions of chemical control as above, the rate was measured at different interfacial areas. The interface was reduced by insertion into the cell of suitably designed rings of different inside diameters. The results obtained are plotted in Fig. 4. A straight line was obtained which passes through the origin. This shows that the rate is proportional to the specific interfacial area and, additionally, that the geometric interfacial area is identical with the area available for reaction.

The volume of one phase was varied by increasing or decreasing the volume of the other phase. Fig. 5 is a plot of the mass flux vs. the volume of the aqueous phase. It is clear that the flux is independent of the phase volumes.

These two sets of results taken together indicate that the controlling reaction occurred at the interface.

(c) The Dependence of the Rate on pH, C_{OI} and C_Z

Runs at $C_Z = 10^{-4}$ and $C_{OI} = 10^{-2}$ kmol m⁻³ were carried out to investigate the dependence of the rate on the initial value of pH. The results are given in Fig. 6. The slopes of the straight lines are unity.

It was observed that under such low concentrations of zinc and HDEHP the pH did not change noticeably after the reaction has reached equilibrium. Some runs were repeated to establish the reproducibility of the results. The average error was about 2% which is quite satisfactory.

Next, the extraction rate was measured at $C_Z = 10^{-4}$ kmol m⁻³ and pH of 2.98 at different HDEHP concentrations. The results are shown in Fig. 7. The slope of the straight line is unity.

It was not possible to measure rates at HDEHP concentrations less than 2×10^{-3} kmol m⁻³ as it was very difficult, due to the very low concentrations, to follow the course of the reaction.

The linear plots of concentration against time during a run were indicative that the reaction was first order with respect to zinc. However, it was necessary to confirm this by actual measurements. This is indeed the case as Fig. 8 shows. The results were obtained at $C_{OI} = 10^{-2}$ kmol m⁻³ and pH of 2.98 at different values of zinc concentration.

The three values of k_I obtained from these results - according to equations (4) - were in very good agreement. The average value is 5.09×10^{-6} s⁻¹.

CONCLUSIONS

The rate equation of chemical change in the extraction of zinc by di (2-ethylhexyl) phosphoric acid in n-heptane was found to be first order with respect to zinc, first order with respect to HDEHP and inverse first order with respect to the hydrogen-ion concentration. The reaction rate constant was found to be 5.1×10^{-6} s⁻¹ at 25°C at an ionic strength of 1.0 kmol m⁻³. Evidence produced by the effect on the reaction rate of the variation of the interfacial area and phase volumes indicates that the controlling reaction occurred at the interface.

ACKNOWLEDGEMENT

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SYMBOLS USED

a	specific interfacial area
C_H	hydrogen ion concentration in the bulk aqueous phase
C_{OI}	HDEHP concentration in the organic phase (on the basis of the molar mass of the monomer)
C_Z	total zinc concentration
C_Z^a	zinc concentration in the aqueous phase at time t
C_Z^o	zinc concentration in the organic phase at time t
k_I	concentration-based forward reaction rate constant in equation (2)
k', k'', k'''	constants in equations (4)
R	molar flux
r_z	reaction rate of zinc
t	time; α, β, γ constants in equation (2).

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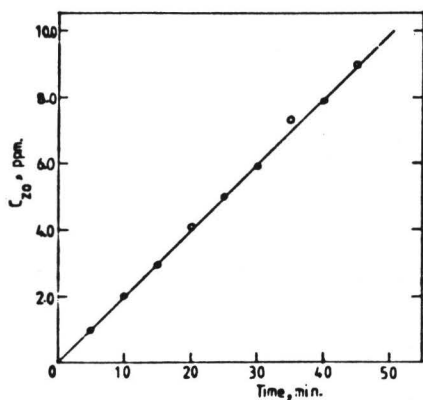


FIG. 2

Change in the concentration of zinc in the organic phase with time. Stirring speed = 200 rpm, $C_{OI} = 0.05$, $C_Z = 10^{-3}$ kmol m^{-3} , pH 2.95.

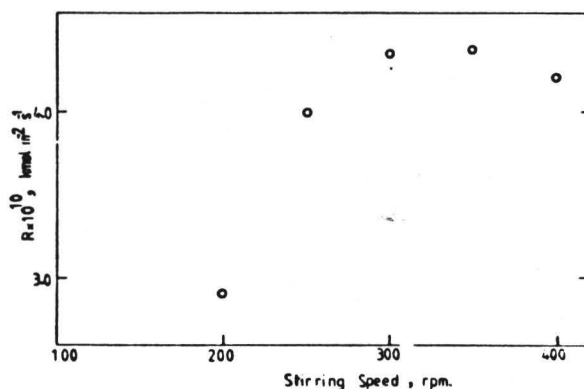


FIG. 3

Effect of the stirring speed on the rate of extraction. $C_{OI} = 10^{-2}$, $C_Z = 10^{-4}$ kmol m^{-3} , pH 2.94.

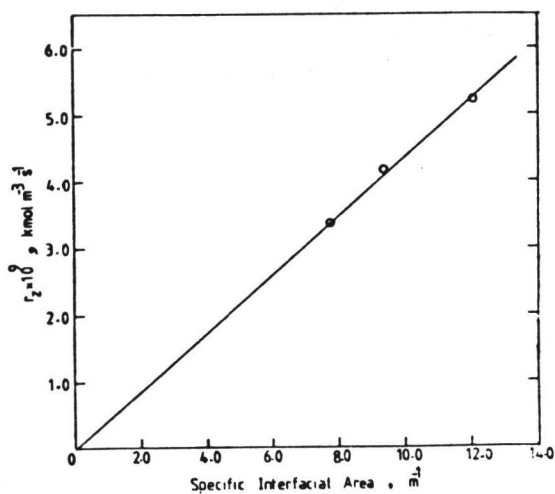


FIG. 4

The dependence of the extraction rate, r_Z , of zinc on the specific interfacial area of the aqueous phase. $C_{OI} = 10^{-2}$, $C_Z = 10^{-4}$ kmol m^{-3} , pH 2.93.

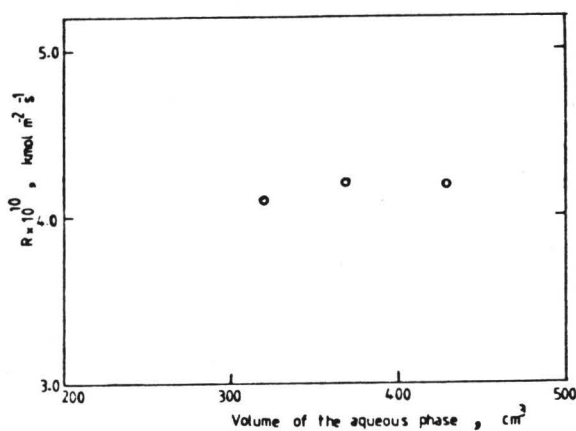


FIG. 5

The dependence of the flux, R , on the volume of the aqueous phase. $C_{OI} = 10^{-2}$, $C_Z = 10^{-4}$ kmol m^{-3} , pH 2.98.

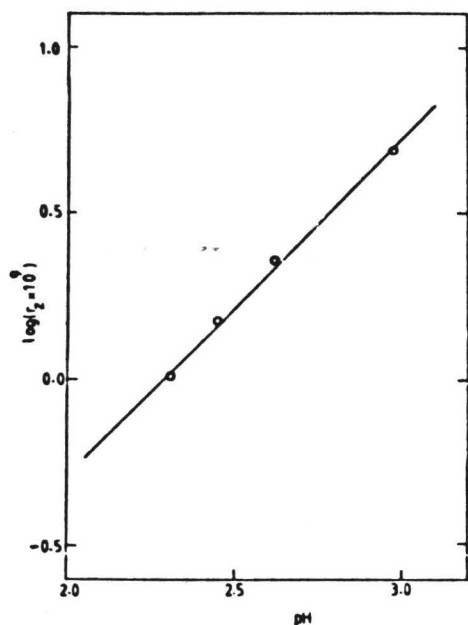


FIG. 6
The extraction rate, r_z , of zinc
as a function of pH.
 $C_{OI} = 10^{-2}$, $C_z = 10^{-4}$ kmol m^{-3} .

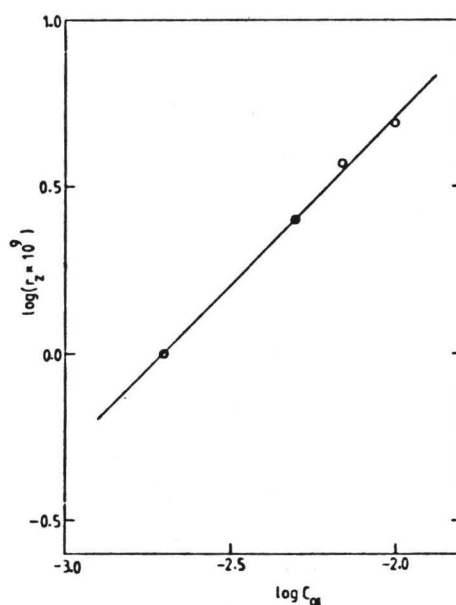


FIG. 7
The extraction rate, r_z , of
zinc as a function of C_{OI}^{-3} .
pH 2.98, $C_z = 10^{-4}$ kmol m^{-3} .

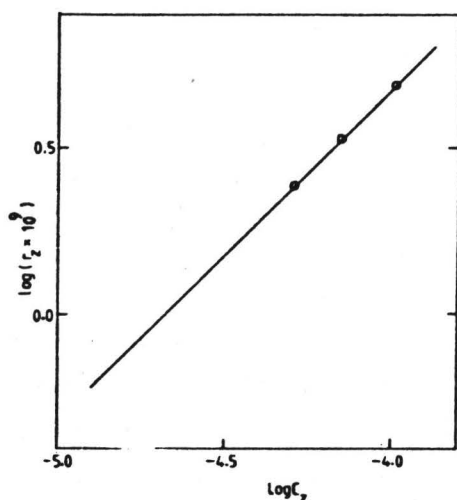


FIG. 8
The extraction rate, r_z , of zinc
as a function of C_z . pH 2.98,
 $C_{OI} = 10^{-2}$ kmol m^{-3} .

KINETICS OF COBALT OXIDATION IN SOLVENT EXTRACTION BY 8-QUINOLINOL AND KELEX 100

P. GUESNET, J.L. SABOT, D. BAUER

Laboratoire de Chimie Analytique des
Processus Industriels - E.S.P.C.I.
10, rue Vauquelin 75231 Paris Cedex 05
PARIS FRANCE

ABSTRACT

During solvent extraction by 8-quinolinol and Kelex 100, Co(II) chelates are irreversibly oxidized by atmospheric oxygen to Co(III) chelates which are poorly strippable. This oxidation is influenced by organic phase features : strong donor compounds stabilize Co(II) by formation of mixed complexes and considerably reduce the oxidation rate. With oxo donor compounds the order of efficiency is in good accordance with the classification proposed by Gutmann (1). When the donor atom is nitrogen, steric hindrance is an important phenomenon. Acidic compounds also stabilize Co(II), the order of efficiency being the order of acid strength. The formation of ion-pair complexes has been proposed.

INTRODUCTION

The oxidation of cobalt chelates during solvent extraction is a very frequent phenomenon which occurs with most extractants of industrial or analytical interest. The Co(III) species resulting from this oxidation are highly stable and a quantitative stripping is impossible with aqueous solutions of diluted acids (2, 3, 4). This paper presents an investigation of the oxidation of Co(II) chelates during solvent extraction by 8-quinolinol and an industrial alkylated 8-quinolinol : Kelex 100. The influence of extractant and additives concentrations has been investigated.

EXPERIMENTAL

All the aqueous solutions were prepared from cobalt sulfate (HOPKIN-WILLIAMS). pH was adjusted to 4.65 by use of an acetate buffer 1 mol l^{-1} or to 8.15 by use of a borate buffer (PROLABO reagents). The extractants used were 8-quinolinol (PROLABO) and β -dodeceny1-8-quinolinol (Kelex 100 ASHLAND).

Extraction procedure and spectrophotometric studies : a solution of 8-quinolinol $3.4 \times 10^{-2} \text{ mol l}^{-1}$ or Kelex 100, 0.155 mol.l^{-1} in 10 ml of toluene (MERCK) was shaken for 1 minute at room temperature with an aqueous solution (10 ml) of cobalt 10^{-3} or $1.5 \times 10^{-3} \text{ mol l}^{-1}$ adjusted to pH 4.65 or 8.15. After centrifugation and separation of the two phases, the organic phase was diluted in various organic solvents containing various amounts of additives or excess of extractants. These diluted organic solutions which contained about $1.2 \times 10^{-4} \text{ mol l}^{-1}$ of cobalt were poured into a glass cell

whose temperature was maintained at 31°C. The atmosphere was continually renewed by a current of air (L'AIR LIQUIDE). Visible and ultraviolet absorption spectra were recorded using a VARIAN 634 S spectrophotometer. Cobalt concentrations were determined in the aqueous phase by atomic absorption spectrophotometry (VARIAN AA 6 spectrophotometer). Concentrations in the organic phase were calculated from these values by difference.

Extraction procedure and electrochemical studies : 10 ml of a solution of 8-quinolinol $17 \times 10^{-2} \text{ mol.l}^{-1}$ in 1-2 dichloroethane (PROLABO) were shaken for 1 minute, at room temperature with an aqueous solution (10 ml) of cobalt $2.10^{-2} \text{ mol l}^{-1}$ adjusted to pH 8.15. After centrifugation the organic phase was diluted 10 times in 1-2 dichloroethane, which is a poorly solvating solvent similar to those usually used in extraction. This diluted solution which contained about $1.3 \times 10^{-3} \text{ mol l}^{-1}$ of cobalt, was introduced into a three electrodes cell whose temperature was maintained at 25°C. 0.1 mol l^{-1} of tetrabutylammonium perchlorate (EASTMAN) was added as supporting electrolyte. This solution was prevented from chemical oxidation by use of an argon atmosphere. A Rotating Platinum Electrode (RPE) was used as working electrode for recording the current voltage curves. The reference electrode consisted of a silver wire covered with silver perchlorate in a 1-2 dichloroethane solution of tetrabutylammonium perchlorate 0.1 mol l^{-1} . Voltammetry was carried out on a TACUSSEL PRT 20.

RESULTS AND DISCUSSION

I - Extraction of cobalt from a borate solution : pH 8.15

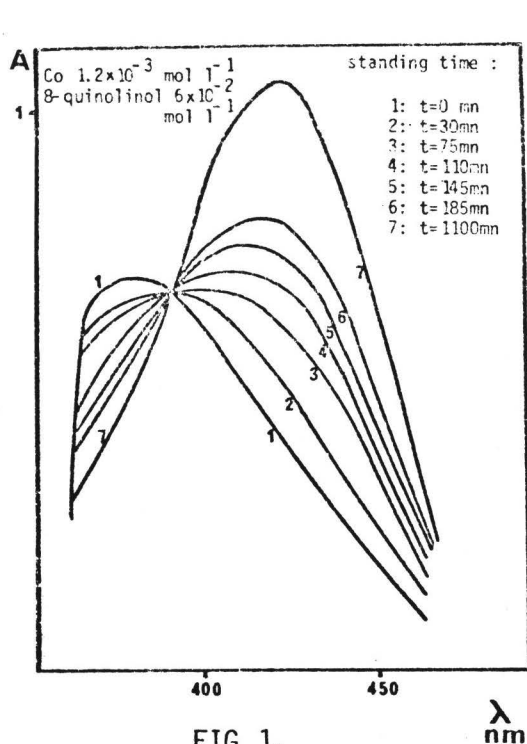


FIG 1.

absorption spectra of cobalt-8-quinolinol chelates in toluene

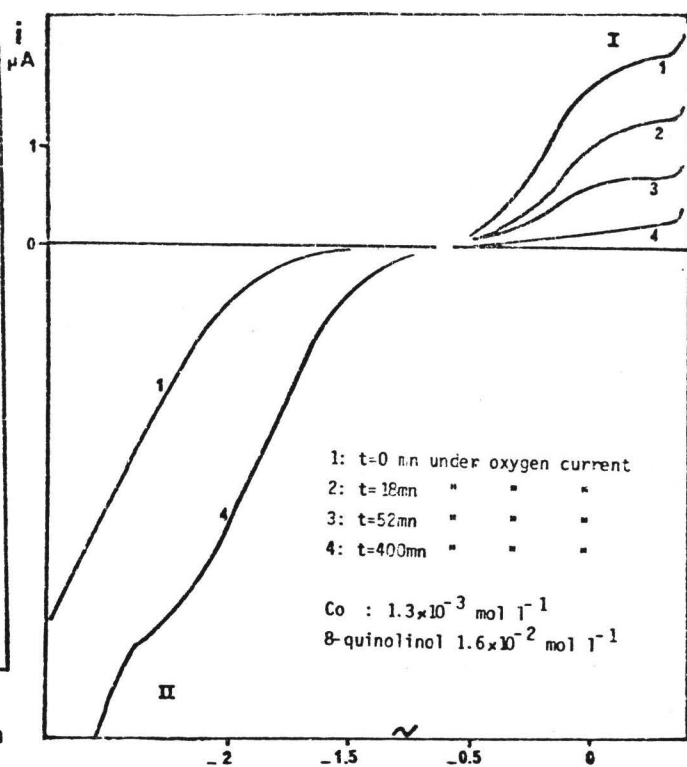


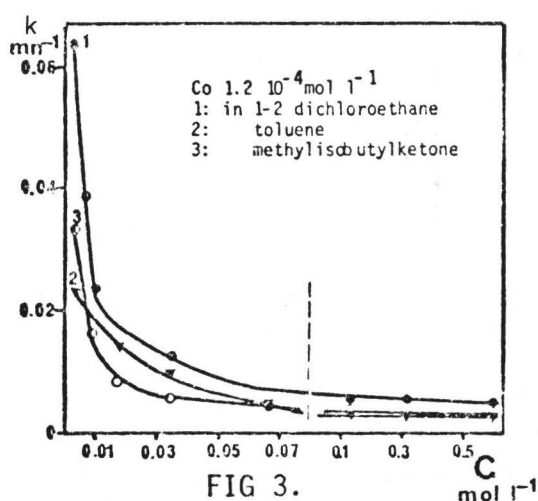
FIG 2.

oxido reduction of cobalt 8-quinolinol chelates: effect of oxygen.

I.1 - After extraction of cobalt by 8-quinolinol, separation from the aqueous phase and dilution, the organic phase shows an absorption maximum around 375 nm in non basic solvents such as toluene, kerosene or 1-2 dichloroethane. This absorption maximum decreases with time whereas a new maximum progressively appears around 420 nm (fig. 1). This phenomenon is due to the oxidation of the extracted Co(II) 8-quinolinol complex-absorption maximum 375 nm - to the Co(III) 8-quinolinol complex CoL_3 - absorption maximum 420 nm.

Thus, when the Co(II) 8-quinolinol complex is oxidized at the rotating platinum electrode, an irreversible diffusion control wave appears. This wave I, ($E^{1/2} = -0,22$ V) which corresponds to the transfer of one electron per cobalt atom, progressively disappears under oxygen atmosphere (fig. 2). Whereas a reduction wave II appears ($E^{1/2} = -1,9$ V). The electrochemical oxidation of the extracted complex, under argon atmosphere, and its chemical oxidation, under air or oxygen atmosphere, lead to the formation of the same wave II and the same absorption maximum (420 nm), whereas the electrochemical reduction of the final complex allows one to regenerate the extracted complex.

The study of the oxidation reaction was performed by measuring the absorbance variations at 420 nm as a function of time. These variations are proportional to cobalt (III) complex concentrations when these concentrations are below $1.5 \cdot 10^{-4} \text{ mol l}^{-1}$. A_∞ , A_0 , A_t being the absorbance at 420 nm, at times infinite, 0, and t respectively, the variations of $\text{Log}((A_\infty - A_0)/(A_\infty - A_t))$ as a function of time are linear (5): the reaction of oxidation is pseudo first order with respect to cobalt (II) complex, the slope of $\text{Log}((A_\infty - A_0)/(A_\infty - A_t))$ as a function of time being the oxidation rate constant k . The variations of this constant K as a function of 8-quinolinol concentration show a decrease of the oxidation rate when the 8-quinolinol concentration increases (fig. 3). Thus, the extracted Co(II) complex is not the 1:2 cobalt(II) 8-quinolinol complex CoL_2 whose absorption maximum is located at 400 nm in non basic solvents (6)² but a complex in which cobalt is coordinated by both bidentate ligands L and molecules of extractant HL. $\text{CoL}_2(\text{HL})$ (7), $\text{CoL}_2(\text{HL})_2$ (8, 9) or $\text{Co}_2\text{L}_4(\text{HL})_2$ (2) have all been proposed by various authors. An increase of extractant concentration HL promotes the formation of these complexes which are more stable therefore less oxidizable than CoL_2 .

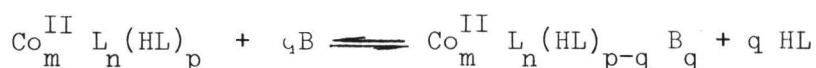


oxidation rate constant k as a function of 8-quinolinol concentration in the organic phase.

If the extraction is performed with Kelex 100, instead of 8-quinolinol, the organic phase shows an absorption maximum around 440 nm in non basic solvents, such as toluene, kerosene, benzene or 1-2 dichloroethane, but the position of this band doesn't change with time and stripping with diluted acids is impossible. These facts suggest that when cobalt is extracted with Kelex 100, the oxidation is as fast as the extraction (5).

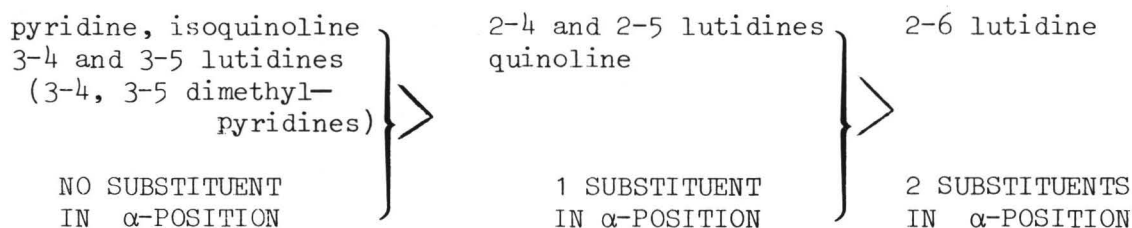
1.2 - Effects of donor compounds:

- The addition of various amounts of oxo donor compounds - that is to say compounds that donate electrons through an oxygen atom - to the organic phase after extraction by 8-quinolinol and separation of the two phases or before extraction by Kelex 100, produces a decrease of the oxidation rate. This effect follows the order trioctylphosphine oxide TOPO > tributyl phosphate TBP > octanol (5) that is in good accordance with the classification proposed by GUTMANN (1) which characterizes a donor compound by its donor number DN. The addition of these oxo donor compounds produces a shift of the absorption maximum of cobalt (II) complexes to the longer wavelengths, whereas the absorption band of the cobalt (III) complex is not modified. This shift indicates a change in the structure of the cobalt (II) complex, which can be explained by the acid-base properties of Co(II) atom and oxo donor compounds which are Lewis acid and Lewis base respectively. The Co(II) atom being an electron acceptor, bonds between Co(II) atom and donor compounds B are formed. These bonds which are stronger when B is a strong donor compound increase the stability of the cobalt (II) complex which becomes less oxidizable. The donor compounds effect can be represented as follows :



species extracted without
additives (immediately oxidized when HL=Kelex)

- The addition of compounds that donate electrons through a nitrogen atom also produces a decrease of the oxidation rate but the steric hindrance round the nitrogen atom of the donor compounds becomes the most important phenomenon. For instance, the effect of pyridine derivatives is dependent on the presence of substituent in the α position. Thus, with Kelex, the efficiency of these compounds (fig. 4) follows the order :



It can be noticed that the formation of self adducts $\text{Co L}(\text{HL})_{\text{p}}^{\text{n}}$ with 8-quinolinol is a similar phenomenon, 8-quinolinol being itselfⁿ a pyridine derivative.

The efficiency of amine compounds is dependent on both basicity and steric hindrance round nitrogen atom and follows the orders (fig. 4):

- primary amines > secondary amines > tertiary amines (inefficient)
(dodecylamine) (piperidine) (triisooctylamine)
- aliphatic amines > unsaturated amines > aromatic amines (inefficient)
(dodecylamine) (diallylamine) (aniline)

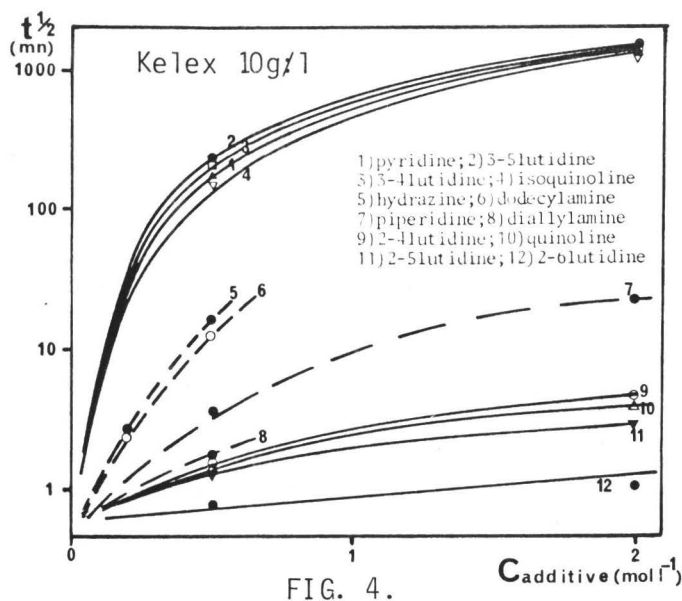


FIG. 4.

OXIDATION: time of half reaction as a function of additive concentration in the organic phase.

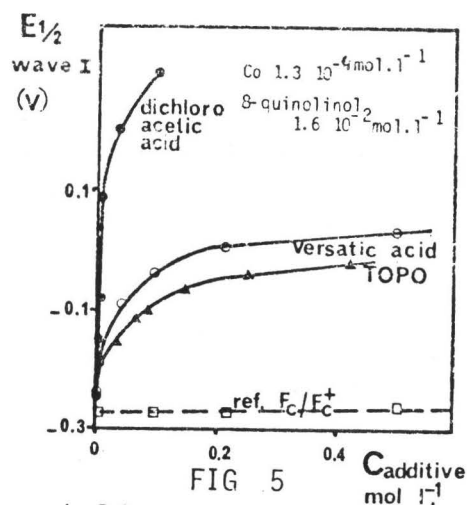


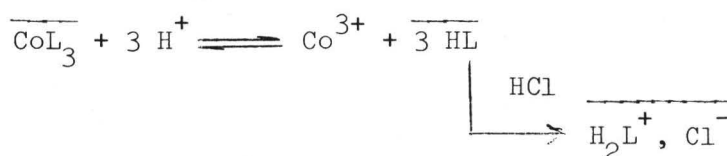
FIG 5

half wave potential as a function of additive concentration.

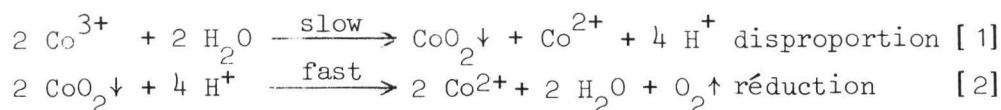
I.3 - Effects of acidic compounds : The addition of various amounts of acidic compounds, such as versatic-10 acid or dichloroacetic acid to the organic phase after extraction by 8-quinolinol and separation of the two phases, produces a decrease of the oxidation rate (5), shifts the absorption maximum of Co(II) complexes to lower wavelengths and shifts the wave I to anodic potentials (fig. 5). The decrease of oxidation rate and the potential shifts are more significant when the acid strength increases. These potential shifts can also be noticed after addition of donor compounds such as TOPO (fig. 5) that is in good accordance with kinetic studies. The same phenomenon of Co(II) complex stabilisation is observed when the extraction of cobalt is performed with Kelex 100 in a solvent containing Versatic 10 acid (5, 3).

I.4. - Stripping studies. Stripping studies confirm the previous effects. After extraction by Kelex 100 and stripping by H_2SO_4 1mol l^{-1} the stripping ratio is closed to zero. When Versatic 10 acid, TOPO or pyridine are added to the organic phase, the stripping equilibrium is reached in less than two minutes but the stripping ratio at equilibrium decreases when the time elapsed between the end of extraction and the beginning of stripping increases (5). These slow decreases of stripping ratio indicates that versatic acid, TOPO or pyridine delay the formation of the Co(III) complex CoL_3 which can't be stripped with diluted acids. On the other hand the stripping of CoL_3 with concentrated acids - particularly with HCl - is possible. The variations of the distribution coefficient D as a function of HCl concentrations in the organic phase are presented fig. 6. Two situations must be considered :

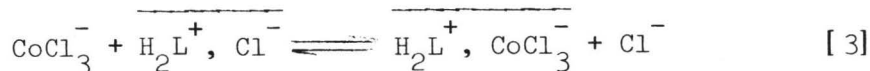
- HCl concentration < 6.5 M : HCl doesn't lead to the formation of anionic complexes and cobalt is stripped by the following reaction :



The stripping equilibrium is reached in 30 hours. Co^{3+} being unstable is slowly disproportionated (10), that leads to the formation of Co^{2+} :

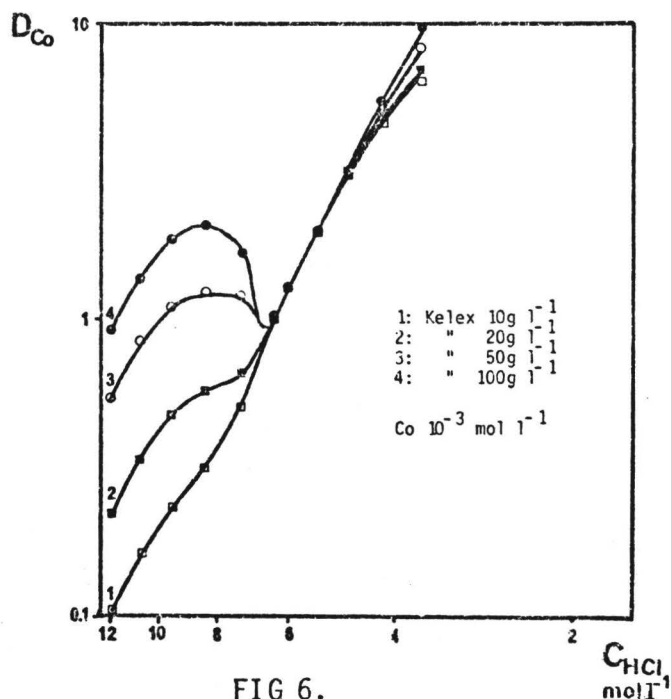


- HCl concentration > 6.5 M : An increase of HCl concentrations leads to the stripping of the Co(II) chloride complex CoCl_3^- . This reaction of "stripping and reduction" is very fast (less than 1 minute with 12 M HCl), but Kelex being in its protonated form H_2L^+ , acts as a tertiary amine and the chloride complex is extracted by the following reaction :



which is similar to those obtained with Ga(III) (11).

If toluene is replaced by kerosene or Solvesso, it becomes necessary to add octanol in order to avoid the precipitation of Kelex.



stripping of cobalt(III) with HCl.

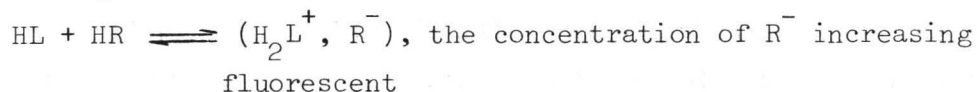
II - Extraction of cobalt from an acetate buffer : When cobalt is extracted from a borate buffer, by Kelex 100 in non donor solvents, the oxidation is as fast as the extraction and the absorption maximum of the cobalt (III) complex CoL_3 is located around 440 nm, whereas, the species extracted from an acetate buffer shows an absorption maximum around 390 nm in non donor solvents (band II masked by band I (fig. 7) and is quantitatively strippable with diluted acids. In this second case, it is possible to separate the two phases before oxidation of the Co(II) complex in the organic phase: Then, the characteristic band of the Co(III) complex CoL_3 (440 nm) appears very slowly

(fig. 7). The variations of $\text{Log}(A_{\infty}-A_0)/(A_{\infty}-A_t)$, where A_{∞} ; A_0 , A_t stand for the absorbances at 440 nm, as a function of time being linear, the reaction of oxidation is pseudo first order with respect to Co(II) complex. The oxidation rate constant K is dependant on the concentrations of Kelex 100, the excess of Kelex 100 being added to the organic phase, only after extraction as usual. The variations of this constant K as a function of $[\text{HL}]^2$ (where $[\text{HL}]$ stands for Kelex 100 concentration) being a straight line (5) the oxidation is pseudo second order with respect to Kelex 100. The addition of various amounts of acidic compounds to the organic phase, after extraction and separation of the two phases, produces a large decrease of the oxidation rate (fig. 8). This decrease is more important with strong acids and follows the order acetic acid $\approx$ benzoic acid $\approx$ versatic acid $<$ monochloroacetic acid $<$ dichloroacetic acid $\approx$ paratoluene sulfonic acid $<$ trichloroacetic acid $\approx$ methane sulfonic acid, that is to say the order of acidities.

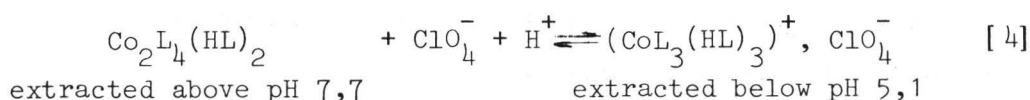
The addition of di 2-ethyl hexyl phosphoric acid (D_2EHPA) has the same effect as versatic acid.

Some authors (12) explain the effect of acidic compounds HR (versatic 10 especially) by the formation of a mixed Co(II) complex, very stable and poorly oxidizable, for example $\text{CoL}_2(\text{HR})_2$, where HR is bonded with cobalt atom. Donor compounds and acidic compounds lead to the same result, a decrease of the oxidation rate but; it's not very likely to explain the effect of these two kinds of additives by the formation of the same kind of complex. The formation of a bond located between acid molecules HR and Co(II) atom is not very likely. The effect of acidic compounds must be explained by the acid-base property of extractant and acidic compounds which are basic and acidic respectively.

Thus, after addition of acidic compounds the organic phase which contains Kelex 100, becomes fluorescent and shows an absorption maximum around 375 nm (Band I fig. 7). This maximum can be noticed even without cobalt in the organic phase and its absorbance increases when the concentration and the strength of the acid increase. This phenomenon well known with 8-quinolinol (13) is due to the protonation of Kelex 100. Thus, the addition of an acidic compounds HR, leads to the equilibrium :



when the concentration (or the strength) of HR increases. This increase of R^- promotes the formation of poorly oxidizable Co(II) - complexes which must contain R^- but not HR, ion-pair complexes $(\text{Co}_n\text{L}_p\text{HL}_q)^{(p-n)+}$, $(p-n)\text{R}^-$ being the most likely. SEKIDO et al. (2) reported a similar effect when cobalt is extracted by 8-quinolinol from a perchlorate solution :



III - Oxygenation and oxidation

A large number of cobalt chelates are capable of reversible reactions with molecular oxygen both in solution and in the solid state (14). This oxygenation is important in biological processes and the formation of binuclear oxygen complexes $\text{A}_2\text{Co} - \text{O}_2 - \text{Co} - \text{A}_2$ called "oxygen carriers", is well known.

During solvent extraction it seems that the reversible oxygenation is only the first step of an irreversible oxidation.

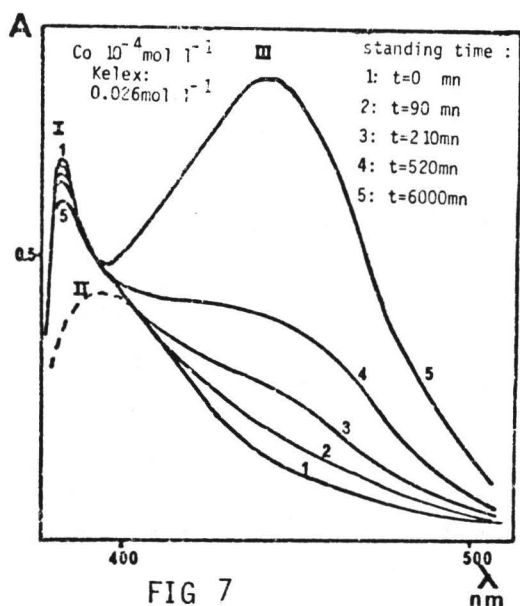


FIG 7
absorption spectra of cobalt-Kelex100 chelates in toluene: extraction from an acetate buffer.

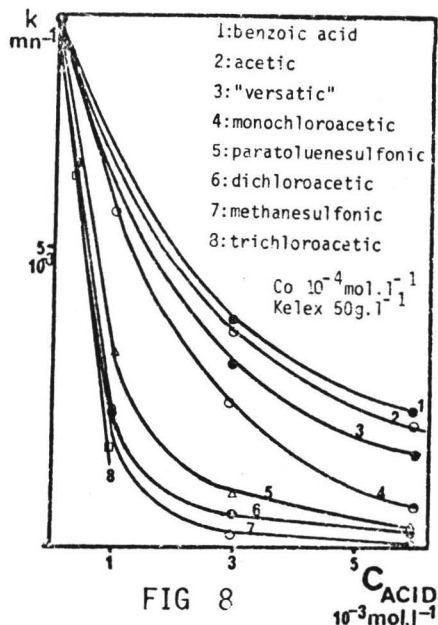
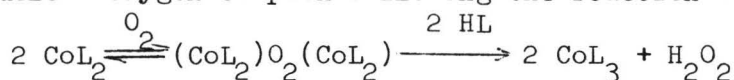


FIG 8
oxidation rate constant k as a function of acid concentration in the organic phase.

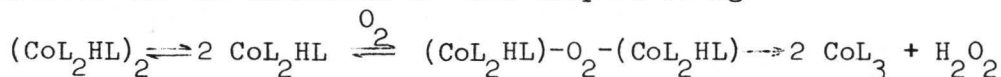
Thus, during solvent extraction by dialkyldithiophosphoric acids HL, the reaction of oxidation of the extracted complex CoL_2 is second order with respect to HL and to cobalt (4). These orders are in good accordance with the formation of a binuclear oxygen complex following the reaction :



the oxidation rate being :

$$v = k [(\text{CoL}_2)_2 \text{O}_2 (\text{L}_2 \text{Co})] [\text{HL}]^2 = k' [\text{CoL}_2]^2 [\text{HL}]^2 [\text{O}_2]$$

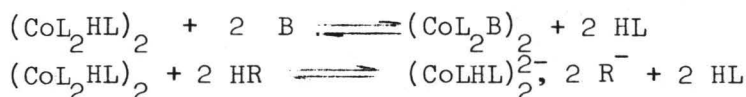
With 8-quinolinol and Kelex 100 the reaction is first order with respect to cobalt that suggests the extraction of a dimeric complex such as $(\text{CoL}_2 \text{HL})_2$, the oxygenation and the oxidation of this complex being :



with :

$$v = k [(\text{CoL}_2 \text{HL})_2 \text{O}_2 (\text{CoL}_2 \text{HL})] = k' [(\text{CoL}_2 \text{HL})_2]^1 [\text{O}_2]$$

With such an hypothesis, the action of donor compounds B and acidic compounds HR, must be represented as follows :



CONCLUSION

- The formation of mixed complexes with donor compounds is a way of enhancing the stability of cobalt (II) chelates. This phenomenon, which is due to the Lewis acid properties of the Co(II) atom, should be observed with other extractants (4).

- The stabilization of cobalt (II) chelates with acidic compounds is due to the basic properties of the extractant. This phenomenon should be observed only with extractants which can be protonated.

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ADSORPTION PHENOMENA AND THEIR EFFECTS ON THE MECHANISM
OF COPPER EXTRACTION BY HYDROXYOXIMES

Yagodin G.A., Ivakhno S. Yu.,
Tarasov V.V.
Mendeleev Institute of Chemical
Technology
Moscow, USSR.

"ABSTRACT". Employing various experimental technique a study has been made of the kinetics of copper extraction by commercial hydroxyoximes. The effect of certain adsorption phenomena has been studied on the kinetic characteristics of the extraction systems in question. It has been shown that the experimental results published elsewhere and those obtained by the authors could be explained within the framework of a heterogeneous chemical reaction of the hydroxyoxime second molecule addition to a positively charged intermediate complex, the reaction proceeding the mechanism of a direct impact and limiting the total process rate.

The amount of publications dealing with investigations into the kinetics and mechanism of metal extraction by hydroxyoximes is ever growing in the scientific literature(1)-(12). Considerable experimental data accumulated over recent years permit us to draw an unambiguous conclusion to the effect that the mass transfer process is in most cases limited by the slow chemical reaction. At the same time many important problems are still unsolved. It is not clear yet how and in which phase the limiting reaction proceeds, why its rate is slow, how to interpret the kinetic data (orders of reaction, activation energies etc.), according to what principle the catalysts should be selected and so on.

To our minds, a more thorough investigation into the effect of adsorption phenomena on the kinetics of copper extraction by hydroxyoximes could render a substantial help in solving these problems. These are dealt with in the present paper.

EXPERIMENTAL

Solutions of copper in sulphuric acid were prepared from blue vitriol of chemically pure grade (CP). The solutions of commercial hydroxyoximes, such as General Mills LIX64N and ABP-2 (13), in aliphatic (octane, grade CP) or aromatic (toluene, CP grade) diluents were used for the extraction.

The copper concentration in the aqueous phase was determined by a complexometric titration with murexide as indicator.

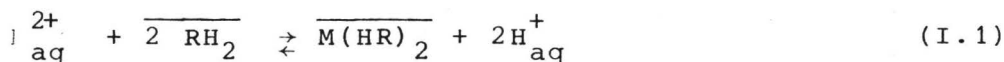
The dynamic interfacial tension in the extraction system was determined by Wilhelmy's equilibrium plate method to an accuracy of $\pm 0.2 \text{ dyn cm}^{-1}$.

To measure the interfacial viscosity a specially designed electromagnetic viscometer of pendulum type was used (14).

The kinetics of copper extraction by hydroxyoximes has been studied by three methods : (i) a short time contacting method (STCM) (15) ; (ii) under emulsion regime in a flow-through reactor with interfacial area determined photographically (16) ; and (iii) with the use of a diffusion cell with stirring (the phase contacting area being $2,03 \times 10^{-3} \text{ m}^2$, the volume of each phase $4,0 \times 10^{-5} \text{ m}^3$, and the stirring speed 120 r.p.m.).

MODEL

Let us consider the simplest case of the extraction of a bivalent metal M^{2+} by a single hydroxyoxime RH_2 . Taking into consideration the possibility of the formation in principle of two compounds of the type $M(HR)_2$ and MR we shall write a summarized equation of the reactions :



Here and subsequently components in the organic phase are distinguished by a superscript $\overline{}$ the subscript aq denotes those of the aqueous phase, and the subscript s the adsorbed compounds. The general scheme of the process with both ionized and unionized forms of the extractant participating could be presented as follows :



The experimental data and, in particular, the limiting order with respect to the concentration of protons, is close to - 1, giving evidence of the fact that the initial extraction rate is limited by a slow chemical reaction (1,9,10). Suppose that this reaction VI.2 could proceed either as : a reversible heterogeneous reaction in an adsorbed state (ss), as a reversible heterogeneous reaction involving a direct attack on a single adsorbed reactant (sv), or as a reversible homogeneous reaction in adjacent layers of the aqueous phase (vv).

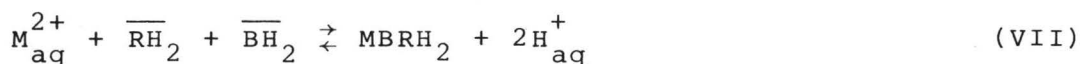
The respective kinetic equations take the following form (17)

$$W = k \underline{K}_{(IV.2)} \left(\frac{C_{M^{2+}} \bar{C}_{RH_2}^2}{C_{H^+} A^v} - \frac{1}{\underline{K}_{(I.1)}} \cdot \frac{\bar{C}_{M(HR)_2} C_{H^+}}{A^v} \right) \quad (1)$$

$$\text{where } A = 1 + b_{RH_2} \bar{C}_{RH_2} + b_{RH^-} C_{RH^-} + b_{R^{2-}} C_{R^{2-}} + b_{MHR^+} C_{MHR^+} + b_{MR} \bar{C}_{MR} + b_{M(HR)_2} \bar{C}_{M(HR)_2} + b_z C_z,$$

b = adsorption coefficient, C = concentration, $\underline{K}$ = the equilibrium constants of the respective reactions, k = the normalized constants of the reaction rates, A = the adsorption factor, z = the index denoting surface-active admixtures, and $v = 2$ for ss-reaction, $v = 1$ for xv-reaction, $v = 0$ for vv-reaction.

In the case where a catalyst is present in the system together with the extractant, it is logical to consider, as the authors of the papers (1,7,10) do, that the former participates in the limiting stage with a subsequent re-solvation of a mixed intermediate complex in the organic phase and that this reaction route becomes the rate-controlling step. The kinetic equations are similar to (1), but they include in place of $\bar{C}_{RH_2}^2$ the product $\bar{C}_{RH_2} \bar{C}_{BH_2}$, and in place of $\underline{K}_{(I.1)}$ the $\bar{C}_{RH_2}$ equilibrium constant $\underline{K}_{(VI.1)}$ of the reaction



The factor A accounts for the adsorption of the catalyst itself in the form of neutral molecules BH_2 and anions BH^- and B^{2-} , as well as the adsorption of the intermediate complex $MBRH_2$.

It is known (10), that oximes undergo polymerization in many organic solvents. If we consider polymerization in terms of the reaction

$$\bar{RH}_2 \rightleftharpoons \frac{1}{m} (\bar{RH}_2)_m, \quad (VIII)$$

then the concentration of monomeric forms will be given by :

$$\bar{C}_{RH_2} \sim (C_{RH_2}^o)^{1/m} \frac{1}{\underline{K}_X^{1/m}} \quad (2)$$

This value could be substituted into the kinetics equation (1). We should do the same if the catalyst polymerizes.

The matter gets more complicated when one of the extractives or, which is more probably, one of intermediate or by-products undergoes polymerization, for instance :

$$\bar{MB} \rightleftharpoons \frac{1}{p} (\bar{MB})_p \quad (IX)$$

This is tantamount to the decrease in the free catalyst concentration C_{BH_2} which now is determined by the equation :

$$p \frac{K^p_{(IX)}}{K^p_{(X)}} \frac{C^p_{M^{2+}}}{C^{2p}_{H^+}} \bar{C}^p_{BH_2} + \bar{C}_{BH_2} - \bar{C}^o_{BH_2} = 0 \quad (3)$$

where $\bar{C}^o_{BH_2}$ is the analytical concentration of the catalyst in the organic phase, $\bar{C}_{BH_2}$ is the concentration of monomeric forms of the catalyst, p is the degree of polymerization, and $K_{(X)}$ is the equilibrium constant of the reaction



The equation (3) will be solved together with equations (I), since in the general case this is possible by numerical methods. The polymerization of compounds MR , $M(RH)_2$, $M(BH)_2$ etc. is taken into account in a similar way.

DISCUSSION

1. The Limiting Reaction Orders.

Consider the case of the extraction of copper from sulfuric acid solutions by the hydroxyoxime LIX65N. The adsorption coefficients required for calculating the adsorption factor A , viz. $b_{R_2H_2}$ and b_{RH} , could be determined from the interfacial tension isotherms determined for the pure extractant at various values of the aqueous phase pH. The interfacial tension in the system H_2SO_4 (aqueous solution)-LIX65N (in toluene or heptane solution) is practically constant within the pH range 2 to 5 (18). Since all the kinetic results under discussion are obtained in this very range of pH, we neglect the contribution of ionized forms of the extractant to the factor A . The parameters (Table 1) were determined graphically from literature values (18) by means

Table 1

THE ADSORPTION CHARACTERISTICS OF LIX65N AND LIX63.

N°	Hydroxyoxime	$b_{RH_2}, m^3 \text{ kmol}^{-1}$	$\Gamma_{\infty}, \times 10^9 \text{ kmol m}^{-2}$
1	LIX65N-anti-form in toluene	720	1,15
2.	LIX65N-sin-form in toluene	980	1,10
3.	LIX63 in toluene	780	0,98
4.	LIX65N-anti-form in hexane	40000	1,70
5.	LIX63 in hexane	9600	1,50

NOTE : aqueous phase - H_2SO_4 solution (pH = 2.0).

of a combination of the Gibbs and Langmuir adsorption isotherms. The values of Γ_{∞} do not differ much from each other (Table 1), the adsorption is evidently close to the Langmuir one. As regards copper oximates, they, as it is well known (6), are considerably less surface-active than oxime itself, whereas under the conditions we are interested in compounds of the type CuR are scarcely formed at all (1,10). Therefore, the contribution of the reaction products to the adsorption factor is also small, especially at a negligible degree of the extractant saturation by metal. The b_{CuRH^+} coefficient more readily satisfies the inequality $b_{\text{Cu(RH)}_2} < b_{\text{CuRH}^+} < b_{\text{RH}_2}$, and since $C_{\text{CuRH}^+} \ll \bar{C}_{\text{RH}_2}$, then $b_{\text{RH}_2} \cdot \bar{C}_{\text{RH}_2} \gg b_{\text{CuRH}^+} \times C_{\text{RHCu}^+}$. The dominating contribution to the adsorption factor is made by unionized forms of the hydroxyoxime, therefore

$$A \approx 1 + b_{\text{RH}_2} \times \bar{C}_{\text{RH}_2} \quad (4)$$

Taking into account that neither LIX65N, nor its complex with Cu polymerize in aromatic hydrocarbons (10), the kinetic equations are to be used in the form of (1). The order for the extractant $\vec{n}_{\text{RH}_2} \rightarrow 1$ (1) gives evidence in favour of a direct attack heterogeneous reaction. Indeed for the anti-form of LIX65N in toluene at $\bar{C}_{\text{RH}_2} = 0.005$ to 0.05 kmol m^{-3} (1) the degree of saturation of the adsorption layer with the extractant varies between 81 to 98 % (an equal content of both active anti- and inactive syn-isomers being assumed). In that case the rate of a heterogeneous reaction in an adsorbed state (ss) should almost be independent of the oxime concentration, whereas for a homogegeous interaction in the aqueous phase the order $\vec{n}_{\text{RH}_2}$ should be close to 2 (see (1)). In the presence of aliphatic LIX63 which does not change the copper distribution coefficients in LIX65N and is added as a catalyst (1,3,10) the factor A includes the produce $b_{\text{BH}_2} \times C_{\text{BH}_2}$, and the kinetic equation should be written in the form:

$$W^{\text{sv}} = \vec{k}^{\text{sv}} \frac{K_{\text{(IV.2)}}}{K_{\text{(IX)}}} \frac{C_{\text{Cu}^{2+}} \bar{C}_{\text{RH}_2} \bar{C}_{\text{BH}_2}}{C_{\text{H}^+} (1 + b_{\text{RH}_2} \bar{C}_{\text{RH}_2} + b_{\text{BH}_2} \bar{C}_{\text{BH}_2})} \frac{1}{\bar{C}_{\text{MBRH}_2} C_{\text{H}^+}} \frac{1}{(1 + b_{\text{RH}_2} C_{\text{RH}_2} + b_{\text{BH}_2} C_{\text{BH}_2})} \quad (5)$$

The order for Cu^{++} and H^+ should be maintained as before $\vec{n}_{\text{Cu}^{2+}} = 1$; $\vec{n}_{\text{H}^+} \approx -1$; $\vec{n}_{\text{H}^+} \approx 1$, while for the extractant they should be somewhat lower, which has been observed experimentally (1,2,10). The order for the catalyst $\vec{n}_{\text{BH}_2} \approx 1$ (average for LIX65N syn- and anti-isomers), $b_{\text{BH}_2} = 780 \text{ m}^3 \text{ kmol}^{-1}$, $C_{\text{RH}_2} = 0.25 \text{ kmol m}^{-3}$, $C = 0.01$ to 0.1 kmol m^{-3} (1), should approach

1 owing to a minor fraction of LIX63 in the adsorption layer which practically increases in proportion to $\bar{C}_{BH_2}$. The actual order $\bar{n}_{BH_2} \approx 0.5$ (1) is most evidently explained by the polymerization of the CuB complex which proceeds in toluene at $\bar{C}_{BH_2} < 0.16 \text{ kmol m}^{-3}$ (19). The set of equations (5) and (3) at $p \approx 2$ (19) gives $\bar{n}_{BH_2} \approx 0.5$, which agrees with experiment.

In aliphatic diluents hydroxyoximes are, as a rule, polymerized (I.10), which should be taken into account by means of equation (6). The orders for the extractant and catalyst should decrease, and that is found to be the case in practice (2,10).

As to the commercial extractants (LIX64N, Kelex 100, ABP), a strict calculation of the adsorption parameters b_{RH_2} and Γ_∞ is difficult owing to the presence of impurities. RH_2 The magnitude of adsorption factor in this case depends mainly on the concentration of ionized oxime and surface active impurities in the organic phase, i.e.

$$A = 1 + b_{RH_2} \bar{C}_{RH_2} + b_Z \bar{C}_Z \quad (6)$$

The substitution of (6) instead of (4) should not affect the orders for metal and hydrogen, and the orders remain as before (1,4), (Table 2). Moreover, the values $\bar{n}_{Kelex}$ are 0.92 to 1.04 (20).

Table 2

LIMITING REACTION ORDERS IN COPPER EXTRACTION BY HYDROXYOXIMES.

Extractant diluent RH_2		Concentration range ^a		Orders		
		pH	$C_{RH_2} \text{ kmol m}^{-3}$	n_{Cu}	n_{H^+}	n_{RH_2}
1. STCM	ABP ^b	2.7-3.15	0.001-0.10	1	-0.88	0.36
2. STCM	ABP ^b	3.15-4.8	0.10	-	-	-
3. STCM	ABP ^c	2.75	0.001-0.10	-	-	0.33
4. STCM	LIX64N ^b	2.95	0.001-0.10	-	-	0.32
5. Diff. cell	ABP ^b	3.5-4.8	0.025-0.12	1	-0.7	1.5

^a for N° 1 $C_{Cu} = 0,003-0,012$ for N° 2,3,4 ; for N° 5 $C_{Cu} = 0,008-0,004$.

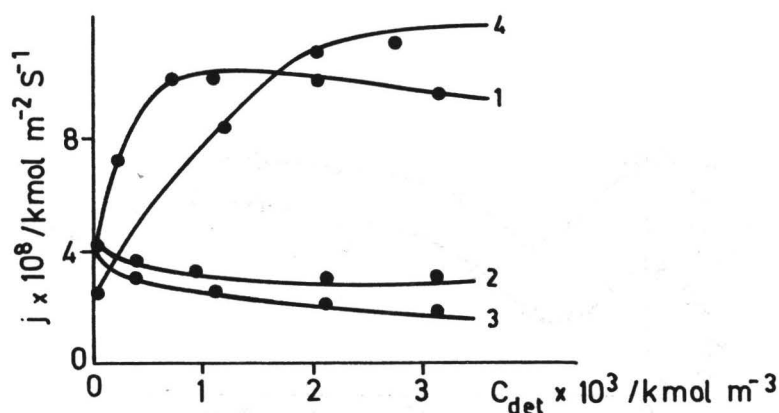
^b diluent - octane.

^c diluent - toluene.

The values $\bar{n}_{ABP}$ in toluene ≈ 0.83 , $\bar{n}_{ABP}$ in octane ≈ 0.36 also comply with the analogous characteristics of LIX65N.

2. The Effects of Adsorption Films on the Extraction Kinetics.

The addition of surfactants considerably affect the rate of a heterogeneous chemical reaction controlling the total rate of copper extraction by hydroxyoximes. On one hand the surfactants compete with an oxime during the adsorption process and partially expel it from the interfacial layer and reduce the rate of the extraction. On the other hand, the ionogenic surfactants are capable of imparting an electric charge to the interface thus affecting the surface reaction proceeding with the participation of charged particles (21). It has been established experimentally (Fig. 1) that the anion active surfactants (laurylsulphate of sodium), negatively charging the surface, accelerate copper extraction by ABP, LIX64N, and other hydroxyoximes. With the cationic-active compounds (cetyltrimethyl ammonium bromide), a reverse picture is observed. The non-ionogenic dodecanol also decreases the initial rate, but not so abruptly (Fig. 1). Most probably, the electrostatic effects are decisive, and this fact directly confirms the correctness of identifying the limiting stage as that in which the second molecule of extractant adds on to the positively charged intermediate complex. It should be stressed herewith, that the anion-active surfactants are effectively catalyzing the extraction in emulsions as well, and here they enhance not only the limiting stage, but also the interfacial surface area by as much as 1.3 to 1.5 fold.

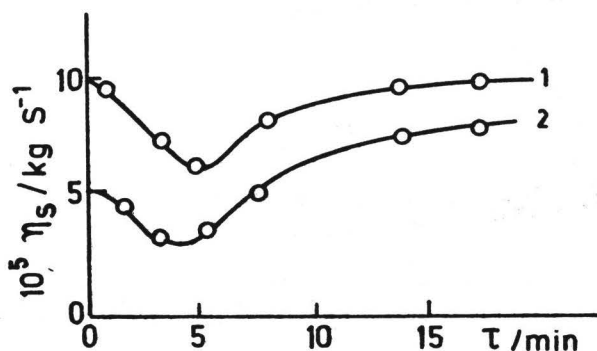


The effect of low molecular weight surfactants on the initial rate of copper extraction by ABP(1,2,3) and by LIX64N (4).

$C_{\text{Cu}} = 0.002 \text{ kg-at m}^{-3}$; $\text{pH} = 2.95$; $\bar{C}_{\text{ABP}} = 0.1 \text{ kmol m}^{-3}$;
 $\bar{C}_{\text{LIX64N}} = 0.5 \text{ kmol m}^{-3}$; diluent was octane ; 1 and 4, sodium laurylsulphate ; 2, dodecanol ; 3, cetyltrimethylammonium bromide.

Compounds forming condensed interfacial films at the interface (proteins, zirconium sulfate complexes) are capable of sharply decreasing the rate of the extraction process both at short time phase contacting and in the emulsion state, a correlation being observed between the durability of a film and its delaying activity.

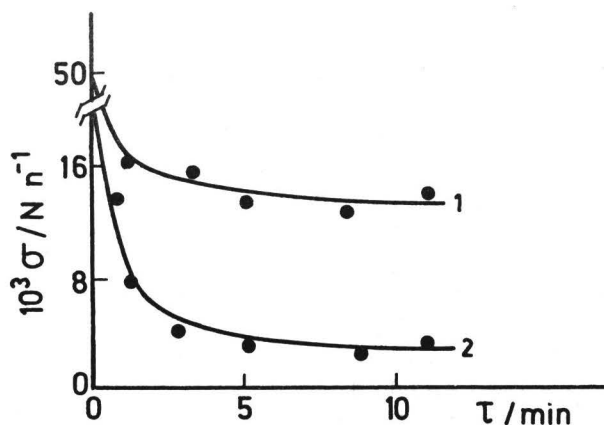
In the extraction systems under discussion an important role is played by the interfacial films consisting of the basic, indispensable components of a system comprising copper complexes with various addenda. The hypothesis of the formation at the interface of an intermediate, surface-blocking compound $\text{Cu}(\text{LIX65N})_2$ during copper extraction has been suggested by Fleming (cited from (6)). Afterwards Flett (6) did not succeed in establishing its validity, so the matter remained unsolved. Our experiments have proved that copper, like Zr when extracted by HDEHP (22,23), stops getting extracted by ABP in a diffusion cell long before equilibrium is attained. At the same time, measurements of the interfacial viscosity made it possible to reveal condensed interfacial films formed in the system under study. The values of the rheological parameters are not readily reproducible and are very dependent on the previous history of the aqueous phase. Evidently, hydrolyzed copper complexes, responsible for the film formation after a long (several hours) hold-up of the aqueous solution, adsorb even at their interface with the air, which results in an enhancement of the surface viscosity (fig. 2). Following its being contacted with the organic phase the adsorbed layer is destroyed, a new interfacial film being formed possibly with participation of the hydroxyoxime. As a result the interfacial viscosity at first drops, then increases again (Fig. 2).



Interfacial viscosity as a function of time at the surface between aqueous copper solutions in sulphuric acid and solutions of LIX64N (1) and ABP (2) in octane.

$C_{\text{Cu}} = 0.026 \text{ kg-atm}^3$; $\text{pH} = 2.03$; $C_{\text{LIX64N}} = 0.09 \text{ kmol m}^{-3}$;
 $C_{\text{ABP}} = 0.10 \text{ kmol m}^{-3}$.

When discussing the reasons for the low rate of copper extraction by hydroxyoximes, the data on the dynamic interfacial tension in the aqueous sulphuric acid copper-hydroxyoxime system could prove rather useful. Hughes et al. (26) have established that the value σ in this system is only slightly dependent on the time τ elapsed after contacting the phases. However, the measurements were taken only for $\tau > 3$ min. Our experiments have shown, that the value of σ decreases markedly during the initial moments (up to 3 to 4 min.) after phase contacting, but afterwards actually reaches a constant value. The curves representing time-dependent variations in the interfacial tension, measured both by means of the Wilhelmy plate and by a stalagmometer, for solutions of two commercial extractants in octane are given in Fig. 3. The minimum values of the interfacial viscosity in the sulphuric acid-aqueous solution of copper - ABP solution in octane system corresponded to the same time interval (3 to 5 minutes). Evidently, the time period of several minutes is required for a complete adsorption of the extractant. The slow adsorption of oximes, in its turn, which undoubtedly proceeds at their so high concentration in the kinetic regime, is most probably controlled by steric factors that could arise also at the formation of the extractable metal complexes. SME-529 which is less branched, and extracts copper more readily than LIX64N, has a higher surface activity and adsorbs faster (Fig. 3).



Interfacial tension as a function of time at the interface between aqueous solution of H_2SO_4 ($\text{pH} = 2.01$) and octane during the hydroxyoxime adsorption.

1, $C_{\text{LIX64N}} = 0.09 \text{ kmol m}^{-3}$; 2, $\bar{C}_{\text{SME-529}} = 0.10 \text{ kmol m}^{-3}$.

CONCLUSIONS

The experimental data obtained on the kinetics of the extraction of copper by hydroxyoximes agree well with the hypothesis that the second molecule of the extractant adds on in an interfacial chemical reaction to a positively charged complex. However, in order to draw a final conclusion with regard to the localization of this reaction it is necessary to consider

diffusion-kinetic equations, the latter accounting for the multistage process and its reversibility and describing the transient regime of a similar homogeneous reaction proceeding in the aqueous phase layers adjacent to the interface.

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SOLVENT EXTRACTION KINETICS OF COPPER BY BENZOYLACETONE

Kazuo Kondo, Teruo Tsuneyuki
and Fumiyuki Nakashio

Department of Organic Synthesis
Kyushu University

Fukuoka 812, Japan

ABSTRACT Studies of the extraction of copper by benzoylacetone were conducted in a stirred transfer cell. It was found that: (1) the initial rate of copper extraction varied inversely as the 0.5 power of hydrogen-ion concentration in the low pH range, but in the high pH range was not affected by hydrogen-ion concentration, (2) the rate was proportional to benzoylacetone concentration in the low pH range, but the rate was scarcely affected by benzoylacetone concentration in the high pH and benzoylacetone concentration ranges, (3) the rate was proportional to the square root of copper concentration in the low pH range and to copper concentration in the high pH range. These results are consistent with a model of copper extraction mechanism, which is presented.

INTRODUCTION

Solvent extraction of metals with chelating agents such as LIX or Kelex reagents(1,7,10,14) has recently attracted practical interest through nuclear, hydrometallurgical and waste-water treatment processes(2,3,8). In the design of extractor in these processes, a knowledge of extraction kinetics is necessary in addition to a knowledge of extraction equilibrium.

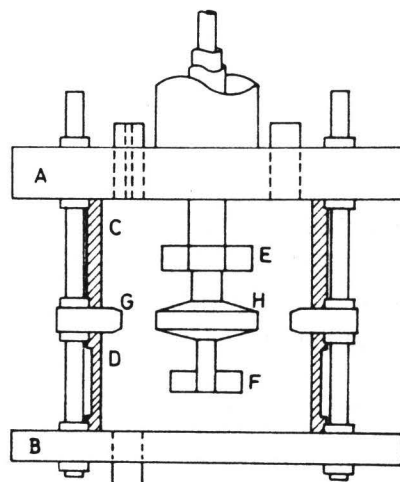
In the present work, the extraction of copper by benzoylacetone in benzene solution was carried out using a stirred transfer cell, and the effect of chelating agent concentration on extraction rate was examined experimentally and theoretically. Then, using the reaction rate constant and the mass transfer coefficient obtained, the experimental results were simulated. Lastly, the mass transfer coefficients were correlated with the stirring speed.

EXPERIMENTAL

Experimental Apparatus

The stirred transfer cell used is shown in FIG. 1. Each compartment had

T. Tsuneyuki is at Kitakyushu Technical College, Kitakyushu 803.



A,B upper and lower flange
 C cylindrical glass wall
 D cylindrical stainless wall
 E,F impeller
 G,H partition plate

FIG. 1

Sketch of the stirred transfer cell

a volume of 120 ml and the area of the interface, A, was 15.3 cm^2 . The aqueous and organic phases in the two compartments were stirred independently by two flat-blade stirrers in opposite directions with equal velocities.

Experimental Procedure

The aqueous solution was prepared by dissolving commercial GR grade copper nitrate in deionized water. The pH of the aqueous solution was adjusted using 1.0 mol/l ammonium nitrate-ammonium hydroxide solution. The ionic strength of the solution was maintained constant during extraction. The organic solution was prepared by dissolving benzoylacetone in benzene purified by distillation. Benzoylacetone was distilled under reduced pressure in an atmosphere of nitrogen.

The aqueous solution was first introduced to the transfer cell from a burette fitted with a constant-temperature jacket, and then the organic solution was placed carefully in such a way as not to disturb the interface. About six small samples (1.0 ml) were taken at intervals from the organic phase, these volumes being too small to affect appreciably the conditions in the cell. The copper concentration was determined by atomic absorption spectrochemical analysis. Using these results, the copper concentration in the aqueous phase was obtained by material balance.

The extraction rates were measured at 30°C under the following conditions: benzoylacetone concentration, C_{HB_0} , was 0.0025–0.050 mol/l, copper concentration, C_{M_0} , 0.0015–0.025 mol/l, pH range 4.5–8.5 and stirring speed, N, 50–200 rpm.

RESULTS

Typical relations between the extent of copper extracted, x, and time are shown in FIG. 2. It is evident from FIG. 2 that the extraction rate increased with pH.

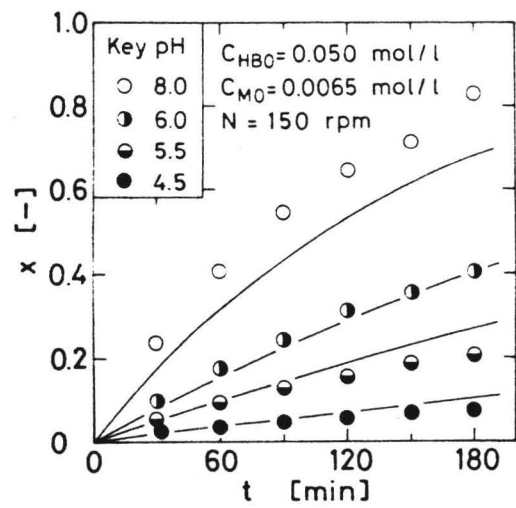


FIG. 2

Relation between extent of copper extracted and time, as a function of pH

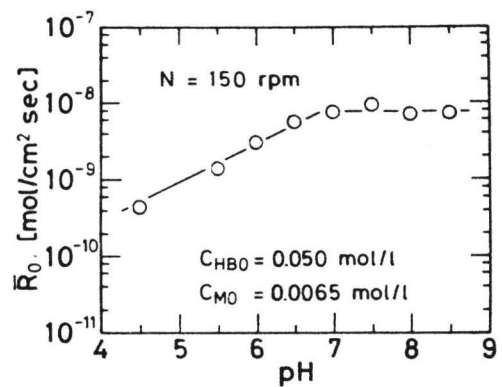


FIG. 3

Effect of pH on initial extraction rate

The effect of pH on the initial extraction rate, $\bar{R}_0$, is shown in FIG. 3. The initial extraction rate was obtained using the same manner as in a previous paper(4). As shown in FIG. 3, the initial extraction rate varied inversely as the 0.5 power of hydrogen-ion concentration, C_H , in the low pH range, but in the high pH range was not affected by hydrogen-ion concentration. Therefore, it was anticipated that the extraction mechanism in the high pH range was different from that in the low pH range.

The effect of benzoylacetone concentration on the initial extraction rate is shown in FIG. 4. From the figure, it was found that the initial extraction rate was proportional to the concentration of benzoylacetone in the low pH range but that the rate was scarcely affected by benzoylacetone concentration in the high pH and benzoylacetone concentration ranges.

The effect of copper concentration on the initial extraction rate is shown in FIG. 5. From the figure, it was evident that the initial extraction rate was proportional to the concentration of copper at pH = 7.5 and to the square root of the copper concentration at pH = 5.5.

The effect of stirring speed on the initial extraction rate is shown in FIG. 6 at three pH values. It was clear from these results that the initial

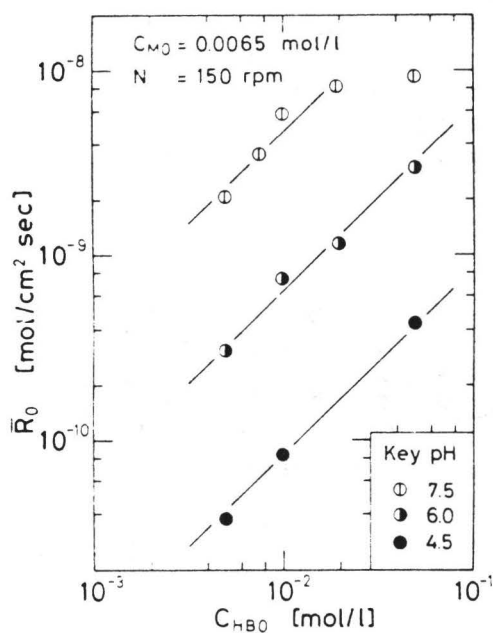


FIG. 4
Effect of benzoylacetone concentration on initial extraction rate

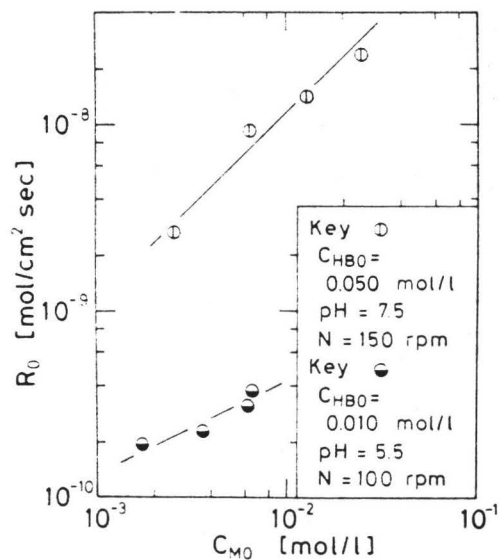


FIG. 5
Effect of copper concentration on initial extraction rate

extraction rate depended fairly strongly on the stirring speed in the high pH range, but that the effect of stirring speed on the rate became weak with decreasing pH value.

These results suggest that the initial extraction rate was slightly affected by diffusion in the low pH range, but that in the high pH range was fairly strongly affected by diffusion.

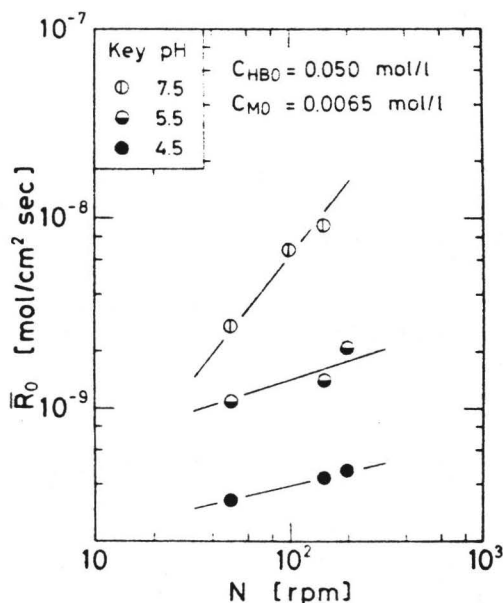


FIG. 6
Effect of stirring speed on initial extraction rate

DISCUSSION

Effect of Diffusion on the Copper Extraction Rate

The extraction mechanism of copper by a chelating agent has been generally considered to be as follows(1). The chelating agent in the organic solution dissolves into the aqueous phase to produce the chelating agent anion and proton by dissociation. The water molecule coordinated to copper ion is replaced by the chelating agent anion to form the metal chelate extracted into the organic phase. With the assumption that copper mono-complex formation reaction with benzoylacetone is the rate-controlling step, the reaction rate, r , can be expressed(4) as

$$r = (k_3 K_2 / C_H) C_M C_{HB} \quad (1)$$

where k_3 is the reaction rate constant of copper mono-complex formation, K_2 is the dissociation constant of benzoylacetone, and C_{HB} is the benzoylacetone concentration in the aqueous phase.

It is evident that the experimental results cannot be explained by Eq. (1). As mentioned before, the experimental results have to be analyzed by taking account of the diffusion accompanying the reaction between copper ion and chelating agent anion in the aqueous phase close to the interface. Basic equations based on the film model are written as follows.

$$D_{HB} (d^2 C_{HB} / dy^2) - 2(k_3 K_2 / C_H) C_M C_{HB} = 0 \quad (2)$$

$$D_M (d^2 C_M / dy^2) - (k_3 K_2 / C_H) C_M C_{HB} = 0 \quad (3)$$

These differential equations are subject to four boundary conditions:

$$\left. \begin{aligned} y = 0 : C_{HB} &= C_{HB}^*, \quad dC_M/dy = 0 \\ y = \delta : C_{HB} &= 0, \quad C_M = C_{M_0} \end{aligned} \right\} \quad (4)$$

where D_i is the diffusion coefficient of i component, C_{HB}^* is the benzoyl-acetone concentration in the aqueous phase adjacent to the interface, which is in equilibrium with the concentration in the organic phase, and δ is the thickness of film.

No analytical solution of these basic equations is available, but Porter (9) solved the equations numerically and presented an approximate solution as follows.

$$E = 1 + (E_i - 1)[1 - \exp\{-(\sqrt{M} - 1)/(E_i - 1)\}] \quad (5)$$

where E is the enhancement factor, E_i is the limiting value of E for instantaneous reaction, and M is the modulus describing the ratio of the reaction rate to the mass transfer rate, as follows.

$$E = \frac{\bar{R}_0}{k_L C_{HB}^*}, \quad E_i = 1 + \frac{2D_M C_{M_0}}{D_{HB} C_{HB}^*}, \quad \text{and} \quad M = \frac{D_{HB} k_3 K_2 C_{M_0}}{k_L^2 C_H} \quad (6)$$

where k_L is the mass transfer coefficient of benzoylacetone in the aqueous phase.

In a region where the reaction is pseudo-first order, E is almost equal to $\sqrt{M}$. Accordingly, from Eq.(6) the following equation is derived:

$$\bar{R}_0 = C_{HB}^* (D_{HB} k_3 K_2 C_{M_0} / 4 C_H)^{1/2} \quad (7)$$

On the other hand, in a region where the reaction is instantaneous, E is almost equal to E_i . Therefore, the following equation is derived from Eq.(6), by taking account of $C_{HB}^* \ll C_{M_0}$:

$$\bar{R}_0 = k_L (D_M / D_{HB}) C_{M_0} \quad (8)$$

Equation (7) shows that the initial extraction rate is proportional to the concentration of benzoylacetone, and that the rate varies as the 0.5 power of the copper concentration and inversely as the 0.5 power of the hydrogen ion concentration. On the other hand, Eq.(8) shows that the initial extraction rate is proportional to the concentration of copper and is affected by the stirring speed. Accordingly, the experimental results in the low pH range can be explained by Eq.(7) and those in the high pH range by Eq.(8).

The reaction rate constant and the mass transfer coefficient could be calculated from the experimental results at constant stirring speed and Eq. (5), that is, $k_3 = 5.2 \times 10^8$ 1/mol sec and $k_L = (5.6 \pm 0.4) \times 10^{-4}$ cm/sec in the case of 50 rpm, by using the values of $D_{HB} = 0.84 \times 10^{-5}$ cm²/sec (15), $D_M = 0.72 \times 10^{-5}$ cm²/sec (12), and $K_2 = 1.1 \times 10^{-9}$ mol/l (11). In the cases of 100

rpm and 150 rpm, the values of $k_L = (8.8 \pm 2.0) \times 10^{-4}$ cm/sec, and $(9.8 \pm 2.7) \times 10^{-4}$ cm/sec were obtained, respectively.

The values of the coefficients k_3 and k_L which were determined in this study were employed in the presentation of the experimental data as a plot of E vs $\sqrt{M}$ which is shown in FIG. 7. $E_i = 1500, 890$ and 420 correspond to $C_{M_0} = 0.0063$ mol/l, 0.0037 mol/l and 0.0018 mol/l, respectively. The solid lines in

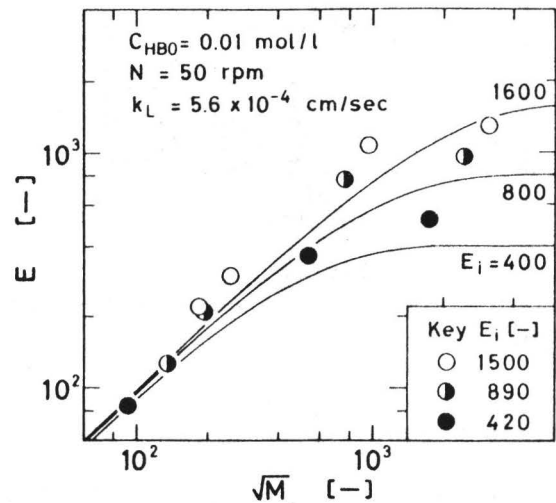


FIG. 7
Relation between E and $\sqrt{M}$ in the case of 50 rpm

FIG.7 were calculated from Eq.(5). It is considered that the experimental results could be explained by the present model.

Simulation for the Extraction of Copper in the Stirred Transfer Cell

The experimental data obtained can now be simulated in terms of the extraction mechanism which is presented.

The change of copper concentration with time can be expressed as

$$V_W C_{M_0} (dx/dt) = A \bar{R} \tag{9}$$

where V_W is the volume of the aqueous phase. From Eqs.(6) and (9), the following equation can be derived.

$$dx/dt = (A/2V_W) K_1 k_L E (C_{HB} / C_{M_0}) \tag{10}$$

where K_1 is the partition constant of benzoylacetone, 7.24×10^{-4} (11). Taking account of Eq.(5), Eq.(10) can be solved by the Runge-Kutta method, with the initial condition being $x = 0$ at $t = 0$. The values of the constants used in the calculation are as presented above. Comparison of the experimental data with calculated results is shown in FIG. 2 for the case 150 rpm. The solid lines represent the calculated results. The calculated values are in good agreement with the experimental results in the cases where the extraction rate of copper is low.

In FIG.8, comparison of the extent of copper extracted between the ob-

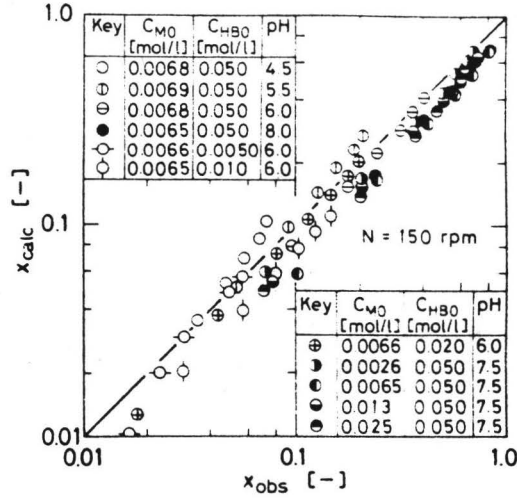


FIG. 8

Comparison of extent of copper extracted between the observed and the calculated

served and the calculated is shown. It is evident that they can be fitted within about $\pm 30\%$.

Correlation of the Mass Transfer Coefficients with the Stirring Speed

The mass transfer coefficients obtained can be correlated with the stirring speed. McManamey(6) presented the following correlation between Sh and Re .

$$Sh_1 = C_8 (Sc_1)^{0.5} We_1^2 [Re_1 + \left(\frac{\nu_2}{\nu_1}\right) Re_2]^{0.5} \left[1 + \left(\frac{\rho_2 \nu_2^2}{\rho_1 \nu_1^2}\right) \left(\frac{Re_2}{Re_1}\right)^2\right]^{0.5} \quad (11)$$

where

$$\left. \begin{aligned} Sh_1 &= k_{L1} L_1 / D_1, \quad Sc_1 = \nu_1 / D_1, \\ We_1 &= N_1 L_1 (\rho_1 L_1 / \sigma_{eq})^{0.5}, \quad Re_i = L_1^2 N_1 / \nu_i \quad (i = 1, 2) \end{aligned} \right\} \quad (12)$$

C_8 is a constant, ν_i and ρ_i are the kinematic viscosity and the density of i phase, respectively. σ_{eq} is the interfacial tension defined by the following equation(6).

$$\sigma_{eq} = \sigma + 0.00562 L_1^2 |\Delta\rho| g \quad (13)$$

where g is acceleration of gravity. L_1 is the length of stirrer blade, in this work, $L_1 = 2.5$ cm and $L_2 = 3.0$ cm. Equation (11) is derived based on an extension to liquid-liquid mass transfer of the Levich model(5) for the approach of an eddy to a free surface. In FIG. 9, k_L ($\equiv k_{L1}$) obtained in this work were plotted according to Eq.(11). In the figure, the mass transfer coefficients in Amberlite LA-2-hydrochloric acid system, obtained by the authors, and those in ethyl acetate-water and n-butanol-water systems by McManamey(6) were plotted too. Since the experimental conditions in Amberlite LA-2-hydrochloric acid system correspond to the region of instantaneous reaction(13), the mass transfer coefficients in the aqueous phase were obtained by using the same stirred transfer cell. McManamey determined both k_{L1} and

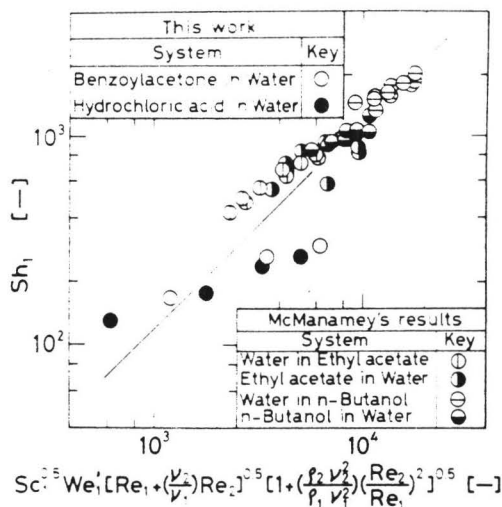


FIG. 9
Effect of stirring speed on mass transfer coefficient

k_{L2} in the same experiment using the mutual saturation technique. It is found from FIG.9 that the mass transfer coefficient obtained can be correlated using McManamey's equation. In other words, it is suggested that the model presented here is reasonable.

CONCLUSIONS

The extraction of copper by benzoylacetone in benzene solution was carried out using a stirred transfer cell and the following information was obtained.

- (1) The initial extraction rate varied inversely as the 0.5 power of the hydrogen-ion concentration in the low pH range, but in the high pH range was not affected by hydrogen-ion concentration.
- (2) The initial extraction rate was proportional to the concentration of benzoylacetone in the low pH range, but the rate was scarcely affected by benzoylacetone concentration in the ranges of both high pH and high concentration of benzoylacetone.
- (3) The initial extraction rate was proportional to the square root of the copper concentration in the low pH range and to the concentration of copper in the high pH range.
- (4) The initial extraction rate depended fairly strongly on the stirring speed in the high pH range, but the effect of stirring speed on the rate became weak with decreasing pH value.

The experimental results mentioned above were analyzed by a diffusion model accompanied by the chelating complex formation to obtain the reaction rate constant of complex formation and the mass transfer coefficient of benzoylacetone in the aqueous phase. The experimental data obtained could be simulated in terms of the diffusion model which was presented. The effect of stirring speed on the extraction rate of copper was discussed. The mass transfer coefficient obtained could be correlated with McManamey's equation. It was suggested that the extraction model presented here was reasonable.

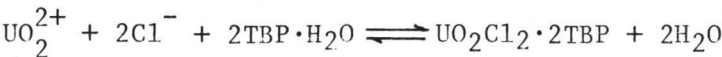
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CALCULATION OF ACTIVITY COEFFICIENT OF NONELECTROLYTES AND
DETERMINATION OF EQUILIBRIUM CONSTANT IN UO₂Cl₂-TBP
SYSTEM BY THE EXTRACTION DISTRIBUTION METHOD

Teng Teng, Li Yi-gui, Zhang Liang-ping
Dept. of Chem. Engrg., Qinghua University
Peking, People's Republic of China

Under our experimental conditions, the extraction reaction in UO₂Cl₂-TBP system, with or without xylene as diluent, may be considered as:



We have used the expressions derived from Gibbs-Duhem equation to treat our experimental distribution data and obtained the activity coefficient for each component in the organic phase. The activity coefficients thus calculated are compared with those calculated from seven models listed in Table 1. The terminal constants within these models and the thermodynamic equilibrium constant of UO₂Cl₂-TBP system are solved on computer simultaneously by using a suitable least-square method. For model 4,5,6,7 the thermodynamic equilibrium constants, K_a, determined are coincident each other, and the activity coefficients f_i computed are fairly approximate to those obtained from treatment of experimental data.

From the results shown in Table 1, we consider that, the last four models may be used to evaluate activity coefficients of nonelectrolytes for UO₂Cl₂-TBP-xylene extraction system. Among these models, the Scatchard-Hildebrand model and Guggenheim quasi-lattice model are simple and convenient, the Wilson model can fit the data flexibly but is somewhat complicated in calculation, the NRTL model is also applicable but time consuming. Besides, based on the comparison of results obtained, we incline to the assumption that, the water in organic phase may be considered as TBP·H₂O complex instead of as free water molecule.

TABLE 1. Models to be examined

models	mean relative deviation of f _i (calc.)	K _a , determined by this paper
1. symmetric regular solution	calculated results de- viated from experiments	
2. Margules-Wohl	unsuitable to be extended to multicompo- nent system	
3. Scatchard-Hamer		
4. Scatchard-Hildebrand $\ln f_i = \frac{V_i (\phi_2^2 A_{12} + \phi_3^2 A_{13} + \phi_2 \phi_3 (A_{12} + A_{13} - A_{23}))}{RT}$	0.009--0.0587	0.0626
5. Guggenheim quasi-lattice $\ln f_i = \frac{q_i (\theta_2^2 A_{12} + \theta_3^2 A_{13} + \theta_2 \theta_3 (A_{12} + A_{13} - A_{23}))}{RT}$	0.008--0.057	0.0646
6. Wilson $\ln f_i = 1 - \ln \sum_j x_j A_{ji} - \sum_j \frac{A_{ij} x_j}{\sum_k A_{kj} x_k}$	0.007--0.106	0.0612
7. NRTL	0.011--0.0891	0.0612

THE EXTRACTION OF MERCURY(II) FROM POTASSIUM IODIDE SOLUTIONS
AND THE EXTRACTION OF COPPER(II), ZINC(II) AND CADMIUM(II) FROM
HYDROCHLORIC ACID SOLUTIONS BY ALIQUAT 336 DISSOLVED IN
CHLOROFORM

R.W. Cattrall and Ainul Hayati Daud

La Trobe University

Bundoora, Victoria, 3083, Australia

Recently we reported the equilibrium constants for the extraction of mercury(II) from hydrochloric acid solutions by aliquat 336 dissolved in chloroform (1). We also suggested that the greater extraction of the monovalent trichloromercurate(II) species when compared with the divalent tetrachloromercurate(II) species could be used to explain the preferred selectivity for the monovalent ion of a coated-wire ion-selective electrode containing the chloromercurate(II) salts of aliquat 336.

In this paper we describe a solvent extraction study of additional systems and report the equilibrium constants for the extraction of the monovalent trihalometal complexes and the divalent tetrahalometal complexes. An attempt is made to correlate these with observed ion-selective electrode behaviours.

The results show that for the systems studied mercury is extracted strongest and copper weakest and that the extraction order is $\text{Hg}(\text{iodide}) > \text{Hg}(\text{chloride}) > \text{Cd} > \text{Zn} > \text{Cu}$. Some interesting correlations can be drawn by comparing the fractions of each complex present in the organic phase for each system with the fractions of the respective anionic complexes present in the aqueous phase. This shows that the monovalent species is preferentially extracted in the case of mercury(II) and copper(II). For zinc(II) and cadmium(II), at low concentrations of HCl, the divalent anion is preferentially extracted. This occurs even though the monovalent and divalent ions are present in the aqueous solution in almost equal amounts for zinc(II) and the monovalent ion predominates in aqueous solutions for cadmium(II). At high HCl concentrations (6.0M) the situation is reversed and the [1,1] complex predominates in the organic phase whereas the amount of the divalent anion present in the aqueous phase has increased greatly. This is explained on the basis of the competition between the hydrogen ion and the quaternary ammonium ion for the anionic metal complex. Thus the divalent tetrachlorometal complex has its negative charge reduced by one and the [1,1] complex formed has the formulation $(\text{R}_3\text{R}'\text{N}^+)(\text{HMC1}_4^-)$.

A correlation can be seen between the extraction behaviour and the response of the appropriate coated-wire ion-selective electrode.

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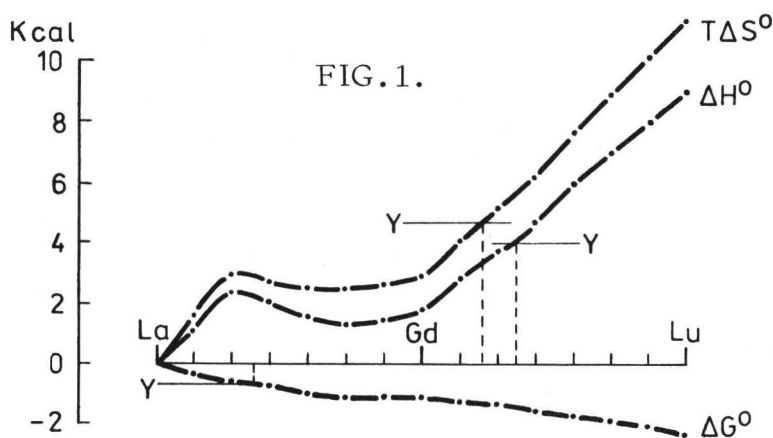
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THE POSITION OF YTTRIUM WITHIN THE LANTHANIDE
SERIES OF ELEMENTS

S. Siekierski

Department of Radiochemistry, Institute
of Nuclear Research,
03-195, Warsaw, Poland

In respect to crystallochemical properties yttrium resembles heavy lanthanides. In respect to free energy of extraction and complex formation, Y can occupy any position within the lanthanide series. In order to explain this behaviour, the position of Y, in respect to ΔG° , ΔH° and ΔS° of extraction and complex formation, has been examined from existing literature data and from extraction experiments performed in this department. It follows from this examination that in respect to both ΔH° and ΔS° the position of Y is that of a heavy lanthanide, although Y is a slightly lighter lanthanide in respect to ΔS° than in respect to ΔH° . The position of Y on the ΔG° vs. Z plot results from this slight difference and from the relative position of the ΔH° and $T\Delta S^\circ$ vs. Z plots. If the curve for ΔH° lies below that for $T\Delta S^\circ$ (the most frequent case) than, in respect to ΔG° , Y is a light lanthanide, Fig.1. The shift towards light lanthanides is the greater, the greater is the difference between the position of Y on the ΔH° and $T\Delta S^\circ$ curves, and the smaller is the distance between the two curves.



Position of yttrium on the ΔG° , ΔH° and $T\Delta S^\circ$ vs. Z plots. Extraction with Adogen- SCN^- from 2 M NH_4SCN . The values of thermodynamic functions are relative to those for lanthanum.

The somewhat earlier appearance of Y on the $T\Delta S^\circ$ vs. Z plot than on the ΔH° vs. Z plot is probably typical for ligands softer than water. For ligands harder than water e.g. fluorides, the order is reversed.

KINETIC ASPECTS OF THE LIQUID-LIQUID EXTRACTION OF GERMANIUM(IV)
WITH THE β -DODECENYL 8-HYDROXYQUINOLINE.

G. COTE and D. BAUER

Laboratoire de Chimie Analytique des
 Processus Industriels (ESPCI),
 10, rue Vauquelin, 75231 Paris Cédex 05,
 France

β -Dodeceny1-8-hydroxyquinoline (Kelex 100 ; HL) has been proposed (1) for the solvent extraction of germanium(IV) with a kerosene + octanol solvent. The formation of two different species in the organic phase has been shown (2) viz : $\text{GeL}_2(\text{OH})_2$ when $\text{pH} > 2$ or 3 ; GeL_3^+ , X^- ($\text{X}^- = \text{HSO}_4^-$, etc.) when $\text{pH} < 3$.

1) Kinetics of the extraction

- The extraction is rapid at $\text{pH} = 0$ but becomes slower as the acidity decreases.
- An increase in the concentration of HL and an addition of n-octanol in the organic phase enhances the kinetics of extraction. However, these two factors are unable to balance the effect of a decrease in the acidity.
- An increase in the temperature decreases the rate of extraction.

The role of the acidity is chemical (transformation of $\text{Ge}(\text{OH})_4$ into more easily extractable cations : $\text{Ge}(\text{OH})_i^{(4-i)+}$, $i = 3$ to 0) but also physical in nature (the interfacial tension between the two phases decreases when the acidity is increased).

2) Kinetics of the stripping

Stripping at uncontrolled interfacial area (mixed-settlers) : GeL_3^+ is stripped more slowly than $\text{GeL}_2(\text{OH})_2$ in alkaline solutions. An increase in the temperature, conversely to what happens at the extraction, accelerates the stripping. But it has little importance in the case of $\text{Ge}_2(\text{OH})_2$ whereas it is determining for GeL_3^+ . The difference between the behaviours of $\text{GeL}_2(\text{OH})_2$ and those of GeL_3^+ are structural in nature.

Stripping of GeL_3^+ , HSO_4^- at constant interfacial area (LEWIS's type cell) (3) : The stripping rate is : first order in respect of the germanium(IV) concentration in the organic phase, and without a simple order in respect of the hydroxide ion and HL concentrations.

CONCLUSION - Liquid-liquid extraction is well adapted to germanium(IV) separation as long as the species are extractable without major structural change. When transformations such as those of $\text{Ge}(\text{OH})_4$ into cations are required kinetic limitations appear although enhancement is possible by addition of modifiers (octanol). The structure of the extracted species plays a dominant role : the ion-pair GeL_3^+ , X^- is stripped more slowly than the species $\text{GeL}_2(\text{OH})_2$.

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LIQUID-LIQUID PARTITION AND HYDRATION OF ZINC
ACETYLACETONATE AND ITS HOMOLOGUES

J. Narbutt

Department of Radiochemistry,
Institute of Nuclear Research,
03-195 Warsaw, Poland

Hydration of metal chelates in the aqueous phase strongly affects their partition between water and organic solvents. Chelates with coordinatively saturated central metal ions are expected to be hydrated in their outer coordination sphere /1/. Chelates with coordinatively unsaturated metal ions are more highly hydrated, apart from the outer - also in the inner coordination sphere, which explains their lower extractability /2/.

Standard thermodynamic functions of partition of coordinatively unsaturated zinc β -diketonates, the ligands being acetylacetone, hexanedione-2,4, heptanedione-2,4 and heptanedione-3,5, in the water/n-heptane system have been evaluated using the temperature coefficient method. All these values are considerably higher than those for analogous coordinatively saturated beryllium chelates /1/, which reflects higher dehydration of the zinc chelates accompanying their transfer from water to the organic phase.

Unexpectedly high values of ΔG° changes per one CH_2 group, -4.5 to -4.7 kJ/mol at 25°C, have been observed in the homologous series of the zinc chelates, while the respective values for coordinatively saturated chelates fall within the usual range -3.1 to -3.8 kJ/mol or become lower when additional effects take place /1/. The contributions from ΔH° and ΔS° also differ from the values due to the changes in the water structure around the CH_2 group merely.

All the effects observed can be explained by assuming that the increase of pK^a in the homologous series of the ligands, indicating an increase of the Zn-O bond strength in the respective chelate series, has been followed by a small decrease of the coordination number of zinc in the chelates /3/. The inner-sphere hydration of the consecutive chelates decreases what additionally promotes their partition coefficients. The same phenomenon has not been observed for coordinatively saturated chelates where the coordination number of the central metal ion remains constant within the homologous series.

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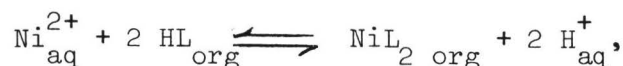
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KINETICS OF SOLVENT EXTRACTION OF NICKEL (II) BY OO'-DIALKYL-HYDROGEN DITHIOPHOSPHATES

O. MAZEROLLES-BOHM, J.-L. SABOT, D. BAUER

Laboratoire de Chimie Analytique des
Processus Industriels - ESPCI
10, rue Vauquelin 75231 Paris Cedex 05
France

The solvent extraction by oo'-dialkyl hydrogen dithiophosphate is a key to successful processing of acidic leach solutions of nickel (1). The overall reaction is as follows (HL = oo'-dialkylhydrogen dithiophosphate) :



The work presented here is concerned with kinetics of mass transfer from aqueous to organic phase, investigated by the single drop experiment. The influence of different reactants was first studied then the role of structural and physical properties of the interfacial zone (2).

1/ - Influence of reactants - The extraction rate, r , could be expressed as follows :

$$r = k |\text{Ni}^{2+}|_{\text{aq}} |\text{L}^{-}|_{\text{aq}} = k' |\text{Ni}^{2+}|_{\text{aq}} |\text{HL}|_{\text{org}} |\text{H}^{+}|_{\text{aq}}^{-1}$$

2/ - Hydration effects - From the comparison of Zn(II) and Ni(II) extraction, it is clear than the slow step is the desolvation of nickel aquo-complex.

3/ - The alkyl chain effect - Following chains have been selected among twenty compounds : 2-ethyl-hexyl, dodecyl, di-iso-butylmethyl, octyl-phenyl and nonyl-phenyl. Steric phenomena and Van der Waals bonding affect the interfacial activity of the extractant.

4/ - The effect of modifiers - The addition of TBP or alcohols greatly enhances the extraction rate at constant interfacial area, whatever the extractant alkyl group is. The observed variation can be explained in term of interfacial properties and solubility of water in the organic phase as it is shown on the figure in the case of the bis(ethyl-2-hexyl) TPA 0,2 M in solvesso 150.

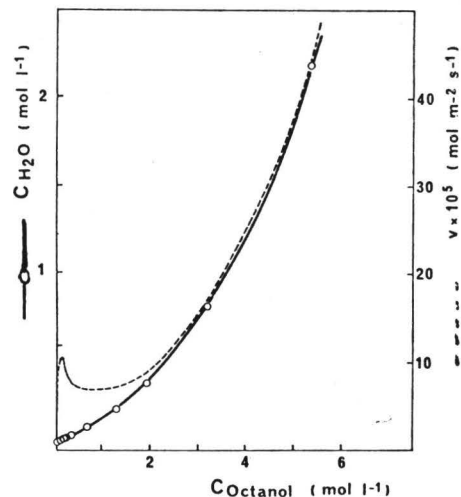
5/ - Interfacial properties - The interface of the water/solvent system has been studied by :

- . Interfacial tension measurements
- . Electron spin resonance of spin labelled long chain quaternary ammonium salts adsorbed at the interface.

The first method can be used to determine the species adsorbed at the interface, the second one is used to measure the rigidity of the interface.

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THE KINETICS OF SOLVENT EXTRACTION OF IRON (III) FROM CHLORIDESOLUTION BY TRI-n-OCTYLAMINE

J.C.S. CASSA and A.J. MONHEMIUS

DEPARTMENT OF METALLURGY AND MATERIALS
SCIENCE, ROYAL SCHOOL OF MINES,
IMPERIAL COLLEGE OF SCIENCE & TECHNOLOGY,
LONDON S.W.7 2BP- ENGLAND

The kinetics of solvent extraction of iron (III) in chloride solutions by tri-n-octylamine (TOA) in toluene has been studied in a stirred cell.

The aim of this work was to elucidate the mechanism of extraction in order to determine whether the reaction involves neutral or anionic metal species (or both), as well as, to investigate how the hydrodynamic conditions in the stirred cell affect the mass transfer process.

The stirred cell used was basically a modified Lewis cell where some variations of the geometry of the cell were possible. Continuous reading of the extracted iron in the organic phase was carried out by circulating the solution through a spectrophotometer. The evaluated rate parameter was the initial mass flux ($t \rightarrow 0$). Forward and reverse kinetics were studied in similar conditions.

The effect of cell geometry was studied in a baffled and unbaffled cell with contra or co-rotating stirrers. It was found that some cell geometries gave no clear plateau, when the extraction rate was plotted against stirrer speed. The geometry found to be most suitable for good mixing in each phase and shows a plateau over a range of stirring speed was the fully-baffled one with contra-rotating stirrers. It was also found that there is a range of chemical composition where a plateau cannot be attained. It was found that the reaction rate was related to the interfacial area of contact between the phases.

The effects of iron (III), TOA and chloride concentrations were studied. The rate of extraction is first order with respect to iron (III) and TOA concentrations and of complex order when related to chloride concentration. A mechanism for the reactions involved is presented. A statistical technique was used to select the most likely mechanism. Because all these mechanisms are based on the published values of the stability constants of chloro-complexes, which unfortunately are not very reliable and often conflicting, further experiments were carried out using radioactive chlorine. The experiments were designed so as to offer the possibility of detecting the transfer of neutral or anionic iron (III) species. The range of chloride concentrations studied varied from 1 to 9 M. It was found that at concentrations below 5 M chloride, iron (III) is extracted as a neutral species and at concentrations above that anionic and neutral species are extracted. The rate of extraction was found to be proportional to the concentration of these species in both cases.

KINETICS OF THE SOLVENT EXTRACTION OF COPPER
WITH A COMMERCIAL EXTRACTION REAGENT

P.S.Ellender, G.Harrison and G.J.Lawson.

Department of Minerals Engineering
University of Birmingham

Birmingham. United Kingdom.

Rates of extraction of copper into kerosene solutions of commercial reagents, determined with a single drop transfer apparatus (SDA), were reported earlier (1,2); the transfer rates depend on the drop size, which varies with the interfacial tension between the organic and aqueous phases, and with other properties of the system. A Lewis-type stirred transfer cell (STC) has now been constructed which offers a constant interfacial area and eliminates the effects of drop size. The STC is arranged for on-line radio-tracer measurement of metal concentrations and readily accommodates changes in experimental parameters, but requires larger amounts of organic reagents than does the SDA, which also permits more rapid overall metal transfer and higher loading of reagent.

The rate of extraction of copper into SME 529/kerosene has been compared by the two methods with respect to variation in copper, extractant and anion concentrations, and pH. Rates by the STC increased linearly with pH from 1.1 to 2.7; those by the SDA were reduced at higher pH levels, but under these conditions the system approached maximum loading, whereas with the STC the reagent was always in large excess. By both methods the rates increased markedly with chloride concentration from 0 to 3M, with negligible increase from 3 to 4M; between 0 and 1.0M a 400 per cent increase was found with the STC. Conversely, with sulphate from 0 to 1.0M the rates decreased; increasing nitrate concentration (0 to 4M) accelerated transfer but the enhancement was less than with chloride. These trends in rate values indicate that the state of complexation of the metal in the aqueous phase strongly affects the overall mass transfer rate. As the copper concentration was increased, the rate increased linearly at low metal concentrations, but the increase became progressively less at higher copper levels. Possibly the initial first order dependence on aqueous copper concentration was superseded by dependence on diffusion of the copper-organic complex from the interface. The STC measurements showed a linear increase in transfer rate with concentration of SME 529 from 1.0 to 20 per cent, the increase lessening thereafter. This linear relation was not readily apparent from SDA measurements, although fewer points were available at low concentrations, and the results may have been influenced by variation in drop size with extractant concentration.

It is concluded that both methods give valuable information on transfer values, and that the results are usefully complementary.

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EXTRACTION KINETICS OF COPPER WITH VERSATIC 10

Katsutoshi Inoue, Hironori Ammano
and Issei Nakamori

Dept. of Industrial Chemistry,
Saga University

Saga 840, Japan

Extraction kinetics of copper (II) from aqueous ammonium nitrate-ammonia mixture with n-hexane solution of Versatic 10 was studied as well as its fundamental extraction properties.

The distribution equilibrium of copper was explained by the following stoichiometric relation between copper and Versatic 10

$$2\text{Cu}_{\text{aq}}^{2+} + 3\text{H}_2\text{R}_{2\text{org}} \rightleftharpoons (\text{CuR}_2 \cdot \text{HR})_{2\text{org}} + 4\text{H}_{\text{aq}}^+ \quad K, \text{ where } K = 1.10 \times 10^{-13}.$$

Aqueous solubility of Versatic 10 was explained taking account of the following equilibriums.

$$\text{H}_2\text{R}_{2\text{org}} \rightleftharpoons 2\text{HR}_{\text{aq}} \quad K_1; \quad \text{HR}_{\text{aq}} \rightleftharpoons \text{H}_{\text{aq}}^+ + \text{R}_{\text{aq}}^- \quad K_2$$

where $K_1 = 9.57 \times 10^{-7}$ [mol/l] and $K_2 = 1.10 \times 10^{-6}$ [mol/l].

Interfacial adsorption equilibrium of Versatic 10 was explained taking account of the Langmuir-type adsorption of R^- and HR at the interface as follows. $\text{HR}_{\text{aq}} \rightleftharpoons \text{HR}_{\text{ad}} \quad K_{A1}; \text{R}_{\text{aq}}^- \rightleftharpoons \text{R}_{\text{ad}}^- \quad K_{A2}$ where K_{A1}, K_{A2} and S , interfacial area occupied by unit mole of R^- or HR , was estimated as follows. $K_{A1} = 2.8 \times 10^{-5}$ [l/cm²], $K_{A2} = 4.2 \times 10^{-6}$ [l/cm²] and $S = 4.1 \times 10^9$ [cm²/mol]. From these results, θ_{R^-} , the fractional coverage of the interface by R^- , was found to be independent of the concentration of Versatic 10 and inversely proportional to that of hydrogen ion in the pH region, pH < 6.

Experiments on extraction kinetics were carried out by the single drop method to examine the effects of the concentrations of each reaction component on the extraction rate during drop rise and also during drop formation.

The overall extent of extraction (E) obtained experimentally was separated into the extent of extraction during drop rise (E_r) and that during drop formation (E_f) as follows.

$$E = E_r + (1 - E_r) \times E_f = E_r + (1 - E_r) \times \beta t_f^p$$

In this equation, p , the exponent of drop formation time (t_f), was found to be 1, which indicates that the extraction rate during drop formation is controlled by an interfacial reaction. Extraction rate mechanism during drop rise was analysed based on the Handlos-Baron's turbulent diffusion model combined with interfacial reaction at drop surface. The interfacial reaction rate was found to be proportional to the concentration of copper and inversely proportional to that of hydrogen ion though it is independent of that of Versatic 10 in a droplet. Similar reaction orders were observed in the analysis of the extraction kinetics during drop formation. These results are considered to indicate that the extraction rate is determined by the reaction between copper ions in the aqueous phase and anionic species of Versatic 10 at the drop surface.

INVESTIGATION INTO THE KINETICS OF HYDROCHLORIC ACID
EXTRACTION BY CERTAIN TERTIARY AMINES.

V.V. Tarasov, T.D. Nikolaeva,
N.E. Kruchinina

Mendeleev Institute of Chemical
Technology
Moscow, USSR

Investigation into the extraction reactions mechanisms under arbitrary hydrodynamic conditions are very difficult. The short-time contact method (STCM) gives the possibility to simplify this problem because the mass transfer may be described by Fick's laws. Using the STCM we have studied the kinetics of HCl extraction by TOA, TDA and TLA in toluene. The equation of the mass transfer rate r in non-stirred quasi-infinite phases is :

$$r = k_1 \{ [\overline{R_3N}] \cdot [HCl]_{aq} - k_2 [\overline{R_3NHCl}] \} / \{ [R_3N] + k_3 \} \sqrt{t}$$

where $k_1 = \sqrt{D_{HCl}} / \pi = 3.14 \times 10^{-5} \text{ m} \times \text{s}^{-1/2}$; k_2 and k_3 are the coefficients placed in the table, t is diffusion time.

Table.

THE VALUES k_2 AND k_3

Coefficients	TOA	TDA ^x	TLA ^x
$k_2, \text{kmol} \times \text{m}^{-3}$	$1,61 \times 10^{-2}$	11.26×10^{-2} 2.38×10^{-2}	16.9×10^{-2} 3.03×10^{-3}
$k_3, \text{kmol} \times \text{m}^{-3}$	3.74×10^{-2}	23.98×10^{-2} 5.05×10^{-2}	37.64×10^{-2} 6.76×10^{-2}

^xNOTE : the higher values of k_2 and k_3 correspond to $[HCl]_{aq} \leq 20^{-3} \text{ M}$.

The equation shows that all reactions are diffusion-controlled because $r \rightarrow \infty$ at $t \rightarrow 0$. Thus the diffusion kinetics may be described by equations identical to chemical kinetics equations suggested by Danesi. The STCM makes it possible to identify these cases since the values of k_1 and k_2/k_3 may be calculated a priori.

The HCl extraction by TDA and TLA when $[HCl]_{aq} \leq 10^{-3} \text{ M}$ was complicated by the formation of thin, highly viscous, interfacial films which sharply decrease the extraction rate (see table). The film formation leads not only to the occurrence of the additional diffusion resistance but also changes the equilibrium constants of the interfacial reactions.

THE EXTRACTION OF LANTHANIDE SALTS FROM BINARY AND
TERNARY SOLUTIONS BY TBP.

V.V. Sergievskij, L.V. Evdokimova,
I.P. Fominov, L.M. Babenko
Mendeleev Institute of Chemical
Technology
Moscow, USSR.

Regularities in the extraction of lanthanide salts by TBP from their binary and ternary solutions have been studied. It has been confirmed that lanthanide nitrate extraction proceeds through the solvate mechanism. In this case the equation for calculation of the extraction constant K_q takes the form

$$K_q = \bar{m} / (a \cdot \bar{m}_s^q) \quad (1)$$

where a is the salt activity in the aqueous phase, $\bar{m}$ and $\bar{m}_s$ are the molar concentrations of the salt and the "free" extractant in the organic phase, q is the solvation number. It has been found that for the majority of lanthanides the values K_3 are practically constant. Thus trisolvates are the main compounds in these systems. The analysis of the organic phase nonideality shows that in systems with nitrates, tetrasolvates of La and Pr are also formed and their concentrations decrease sharply when the organic phase has been saturated.

Data on the extraction of lanthanide chlorides and perchlorates by TBP show that these salts dissociate partially in the organic phase. Supposing that the dissociation proceeds only through the first step distribution of salts can be described by the equation

$$\begin{aligned} \bar{m} = & \sqrt{K_{+q} a \bar{m}_s^q \exp [h_{+q} (1-a_w)]} + \\ & + K_q a \bar{m}_s^q \exp [h_q (1-a_w)] \end{aligned} \quad (2)$$

where K_{+q} is the thermodynamic constant of the extraction, h_{+q} and h_q are the degrees of hydration of ions and solvates at $a_w = 1$, a_w is the water activity. It has been established that perchlorates usually form hydrated tetrasolvates.

The equations (1) and (2) describe the data on the extraction of chlorides from their mixtures with lanthanide nitrates. In that case the values of a have been calculated from the Mikulin equation assuming that for the aqueous solutions in question Zdanovskij's rule is valid.

ON SOME REGULARITIES FOR THE EXTRACTION SEPARATION
OF ELEMENTS WITH SIMILAR PROPERTIES.

A.I. Mikhailichenko, M.A. Klimenko,
T.V. Fedulova, V.P. Karmannikov,
R.M. Ageeva
Institute of Rare Metals, Giredmet,
Moscow, USSR.

To reveal the main factors that influence the separation of elements with similar properties we considered the interconnection between selectivity and metal complex structures in equilibrium phases (in particular the structure of extractants) on the basis of experimental data for the extraction of rare earth, alkaline earth, and alkaline elements with extractants of different classes.

The attempt to find a definite correlation between the selectivity and the parameters characterising metal states in one of the equilibrium phases, may be successful only in special cases, for example when considering the regularities of changes in separation factors through the series of monocarboxylic acids.

In general case on searching for factors that influence the efficiency of the separation in any system, it is necessary to look upon the extraction systems from the point of view of the difference in the structure of complexes in the equilibrium phases.

The analysis of all the data gives us the right to formulate the following recommendations for the choice of effective systems. To achieve the best selectivity on separating elements with similar properties by liquid-liquid extraction method it is necessary that the complexes, which exist in aqueous and organic phases and between which there is chemical exchange, to differ in many ways. Such ways are : the coordination number of a metal in the complex, the coordination polyhedron formed, the type of coordination atoms (oxygen or nitrogen) or molecules and the quantitative ratio among them in the inner sphere of the complex, the bonding energy between the metal and donor atoms.

EFFECT OF DILUENTS ON EXTRACTION (PHYSICO-CHEMICAL PRINCIPLES).

A.M. Rozen, V.G. Yurkin

State Committee for Utilization
of Atomic Energy

Moscow

USSR

The physico-chemical nature of the effect of "inert" diluents on extraction is considered. According to the thermodynamic equations for extraction equilibrium this effect is determined by the magnitude of the diluent parameter $DIL = (\gamma_S)^q / \gamma_C$ where γ_S and γ_C are activity coefficients for an extractant (S) and a complex (C); q is a solvate number. From extraction data alone it is impossible to gain information on the nature of interactions and the appearance of non-ideality in systems with the same values of DIL may result from opposite causes. The nature of DIL may only be established by studying γ_S and γ_C separately in mixtures with diluents (D). Our measurements were carried out by the isoteniscope method with binary mixtures of C_6H_{14} , C_6H_6 , CCl_4 and $CHCl_3$ with $S = TBP$, $D2EHPA(HR)_2$, and $TOAHNO_3$ and with $C = UO_2(NO_3)_2(TBP)_2$, $UO_2(HR)_2$ and $TOA, H_2UO_2(NO_3)_3$. The agreement between the values of DIL calculated from experimental values of γ_S and γ_C and the extraction ones is quite good. The contribution of each of the three possible causes of non-ideality ($\gamma \neq 1$) in γ is identified: (1) versatile Van der Waals interactions (they are always present and make $\gamma < 1$); (2) A combined athermic effect (which increases with the difference in the sizes of component molecules and makes $\gamma < 1$); (3) the chemical interreactions between components, resulting in $\gamma < 1$. In mixtures of C_6H_{14} with TBP, $TOAHNO_3$ and their complexes, effect (1) prevails (for $TOAHNO_3 \gamma \approx 10^3$, limited phase miscibility). However for $(HR)_2$ (1) is exceeded by the action of (2), intensified due to a large size of the molecules $(HR)_2$ and C ($\gamma < 1$ although (3) is absent). In systems with $CHCl_3$ considerable negative non-ideality is observed ($\gamma \approx 10^{-2}$) due to the formation of a hydrogen bond. In systems with CCl_4 and C_6H_6 (2) and weak (3) prevails ($\gamma < 1$). Despite a wide range of variations of γ (from 10^3 to 10^{-4}) the values of DIL are about 1 and depend only slightly on the nature of D (with the exception of systems with $CHCl_3$, where DIL is 10^{-2}). This is explained by the similar character of interactions D with S and C, by the mutual compensation of the effect of factors (1) and (2) (and sometimes (3)) on γ_S and γ_C . The DIL value, and the place of this D in the extraction series D is determined basically by the effect of factor (3). In compensated systems $\gamma_S = k_1 + k_2 \gamma_C$ and a single-parameter correlation of DIL with only one characteristic of D is possible. In systems with specific interactions (e.g. with $CHCl_3$) the correlation breaks down.

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Extractants and diluents

Session 16

Co-chairmen : D.S. Flett (Warren Spring Lab., Stevenage, U.K.)
Y.A. Zolotov (Academy of Sciences, Moscow, U.S.S.R.)

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G.N. Rao and S. Narayanan, Indian Institute of Technology, New Delhi, India.

ON THE EXTRACTANT PROPERTIES OF DIBUTYLPHENACYLPHOSPHONATE

U. Olofsson, J.P. Brunette^{*}, B. Allard
and A. Selme

Department of Nuclear Chemistry
Chalmers University of Technology
S-412 96 Göteborg, Sweden

ABSTRACT

The dissociation of dibutylphenacylphosphonate (HDBPP) in 1 M sodium perchlorate solution and the di- and trimerization in n-hexane and n-heptane have been studied and the corresponding stability constants have been determined at 25°C.

The distribution of thorium between n-heptane containing dibutylphenacylphosphonate and 1 M sodium perchlorate or 1 M sodium nitrate solutions has been investigated in the pH-range 1-7. In the perchlorate system the extracted species are $\text{Th}(\text{DBPP})_4 \cdot x\text{HDBPP}$, $x = 0-2$. Preliminary stability constants have been determined at 25°C. In the nitrate system formation of extractable species such as $\text{Th}(\text{NO}_3)_n(\text{DBPP})_{4-n} \cdot x\text{HDBPP}$, $n = 1-1.5$, seems probable.

INTRODUCTION

Since the first reported instance of synergistic effects in solvent extraction (1), a large number of combinations of chelating agents and neutral donors has been investigated, especially in metal systems such as the lanthanides and the actinides, where hydration hampers the extraction. Particularly combinations of β -diketones and formally neutral phosphoryl compounds, G_3PO , where G is an alkyl or alkoxy group, have been studied in detail, which have been reported in several comprehensive reviews (2-5). For a tetravalent metal like thorium extractable species such as $\text{ThA}_4 \cdot \text{S}$ are formed, A being the chelating agent and S being the neutral phosphoryl compound (6-8). In the absence of a chelating agent solvates like $\text{Th}(\text{NO}_3)_4 \cdot 2\text{S}$, S being the neutral donor, or $\text{Th}(\text{NO}_3)_3\text{S}'_3$, S' being the anion of e.g. a phosphoric acid, are formed (9,10).

A β -ketophosphonate such as dibutylphenacylphosphonate (HDBPP) with the composition $[(\text{C}_6\text{H}_5)\text{C}(\text{O})\text{CH}_2\text{P}(\text{O})(\text{OC}_4\text{H}_9)_2]$ may act both as a neutral or anionic adduct forming agent or as a chelating agent and would therefore be able to form either extractable chelates like $\text{Th}(\text{DBPP})_4 \cdot x\text{HA}$ with thorium or adduct species of the composition $\text{Th}(\text{NO}_3)_4 \cdot y\text{HDBPP}$ or $\text{Th}(\text{NO}_3)_n(\text{DBPP})_{4-n} \cdot y'\text{HDBPP}$. The similar carbamylmethylenephosphonates, $[\text{R}_2\text{NC}(\text{O})\text{CH}_2\text{P}(\text{O})(\text{OR}')_2]$ have been found to act as bidentate reagents in the extraction of trivalent actinides and do also form adducts (11).

^{*}Present address: Laboratoire de Chimie Minérale,
Ecole Nationale Supérieure de Chimie
B.P. 296 R8 67008 Strasbourg Cedex, France

Although a number of metal systems has been studied using various β -keto-phosphonates as ligands (12-21), the information on extractant properties of this group of complexing agents is unsatisfactory. In the present work dissociation, distribution and polymerization of HDBPP have been studied in two-phase systems as well as the extraction of thorium.

EXPERIMENTAL

The distribution measurements were performed in a thermostated vessel ($25.0 \pm 0.2^\circ\text{C}$) using a batch technique (22). For the determination of distribution coefficients, D , aliquots of each phase were withdrawn and analyzed.

In the studies of dissociation, distribution and polymerization of HDBPP itself, the aqueous phase was 1.0 M (Na,H)ClO₄ solution and the organic phase n-heptane or n-hexane with the initial HDBPP concentration varied between 10^{-4} and 1.7×10^{-3} M. The withdrawn samples were diluted with ethanol and the UV spectrum recorded. The strong absorption band at 246 nm was used for the determination of HDBPP concentrations.

In the thorium extraction studies the aqueous phase was 1.0 M (Na,H)ClO₄ or 1.0 M (Na,H)NO₃ solutions and the organic phase n-heptane with the initial HDBPP concentration varied between 0.025 and 0.1 M. The total initial thorium concentration in the aqueous phase was 4×10^{-3} M or less. The thorium concentration was determined by a liquid scintillation counting technique using ²³⁰Th as a radiotracer.

HDBPP was prepared as previously described (20). Sodium perchlorate was prepared and purified according to conventional methods (23). All other chemicals were of p.a. quality and used without further purifications.

PROPERTIES OF HDBPP

The dissociation, distribution and polymerization of HDBPP (here denoted by HA) in a two-phase system can be described by the following equilibria, neglecting any aggregation in the aqueous phase and dissociation in the organic phase (overline refers to organic phase):



The distribution ratio D can be expressed as

$$D = \frac{\sum_1^n n [(\overline{\text{HA}})_n]}{[\text{HA}] + [\text{A}^-]} = \frac{K_d + \sum_2^n n K_n K_d^n [\text{HA}]^{n-1}}{1 + K_a [\text{H}^+]^{-1}} \quad (4)$$

For $\text{pH} \ll \text{p}K_a$, giving $K [\text{H}^+]^{-1} \ll 1$, a plot of D vs $[\text{HA}]$ permits a determination of K_d (for $[\text{HA}] = 0$) and K_n . Eqn (4) can be rewritten as

$$pH = \log\{(K_d + \frac{\sum n K_d^n}{2} [HA]^{n-1})/D - 1\} + pK_a \tag{5}$$

At low values of [HA], giving $n K_d [HA]^{n-1} \ll K_d$, a plot of pH vs $\log (K_d/D - 1)$ permits a determination of pK_a . Distribution coefficients for HDBPP in the n-heptane/1.0 M (Na,H)ClO₄ system at pH 4 are given in Fig. 1. The non-linearity of the curve is consistent with a polymerization in the organic phase. Assuming a formation of dimers and trimers the experimental data can be described by the following equations:

$D(\text{n-hexane}) = 35.0 + 16400[HDBPP] + 19.5 \times 10^6[HDBPP]^2 \tag{6}$

$D(\text{n-heptane}) = 29.8 + 13800[HDBPP] + 16.3 \times 10^6[HDBPP]^2 \tag{7}$

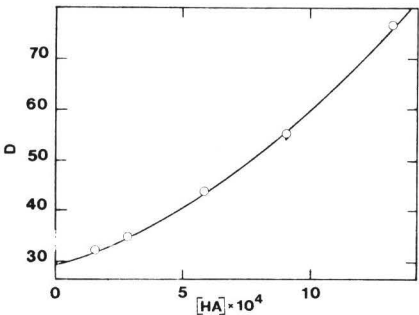


FIG. 1

The distribution coefficient (D) for HDBPP (HA) as a function of the concentration. (Aqueous phase: 1.0 M(Na,H)ClO₄, pH 4; organic phase: n-heptane)

The corresponding distribution constants and polymerization constants are given in Table 1. The distribution coefficient was constant and the UV-spectrum did not change for pH between 2 and 10 (24). Thus, HDBPP seems to be stable and non-dissociated in this pH-range. The non-linearity of D vs [HDBPP] in Fig. 1 can not be ascribed to the extraction of HClO₄.

TABLE 1

Distribution and polymerization constants for HDBPP (Aqueous phase: 1.0 M (Na,H)ClO₄)

Solvent	K_d	K_2	K_3
n-hexane	35.0	6.7	150
n-heptane	29.8	7.9	210

By the use of eqn (5) a pK_a -value of 12.30 ± 0.03 was obtained for HDBPP (c.f. Fig. 2). The dissociation at pH above 10 progressively changed the UV-spectrum. The spectrum for DBPP shows a broad band at 280 nm with an ϵ_{max} of $7000 \text{ M}^{-1}\text{cm}^{-1}$ which could easily be distinguished from the peak for HDBPP at 246 nm with an ϵ_{max} of $11200 \text{ M}^{-1}\text{cm}^{-1}$ (24). The dissociation was reversible and undissociated HDBPP was quantitatively obtained at the decrease of pH.

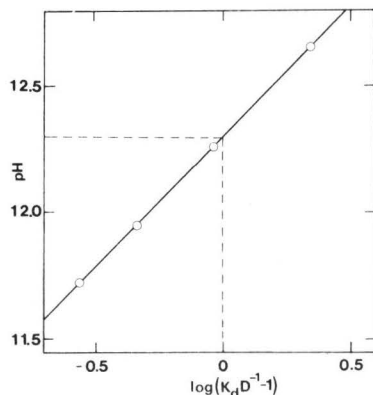


FIG. 2

Determination of the dissociation constant (K_a) for HDBPP; pH vs $\log(K_d D^{-1} - 1)$ (Aqueous and organic phases as in Fig. 1)

EXTRACTION OF THORIUM

In an extraction system containing a metal M, an acidic complexing agent HA, anions B of the salt medium in the aqueous phase, and an organic diluent Org, complexes with the general composition $M^m A^n (OH)^p B^q (HA)^r (Org)^s (H_2O)^t$ may be formed, even if not all of the subscripts are greater than zero simultaneously. Neglecting solvent interactions and assuming mononuclear complexes the general complex can be written as $MA^n (OH)^p (HA)^r$, or $M(HA)_x (H)^{-y}$, where $x = n + r$ and $y = n + p$ (25). The distribution of M in a two-phase system may be written as

$$D = \frac{[M(HA)_x (H)^{-y}]_{org}}{\sum_{xy} [M(HA)_x (H)^{-y}]_{aq}} = \frac{\sum_{xN} K_{xN} \Lambda_{xN} [HA]^x [H]^{-N}}{\sum_{xy} K_{xy} [HA]^x [H]^{-y}} \quad (8)$$

where

$$K_{xy} = \frac{[M(HA)_x (H)^{-y}]_{org}}{[M] [HA]^x [H]^{-y}} \quad (9)$$

and

$$\Lambda_{xy} = \frac{[M(HA)_x (H)^{-y}]_{org}}{[M(HA)_x (H)^{-y}]_{aq}} \quad (10)$$

N represents the maximum charge of the central ion. All charges have been omitted for simplicity. It is assumed that only uncharged species of M are extracted to the organic phase and that the formation of ion-pairs can be neglected.

From eqn (1)-(4) and a mass balance for HA, corresponding values for $[HA]$, $[H]$ and $[A]$ can be calculated.

In Fig. 3-4 distribution coefficients are given for thorium as a function of pH and pA at various total HDBPP concentrations, the organic phase being n-heptane and the aqueous phase being 1.0 M (Na,H)ClO₄ or 1.0 M (Na,H)NO₃ solutions (25°C). The formation of extractable species of the general composition MA(OH)(HA)_n is indicated.

In Fig. 5. Distribution coefficients are given for thorium as a function of the HDBPP concentration in the aqueous phase at constant pH.

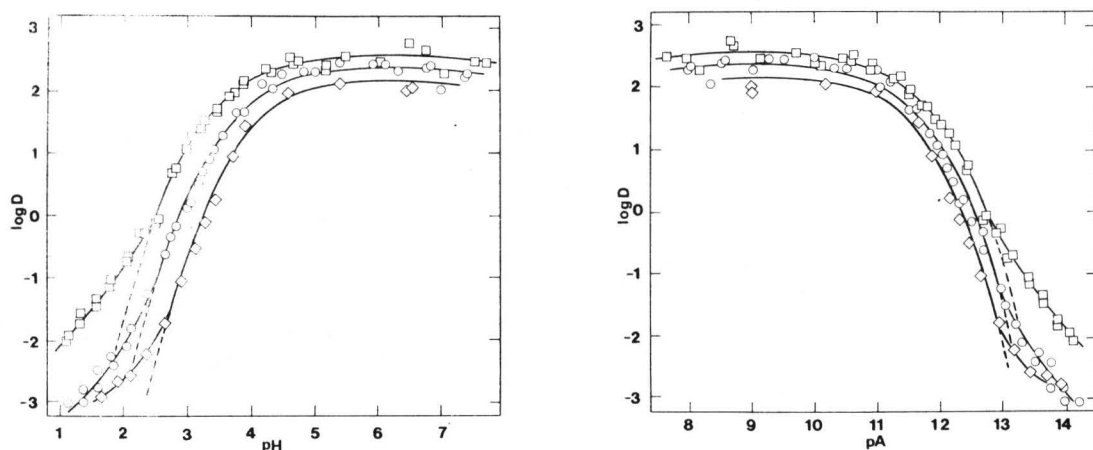


FIG. 3

Distribution coefficients ($\log D$) for Th as a function of pH and pA at various total HDBPP concentrations. (Aqueous phase: 1.0 M (Na,H)ClO₄; organic phase: n-heptane; initial HDBPP concentration in the organic phase: $\square$ 0.1007 M, $\circ$ 0.0504 M, $\diamond$ 0.0252 M; 25.0°C)

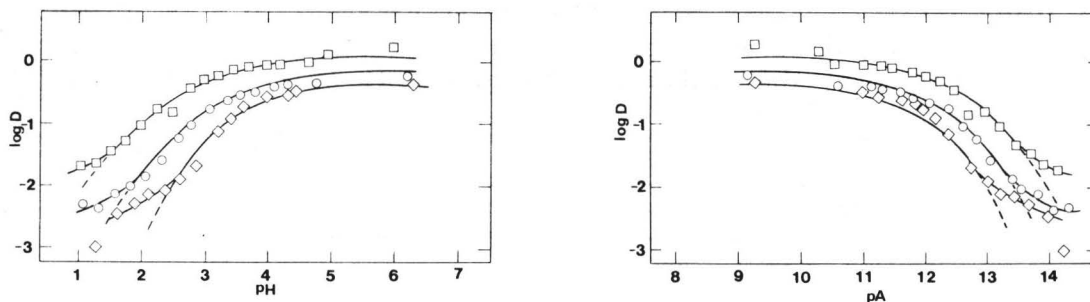


FIG. 4

Distribution coefficients ($\log D$) for Th as a function of pH and pA at various total HDBPP concentrations. (Aqueous phase: 1.0 M (Na,H)NO₃; organic phase: n-heptane; symbols as in Fig. 3.)

Species in the perchlorate system

The extrapolated curves of Fig. 3 in the low pH- and high pA-range, respectively, (dashed lines) have a limiting slope of 4, indicating an A/M ratio of 4. The slopes in Fig. 5 of $\log D$ vs $\log [HA]$, however, indicate an HA/M ratio of at least 5, and even in the plateau region above pH 5, where the distribu-

tion coefficient is independent of pH, the limiting slope is between 1 and 2, indicating an adduct formation with an HA/M ratio of 1-2. Thus, formation of extractable species with the composition $\text{ThA}_4 \cdot x\text{HA}$, $x = 1-2$, seems to be possible.

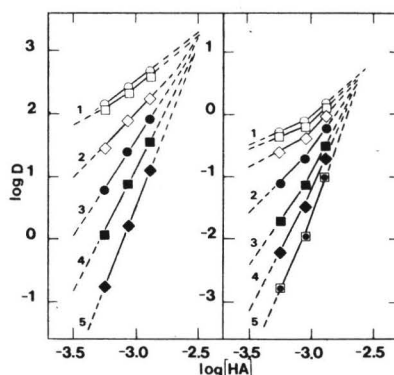


FIG. 5

The dependence of $\log D$ on $\log[\text{HDBPP}]$ (denoted by HA) for Th at different values of pH. The slopes of the lines are given in the figure. (Left figure: 1.0 M (Na,H)ClO₄; ○ pH 6, □ pH 5, ◇ pH 4, ● pH 3.6, ■ pH 3.3, ◇ pH 3.0; right figure: 1.0 M (Na,H)NO₃; ○ pH 6, □ pH 5, ◇ pH 4, ● pH 3.2, ■ pH 2.7, ◆ pH 2.4, ◼ pH 2.0)

From corresponding values of D , $[\text{HA}]$ and $[\text{H}]$, as given by the smooth curves of Fig. 3, preliminary values of the constants K_{xy} and Λ_{x4} in eqn (8)-(10) have been calculated, using the limiting value method (25, 26). These constants with graphically estimated error limits are given in Table 2.

TABLE 2

$\text{Th}(\text{HA})_x(\text{H})_{-y}$ -species present in the Th-HDBPP-n-heptane/1.0 M NaClO₄-system as indicated by graphical evaluation, and the corresponding stability constants as obtained by the limiting value method (x and y refer to eqn (8)-(10))

$x \setminus y$	$\log K_{xy}$				$\log \Lambda_{x4}$
	1	2	3	4	
0	-2.82 ± 0.03	< -7			
1	-0.30 ± 0.15				
2	1.55 ± 0.20	0.00 ± 0.22			
3	5.04 ± 0.25	3.15 ± 0.19	-0.52 ± 0.26		
4	7.43 ± 0.09	5.90 ± 0.21	2.98 ± 0.10	-2.30 ± 0.45	2.56 ± 0.45
5		9.40 ± 0.22		1.54 ± 0.14	1.93 ± 0.44
6		12.60 ± 0.55		4.78 ± 0.12	1.92 ± 0.21

Since

$$K_{xy} = \beta_{npr} K_a^n K_w^p \quad (11)$$

where

$$K_w = [H][OH]/[H_2O] \tag{12}$$

and

$$\beta_{npr} = [MA_n(OH)_p(HA)_r]/[M][A]^n[OH]^p[HA]^r \tag{13}$$

a possible set of β_{npr} -values can be generated and probable species identified, Table 3, considering the K_{xy} -constants and the actual pH and HDBPP concentrations and the corresponding $\partial(\log D)/\partial(\log[A])$ -values. Some of the corresponding stability constants are given in Table 4.

TABLE 3

ThA_n(OH)_p(HA)_r-species present in the Th-HDBPP-n-heptane/1.0 M NaClO₄-system. (Extractable species denoted by an asterisk)

x\y	1	2	3	4
0	MOH ³⁺			
1	MA ³⁺			
2		MA ₂ ²⁺		
3		MA ₂ ²⁺ ·HA	MA ₃ ⁺	
4		MA ₂ ²⁺ ·2HA	MA ₃ ⁺ ·HA	MA ₄ [*]
5		MA ₂ ²⁺ ·3HA		MA ₄ ·HA [*]
6		MA ₂ ²⁺ ·4HA		MA ₄ ·2HA [*]

TABLE 4

Preliminary stability constants in the Th-HDBPP-system

Th ⁴⁺ + OH ⁻ = Th(OH) ³⁺	logK = 11.2±0.2
Th ⁴⁺ + 2OH ⁻ = Th(OH) ₂ ²⁺	logK < 21
Th ⁴⁺ + A ⁻ = ThA ³⁺	logK = 12.0±0.2
Th ⁴⁺ + 2A ⁻ = ThA ₂ ²⁺	logK < 24.5
Th ⁴⁺ + 3A ⁻ = ThA ₃ ⁺	logK = 36±0.5
Th ⁴⁺ + 4A ⁻ = ThA ₄	logK = 46.9±0.4
ThA ₄ + HA = ThA ₄ ·HA	logK = 3.8±0.4
ThA ₄ + 2HA = ThA ₄ ·2HA	logK = 6±1
ThA ₄ = ThA ₄	logK = 2.56±0.5
ThA ₄ ·HA = ThA ₄ ·HA	logK = 1.93±0.4
ThA ₄ ·2HA = ThA ₄ ·2HA	logK = 1.92±0.2

Thus, in the high pH-region adduct species with a coordination number of 9 and possibly also 10 seem to be formed. In the present [HA]-[A]-range no mixed MA_n(OH)_p(HA)_r-complexes with p > 0 would dominate at any pH.

The observed decrease of $\partial(\log D)/\partial(\log[A])$ at low [A] (pA > 13) with a limiting value of 1, as well as $\partial(\log D)/\partial(\log[HA])$ -values of >1 indicate a formation of ion-pairs with the composition Th(ClO₄)_nA_{4-n}, n < 3. This effect is more pronounced at the lowest total [HA]-concentration, as expected. However, the change of the slope of the curve in the low pH-region could also to some extent be attributed to the presence of complexing impurities at trace

levels in the phosphonate. Without several prewashes (with NaOH and HClO_4 of various concentrations) of the organic phase before the extraction experiment considerable higher distribution coefficients were observed in the low pH-region. Moreover, these distribution coefficients showed a slight dependence on the metal concentration in the pH-region below 3, unless a prewash was performed. Even with a thorough prewash procedure the data at low pH were difficult to reproduce, and any rigorous numerical treatment of these data are probable useless.

Refinement of the preliminar stability constants in Table 2 (related to the extrapolated curves in Fig. 3) by a least squares method (27) is in progress (24).

Species in the nitrate system

The extrapolated curves of Fig. 4 in the low pH- and high pA-range, respectively, (dashed lines) seem to have a limiting slope of at least 2, while the slopes of $\log D$ vs $\log[\text{HA}]$, Fig. 5, are about 5 at low pH-values, indicating an extraction of ion-pairs with the composition $\text{Th}(\text{NO}_3)_x\text{A}_{4-x}\cdot y\text{HA}$, $x = 1-2$ (or > 2 at low pH).

In Fig. 6 distribution coefficients are compared for the nitrate and perchlorate systems at pH 2 and 6. In the perchlorate system the nitrate concentration is about $0.4-1.6 \times 10^{-2}$ M due to the addition of thorium as $\text{Th}(\text{NO}_3)_4$. At high pH values of $\partial(\log D)/\partial(\log[\text{NO}_3])$ of about 1-1.5 are obtained, in agreement with the suggested composition of extractable ion-pairs given above. Calculations of stability constants are in progress.

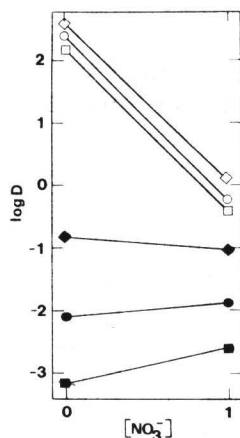


FIG. 6

Distribution coefficients ($\log D$) for Th in 1.0 M $(\text{Na,H})\text{ClO}_4$ ($[\text{NO}_3] \approx 0.4-1.6 \times 10^{-2}$ M; given as 0 in the figure) and 1.0 M $(\text{Na,H})\text{NO}_3$ at various total HDBPP concentrations. (Initial concentrations in the n-heptane phase: $\diamond$ 0.1007 M, $\circ$ 0.0504 M, $\square$ 0.0252 M; open symbols: pH 6, filled symbols: pH 2)

Solid thorium-HDBPP complex

By evaporation of the organic phase of the perchlorate system (at pH 5-6 of the aqueous phase) crystalline $\text{Th}(\text{DBPP})_4$ was obtained. The complex could be heated to the melting point ($72 \pm 1^\circ\text{C}$) without decomposition. No solid adducts with the composition $\text{Th}(\text{DBPP})_4 \cdot x\text{HDBPP}$, $x > 0$, were obtained.

From IR- and Raman spectra, indications of a chelate type structure were

obtained from shifts both in the C=O and P=O frequencies (from 1685 to 1535 and from 1265 to 1155 cm^{-1} , respectively) (24).

The proton NMR spectrum of $\text{Th}(\text{DBPP})_4$ has been registered using CCl_4 as solvent and TMS as internal standard. The chelate cycle proton resonance appears as a doublet at 4.45 ppm ($J_{\text{PH}} = 14.5$ Hz). A chemical shift of 0.95 ppm towards the low fields is observed by comparison with the free ligand methylene proton resonance at 3.50 ppm ($J_{\text{PH}} = 23.5$ Hz). This observation is well-consistent with a chelate type structure.

CONCLUSIONS

In the Th -HDBPP- n -heptane/aq-system species of the general composition $\text{Th}(\text{DBPP})_n\text{B}_q \cdot r\text{HDBPP}$ are formed. At pH above 3-4 chelate and adduct formation occurs with $n = 1-4$ and $q = 0$ for $\text{B} = \text{ClO}_4^-$ and $q = 1-1.5$ for $\text{B} = \text{NO}_3^-$; neutral species with $r = 0-2$ will be extracted.

Formation of ion-pairs is probably significant at pH below 2-3 even in the perchlorate system with $q = 1-3$.

As can be expected, considering the high pK_a -value for HDBPP (12.3), the corresponding thorium complex is strong ($\log \beta_4/4 = 11.7$).

Only the chelate $\text{Th}(\text{DBPP})_4$ was obtained by evaporation of the organic phase of the perchlorate extraction system at high pH.

The HDBPP itself existed largely as di- and trimers in an inert diluent like n -heptane.

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ALKALI EXTRACTIONS AND RELATED ION-PAIRING METAL
EXTRACTIONS BY POLY(OXYETHYLENE) DERIVATIVES OF
ORGANIC CARBONATES.

A. ROLLAT, M. BURGARD, M. J. F. LEROY, H. S. PARK.
Laboratoire de Chimie Minérale, Ecole Nationale
Supérieure de Chimie, Université Louis Pasteur,
B.P. 296/R8. 67008 Strasbourg Cedex (France)
J. C. GAUTIER, S. LECOLIER.
Société Nationale des Poudres et Explosifs,
Centre de Recherches du Bouchet,
Le Bouchet, 91710 Vert Le Petit (France)

ABSTRACT

Ion pairing metal extraction properties of some poly (oxyethylene) derivatives of organic carbonates are presented in the case of Co^{2+} in MSCN media and Au^{3+} in MCl media ($\text{M} = \text{Na}^+, \text{NH}_4^+, \text{K}^+$). The trends of extractability are compared with those observed for KSCN . The stoichiometries of Alkali-extractant complexes are determined by the solvent extraction method. On the basis of an infrared study, the contribution of the various organic functions to the coordination of the alkali is discussed for some complexes.

INTRODUCTION

Poly(oxyethylene) compounds and crown ethers are known to extract Ia and IIa metal ions (1) (2). They have also been used for extractions of other metals by ion-pairing processes (3) (4) in which the most important chemical factor is the extractant's ability to solvate the alkali ion in the organic phase, while the metal itself is extracted as a lipophilic anionic complex. Thus, several metals can be extracted from alkali thiocyanate and iodide media (3) (4). These extractions are interesting principally in analytical chemistry. However, an example of industrial application is the extraction of gold(III) from acid solutions having high concentrations of NaCl by diethyleneglycol dibutyl ether (Butex) (5). Cyclic carbonates are also known to solvate alkali ions (6) (7) and the use of propylene carbonate for the extraction of gold (III) is mainly due to the solvating ability of the cyclic carbonate function (8). In this paper, we present a study of ion-pairing metal extractions of Co(II) and Au(III) and their relations with alkali extractions using extractants which can be expected to solvate the alkali ions well.

EXPERIMENTAL

K, Co, and Au analyses were carried out by Atomic Absorption Spectrophotometry (Apparatus : IL 453). Organic phases were previously mineralized with nitric acid-hydrochloric acid solutions. Induction-coupled plasma spectrometry (Model : ICP 2500) was also used for direct

Table 1. The extractants

COMPOUNDS

I $n = 1$

II $n = 2$

III $n = 3$

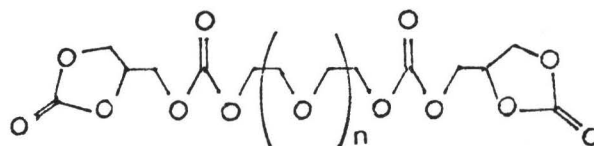
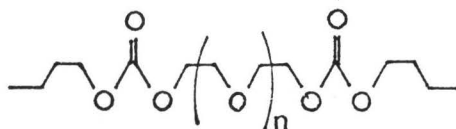
IV $n = 1$

V $n = 2$

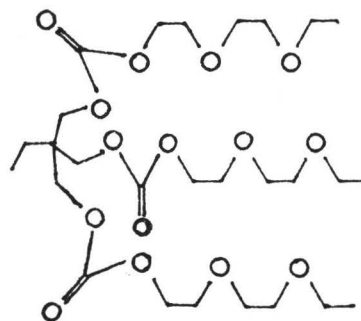
VI $n = 3$

VII $\bar{n} = 5.4$

VIII $\bar{n} \approx 12.3$



IX



BUTEX



analysis of gold in the organic phases after dilution in ethanol. Infrared spectra were obtained with a Beckman IR 10 spectrometer.

THE EXTRACTANTS

The extractants are poly(oxyethylene) derivatives of phosgene containing polyether functions, carbonate functions and/or cyclic carbonate functions. The compounds used were of three types (see table 1).

- A) Poly(oxyethylene)dibutyl carbonates ; ($n = 1, 2, 3$), compounds I, II, III.
- B) Poly(oxyethylene) chains with a carbonate-cyclic carbonate sequence at each end ; ($n = 1, 2, 3, \bar{n} = 5.4, \bar{n} = 12.3$), compounds IV-VIII.
- C) A three branch polyether carbonate ; compound IX.

FIG. 1

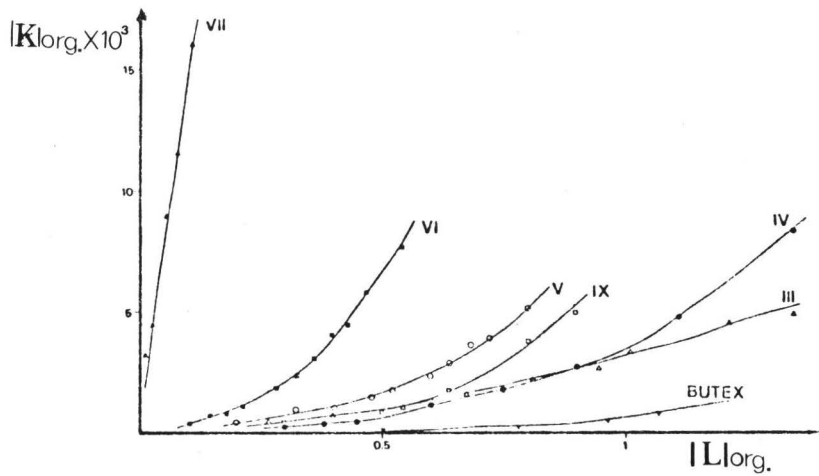


FIG. 2

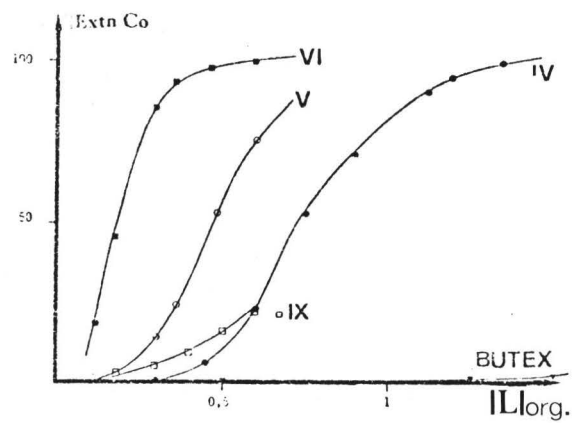


FIG. 3

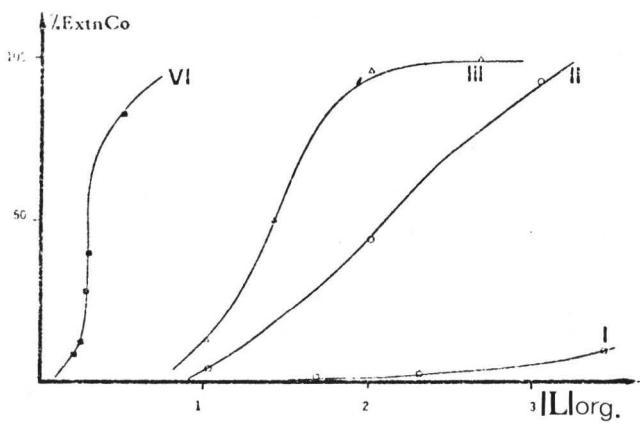


FIG. 1

The extraction of KSCN as a function of $|L|_{org}$.
organic phase ; extractants (M) in dichloro 1.2. ethane
aqueous phase ; 1M KSCN, pH~2, phase ratio 1 to 1 at 25°C.

FIG. 2

The extraction of Co(II) as a function of $|L|_{org}$.
organic phase ; extractants (M) in dichloro 1.2. ethane
aqueous phase ; 100ppm Co(II), 1M KSCN, pH~2, phase ratio 1 to 1 at 25°C.

FIG. 3

The extraction of Co(II) as a function of $|L|_{org}$.
organic phase ; extractants (M) in chloroform
aqueous phase ; 100ppm Co(II), KSCN 1M, pH~2, phase ratio 1 to 1 at 25°C.

EXTRACTIONS OF KSCN AND Co(II) IN KSCN MEDIUM

Extraction of Co(II) in KSCN is more efficient than that of KSCN itself. However both cases show very similar trends : (see FIG.1,2,3) : An increase in the extractability with the increasing length of the poly(oxyethylene) chain is observed within the series A and B. Otherwise, the compounds of the B series are systematically better extractants than the corresponding compounds having the same poly(oxyethylene) chain lengths in the A series. Moreover, most of the compounds have better extraction ability than Butex.

FIG. 4

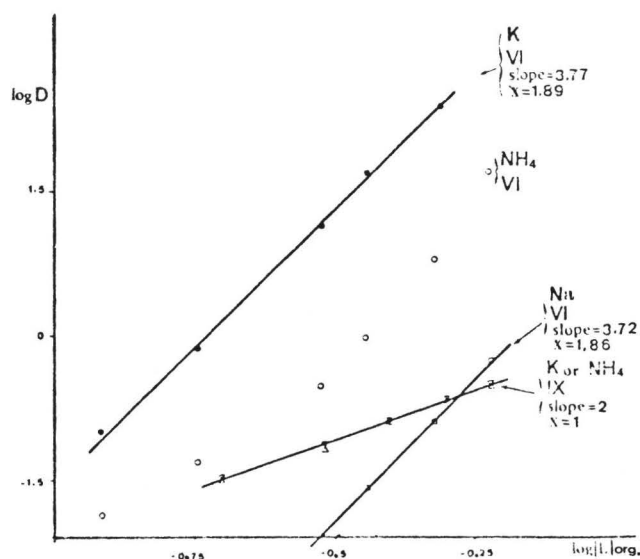


FIG. 4

The stoichiometry of M in the extraction of Co(II) by extractants VI and IX (in the MSCN media).

FIG. 5

The stoichiometry of K in the extraction of Co(II) and Au(III) by extractants V and IX (Co(II); KSCN medium. Au(III); KCl medium).

Table 2. The stoichiometry of the ligand-alkali ion complexes.

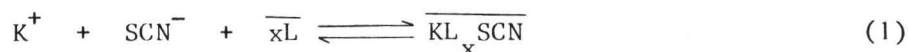
Extractants	x's values from KSCN extractions	x's values from Co ²⁺ /MSCN extract.	x's values from Au ³⁺ /KCl extract.
IV	2.6	2.6 (K ⁺)	
V	2.2	2.15(K ⁺); 2.2(NH ₄ ⁺)	2.15
VI	1.9	1.9 (K ⁺); 1.9(Na ⁺)	
VII	0.9		
IX	1.15	1.0 (K ⁺); 1.0(NH ₄ ⁺)	1.0

Assuming that there are no complications due to the distributions of the extractants between the two phases, these trends could reflect the relative complexing abilities of the extractants toward the potassium ion.

COMPLEXATION OF THE ALKALI IONS IN THE ORGANIC PHASE

a) SOLVENT EXTRACTION STUDY

For the extraction of KSCN, a simple extraction reaction can be proposed:



For the extraction of Co²⁺ in MSCN media and Au³⁺ in MCl media (M = Na⁺, NH₄⁺, K⁺), the following reactions are respectively assumed:

FIG. 6

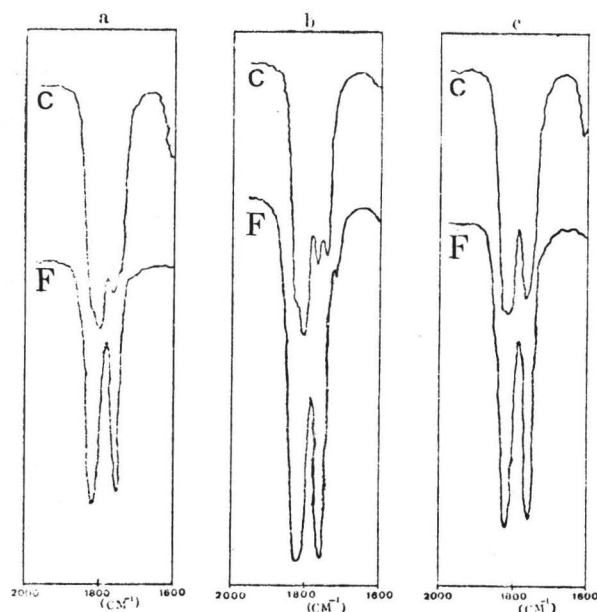


FIG. 6

Infrared spectra in the range $1600-1900\text{ cm}^{-1}$ for compounds V(a), VI(b), VII(c).
 F : free ligand
 C : F solution + $\text{NaB}\phi_4$

FIG. 7

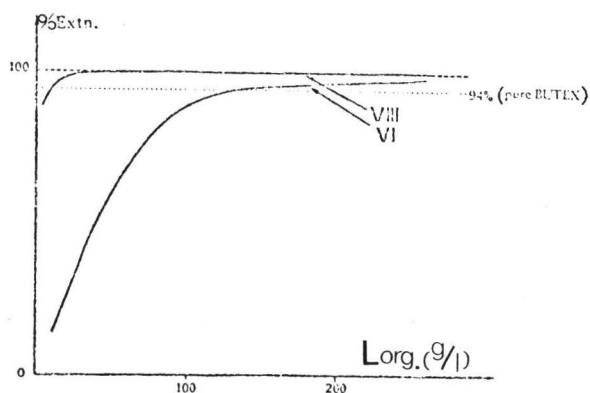
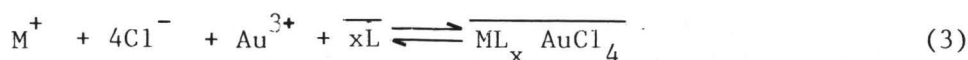
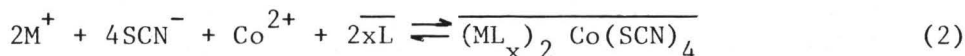


FIG. 7

The extraction of gold(III) by extractants VI and VIII
 organic phase ; several concentrations of VI or VIII in dichloro 1,2-ethane (3ml)
 aqueous phase ; 1000ppm Au , 2M NaCl, 0.05 N HCl (5ml).



Appropriate log/log plots lead to the determination of x values which provide useful information on the coordination of the alkali ions. Since KSCN is only weakly extracted we plotted $\log |\text{K}^+|_{\text{org.}}$ as a function of $\log |\text{L}|_{\text{org.}}$. For the cobalt and gold extraction systems $\log \frac{|\text{Co}|_{\text{org.}}}{|\text{Co}|_{\text{aq.}}}$ and $\log \frac{|\text{Au}|_{\text{org.}}}{|\text{Au}|_{\text{aq.}}}$ are respectively plotted as a function of $\log |\text{L}|_{\text{org.}}$. Some experimental lines obtained are given in FIG. 4 and 5. The overall results are summarized in Table 2. The constancy of the x values found for a given extractant and various extraction systems gives an *a posteriori* validity to the extraction reactions proposed above and suggests the existence of definite complexes between the alkali ions and the extractants in the organic phase. In the B series, the decrease of x values with the increase of the poly(oxyethylene) chain length shows a progressive contribution of the poly(oxyethylene) groups to the coordination of the potassium ion. The corresponding increase of the extraction ability is noteworthy. A value of x close to one is found for a poly(oxyethylene) chain corresponding to $\bar{n} = 5.4$. This result is in agreement with earlier findings on other POE derivatives having similar

chain lengths(2a). For compound IX, the 1:1 stoichiometry is also remarkable and is consistent with the existence of a K^+ or NH_4^+ "acyclic cryptate"(9) in the organic phase.

b) AN INFRARED STUDY

Infrared spectroscopy was used to characterize solvation of some monovalent ions in propylene carbonate (7). As an aid in evaluating the possible contribution of carbonate and cyclic carbonate groups to the coordination of the alkali, infrared spectra of dilute solutions of the B series compounds were studied in the range $1700 - 1900\text{ cm}^{-1}$. In this region they exhibit two bands near 1760 and 1815 cm^{-1} which correspond to the carbonate $\nu(C=O)$ and the cyclic carbonate $\nu(C=O)$. When some amounts of $NaBO_4$ are dissolved in solutions V and VI, new bands or shoulders appear which correspond to shifted $(C=O)$ bands. The shifts are of ca. 20 and 15 cm^{-1} for carbonate and cyclic carbonate $\nu(C=O)$ respectively and show therefore strong ligand-sodium interactions through carbonate and cyclic carbonate groups. In the case of mixture VII the shifts are weaker and correspond to weaker Na^+ -ligand through the $(C=O)$ bonds. We conclude that in this case the Na^+ -ligand interaction is mainly a poly(oxyethylene)- Na^+ interaction.

EXTRACTION OF GOLD(III)

These compounds were investigated for the extraction of gold(III) in conditions similar to those described by RIMMER (5) for the Butex process. In those conditions they follow trends similar to those shown above for KSCN and Co^{2+} in thiocyanate media. Dilute dichloroethane solutions of certain extractants have given very efficient extractions as shown in FIG. 7.

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EXTRACTANT SYSTEMS FOR NICKEL AND COBALT
BASED ON ORGANIC SULFONATES

R. R. Grinstead

Dow Chemical U.S.A.

Western Division Research & Development

2800 Mitchell Drive

Walnut Creek, California, 94598, USA

ABSTRACT

A number of two-component systems consisting of a high molecular weight amine chelating agent and dinonylnaphthalenesulfonic acid (DNNS) have been identified as possible extractants for nickel and cobalt from acid solutions in the pH region above 2. Several systems are described which extract nickel well in this range. Cobalt performance varies, from picolylamine derivatives, which prefer nickel to cobalt by about 100 fold, through bis-picolylamine derivatives, which prefer cobalt slightly over nickel. Hexadecyl picolinate/DNNS systems gave good extraction of nickel from a typical laterite leach composition, with separation factors over the major contaminating ions of 25 or more. Separation factors for cobalt were about 5-fold less. Stripping of nickel and cobalt from the organic phase is readily accomplished with 0.5 N sulfuric acid.

Although extractant systems for processing copper have become commonplace within the past several years, comparably effective systems for nickel and cobalt have yet to appear. Recently, work has been reported on the use of dinonylnaphthalenesulfonic acid (DNNS) and related compounds, in conjunction with the commercial extractant LIX 63, to extract copper, nickel and other metals. (1,2,3,4,5). Under certain conditions this system exhibits good selectivity for nickel and copper over the undesirable species iron(III) and aluminum, but appears to be difficult to strip and unstable toward hydrolysis.

We have worked extensively with DNNS/amine extractant system, and because of the potential interest in nickel processing in particular, we are prompted to describe at this time a few of these systems. Although development of such systems for commercial application is still in the early stages, we believe the data presented here will demonstrate the versatility and some of the potential of such systems.

GENERAL BEHAVIOR OF DNNS SYSTEMS

Because of the strong acidity of the sulfonic acid group DNNS is a liquid ion exchanger, capable of existing either as the acid or as a metal salt in organic solvents. (6,7). The selectivity characteristics are not particularly interesting to metallurgists, however, as the data in the first experiment in Table I show. This is because, of the metal ions of interest, iron(III) is preferred to all of the valuable ions copper, nickel and cobalt.

TABLE I

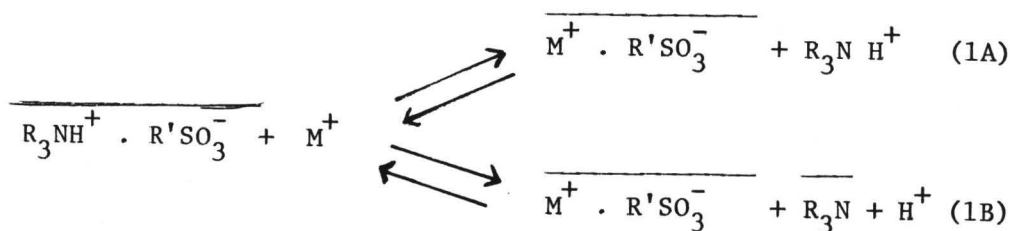
BEHAVIOR OF DNNS/AMINE EXTRACTION SYSTEMS. Organic, 0.20 M DNNS + amines as shown in Napoleum 470, a primarily aliphatic hydrocarbon diluent. Aqueous, 1 g/l each metal ion, as indicated.

Amine	pH	Dc, Distribution Coefficient			
		Cu	Ni	Co	Fe(III)
None	1.5	1.7	1.13	1.33	1.95
0.20M Trioctylamine	2.0	0.009	--	--	0.013
0.20M Quinoline	1.9	0.68	--	--	0.82
0.20M PBA*	1.7	41	--	--	0.008

*n-picolyl-p-(n-butyl)-aniline

One factor which affects the ion exchange equilibria is the hydrophobicity of the ion. If one uses the trioctylammonium (TOA) salt of DNNS, one finds, as the second test in Table I shows, that practically no extraction of either copper or iron(III) occurs. That is, the extractant system exhibits a high preference for the trioctylammonium cation over the metal cations present.

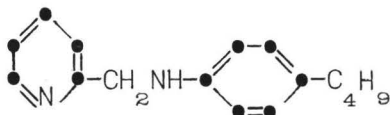
An intermediate situation can be observed if we use quinoline instead of trioctylamine. As the table shows a rather significant amount of both copper and iron is extracted, although not nearly as much as with no amine present at all. Iron is still preferred over copper. A simple explanation which seems to fit all of the observations is that although in the organic phase quinoline certainly forms a protonated species which would be expected to resist exchange into the aqueous phase, it is, after all, a rather weak base. As a result some dissociation of the proton can occur into the aqueous phase, which allows an equivalent amount of metal ions to transfer into the organic phase. This situation described by equation (1), which indicates the two mechanisms by which metal ion exchange can occur: first (1A) by exchange of the entire amine cation, and second (1B), by dissociation of the proton, leaving the amine in the organic phase. (Barred species are in the organic phase).



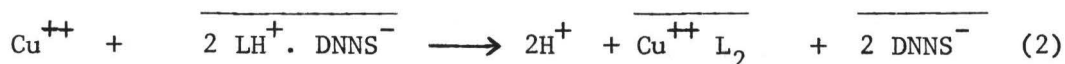
If only mechanism (1A) operates the selectivity should not be much different from DNNS alone, since the metal is simply a counterion to the DNNS anion. To the extent that (1B) occurs some change in selectivity may be observed, since the free base amine in the organic phase may selectively solvate certain metal ions. With monofunctional hydrophobic amines of moderate base strength, however, little extraction will occur because of the difficulty of displacing the amine cation into the aqueous phase or of dissociating the proton into the aqueous phase.

To describe the situation another way, the amine is a blocking agent, allowing only a small non-selective extraction of metal ions. This non-selective extraction will be a function of two properties: the strength of the amine as a base, and its hydrophobicity.

The last experiment in Table I shows extraction data for the compound N-(picolyl)-p-butylaniline, (PBA),



The comparison with the preceding compounds is striking, the latter extracting most of the copper and practically none of the iron. This is most simply explained as a result of the ability of the copper ion to form a chelate with the amine, the proton being displaced and transferred into the aqueous phase. Iron, which does not form a chelate with this amine, cannot displace the proton and is therefore not extracted. The net reaction for the extraction of copper can be expressed as:



Here DNNS^- denotes the deprotonated DNNS molecule, L represents the free base chelating agent and bars denote species in the organic phase. The equation is written for the formation of a 2:1 complex, although other stoichiometries can be accommodated as well.

From the discussion above we can now list the minimum requirements for using DNNS in a selective extraction system. One needs first a chelating agent which has the appropriate selectivity characteristics, and also adequate activity in the pH range of interest. Second, the agent should contain at least one amine group which is sufficiently basic to retain its proton in the presence of exchangeable non-chelating cations in the aqueous phase.

We have examined a large number of potential chelating agents in conjunction with DNNS and have found several which can be used to extract copper, nickel and cobalt, together or singly. This paper will discuss only the extraction of nickel and cobalt; obviously copper extraction is another useful area of application, but is beyond the scope of this discussion.

VARIATIONS IN THE AMINE COMPONENT

Some of the systems examined for their behavior in extracting nickel and cobalt are shown in Table II.

TABLE II

EXTRACTION OF METAL IONS BY DNNS SYSTEMS. VARIATION OF THE AMINE COMPONENT. 0.20 M DNNS/Napoleum 470/amine as shown. Initial aqueous contained 1 g/l of each ion shown. Phase ratio (O:A) = 1:3

Amine Component	R	pH	Ni	D A		
				Co	Al	Fe(III)
N-picolyl-p-butyl aniline (PBA)	1.00	1.8	0.46	0.006	0.012	
N-picolyl nonyl glycinate (PNG)	1.10	1.3	18	0.18	0.003	
N-p-dodecylbenzyl)-bis-picolyl-amine (DBPA) ^a	1.05	1.6	0.45	0.72		0.015
2-ethylhexyl picolinate (EHP)	1.05	1.5	3.2	1.1		0.50
Hexadecyl ^b picolinate (EHP)	1.05	1.6	2.3	1.3		0.60
Tridecyl ^c picolinamide (TDP)	1.05	1.5	0.38	0.73		0.15
Di-(n-butyl) picolinamide (DBP)	1.05	1.5	2.1	0.67		0.70
Bis-(2-ethylhexyl)picolinamide (BEP)	1.00	1.7	0.70	0.33	0.45	

a. Diluent is Chevron 3, an aromatic hydrocarbon diluent.

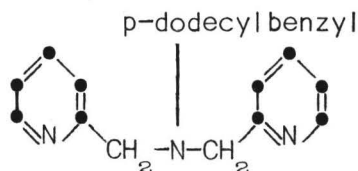
b. Derived from 2-octyl octanol and similar isomers (Exxon Corporation)

c. Derived from a branched chain tridecylamine (Rohm & Haas Corporation)

Each experiment was a single extraction containing three of the metals in a single aqueous phase. The first three compounds are derivatives of picolylamine, the structure for one of which was given above. Structures of the other two compounds are:



N-(picolyl) nonyl glycinate (PNG)



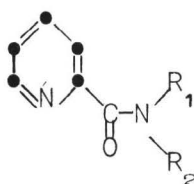
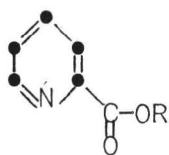
N-(p-dodecylbenzyl)-bis-picolylamine (DBPA)

The compound PBA is seen to be a fair nickel extractant in this pH range, but relatively poor for cobalt. Of course it should be realized that better extraction of most metal ions can be realized at higher pHs, and the 1.5-1.8 range was selected here simply as a convenient one for comparison.

The second compound, PNG, contains an additional coordinating group in the form of the ester carbonyl, and extraction of both nickel and cobalt is considerably higher. Both compounds, however, have a high preference for nickel over cobalt, of the order of 100 to 1.

Finally, the compound DBPA exhibits the interesting characteristic of extracting cobalt somewhat more strongly than nickel.

Two other classes of compounds examined are the esters and amides of picolinic acid, which can be represented by the general structures

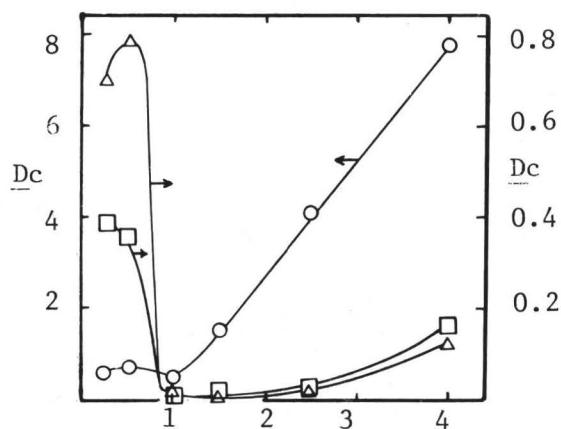


The behavior of the two groups is similar, extracting both nickel and cobalt reasonably well, but also extracting aluminum and iron(III) significantly.

An additional observation, not shown in the data, was that the phase separation characteristics of the picolinic acid derivatives were significantly better than the picolylamine derivatives, for reasons which are not entirely clear, and most of the subsequent effort has been focussed on the former compound.

EFFECT OF EXTRACTANT MOLE RATIO

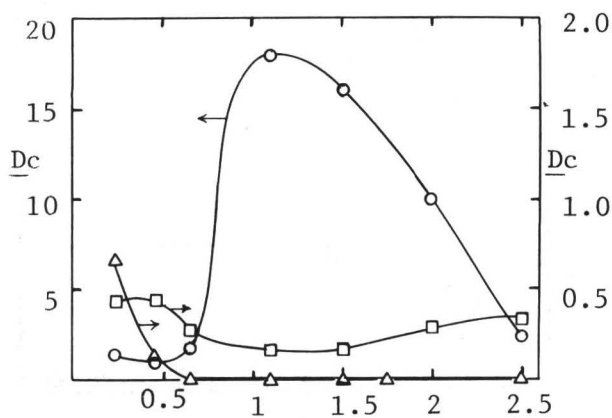
Equation (2) suggests that the mole ratio of amine to DNNS should be important in determining the behavior of this system. In Figure 1 is shown the effect of this ratio on the distribution coefficient for nickel, cobalt and aluminum for the system DNNS/picolyl butylaniline.



Extractant Mole Ratio R, Amine/DNNS

FIG. 1

DNNS/PICOLYL BUTYLANILINE EXTRACTION SYSTEM. Organic, 0.20 M DNNS in Napoleum 470, plus chelator as shown. Aqueous, 1 g each ion per liter; equilibrium pH 1.9 ± 0.1 . $\circ$ Ni, $\square$ Co, $\triangle$ Al.



Extractant Mole Ratio (Amine/DNNS)

FIG. 2

DNNS/NONYL N-PICOLYL GLYCINATE EXTRACTION SYSTEM. Organic, 0.20 M DNNS in Napoleum 470, plus chelator as shown. Aqueous, 1 g each ion/l, equilibrium pH 2.1 ± 0.1 . $\circ$ Ni, $\square$ Co, $\triangle$ Al.

At low amine concentrations aluminum is preferred slightly to nickel and cobalt, presumably because there are insufficient amine cations to balance the DNNS anions and thus block the extraction of aluminum. As the extractant ratio approaches one, however, aluminum extraction drops sharply and is relatively low at higher ratios. Beyond a ratio of 1 the system is fairly selective for nickel, with extraction increasing even at ratios as high as 4.

A somewhat different behavior is shown by the compound PNG, the data for which are shown in Figure 2. Here nickel extraction peaks at an extractant ratio of about 1, in contrast to PBA, where extraction increased steadily with excess amine. As before, aluminum extraction drops with increasing extractant ratio, but becomes negligible at a ratio of about 0.5, in contrast with the ratio of about one which was required for PBA. Because of the strongly basic aliphatic nitrogen in this molecule it seems likely that both nitrogens are protonated at the ratio of 0.5, providing the one cation per DNNS necessary to block aluminum extraction. In PBA, presumably, the more weakly basic nitrogens do not both protonate, and thus one amine is required per DNNS to provide the required number of cations.

A different type of compound is hexadecyl picolinate (HDP), behavior of which is shown in Figure 3. Both cobalt and nickel are extracted fairly well, and substantially better than aluminum.

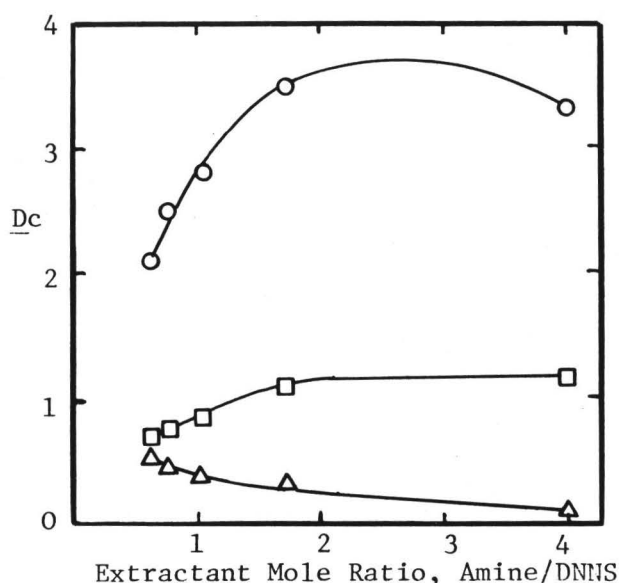


FIG. 3
DNNS/HEXADECYL PICOLINATE EXTRACTION SYSTEM. Organic, 0.20 M DNNS in Napoleum 470, plus chelator as shown. Aqueous, 1 g each ion per liter; equilibrium pH 1.7 ± 0.1 . $\circ$ Ni, $\square$ Co, $\triangle$ Al.

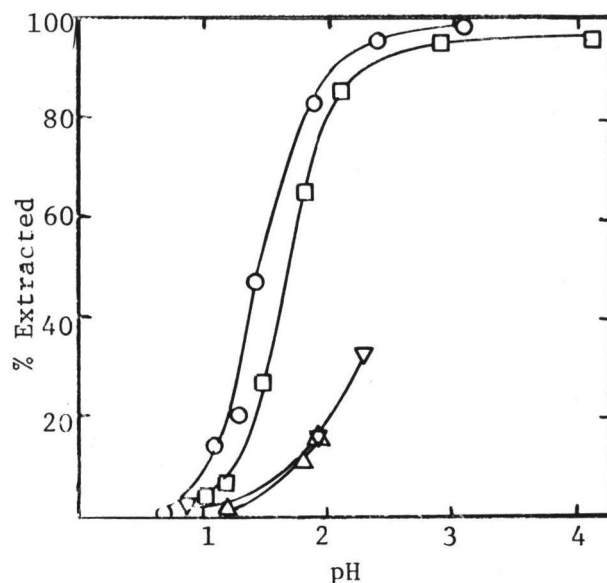


FIG. 4
DNNS/HEXADECYL PICOLINATE EXTRACTION SYSTEM. EFFECT OF pH. Organic, 0.20 M DNNS, 0.60 M amine, Napoleum 470. Aqueous, 1 g/l each ion. Phase ratio (O:A) = 1:3. $\circ$ Ni, $\square$ Co, $\triangle$ Fe(III), ∇ Al.

EFFECT OF pH ON EXTRACTION

In order to observe the effect of pH on extraction a series of experiments was done with each metal ion separately, at an initial concentration of 1 g/l. The data for HDP are given in Figure 4. The usual S-shaped curve was obtained when percent extraction was plotted against pH. This compound exhibits a moderate selectivity for both nickel and cobalt over both aluminum and iron(III).

NICKEL DISTRIBUTION CURVES

Distribution data were obtained for nickel in HDP systems at a series of pH values, and are shown in Figure 5.

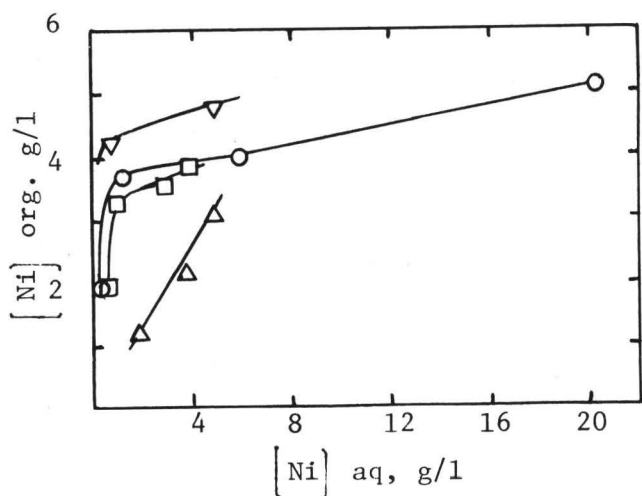


FIG. 5

DISTRIBUTION OF NICKEL BETWEEN AQUEOUS SULFATE SOLUTIONS AND DNNS/HDP SYSTEMS. Organic Phase, 0.20 M DNNS/0.60 M HDP/Napoleum 470. Aqueous phase, $\text{NiSO}_4/\text{Na}_2\text{SO}_4$ Solutions. 0.10 M Sulfate: Δ pH 1.5, $\square$ pH 1.8; 0.43 M Sulfate: $\circ$ pH 2.4, ∇ pH 3.0-3.3

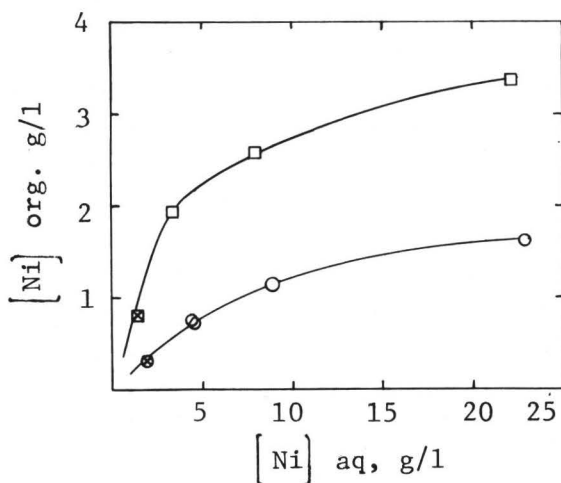


FIG. 6

NICKEL DISTRIBUTION BETWEEN AQUEOUS SULFURIC ACID AND HDP SYSTEMS. Organic, 0.20 M DNNS/0.60 M HDP/Napoleum 470. Aqueous, sulfuric acid as shown. Open points from extraction of nickel from sulfuric acid, filled points from stripping of nickel from loaded organic. $\circ \otimes$, 0.55 N H_2SO_4 ; $\square \boxtimes$, 0.27 N H_2SO_4 .

In all of these experiments the total sulfate concentration was maintained constant by using various proportions of nickel and sodium sulfates. Distribution of nickel into the organic phase is quite strong up to a concentration of about 3 g Ni/l (0.05 M), after which the distribution curve rises only slowly with increasing aqueous nickel concentration. The data at the higher pH levels indicate that the theoretical limit of 0.10 M is being approached, albeit slowly, as the aqueous nickel concentration rises. At the 0.05 M level there is one nickel ion in the organic phase for each four DNNS molecules, and the existence of the pronounced knee in the curves suggests there is some relatively stable complex formed in the organic phase involving this ratio. Further speculation seems unproductive until further data are obtained on the mechanism of extraction.

REMOVAL OF NICKEL FROM THE ORGANIC PHASE

Because of the dependence of the extraction of metal ions on pH dilute mineral acid is quite suitable for stripping or removal of the extracted ions back into an aqueous phase. In Figure 6 is shown distribution data for nickel between HDP systems and dilute sulfuric acid. As expected, the higher acid concentration is the better stripping agent. Judging from the curves fairly adequate stripping will probably require acid of at least 0.5 N, but it should easily be possible to obtain strip solutions of considerably more than 20-25 g Ni/l with this concentration.

SOLUBLE LOSS AND HYDROLYTIC STABILITY

These properties of HDP were determined by contact with the desired aqueous phases, followed by filtration of the aqueous phase and determination of the UV absorbance. The picolinic acid ring exhibits a strong absorbance peak at about 280 nm, whether it is present in the form of an ester, amide or the free acid. Thus, initial determinations could be used for distribution or soluble loss data, and subsequent determinations could be used to determine the rate of hydrolysis, since the picolinic acid formed in this process appears in the aqueous phase.

The distribution or soluble loss so obtained was 10 ppm in a 0.25 M sodium sulfate solution at pH 2, and 34 ppm in a 0.5 N sulfuric acid solution. In contact with either solution a loss of about 10% per month due to hydrolysis was observed. The distribution loss figures are probably acceptable, and in any case can probably be reduced by using a larger alkyl group. The major loss in use would probably be due to hydrolysis of the compound.

PHASE SEPARATION AND EXTRACTION KINETICS

We shall report only some qualitative observations here, since no extensive study of these parameters has been made. Extraction of metal ions under most conditions is fairly rapid, as judged by achievement of a constant pH within 5 minutes during extraction tests. Kinetics of the removal of nickel ion from HDP systems by dilute sulfuric acid were examined briefly by sampling a stirred system, and equilibrium was also found to occur in less than 5 minutes.

Phase separation was generally good, but was faster in solutions of lower acidities. Systems of volumes of 50-100 ml separated to a sharp meniscus within a few minutes under extraction conditions (pH 1-3), while strip systems (0.2-3N acid) were usually separated in 5-10 minutes.

EXTRACTION OF METAL IONS FROM A TYPICAL LEACH SOLUTION

To obtain a more accurate picture of the behavior of this type of system in an actual situation some extractions were carried out with HDP on solutions approximating the composition of those obtained from acid leaching of laterite ore. In each case a single organic phase was contacted with three volumes of the aqueous solution and then stripped with sulfuric acid. In the first experiment all of the usual ions were present, while in the second nickel was absent to observe the behavior of the system on extraction of cobalt. The data for these tests are given in Table III.

TABLE III

EXTRACTION OF TYPICAL LATERITE LEACH WITH HDP/DNNS. Organic, 0.60 M HDP/0.20 M DNNS/Napoleum 470. Organic phase contacted successively with three portions of aqueous phase @ O:A = 1:3.

		Concentrations, g/l					
	pH	Ni	Co	Mn	Mg	Al	Fe(III)
<u>Nickel Present</u>							
Feed		1.00	0.22	3.27	6.1	1.55	1.79
3rd Aqueous Raffinate	2.0	0.87	0.23	3.25	6.1	1.53	1.78
Final Organic		2.50	0.15	0.33	0.24	0.081	0.069
Dc for 3rd Contact		2.9	0.65	0.102	0.039	0.053	0.039
<u>Nickel Absent</u>							
Feed			0.22	3.24	5.72	1.58	1.84
3rd Aqueous Raffinate	2.7		0.18	3.21	6.38	1.60	1.75
Final Organic			0.67	0.76	0.27	0.062	0.12
Dc for 3rd Contact			3.7	0.24	0.042	0.039	0.069

In the first test with nickel present the distribution coefficients clearly show the substantially greater extraction tendency for nickel and cobalt. And, in fact, the organic phase contains primarily nickel after loading. But because of the low cobalt level and the high levels of other ions, the separation of cobalt from these ions is only fair. This is more clearly seen in the second test where nickel was omitted. Again the actual distribution coefficient for cobalt was considerably higher than for any other ion, but the organic actually contained more manganese than cobalt.

DISCUSSION

This report has described in a preliminary way some features of DNNS systems which we believe indicate a good potential for the development of practical selective extraction systems, particularly for nickel and cobalt. Considerable variation is available in the relative extraction tendencies of nickel and cobalt, ranging from a 100 fold preference for nickel to a slight preference for cobalt. Similarly, considerable leeway in the choice of the usable pH range is available. We have chosen to focus on a picolinate ester in this paper as an example of a fairly simple system which may offer practical solutions to some processing problems. The ester does not provide the selectivity of some other systems, but does exhibit reasonably useful physical behavior.

From a process standpoint the separation factors exhibited by HDP for nickel and cobalt over the other species are probably both sufficiently high to allow a separation process to be designed. Distribution coefficients for both ions are high enough to allow fairly complete recovery to be obtained in a multistage extraction process. And, even though considerable coextraction of undesirable species occurs, it is clear that in most cases over 90% of the contaminating species will be rejected into the raffinate. Further separation of the undesirable species can probably be obtained most readily by use of scrubbing or reflux techniques, since the separation factors (ratios of distribution coefficients) for both nickel and cobalt over the other ions are fairly substantial.

The major disadvantage is the instability toward hydrolysis, and will restrict its usefulness. However, other compounds are under examination, and a number of them have been identified which appear to combine some of the useful features of these systems with a considerably greater stability. These will be reported on at a future date.

ACKNOWLEDGMENTS

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THE EXTRACTION OF DIVALENT MANGANESE, COBALT, NICKEL, COPPER, ZINC, CADMIUM AND MERCURY FROM AQUEOUS CHLORIDE SOLUTIONS BY LONG-CHAIN ALKYLAMMONIUM CARBOXYLATE

Taichi SATO, Masahiro YAMAMOTO and Hiroshi WATANABE
Department of Applied Chemistry,
Faculty of Engineering,
Shizuoka University
Hamamatsu, Japan

ABSTRACT The extraction of divalent manganese, cobalt, nickel, copper, zinc, cadmium and mercury from aqueous chloride solutions by the long-chain alkylammonium carboxylates, prepared by combination of tricaprylmethylammonium chloride ($R_3R'NCl$) and carboxylic (caprylic, capric and lauric) acids ($R''COOH$) in benzene, has been investigated under different conditions. The organic phases are examined by spectrophotometry and infrared spectral measurement. As a result, it is found that the extraction efficiency follows the order $Hg \gg Cu > Zn > Cd > Co \approx Ni > Mn$ when the quaternary compound is present in excess, and that the extraction process is expressed as $M^{2+}(aq) + 2Cl^-(aq) + 3R_3R'NR''COO(org) \rightleftharpoons (R_3R'N)[M(R''COO)_3](org) + 2R_3R'NCl(org)$ in which $M = Mn, Co, Ni, Cu$ and Zn . The extracted species of divalent manganese, cobalt, nickel, copper and zinc exist as the complexes $(R_3R'N)[M(R''COO)_3]$ in an octahedral arrangement.

INTRODUCTION

The extraction of metals from acid solutions by high molecular weight amines has been reported by a number of investigators, but there are few observations on the extraction of metals from aqueous solutions in the vicinity of neutral range. In contrast, although carboxylic acids are a possible group of reagents to extract the metals in the vicinity of neutral range¹⁾, their extraction efficiencies depend on the pH of the aqueous phase remarkably. Accordingly the mixed ionic solvent system, consisting of long-chain alkylammonium carboxylates, is considered effective for the such extraction. This is mainly applied to the extraction of magnesium²⁻⁴⁾, but observations on the extraction of other metals are limited. We have also studied this extraction system with long-chain alkylammonium compounds⁵⁾. The present study extends the work to the extraction of divalent manganese, cobalt, nickel, copper, zinc, cadmium and mercury from aqueous chloride solutions by alkylammonium carboxylates.

EXPERIMENTAL

Reagent

The alkylammonium carboxylates were prepared by mixing calculated amounts (equal volumes of solutions in 0.5 M each) of tricaprylmethylammonium chloride (General Mills, $R_3R'NCl$, Aliquat-336) and carboxylic acids (caprylic, capric, and lauric acids represented as $C_nH_{2n+1}COOH$ in $n = 7, 9$ and 11 , respectively or $R''COOH$), and treated with a stoichiometric excess of sodium hydroxide, and then washed thoroughly with distilled water to remove the ions of sodium and

chloride. The resulting materials ($R_3R'NR''COO \cdot 5H_2O$) which exhibit the properties illustrated in Table 1 are diluted with benzene. The aqueous solutions of the chlorides of divalent metals were prepared by dissolving their salts ($MnCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $ZnCl_2$, $CdCl_2 \cdot 2.5H_2O$, $HgCl_2$) in water and those pH values were adjusted by adding perchloric acid. The reagents used were of analytical grade.

Extraction and analytical procedures

The procedure for obtaining the distribution coefficient (the ratio of the equilibrium concentration of metal in the organic phase to that in the aqueous phase), D , was as described previously⁶): equal volumes (15 ml) of the organic and aqueous phases were shaken for 10 min, and then metal in the organic phase was stripped with 1 M hydrochloric acid. The concentration of metals was determined by EDTA titration using the following indicators: BT (Eriochrome Black T) for manganese⁷), zinc⁸), cadmium⁸) and mercury⁹); XO (xylenol orange) for cobalt¹⁰); Cu-PAN (1-(2-pyridylazo)-2-naphtol) for nickel¹¹); PAN for copper¹²). The concentration of chloride in the organic phase was determined by Volhard's method, and the water content of the organic phase by Karl-Fischer titration. The complexes freed from benzene were prepared by drying the metal saturated organic phase in vacuo at 50 °C.

Spectrophotometry and infrared measurement

The absorption spectra were obtained on a Shimadzu Model QV-50 spectrophotometer, using matched 1.00 cm fused silica cells, and the infrared spectra obtained on a Japan Spectroscopic Co. Ltd. Model IRA-1 grating infrared spectrophotometer for measurement at 4000-650 cm^{-1} , and Model IR-F grating type for measurement at 700-200 cm^{-1} , using a capillary film between thallium halide or polyethylene plates.

RESULTS AND DISCUSSION

Extraction isotherm

When nickel(II) is extracted with tricaprylmethylammonium laurate from aqueous nickel chloride solution at 1 g/l varying pH value, the distribution coefficient steeply rises with increasing the pH value in the range of pH 2-3, and then becomes almost constant at $pH > \sim 3$, as shown in Fig.1. The lowering in the distribution coefficient at low pH arises from the decrease of the available extractant, caused by the extraction of acid from aqueous solution. This interpretation is supported by the fact that hydrochloric acid is extracted by the quaternary compound by the reaction



in which (a) and (o) are aqueous and organic phases, respectively. In order to elucidate further the reaction between a benzene solution of quaternary compound and aqueous hydrochloric acid solution, when the variation of the chloride concentration in the organic phase with the initial hydrochloric acid concentration of the aqueous phase is examined by the extraction of aqueous solutions, containing hydrochloric acid in the absence of nickel chloride with 0.02 M quaternary ammonium laurate in benzene at 20 °C, the chloride concentration in the organic phase reveals a constant value of 0.02 M at an aqueous hydrochloric acid concentrations above 0.02 M (Fig.2). Additionally, the infrared spectra of those organic phases show the absorptions due to the formation of dimeric carboxylic acid, supporting the reaction in Eqn.(1). Furthermore, as a similar result is obtained in the extraction of perchloric acid with quaternary compound, it is expected that a reaction analogous to Eqn.(1) also holds for the extraction of perchloric acid. Accordingly, because the quaternary compound is easily decomposed by acid, it can be used to extract metals from nearly neutral aqueous solutions at pH 5-8.

In the extraction of aqueous solutions containing nickel chloride at a

Table 1 Properties of tricaprylmethylammonium carboxylate

Property	R ₃ R'NR''COO·5H ₂ O			Aliquat-336
	Caprylate	Caprate	Laurate	
Molecular weight ^{a)}	607	660	679	442
Appearance at room temperture	Viscous liquid	Viscous liquid	Viscous liquid	Viscous liquid
Colour	Yellowish brown	Light brown	Light brown	Yellowish brown
Specific gravity at 20°C	0.884	0.885	0.894	0.884
Refractive index at 20°C	1.4594	1.4593	1.4592	1.4733
Viscosity at 20°C, cp	1585	1590	1636	2550
Solubility ^{b)} in				
Benzene	>100	>100	>100	>100
Kerosene	>100	>100	>100	<2
Cyclohexane	>100	>100	>100	>100
Isopropanol	>100	>100	>100	>100
Carbon tetrachloride	>100	>100	>100	>100
Water	<1	<1	<1	<1

- a) Apparent molecular weight determined by using benzene on a Hitachi Model 115 isothermal molecular weight apparatus.
b) Solubility in grams per solvent in 100 grams.

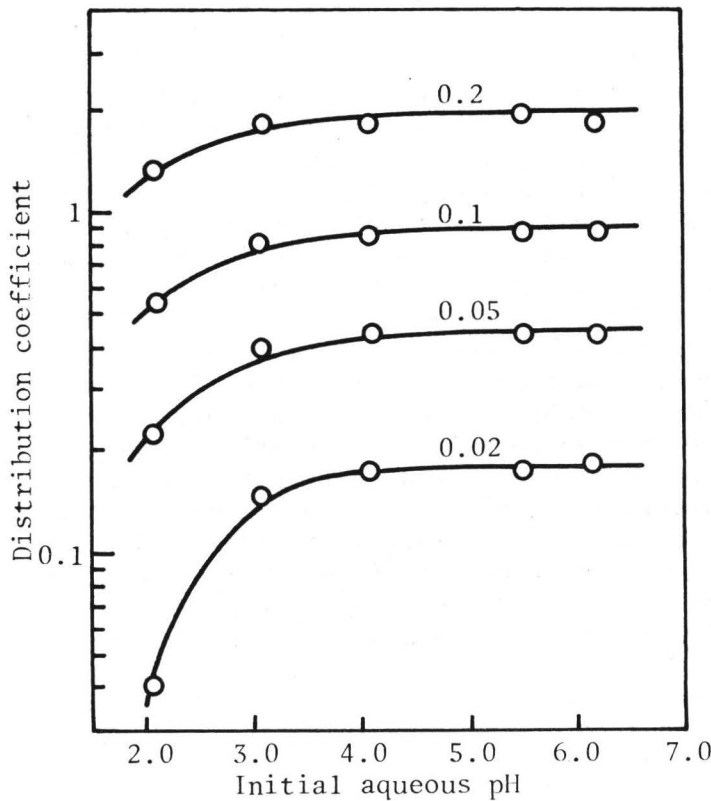
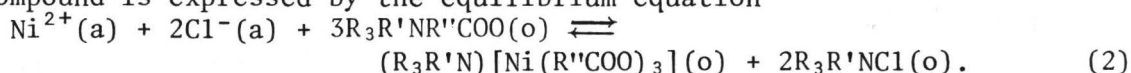


Fig.1 Extraction of nickel chloride from aqueous solutions containing perchloric acid by tricaprylmethylammonium laurate in benzene (numerals on curves are quaternary compound concentrations, M).

constant pH of 5.5 with 0.01 M quaternary compound in benzene at 20 °C, the molar ratio of the concentrations of quaternary compound and chloride to the nickel concentration in the organic phase plotted as a function of the initial aqueous nickel concentration approaches the limiting values of three and two, respectively, indicating the composition of the organic phase in the molar ratio of nickel/chloride/quaternary compound = 1 : 2 : 3. However, when the initial aqueous nickel concentration increases above 10 g/l. the latter molar ratio becomes over two, because the hydrochloric acid arising from the hydrolysis of nickel chloride in the aqueous phase is extracted into the organic solution. This stoichiometry corresponds to the result for the continuous variation method. In the extraction at constant chloride concentration of 0.1 M, the variation of the nickel concentration in the organic phase as a function of the initial aqueous nickel concentration and quaternary compound at a fixed concentration of 0.1 M gives a maximum at a molar ratio of initial aqueous nickel concentration to quaternary compound of 1 : 3. Accordingly the extraction of nickel chloride from aqueous solutions by tricaprylmethylammonium compound is expressed by the equilibrium equation



This is also supported by the dependencies of the distribution coefficient on the concentrations of extractant and aqueous chloride. Eqn.(2) leads to the relationship

$$K = \frac{[(\text{R}_3\text{R}'\text{N})[\text{Ni}(\text{R}''\text{COO})_3]]_{\text{org}}[\text{R}_3\text{R}'\text{NCl}]_{\text{org}}^2}{[\text{Ni}^{2+}]_{\text{aq}}[\text{Cl}^{-}]_{\text{aq}}^2[\text{R}_3\text{R}'\text{NR}''\text{COO}]_{\text{org}}^3} \quad (3)$$

in which K is the equilibrium constant. If we assume that $D = [\text{Ni}]_{\text{org}}/[\text{Ni}]_{\text{aq}}$, $[\text{Cl}]_{\text{aq}} = 2[\text{Ni}]_{\text{aq}}$ and $[\text{R}_3\text{R}'\text{NCl}]_{\text{org}} = 2[\text{Ni}]_{\text{org}}$, the following relation is derived:

$$K = D[\text{R}_3\text{R}'\text{NCl}]_{\text{org}}^2/[\text{Cl}^{-}]_{\text{aq}}^2[\text{R}_3\text{R}'\text{NR}''\text{COO}]_{\text{org}}^3 \quad (4)$$

$$= D^3/[\text{R}_3\text{R}'\text{NR}''\text{COO}]_{\text{org}}^3. \quad (5)$$

Thus Eqns.(4) and (5) should be satisfied by

$$\log \{D[\text{R}_3\text{R}'\text{NCl}]_{\text{org}}^2/[\text{R}_3\text{R}'\text{NR}''\text{COO}]_{\text{org}}^3\} = \log K + 2\log [\text{Cl}^{-}]_{\text{aq}} \quad (6)$$

and

$$\log D = (1/3)\log K + \log [\text{R}_3\text{R}'\text{NR}''\text{COO}]_{\text{org}} \quad (7)$$

In the extraction of nickel chloride from aqueous solutions containing perchloric acid, the log-log plots of D vs. the free quaternary compound concentration, $[\text{R}_3\text{R}'\text{NR}''\text{COO}]_{\text{org}}$, give straight lines with the slopes of 1.0 and 1.1 for the initial aqueous acidities of 0 and 0.01 M, respectively, suggesting a first-power dependence of the distribution coefficient on the solvent concentration. For the extraction of nickel chloride from aqueous solutions containing lithium chloride, the distribution coefficient rises with increasing initial aqueous lithium chloride concentration as shown in Table 2. However, when the extraction of aqueous lithium chloride solutions in the absence of nickel chloride is examined as in the case of acid extraction (Fig.2), it is found that the increase of the chloride concentration in the organic phase is slight with the aqueous lithium chloride concentration as indicated in Table 2. Therefore it is considered that in the extraction of nickel chloride from aqueous solutions containing lithium chloride, the increase of the distribution coefficient with the initial aqueous lithium chloride concentration is attributed to the salting-out effect of lithium chloride. In this extraction, the log-log plots of $D[\text{R}_3\text{R}'\text{NCl}]_{\text{org}}^2/[\text{R}_3\text{R}'\text{NR}''\text{COO}]_{\text{org}}^3$ vs. $[\text{Cl}^{-}]_{\text{aq}}$ suggest a second-power dependence of the distribution coefficient on the aqueous chloride concentration.

The results for the extraction of divalent manganese, cobalt, copper, zinc, cadmium and mercury from aqueous solutions containing their chlorides at 1 g/l in the absence of perchloric acid with tricaprylmethylammonium laurate are shown in Table 3, compared with that for nickel(II). From this it is seen that the extraction efficiency is in the order of $\text{Hg} \gg \text{Cd} > \text{Cu} > \text{Zn} > \text{Co} \approx \text{Ni}$

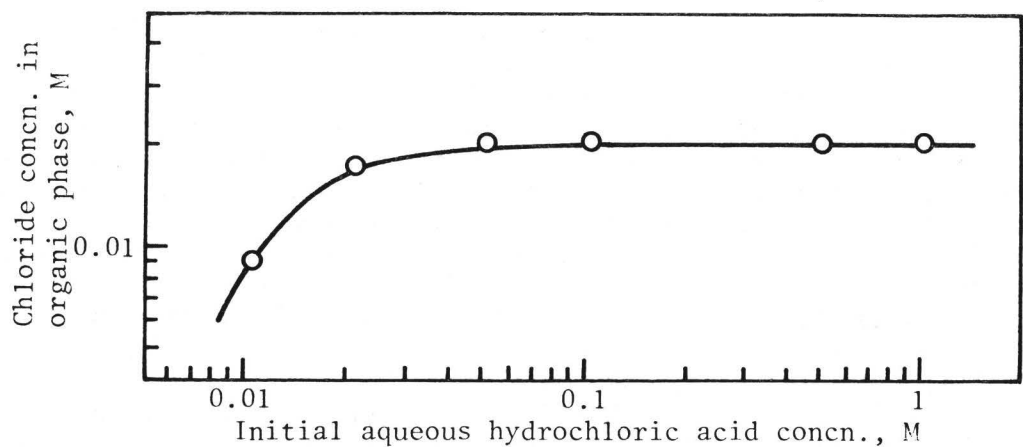


Fig.2 Variation of the chloride concentration in the organic phase with initial aqueous hydrochloric acid concentration for the extraction of hydrochloric acid by 0.02 M tricaprylmethylammonium laurate in benzene.

Table 2 Extraction of aqueous solutions containing lithium chloride in the absence or the presence of nickel chloride at 1 g/l with tri-caprylmethylammonium laurate in benzene at 20 °C

Initial aq. [LiCl], M	[Cl] _{org} x 10 ³ M ^{a)}	D
0.01	0.657	0.178
0.02	0.750	0.269
0.05	0.938	0.385
0.1	1.31	0.495
0.2	1.78	0.645
0.5	3.10	1.03
1.0	4.40	1.36

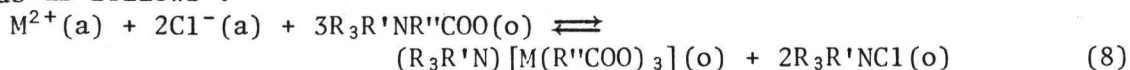
a) The extraction in the absence of nickel chloride.

Table 3 Extraction of divalent manganese, cobalt, nickel, copper, zinc, cadmium and mercury from aqueous solutions containing their chlorides at 1 g/l with tricaprylmethylammonium laurate in benzene

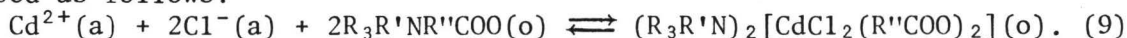
[R ₃ R'NR''COO], M	Distribution coefficient, D						
	Mn	Co	Ni	Cu	Zn	Cd	Hg
0.01	0.0575	0.0912	0.0908	0.579	0.440	1.19	>1000*
0.02	0.140	0.204	0.175	1.92	0.975	2.10	>1000
0.05	0.325	0.450	0.451	12.4	3.12	3.61	>1000
0.1	0.637	0.941	0.938	42.3	9.18	6.56	>1000
0.2	1.24	1.93	1.99	118	20.8	10.8	>1000

* Mercury is wholly extracted to the organic phase.

> Mn for $[R_3R'NR''COO] \leq 0.05$ M and of $Hg \gg Cu > Zn > Cd > Co \approx Ni > Mn$ for $[R_3R'NR''COO] > 0.05$ M, when the quaternary compound is present in excess. Further the log-log plots of D vs. $[R_3R'NR''COO]_{org}$ for divalent manganese, cobalt, copper and zinc give straight lines with the slope of approximately unity, suggesting that their equilibria are indicated by the same expression as the extraction of nickel(II) according to the Eqn.(2). These facts are also supported by the variation in the stoichiometric composition of their organic phases as a function of the initial aqueous metal concentration, and in addition by the continuous variation method for the concentrations in their organic phases. Hence it is presumed that the extraction of divalent transition metals from aqueous chloride solutions by quaternary compound proceeds as follows :



where M = Mn, Co, Ni, Cu and Zn. For the extraction of cadmium(II), the variation of the composition of the organic phase as a function of the initial aqueous cadmium concentration gives the molar ratio of cadmium/chloride/quaternary compound = 1 : 2 : 2, indicating the stoichiometry $(R_3R'N)_2[CdCl_2(R''COO)_2]$. This is also supported by the result for the continuous variation method. It is thus thought that the extraction equilibrium of cadmium(II) is expressed as follows:



In the extraction of mercury(II), however, the mercury concentration in the organic phase increases with increasing initial aqueous mercury concentration above the molar ratio $[R_3R'NR''COO]_{org}/[Hg]_{aq} \approx 1$, and then a third layer is formed below this ratio. Accordingly it is inferred that the extraction of mercury proceeds by a reaction involving the formation of a polymeric species.

Temperature effect

The extraction of aqueous solution (pH 5.5) containing nickel chloride at 1 g/l with 0.02 M tricaprylmethylammonium laurate in benzene at temperature between 10 and 50 °C gave the result that the distribution coefficient is little influenced by varying the temperature. When the similar experiments were carried out for the extraction of divalent manganese, cobalt, copper and zinc, the effect of temperature on the distribution coefficients was slight as shown in Fig.3. From the thermodynamic values (the changes in free energy, enthalpy and entropy) for the Eqn.(8) estimated together with the equilibrium constants at 20 °C (Table 4), it is deduced that although the individual change in enthalpy or entropy does not indicate a reciprocal relation with the extraction efficiency, the order $Cu > Zn > Co \approx Ni > Mn$ corresponds to the increase in the change in free energy and/or the decrease in the equilibrium constant.

Infrared and absorption spectra

The infrared spectra of the organic extracts from the extraction of aqueous solutions at initial nickel chloride concentration of 1, 5, 10, 20 and 50 g/l with 0.01 M tricaprylmethylammonium laurate in benzene at 20 °C were compared with that of quaternary ammonium compound. In the infrared spectrum of carboxylic acid, the C-O stretching band appears at 1710 and 1400-1200 cm^{-1} (13). However, since the quaternary compound shows the C-O stretching vibrations at 1560 and 1380 cm^{-1} , it is considered that the extractant exists in the organic phase as a carboxylate (14), $R_3R'NR''COO \cdot 5H_2O$. For the infrared spectra of the organic extracts, the C-O stretching modes appear at the same frequencies as those of the quaternary compound. The relative intensities of the bands due to the CH_3 degenerate bending and CH_2 scissoring and C-O stretching vibration superposed on the CH_3 symmetrical bending absorption become converse. Accordingly it is deduced that the $R''COO^-$ group coordinates to nickel ion as bidentate ligand. At higher loading, the C-O stretching bands appear at 1720, 1425 and 1180 cm^{-1} , ascribed to the presence of carboxylic acid formed by the

Table 4 Thermodynamic values^{a)} estimated from the temperature-dependence of distribution coefficients for divalent transition metals, compared with the equilibrium constants

Metal	ΔG , kJ/mol	ΔH , kJ/mol	ΔS , kJ/mol·K	$K^b)$
Mn	-15.65	-5.06	36.11	6.2×10^2
Co	-18.62	14.48	113.0	2.1×10^3
Ni	-17.66	0	60.25	1.4×10^3
Cu	-43.85	-25.10	64.02	6.6×10^7
Zn	-34.18	14.06	164.4	1.3×10^6

a) ΔG , ΔH and ΔS represent the changes in free energy, enthalpy and entropy, respectively.

b) K denotes the equilibrium constant at 20 °C for Eqn.(8).

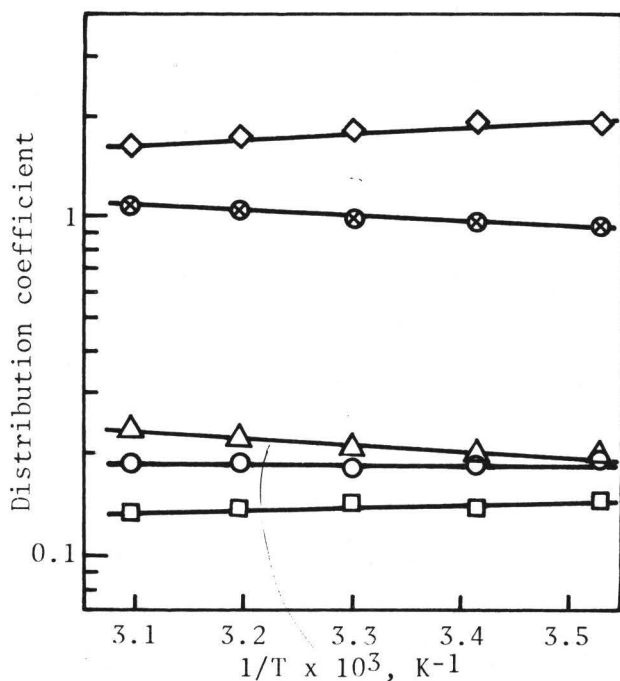


Fig.3 Temperature-dependence of distribution coefficient for the extraction of divalent transition metals from aqueous solutions containing their chlorides at 1 g/l by 0.02 M tricaprylmethylammonium laurate in benzene ($\diamond$, $\triangle$, $\circ$ and $\otimes$ represent the extractions of manganese, cobalt, nickel, copper and zinc, respectively).

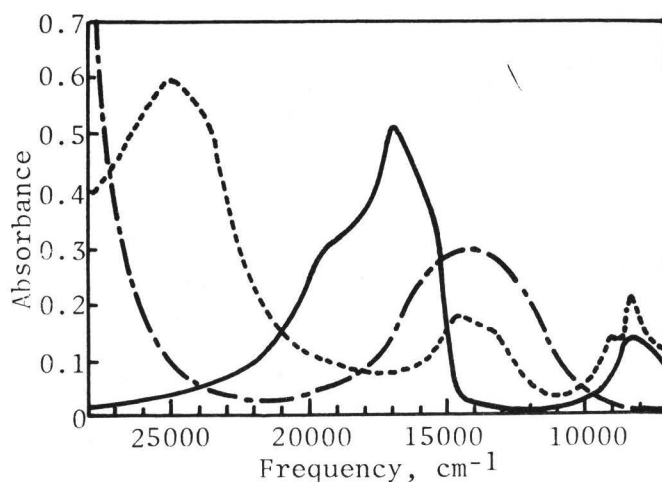


Fig.4 Absorption spectra of the organic solutions from the extraction of aqueous solution containing chlorides of cobalt, nickel and copper at 100, 100 and 20 g/l, respectively, with 0.05 M tricaprylmethylammonium laurate in benzene (continuous, broken and chain lines represent the organic solutions of cobalt, nickel and copper, respectively).

Table 5 Infrared spectral data for the organic extracts from aqueous solutions containing chlorides of manganese, cobalt, nickel, copper and zinc with 0.01 M tricaprylmethylammonium laurate in benzene

Frequency, cm-1								Probable assignment
R ₃ R'NC1	R ₃ R'NR''COO	Organic extract						
		Mn(II)	Co(II)	Ni(II)		Cu(II)	Zn(II)	
		10 g/l**	10 g/l	1 g/l	20 g/l	1 g/l	1 g/l	
3420(mb) *	3320(mb)	3380(mb)	3380(mb)	3370(mb)	3400(mb)	3360(mb)	3400(mb)	OH stretching
2920(s)	2920(s)	2920(s)	2920(s)	2920(s)	2920(s)	2920(s)	2920(s)	}CH stretching
2860(ms)	2860(ms)	2860(ms)	2860(ms)	2860(ms)	2860(ms)	2860(ms)	2860(ms)	
		2600(sh)	2600(sh)		2600(sh)	2600(sh)	2600(sh)	OH stretching
		1720(sh)	1720(sh)		1720(w)	1720(w)	1720(w)	CO stretching
1625(wb)	1650(sh)	1640(w)	1640(sh)	1640(sh)	1640(sh)	1640(sh)	1640(sh)	OH bending
	1560(m)	1560(m)	1560(m)	1560(m)	1560(m)	1560(m)	1560(m)	CO stretching
1465(m)	1465(m)	1465(m)	1465(m)	1465(m)	1465(m)	1465(m)	1465(m)	{CH ₃ degenerate bending
								{CH ₂ scissoring
					1425(m)	1410(m)		{CO stretching
								{OH bending
1375(m)	1380(m)	1380(m)	1380(m)	1380(m)	1380(m)	1380(m)	1380(m)	CO stretching }and/or
								CH ₃ sym.bending
					1180(w)			{CO stretching
								{OH bending
725(w)	725(w)	725(w)	725(w)	725(w)	725(w)	725(w)	725(w)	CH ₂ rocking

* s = strong, ms = medium strong, m = medium, w = weak, b = broad, sh = shoulder

** This represent initial aqueous metal chloride concentration.

combination of a part of the extractant with hydrochloric acid which results from the hydrolysis of nickel chloride in the aqueous phase because its concentration is high. Further, as the absorption due to the Ni-Cl vibration is not observed in the far-infrared region, it is confirmed that the chloride ion in the organic phase is not coordinated to nickel. Similar infrared results are also observed in the organic extracts from the extraction of aqueous solutions containing chlorides of manganese, cobalt, copper and zinc, as indicated in Table 5. In contrast, the infrared spectrum of the organic cadmium extract reveals the Cd-Cl vibration at 225 cm^{-1} .

Additionally the absorption spectra of the organic solutions from the extraction of aqueous solutions containing chlorides of manganese, cobalt, nickel and copper with quaternary compound in benzene at 20 °C were examined under various conditions. Some representative results are illustrated in Fig. 4. In the spectrum of the organic nickel(II) species, the absorption bands reveal the characteristic feature of a six-coordinated complex ion¹⁵⁾, showing the absorption bands at 25000, 14700, 13300 and 8300 cm^{-1} ascribed to three spin-allowed transitions from the ground state $^3A_{2g}(F)$ to the states $^3T_{1g}(P)$, $^3T_{1g}(F)$ and $^3T_{2g}(F)$, respectively. The value of the ligand field parameter for the complex $(R_3R'N)[Ni(R''COO)_3]$ is calculated by using the elements of the matrices determined by Tanabe and Sugano¹⁶⁾: $B = 950 \text{ cm}^{-1}$ and $10 Dq = 8550 \text{ cm}^{-1}$, in which B represents the Racah parameter for electron repulsion. The difference between the calculated value of $10 Dq$ in the nickel(II) complex and its observed one (8300 cm^{-1}) may be attributed to the assignment for the absorption at 8300 cm^{-1} regarded as the state $^3T_{2g}(F)$. Nevertheless the absorptions at 8200 and 8300 cm^{-1} appear in the spectrum because the state $^3T_{2g}(F)$ should be split into two state 3E and 3A_1 , if the point group symmetry of the complex is lowered from O_h to D_3 ¹⁷⁾. Further the factor β in the nephelauxetic series^{18, 19)} (i.e. the ratio between the value of representative parameter of interelectronic repulsion in the complex and in the corresponding free ion), is estimated to be 0.88, implying that the extent to which covalent bond formation occurs in the nickel(II) complex is relatively low. The spectrum of the organic cobalt(II) species exhibits the typical absorptions of a six-coordinated complex ion at 19230, 16950 and 8260 cm^{-1} , due to the transition from the ground state $^4T_{1g}(F)$ to the states $^4T_{1g}(P)$, $^4A_{2g}(F)$, respectively. Accordingly it is found that the value of $10 Dq = 9500 \text{ cm}^{-1}$ in the cobalt(II) in aquo ion $[Co(H_2O)_6]^{2+}$ ¹⁵⁾. For the organic extract of copper(II), the value of $10 Dq = 13990 \text{ cm}^{-1}$ is obtained from the spectrum, which resembles that in the hexa-aquo copper(II) species. In contrast, the spectrum of the organic manganese(II) extract reveals the strong charge-transfer absorption band at 34000–20000 cm^{-1} , covering the weak absorption due to the spin forbidden transitions.

It is therefore concluded that the extracted species of divalent manganese, cobalt, nickel, copper and zinc from aqueous chloride solutions by tri-caprylmethylammonium carboxylate exist as the complex $(R_3R'N)[M(R''COO)_3]$ in an octahedral arrangement.

Effect of carboxylic acid

In the extraction of aqueous solution (at pH 5.5) containing nickel chloride at 1 g/l by quaternary ammonium compounds with caprylic, capric and lauric acids in benzene at 20 °C, the log-log plots of the distribution coefficient vs. the free quaternary compound concentration gave straight lines with slopes nearly unity for respective carboxylates (Fig.5). From this it is seen that the effect of the kind of carboxylic acid on the extraction efficiency of carboxylates for nickel is not remarkable, although their efficiencies increase in the order of caprylic, capric and lauric acids. It is thus presumed that the extraction mechanism of nickel by quaternary compounds is almost the same as expressed in the Eqn.(2) for each carboxylate. Moreover similar results are also obtained for the extraction of divalent manganese, cobalt, copper and zinc from aqueous chloride solutions by quaternary compound.

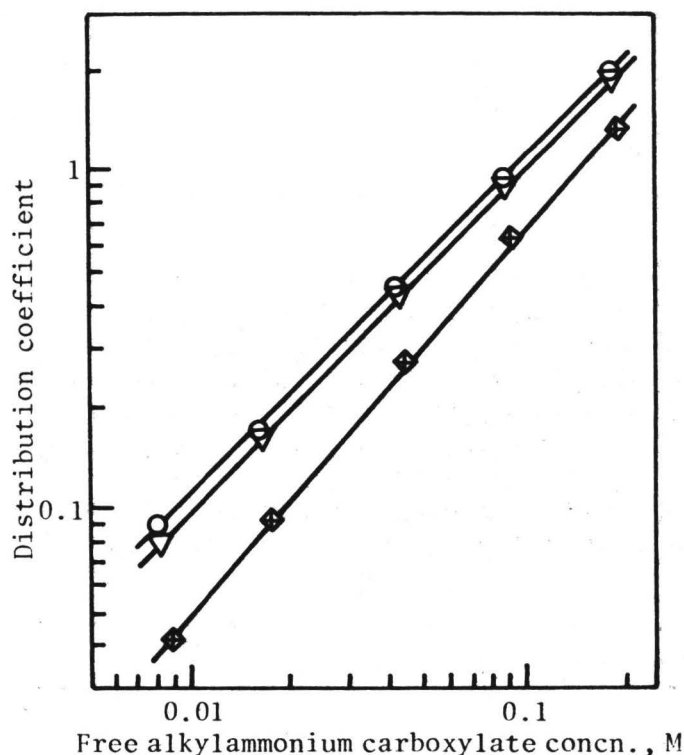


Fig.5 Log-log plots of distribution coefficient vs. free alkylammonium carboxylate concentration for the extraction of aqueous solution containing nickel chloride by quaternary compounds (◇, ▽ and ○ represent quaternary compounds with caprylic, capric and lauric acids).

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THE EFFECT OF DILUENT ON THE EXTRACTION OF DIVALENT MANGANESE,
COBALT, COPPER, ZINC AND CADMIUM FROM HYDROCHLORIC ACID SOLUTIONS
BY TRICAPRYLMETHYLAMMONIUM CHLORIDE

Taichi SATO, Tadashi SHIMOMURA, Takato
NAKAMURA and Teruo FUJIMATSU
Department of Applied Chemistry,
Faculty of Engineering,
Shizuoka University
Hamamatsu, Japan

ABSTRACT In order to investigate the correlation between the distribution coefficient and the physicochemical properties of diluent, the extraction of divalent manganese, cobalt, copper, zinc and cadmium from hydrochloric acid solutions by tricaprylmethylammonium chloride (Aliquat-336) in organic solvent has been examined by using various diluents such as benzene, chlorobenzene, o-dichlorobenzene, toluene, o-xylene, m-xylene, nitrobenzene, carbon tetrachloride, chloroform and 1,2-dichloroethane. As a result, it is found that by assuming a regular solution, the distribution coefficient and the enthalpy change associated with metal extraction are expressed in terms of the solubility parameters of Aliquat-336, diluent and the complex formed in the organic phase and their molar volumes, and in addition that there is an empirical relationship between distribution coefficient and the viscosity of diluent.

INTRODUCTION

The influence of diluent on the solvent extraction of metals has been studied by a number of researchers, attempting to connect the distribution of metal between organic and aqueous phases with the physicochemical properties of organic solvent such as dielectric constant^{1,2)}, dipole moment¹⁾ and solubility parameter³⁻⁸⁾. Nevertheless the role of diluent in the extraction process of metal has not yet been elucidated satisfactorily.

In the extraction of cadmium(II), zinc(II), lead(II) and copper(II) from 2 M hydrochloric acid solutions by octadecyldimethylbenzylammonium chloride in various diluents, Leszko et al⁸⁾ have suggested that the relationship between the distribution coefficient and the solubility parameter of diluent, derived by Vdovenko et al⁵⁾, is not applicable to the extraction of lead(II) and copper(II), but applicable to the extraction of cadmium(II) and zinc(II). We have also studied the extraction of zirconium(IV)⁹⁾, vanadium(IV)¹⁰⁾ and uranium(VI)¹¹⁾ from hydrochloric acid solutions by tricaprylmethylammonium chloride (Aliquat-336, $R_3R'NCl$). In the present work, therefore, the effect of diluent on the extraction of divalent manganese, cobalt, copper, zinc and cadmium is examined with Aliquat-336 in various organic solvents, in order to investigate the correlation between the distribution coefficient and the physicochemical properties of the diluent.

EXPERIMENTAL

Aliquat-336 (General Mills) purified by washing several times with aqueous sodium chloride solution and n-hexane⁹⁾ was diluted in benzene,

chlorobenzene, o-dichlorobenzene, toluene, o-xylene, m-xylene, nitrobenzene, carbon tetrachloride, chloroform and 1,2-dichloroethane. The concentration of Aliquat-336 in organic solvents was determined by Volhard's method with nitrobenzene. Aqueous solutions of divalent manganese, cobalt, copper, zinc and cadmium were prepared by dissolving their chlorides ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 and $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$) in hydrochloric acid. The chemicals used were of analytical reagent grade.

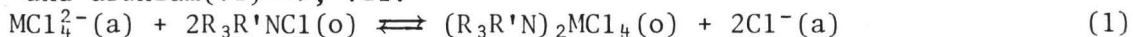
Extraction and analytical procedures

Equal volumes (15 ml) of organic and aqueous phases, placed in 50 ml stoppered conical flasks, were shaken for 10 min (preliminary experiments showed that equilibration was complete in 10 min) in a water-bath maintained at a required temperature. The initial concentration of metal chloride in the aqueous phase was 0.01 M. After equilibrium, the mixture was centrifuged and separated and then aliquots of both phases were pipetted to determine the distribution coefficient (the ratio of the equilibrium concentration of metal in the organic phase to that in the aqueous phase, D). Manganese, cobalt, copper and zinc in the organic phase were stripped with 0.1 M HCl, and cadmium in the organic phase with 1 M HNO_3 . The concentration of metal in the aqueous solutions was determined by EDTA titration using the following indicator: XO (xylenol orange) for cobalt¹²⁾, copper¹²⁾ and zinc¹³⁾; BT (Eriochrome Black T) for manganese¹⁴⁾; Cu-PAN (PAN = 1-(2-Pyridylazo)-2-naphthol for cadmium¹⁵⁾.

RESULTS AND DISCUSSION

Extraction isotherm

When divalent manganese, cobalt, copper, zinc and cadmium are extracted into benzene solution of Aliquat-336 from their aqueous chloride solutions at 0.01 M containing hydrochloric acid of varying acidity at 20 °C, the extraction efficiency is in the order of $\text{Cd} > \text{Zn} > \text{Cu} > \text{Co} > \text{Mn}$ for $[\text{HCl}] < 5$ M and of $\text{Cd} > \text{Zn} > \text{Co} > \text{Cu} > \text{Mn}$ for $[\text{HCl}] > 5$ M, as shown in Fig.1. The distribution coefficient rises with increasing aqueous acidity to a maximum which occurs at initial hydrochloric acid concentrations of 8, 8, 5, 2 and 1 M for manganese, cobalt, copper, zinc and cadmium, respectively, and then falls again. The shape of the extraction curves is not much influenced by the kind of diluent, as illustrated in Table 1. Accordingly the extractions are expressed by the reaction similar to those for zirconium(IV)⁹⁾, vanadium(IV)¹⁰⁾ and uranium(VI)¹¹⁾, viz.



where $\text{M} = \text{Mn}, \text{Co}, \text{Cu}, \text{Zn}$ and Cd , (a) and (o) represent aqueous and organic phases, respectively. This is supported by the results for the dependencies of the distribution coefficients on the extractant concentration and the variation of the metal concentration in the organic phase as a function of initial aqueous metal concentration at constant aqueous acidity.

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THE EFFECT OF DILUENT ON THE EXTRACTION OF DIVALENT MANGANESE,
COBALT, COPPER, ZINC AND CADMIUM FROM HYDROCHLORIC ACID SOLUTIONS
BY TRICAPRYLMETHYLAMMONIUM CHLORIDE

Taichi SATO, Tadashi SHIMOMURA, Takato
NAKAMURA and Teruo FUJIMATSU
Department of Applied Chemistry,
Faculty of Engineering,
Shizuoka University
Hamamatsu, Japan

ABSTRACT In order to investigate the correlation between the distribution coefficient and the physicochemical properties of diluent, the extraction of divalent manganese, cobalt, copper, zinc and cadmium from hydrochloric acid solutions by tricaprylmethylammonium chloride (Aliquat-336) in organic solvent has been examined by using various diluents such as benzene, chlorobenzene, o-dichlorobenzene, toluene, o-xylene, m-xylene, nitrobenzene, carbon tetrachloride, chloroform and 1,2-dichloroethane. As a result, it is found that by assuming a regular solution, the distribution coefficient and the enthalpy change associated with metal extraction are expressed in terms of the solubility parameters of Aliquat-336, diluent and the complex formed in the organic phase and their molar volumes, and in addition that there is an empirical relationship between distribution coefficient and the viscosity of diluent.

INTRODUCTION

The influence of diluent on the solvent extraction of metals has been studied by a number of researchers, attempting to connect the distribution of metal between organic and aqueous phases with the physicochemical properties of organic solvent such as dielectric constant^{1,2)}, dipole moment¹⁾ and solubility parameter³⁻⁸⁾. Nevertheless the role of diluent in the extraction process of metal has not yet been elucidated satisfactorily.

In the extraction of cadmium(II), zinc(II), lead(II) and copper(II) from 2 M hydrochloric acid solutions by octadecyldimethylbenzylammonium chloride in various diluents, Leszko et al⁸⁾ have suggested that the relationship between the distribution coefficient and the solubility parameter of diluent, derived by Vdovenko et al⁵⁾, is not applicable to the extraction of lead(II) and copper(II), but applicable to the extraction of cadmium(II) and zinc(II). We have also studied the extraction of zirconium(IV)⁹⁾, vanadium(IV)¹⁰⁾ and uranium(VI)¹¹⁾ from hydrochloric acid solutions by tricaprylmethylammonium chloride (Aliquat-336, $R_3R'NCl$). In the present work, therefore, the effect of diluent on the extraction of divalent manganese, cobalt, copper, zinc and cadmium is examined with Aliquat-336 in various organic solvents, in order to investigate the correlation between the distribution coefficient and the physicochemical properties of the diluent.

EXPERIMENTAL

Aliquat-336 (General Mills) purified by washing several times with aqueous sodium chloride solution and n-hexane⁹⁾ was diluted in benzene,

chlorobenzene, o-dichlorobenzene, toluene, o-xylene, m-xylene, nitrobenzene, carbon tetrachloride, chloroform and 1,2-dichloroethane. The concentration of Aliquat-336 in organic solvents was determined by Volhard's method with nitrobenzene. Aqueous solutions of divalent manganese, cobalt, copper, zinc and cadmium were prepared by dissolving their chlorides ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 and $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$) in hydrochloric acid. The chemicals used were of analytical reagent grade.

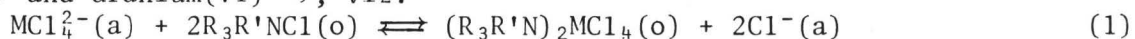
Extraction and analytical procedures

Equal volumes (15 ml) of organic and aqueous phases, placed in 50 ml stoppered conical flasks, were shaken for 10 min (preliminary experiments showed that equilibration was complete in 10 min) in a water-bath maintained at a required temperature. The initial concentration of metal chloride in the aqueous phase was 0.01 M. After equilibrium, the mixture was centrifuged and separated and then aliquots of both phases were pipetted to determine the distribution coefficient (the ratio of the equilibrium concentration of metal in the organic phase to that in the aqueous phase, D). Manganese, cobalt, copper and zinc in the organic phase were stripped with 0.1 M HCl, and cadmium in the organic phase with 1 M HNO_3 . The concentration of metal in the aqueous solutions was determined by EDTA titration using the following indicator: XO (xylenol orange) for cobalt¹², copper¹² and zinc¹³; BT (Eriochrome Black T) for manganese¹⁴; Cu-PAN (PAN = 1-(2-Pyridylazo)-2-naphthol for cadmium¹⁵).

RESULTS AND DISCUSSION

Extraction isotherm

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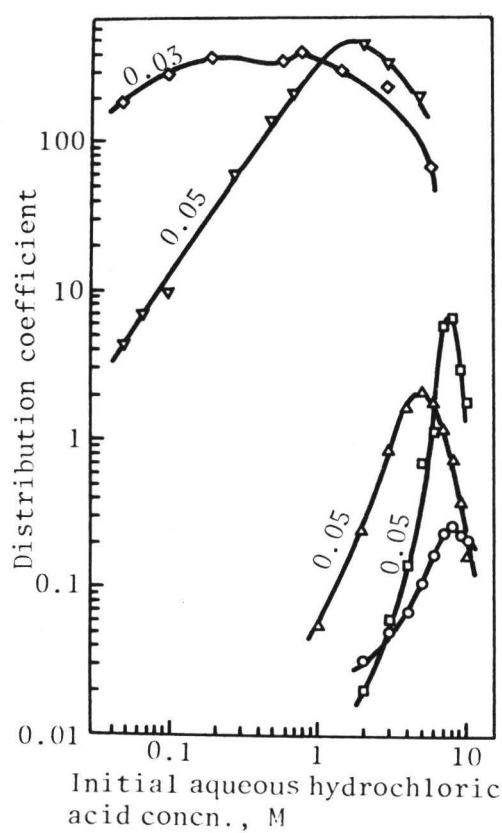


Fig.1 Extraction of divalent manganese, cobalt, copper, zinc and cadmium from hydrochloric acid solutions by Aliquat-336 in benzene (numerals on curves are Aliquat-336 concentrations, M; $\circ$ Mn, $\square$ Co, Δ Cu, ∇ Zn, $\diamond$ Cd).

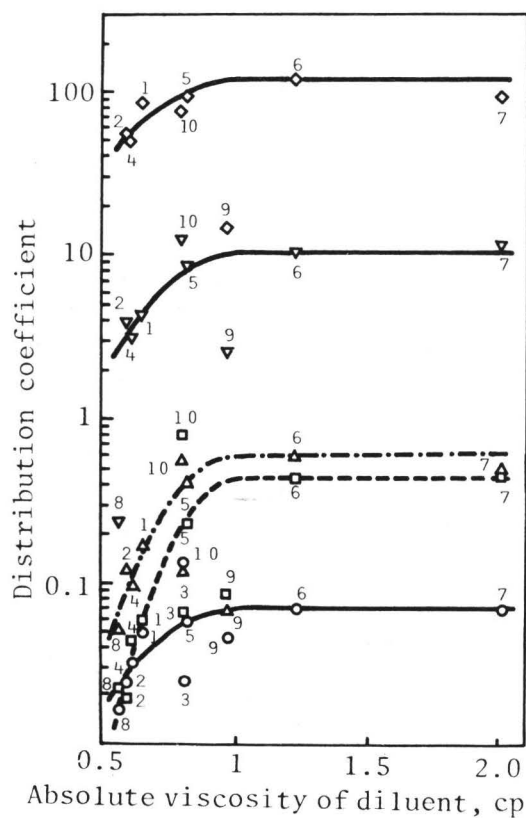


Fig.2 Dependence of the distribution coefficient of divalent manganese, cobalt, copper, zinc and cadmium on absolute viscosity of diluent ($\circ$, $\square$, Δ , ∇ and $\diamond$ represent the extractions of Mn(II) from 3 M HCl soln., Co(II) from 3 M HCl soln., Cu(II) from 2 M HCl soln., Zn(II) from 0.05 M HCl soln. and Cd(II) from 0.02 M HCl soln., respectively): 1)benzene, 2)toluene, 3) o-xylene, 4)m-xylene, 5)chlorobenzene, 6) o-dichlorobenzene, 7)nitrobenzene, 8)chloroform, 9)carbon tetrachloride, 10)1,2-dichloroethane.

Table 1. The distribution coefficient for divalent manganese, cobalt, copper, zinc and cadmium in the extraction from hydrochloric acid solutions by Aliquat-336 in various diluents

Metal	[HCl] _{aq} , M	Distribution coefficient ^{a)}									
		C ₆ H ₆	C ₆ H ₅ CH ₃	o-C ₆ H ₄ (CH ₃) ₂	m-C ₆ H ₄ (CH ₃) ₂	C ₆ H ₅ Cl	o-C ₆ H ₄ Cl ₂	C ₆ H ₅ NO ₂	CHCl ₃	CCl ₄	1,2-C ₂ H ₄ Cl ₂
Mn	3	0.0498	0.025	0.025	0.033	0.059	0.072	0.71	0.017	0.047	0.135
	5	0.0105	0.059	0.04	0.07	0.17	0.26	0.15	0.04	0.1	1.01
	7	0.22	0.17	0.13	0.14	0.40	0.61	0.33	0.11	0.19	2.10
	8	0.25	0.23	0.15	0.17	0.43	0.68	0.36	0.15	0.24	1.39
Co	3	0.06	0.02	0.068	0.045	0.24	0.44	0.47	0.023	0.09	0.827
	5	0.68	0.51	0.51	0.58	2.70	4.14	3.67	0.16	0.39	7.02
	7	5.84	2.49	2.45	2.79	8.80	12.4	6.93	1.19	2.17	10.4
	8	6.22	2.67	3.00	3.36	8.37	15.9	4.91	1.58	2.63	7.32
Cu	2	0.178	0.126	0.121	0.0967	0.415	0.614	0.485	0.052	0.0721	0.574
	3	0.568	0.428	0.391	0.329	1.12	1.55	1.41	0.064	0.0253	
	5	1.12	0.913	0.908	0.824	2.10	3.17	2.45	0.213	0.765	6.03
	8	0.492	0.378	0.372	0.350	0.862	1.15	0.75	0.292	0.280	1.35
Zn	0.05	4.36	3.99	—b)	3.14	8.55	10.4	11.7	0.25	2.54	12.7
	0.1	9.27	8.79	—	7.28	18.3	27.2	25.8	0.36	4.75	36.6
	0.5	134	112	—	75.1	289	305	236	1.90	83	208
	1	420	290	—	156	476	596	523	3.46	214	560
Cd	0.02	86.5	55.7	—	49.4	96.9	121	94.8	0.488	14.8	76.2
	0.1	297	205	—	190	291	306	252	0.929	49.5	250
	1	276	308	—	266	261	213	306	1.64	133	200
	8	6.70	4.62	—	4.82	7.77	10.0	6.69	0.756	3.59	10.4

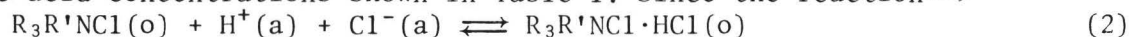
a) The concentration of Aliquat-336 is 0.05 M for manganese, cobalt, and zinc, 0.025 M for copper and 0.03 M for cadmium.

b) No data.

chloroform reveals a very poor extraction because of hydrogen bonding with the extractant. However, there is no simple relationship between the distribution coefficient and the dipole moment and dielectric constant of diluent which represent the polarities of molecule and solution, respectively.

Effect of viscosity

The variation of the distribution coefficient for divalent manganese, cobalt, copper, zinc and cadmium plotted as a function of the absolute viscosity of diluent, η_d , are given in Fig.2. In this case, the values of η_d are indicated in Table 2. Additionally the distribution coefficients for manganese, cobalt, copper, zinc and cadmium are indicated by using the data for the extractions at 3, 3, 2, 0.05 and 0.02 M, respectively, in the lowest hydrochloric acid concentrations shown in Table 1. Since the reaction¹⁵⁾



occurs at higher aqueous acidity, the data at low acidity are used to avoid the reduction of the distribution of metal resulting from the competition between reactions (1) and (2).

In Fig.2, the distribution coefficient increases with increasing viscosity of diluent at $\eta_d \leq 1$ cp, but little change occurs at $\eta_d > 1$ cp. In all of the extraction systems studied, it is interesting that the distribution coefficient becomes constant as the viscosity of diluent approaches that of water. An empirical correlation between the distribution coefficient and the viscosity of diluent can be derived in the range of $\eta_d \leq 1$ cp:

$$\log D/D_o = A(\eta_d - 1)^2 \quad (3)$$

in which D_o is the distribution coefficient for o-dichlorobenzene, and A denotes the slope obtained when $\log D/D_o$ is plotted against $(\eta_d - 1)^2$. Values of the slope calculated by the method of least squares are shown in Table 3.

Effect of solubility parameter

From the Hildebrand-Scatchard equation¹⁶⁾ for the excess free energy of a regular solution, an expression for the distribution coefficient in terms of the solubility parameter has been developed by Vdovenko et al⁵⁾:

$$\log D = (2/2.3RT)(V_c\delta_c - nV_e\delta_e)\delta_d + \{(nV_e - V_c)/2.3\}(\delta_d^2/RT - 1/V_d) + \text{const} \quad (4)$$

where V and δ represent molar volume and solubility parameter, respectively, and the subscripts c, e and d are the complex formed in the organic phase, extractant and diluent, respectively. Assuming that the composition in the aqueous phase and the concentration of extractant in various diluent hold constant, and that the molar volumes of diluents are not different from each other, the following relation can be derived:

$$\{1/(\delta_d - \delta_s)\} \log(D/D_s) = \{(nV_e - V_c)/2.3RT\}(\delta_d + \delta_s) + 2(V_c\delta_c - nV_e\delta_e)/2.3RT \quad (5)$$

in which the subscript s refers to the diluent chosen as standard.

In Fig.3 exhibiting the plots of $\log D$ vs. δ_d , the solid lines are obtained from the values of $(nV_e - V_c)/2.3RT$ and $2(V_c\delta_c - nV_e\delta_e)/2.3RT$, given in Table 4, which are estimated by using Eqn.(5) with nitrobenzene as standard. In this case, the value of δ_d are indicated in Table 2. The parabolic dependence of distribution coefficients on the solubility parameter is obtained, suggesting that Eqn.(4) gives a good estimate for the value of distribution coefficients in the extraction of these divalent metals from hydrochloric acid solutions by Aliquat-336. However, since large deviations from the parabola are observed in the extraction with chloroform, it is considered that the negative deviation arises from the unsymmetrical interaction due to hydrogen bonding between chloroform and Aliquat-336.

Temperature effect

The equilibrium constant in reaction(1) and the distribution coef-

Table 2 Value of η_d and δ_d for various diluents

Diluent	η_d , cp	δ_d
Benzene	0.65a)	9.1
Toluene	0.59	8.9
o-Xylene	0.81	9.0
m-Xylene	0.61	8.8
Chlorobenzene	0.82	9.6
o-Dichlorobenzene	1.23	10.0
Nitrobenzene	2.01	10.9
Chloroform	0.56	9.3
Carbon tetrachloride	0.97	8.7
1,2-Dichloroethane	0.80	9.9

a) The value at 20 °C.

Table 3 Estimated values of A

Metal	A
Mn	-2.59
Co	-7.04
Cu	-4.93
Zn	-2.94
Cd	-2.03

Table 4 Calculated values of $(nV_e - V_c)/2.3RT$ and $2(V_c\delta_c - nV_e\delta_e)/2.3RT$

Metal	$(nV_e - V_c)/2.3RT$	$2(V_c\delta_c - nV_e\delta_e)/2.3RT$
Mn	-0.165	3.45
Co	-5.10	10.7
Cu	-0.370	7.64
Zn	-0.200	4.22
Cd	-0.210	4.27

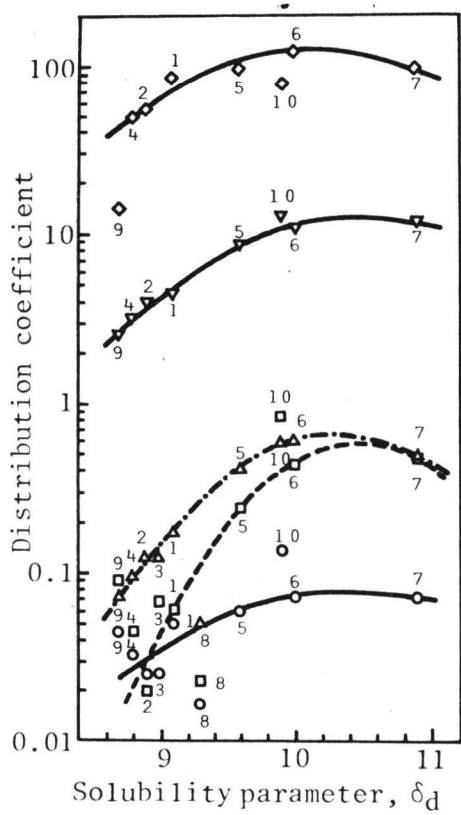


Fig.3 Dependence of the distribution coefficient of divalent manganese, cobalt, copper, zinc and cadmium on the solubility parameter of diluent (○, □, △, ▽ and ◇ represent the extractions of Mn(II) from 3 M HCl soln., Co(II) from 3 M HCl soln., Cu(II) from 2 M HCl soln., Zn(II) from 0.05 M HCl soln. and Cd(II) from 0.02 M HCl soln., respectively): 1)benzene, 2)toluene, 3)o-xylene, 4)m-xylene, 5)chlorobenzene, 6)o-dichlorobenzene, 7)nitrobenzene, 8)chloroform, 9)carbon tetrachloride 10)1,2-dichloroethane.

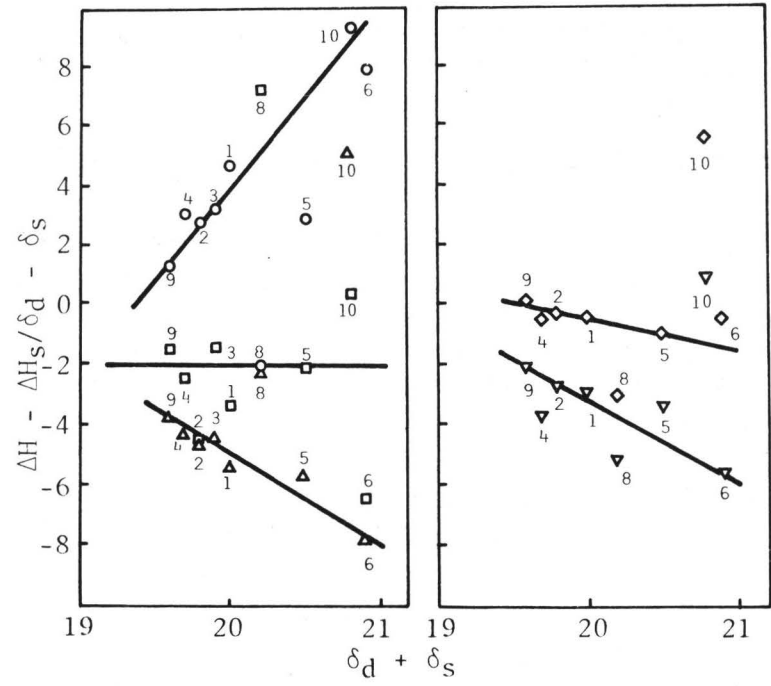


Fig.4 Correlation between $\Delta H - \Delta H_s / \delta_d - \delta_s$ and $\delta_d + \delta_s$ for the extraction of divalent manganese, cobalt, copper, zinc and cadmium from hydrochloric acid solutions by Aliquat-336 in various diluents (○ Mn, □ Co, △ Cu, ▽ Zn, ◇ Cd): 1)benzene, 2)toluene, 3)o-xylene, 4)m-xylene, 5)chlorobenzene, 6)o-dichlorobenzene, 7)nitrobenzene, 8)chloroform, 9) carbon tetrachloride, 10) 1,2-dichloroethane.

ficient are given by

$$K = [(R_3R'N)_2MCl_4][Cl^-]^2/[MCl_4^{2-}][R_3R'NCl]^2 \quad (6)$$

and

$$D = [(R_3R'N)_2MCl_4]/[M^{2+}](1 + \sum \beta_i [Cl^-]^i) \quad (7)$$

where β_i refers to the overall stability constant in the reaction



From Eqns.(6) and (7) the following relationship can be obtained:

$$K = D(1 + \sum \beta_i [Cl^-]^i)/\beta_4 [Cl^-]^2. \quad (9)$$

By assuming that the values of overall stability constant β_4 and the term $(1 + \sum \beta_i [Cl^-]^i)$ do not change significantly in the temperature range studied, the change in enthalpy, ΔH , associated with reaction(1) can be estimated by using the Van't Hoff's equation. The distribution coefficients for divalent manganese, cobalt, copper, zinc and cadmium from aqueous hydrochloric acid solutions with the solutions of Aliquat-336 in various diluents, measured in the temperature range 10-40 °C, are compiled in Table 5 in comparison with the values of ΔH .

The extraction process of divalent metals is considered by a Born-Haber type of cycle. The change in enthalpy observed is the sum of five terms which are of enthalpies for dehydration of the species MCl_4^{2-} (ΔH_1), for desolvation of $R_3R'NCl$ (ΔH_2), for the reaction of MCl_4^{2-} with $R_3R'NCl$ (ΔH_3), for hydration of Cl^- (ΔH_4) and for dissolution of the complex $(R_3R'N)_2MCl_4$ into organic phase (ΔH_5). Therefore the magnitude and sign of the change in enthalpy observed depend on the contribution from enthalpies in these processes. The ΔH_1 and ΔH_4 values correlate to the composition of aqueous acidity, because the water activity decreases as hydrochloric acid concentration is increased, while the ΔH_3 value is independent of the kind of diluent. If the concentration of hydrochloric acid in the aqueous phase remains constant, therefore, the change in enthalpy observed can be expressed as

$$\Delta H = -2\Delta H_2 + \Delta H_5 + \text{const.} \quad (10)$$

Partial molar enthalpies for dissolution of Aliquat-336 and the complex $(R_3R'N)_2MCl_4$ into organic solvent given by $V_e\phi_d^2(\delta_d - \delta_e)^2$ and $V_c\phi'_d{}^2(\delta_d - \delta_c)^2$ from regular solution theory¹⁷⁾, yield the equation

$$\Delta H = -2V_e\phi_d^2(\delta_d - \delta_e)^2 + V_c\phi'_d{}^2(\delta_d - \delta_c)^2 + \text{const} \quad (11)$$

where ϕ_d and ϕ'_d refer to the volume fraction of diluent. This provides the equation

$$\Delta H = (V_c\phi'_d{}^2 - 2V_e\phi_d^2)\delta_d^2 + 2(2V_e\phi_d^2\delta_e - V_c\phi'_d{}^2\delta_c)\delta_d + \text{const.} \quad (12)$$

It is thus expected that when ΔH_2 is plotted against δ_d , its shape depends on the magnitude of the term $(V_c\phi'_d{}^2 - 2V_e\phi_d^2)$. For $V_c\phi'_d{}^2 < 2V_e\phi_d^2$ or $V_c\phi'_d{}^2 > 2V_e\phi_d^2$, the plot should exhibit a parabola with a maximum or minimum at $\delta_d = (V_c\phi'_d{}^2\delta_c - 2V_e\phi_d^2\delta_e)/(V_c\phi'_d{}^2 - 2V_e\phi_d^2)$. In contrast, a linear relationship is expected for $V_c\phi'_d{}^2 = 2V_e\phi_d^2$. The value of $(V_c\phi'_d{}^2 - 2V_e\phi_d^2)$ can be determined by using the equation

$$(\Delta H - \Delta H_5)/(\delta_d - \delta_s) = (V_c\phi'_d{}^2 - 2V_e\phi_d^2)(\delta_d + \delta_s) + 2(2V_e\phi_d^2\delta_e - V_c\phi'_d{}^2\delta_c). \quad (13)$$

Thus $(V_c\phi'_d{}^2 - 2V_e\phi_d^2)$ and $2(2V_e\phi_d^2\delta_e - V_c\phi'_d{}^2\delta_c)$ are the slope and intercept of the line, respectively, when $(\Delta H - \Delta H_5)/(\delta_d - \delta_s)$ is plotted as a function of $(\delta_d + \delta_s)$. The plots for manganese, cobalt, copper, zinc and cadmium exhibit the linear relationship as presented in Fig.4, although the points for chloroform and 1,2-dichloroethane are off the lines in all cases studied. The values obtained for $(V_c\phi'_d{}^2 - 2V_e\phi_d^2)$ indicate that $V_c\phi'_d{}^2 > 2V_e\phi_d^2$ is

Table 5. Temperature dependence of distribution coefficient for the extraction of divalent manganese, cobalt, copper, zinc and cadmium from hydrochloric acid solutions* by Aliquat-336** in various diluents

Metal	Diluent	Distribution coefficient				Change in enthalpy, Kcal/mol
		10°C†	20°C†	30°C†	40°C†	
Mn	C ₆ H ₆	0.0497	0.0498	0.0499	0.050	0.04
	C ₆ H ₅ CH ₃	0.023	0.025	0.033	0.038	2.91
	o-C ₆ H ₄ (CH ₃) ₂	0.023	0.025	0.034	0.035	2.37
	m-C ₆ H ₄ (CH ₃) ₂	0.028	0.033	0.035	0.039	1.99
	C ₆ H ₅ Cl	0.044	0.059	0.077	0.100	4.72
	o-C ₆ H ₄ Cl ₂	0.084	0.072	0.098	0.107	1.50
	C ₆ H ₅ NO ₂	0.037	0.071	0.118	0.17	8.60
	CHCl ₃	0.007	0.017	0.034	0.055	11.9
	CCl ₄	0.030	0.047	0.066	0.071	5.57
Co	1,2-C ₂ H ₄ Cl ₂	0.146	0.135	0.132	0.125	-0.823
	C ₆ H ₆	0.045	0.06	0.09	0.12	5.62
	C ₆ H ₅ CH ₃	0.015	0.02	0.04	0.07	8.72
	o-C ₆ H ₄ (CH ₃) ₂	0.054	0.068	0.075	0.091	2.23
	m-C ₆ H ₄ (CH ₃) ₂	0.035	0.045	0.085	0.09	4.67
	C ₆ H ₅ Cl	0.21	0.24	0.28	0.37	2.42
	o-C ₆ H ₄ Cl ₂	0.31	0.44	0.60	0.73	5.43
	C ₆ H ₅ NO ₂	0.60	0.47	0.48	0.57	-0.293
	CHCl ₃	0.05	0.023	0.015	0.007	-11.4
Cu	CCl ₄	0.08	0.09	0.10	0.13	2.88
	1,2-C ₂ H ₄ Cl ₂	0.846	0.827	0.796	0.745	-0.709
	C ₆ H ₆	0.129	0.178	0.266	0.221	6.79
	C ₆ H ₅ CH ₃	0.0911	0.126	0.172	0.168	6.33
	o-C ₆ H ₄ (CH ₃) ₂	0.0857	0.121	0.150	0.177	5.43
	m-C ₆ H ₄ (CH ₃) ₂	0.0685	0.967	0.136	0.142	5.96
	C ₆ H ₅ Cl	0.346	0.415	0.493	0.502	4.43
	o-C ₆ H ₄ Cl ₂	0.542	0.614	0.720	0.814	4.05
	C ₆ H ₅ NO ₂	0.553	0.485	0.442	0.396	-2.90
Zn	CHCl ₃	0.0537	0.0517	0.0538	0.0527	0.457
	CCl ₄	0.0680	0.0721	0.106	0.142	5.14
	1,2-C ₂ H ₄ Cl ₂	0.847	0.574	0.485	0.323	-7.99
	C ₆ H ₆	4.59	4.36	3.49	4.05	-0.8
	C ₆ H ₅ CH ₃	4.03	3.99	3.76	3.75	-0.53
	m-C ₆ H ₄ (CH ₃) ₂	2.8	3.14	3.36	3.49	1.76
	C ₆ H ₅ Cl	9.55	8.55	7.83	7.78	-1.69
	o-C ₆ H ₄ Cl ₂	15.3	10.4	13.3	13.2	-1.06
	C ₆ H ₅ NO ₂	18.1	11.7	7.80	5.20	-6.1
Cd	CHCl ₃	0.2	0.25	0.29	0.33	2.12
	CCl ₄	2.69	2.54	2.26	2.12	-1.33
	1,2-C ₂ H ₄ Cl ₂	16.3	12.7	8.71	5.83	-7.00
	C ₆ H ₆	101	86.5	61.0	46.2	-4.93
	C ₆ H ₅ CH ₃	78.3	55.3	42.1	29.8	-6.20
	m-C ₆ H ₄ (CH ₃) ₂	67.5	49.4	39.6	31.0	-4.67
	C ₆ H ₅ Cl	128	96.9	70.9	62.5	-4.45
	o-C ₆ H ₄ Cl ₂	151	121	139	133	-2.03
	C ₆ H ₅ NO ₂	104	94.8	61.5	42.8	-5.66
Cd	CHCl ₃	0.519	0.448	0.482	0.471	-0.872
	CCl ₄	23.3	14.8	11.4	8.53	-6.12
	1,2-C ₂ H ₄ Cl ₂	151	76.2	41.9	26.1	-11.3

* The concentration of hydrochloric acid is 3 M for manganese and cobalt, 2 M for copper, 0.05 M for zinc and 0.02 M for cadmium.

** The concentration of Aliquat-336 is 0.05 M for manganese, cobalt and zinc, 0.025 M for copper and 0.03 M for cadmium.

† Temperature of extraction.

satisfied for manganese (as 6.2), $V_c\phi'_d{}^2 = 2V_e\phi_d{}^2$ for cobalt (as zero), and $V_c\phi'_d{}^2 < 2V_e\phi_d{}^2$ for copper, zinc and cadmium (as -0.62, -0.55 and -0.21, respectively). In addition the plots of ΔH against δ_d confirm that Eqn.(12) holds for the enthalpy change for various diluents. These facts suggest that the change in enthalpy for the extraction of divalent manganese, cobalt, copper, zinc and cadmium by Aliquat-336 in various diluents depends on the solubility parameter of diluent, the molar volumes of the complex formed in the organic phase with Aliquat-336, and the volume fraction of diluent.

CONCLUSION

A parabolic dependency of the distribution coefficient on the solubility parameter of diluent is obtained in the extraction by Aliquat-336 in organic solvents except chloroform and 1,2-dichloroethane, indicating that Eqn.(4) derived from the regular solution theory is satisfied. The enthalpy change associated with metal extraction is also explained by assuming a regular solution. Hence it is concluded that in the extraction of divalent manganese, cobalt, copper, zinc and cadmium from hydrochloric acid solutions by Aliquat-336 in various diluents, the distribution coefficient depends on the mutual solubility between the complex formed in the organic phase and the diluent, and that the solubility parameter is an important factor to evaluate the distribution coefficient.

Further a progressive increase in distribution coefficient with increasing viscosity of diluent is observed in the range of $\eta_d \leq 1$ cp, and there is an empirical relation between them. Additionally it is found that in the extraction by Aliquat-336 in aromatic solvents, the distribution coefficient in the diluents with an electron-accepting radical is higher than that with an electron-donating one.

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PYRAZOLONES AS EXTRACTING AGENTS FOR ALKALINE EARTH METALS

Bo Nilsson and Robert Lundqvist

Department of Nuclear Chemistry
Chalmers University of Technology

412 96 Göteborg, Sweden

Pyrazolones are very useful extraction reagents which can be used even in strongly acidic media¹. For 1-phenyl-3-methyl-4-caproyl-pyrazolone-5 (PMCyP) however partition constants were lacking and we have therefore determined K_d -values ($\text{PMCyP} \rightleftharpoons \text{PMCyP}(\text{org})$) for six different solvents, TABLE 1., and 0.1 M NaNO_3 as aqueous phase. The determinations were made by two-phase titration, FIG. 1. By comparing the $\log K_d$ -values for the pyrazolones with the corresponding $\log K_d$ -values for a similar chelating β -diketone acetylacetone (HAA) it was concluded that the interactions between PMCyP and the used solvents were similar as for HAA, FIG. 2. The separation of alkaline earth metals (Be^{2+} , Sr^{2+} , Ba^{2+}) is studied by determining extraction constants K_{ex} and formation constants β_n employing the AKUFVE technique³.

TABLE 1

nr	solvent	$\log K_d K_a^{-1}$	$\log K_d$
1	n-hexane	8.66 $\pm$ 0.04	3.56
2	carbontetrachloride	9.680 $\pm$ 0.008	4.59
3	toluene	9.748 $\pm$ 0.007	4.66
4	chloroform	10.386 $\pm$ 0.005	5.30
5	benzene Ref.2.	10.03	4.94
6	octanol	7.67 $\pm$ 0.02	2.58
7	iso-amylalcohol	6.74	1.56

$(\log K_a^{-1} = 5.09)$

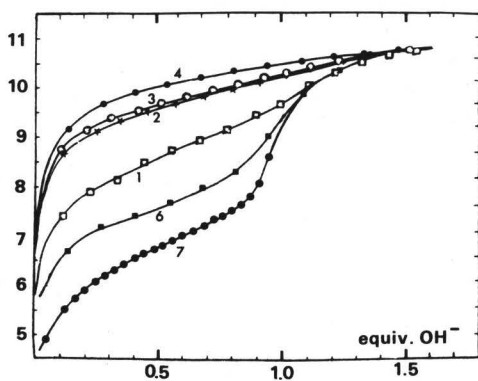


FIG. 1.

Two phase titration curves for PMCyP.

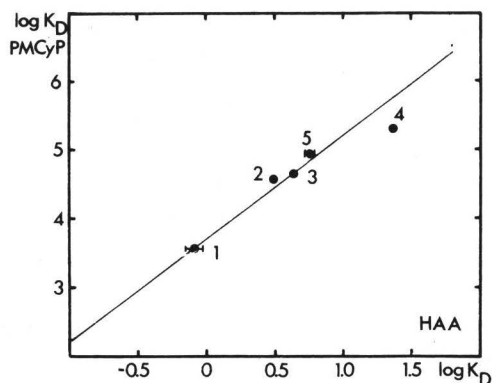


FIG. 2.

Correlation between the partition constants of PMCyP and HAA for various solvents.

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EXTRACTION OF SOME DIVALENT AND TRIVALENT METALS
BY DICARBOLIDE SOLUTION IN THE PRESENCE OF VARIOUS
POLYETHYLENEGLYCOLS

P. Vaňura, E. Makrlík, J. Rais and
 M. Kyrš

Nuclear Research Institute, Řež by
 Prague

Czechoslovakia

Extraction of Sr^{2+} , Ba^{2+} , Eu^{3+} , Ce^{3+} by nitrobenzene solutions of dicarbolid (HB) in the presence of commercial polyethyleneglycols PEG 200, PEG 300, PEG 400, PEG 600, and PEG 1000 (L) by nitrobenzene solutions of the acid form of cobalt dicarbolid $\text{H}^+[(\text{C}_2\text{B}_9\text{H}_{11})\text{Co}]^-(\text{HB})$ was investigated. The occurrence of maxima (up to one order of magnitude) on the metal distribution ratios (D_{Sr} , D_{Ba} , D_{Eu} , D_{Ce}) vs. the total PEG concentration plots was explained in terms of the competition between the charged metal-PEG complex (SrL^{2+} , BaL^{2+} , $\text{EuH}_{-1}\text{L}^{2+}$, $\text{EuH}_{-1}\text{BL}^+$) and protonized PEG (HL^+) in the process of partitioning into the organic phase due to the limited concentration of negatively charged hydrophobic anions (B^-) of the extractant. For the PEG 600 and PEG 1000 also other reactions, probably formation of particles of the type SrLH^{3+} , BaLH^{3+} , LH_2^{2+} take place.

The addition of PEG to the extraction systems increases the selectivity ($S = D_{\text{Ba}}/D_{\text{Sr}}$) for metal cation pairs both for Ba/Sr and Ce/Eu. For the pair Ba/Sr the increase is from $S=1.4$ for the system in the absence of PEG to $S=100$ for the systems with sufficient concentration of PEG. In the case of Ce/Eu pair the value of S increases only from 1.2 to 2. In both cases the selectivity is almost independent of the molecular weight of PEG in the region of PEG 200 - 1000.

Equilibrium constants for all reactions investigated were calculated. In the computerized method of the calculation of the extraction constant K_{ex} (Me compl) (Me compl = PEG complexes of the metal used), the value of $K_{\text{ex}}(\text{HL}^+)$ is yielded simultaneously.

The coincidence of the latter values of the systems with different metals could be considered as a corroboration of the correctness of the mechanism proposed. In the present study the agreement in all $\log K_{\text{ex}}(\text{HL}^+)$ values found was better than ± 0.1 .

ROLE OF SOLVENTS IN DISTRIBUTION OF METAL CHELATES WITH
I. 4-BENZOYL 2;4-DIHYDRO 5-METHYL 2-PHENYL 3H-PYRAZOL
3-ONE (BMPP) AND ADDUCT FORMATION WITH TRI BUTYL
PHOSPHATE (TBP)
II. SALICYLADOXIME.

G.N. RAO AND S. NARAYANAN
 Chemistry Department
 INDIAN INSTITUTE OF TECHNOLOGY
 NEW DEHLI, INDIA.

Some quantitative studies on the role of solvents, as applied to regular solution theory, have been made¹ but these have been mainly confined to Thenoyl Trifluoro Acetone^{2,3}. To investigate the validity of the solubility parameter concept in general, we have studied the extraction of metals using other ligands like BMPP and salicylaldoxime with various organic solvents viz. Benzene, Toluene, Chlorobenzene, o-Dichlorobenzene, Chloroform, Methylenechloride, Carbontetrachloride, Cyclohexane and Hexane. Synergism in the TBP-BMPP system was also studied on the same lines.

Zn-65, Co-60 and Eu-152+154 as radiotracers in acetate buffer medium were equilibrated with BMPP in eight inert organic solvents. The distribution ratio K_d was found after measuring γ activity in the two phases. Plots of $\log K_d$ -pH and $\log K_d$ - $\log (HA)$ reveal the mechanism of extraction. The extracted species were found to be ZnA_2 , CoA_2 and EuA_2^+ . $Ac.HA$ where HA is ligand, A^- is the ligand anion and Ac is the acetate ion. In synergistic studies, the species were found to be $ZnA_2.TBP$; $CoA_2.TBP$; $EuA_2^+.Ac.HA.TBP$. The solubility parameter and molar volume of BMPP were calculated to be 9.4 ± 0.4 and 430 respectively. The relation $\log K_d = n \log P_{HA} + \text{const.}$, where P_{HA} is the distribution ratio of BMPP in different solvents, was found to fit well for most of the systems. Synergism is also explained on the basis of regular solution theory.

Aqueous acetate buffered solutions containing Zn(II), Cu(II), Co(II) ions were equilibrated with eight inert solvents containing the salicylaldoxime. The distribution ratio K_d was found after measuring the concentration of metal in the phases using Atomic Absorption Spectrophotometry. Plots as in the BMPP system were made to study the mechanism of extraction. The relation $\log K_d = n \log P_{HL} + \text{const.}$ was found to fit satisfactorily. Hexane and Cyclohexane showed abnormal behaviour with Cu(II) and no extraction with Zn(II) was possible to the desired level with these two solvents.

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Metal Extraction

Session 17

Co-chairmen : A.W. Ashbrook (Eldorado Nuclear Ltd., Ottawa, Canada)
J. De Cuyper (University of Louvain, Belgium)

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- 80-234 Homogenous liquid-liquid extraction.
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City University of New York, Brooklyn College, New York, U.S.A.

THE APPLICATION OF SOLVENT EXTRACTION TO PLATINUM GROUP METALS
REFINING

L.R.P. Reavill and P. Charlesworth

Matthey Rustenburg Refiners (UK) Ltd.,
Orchard Road,
Royston,
HertfordshireABSTRACT

The paper reviews a new integrated refining scheme for separating the precious metals Au, Pt, Pd, Ru, Rh, Ir and Os. Some of the factors contributing to the development of this process to a commercially viable state are discussed.

1. INTRODUCTION

The platinum group metals (Pt, Pd, Rh, Ir, Ru and Os) occur in minute quantities in deposits of copper-nickel sulphide ore. This material is mined commercially in a number of places in the world, but the three principal areas are in Canada, USSR and the Merenskey Reef, Transvaal, South Africa, (1). The Merenskey deposits, though the richest currently worked in significant quantities, produce less than one troy ounce of platinum group metals per ton of mined seam.

The ore is concentrated by mineralurgical and fire-metallurgical methods. The concentrate so produced generally contains about 50% of platinum group metals, the remainder consisting of gold, silver, copper, nickel and other base metals, amphoteric elements etc ... Further refining of the precious metals has conventionally been done by chemical means. The non-precious metals components of the concentrate are removed. The precious metals are separated from one another, and refined to individual metals of very high purity, generally 99.95% or above.

2. PHILOSOPHY OF REFINING PLATINUM GROUP METALS CONCENTRATES

Theoretically it is possible to separate eight precious metals present in a mixture into single element streams in a number of ways. By analogy with structural organic chemistry, one can consider either a "straight chain" or a "branched chain" method. In the "straight chain" approach, metals are removed from the mixture one at a time, or in like pairs. In the "branched chain" approach, the elements are split into two groups, say 4 and 4, or 5

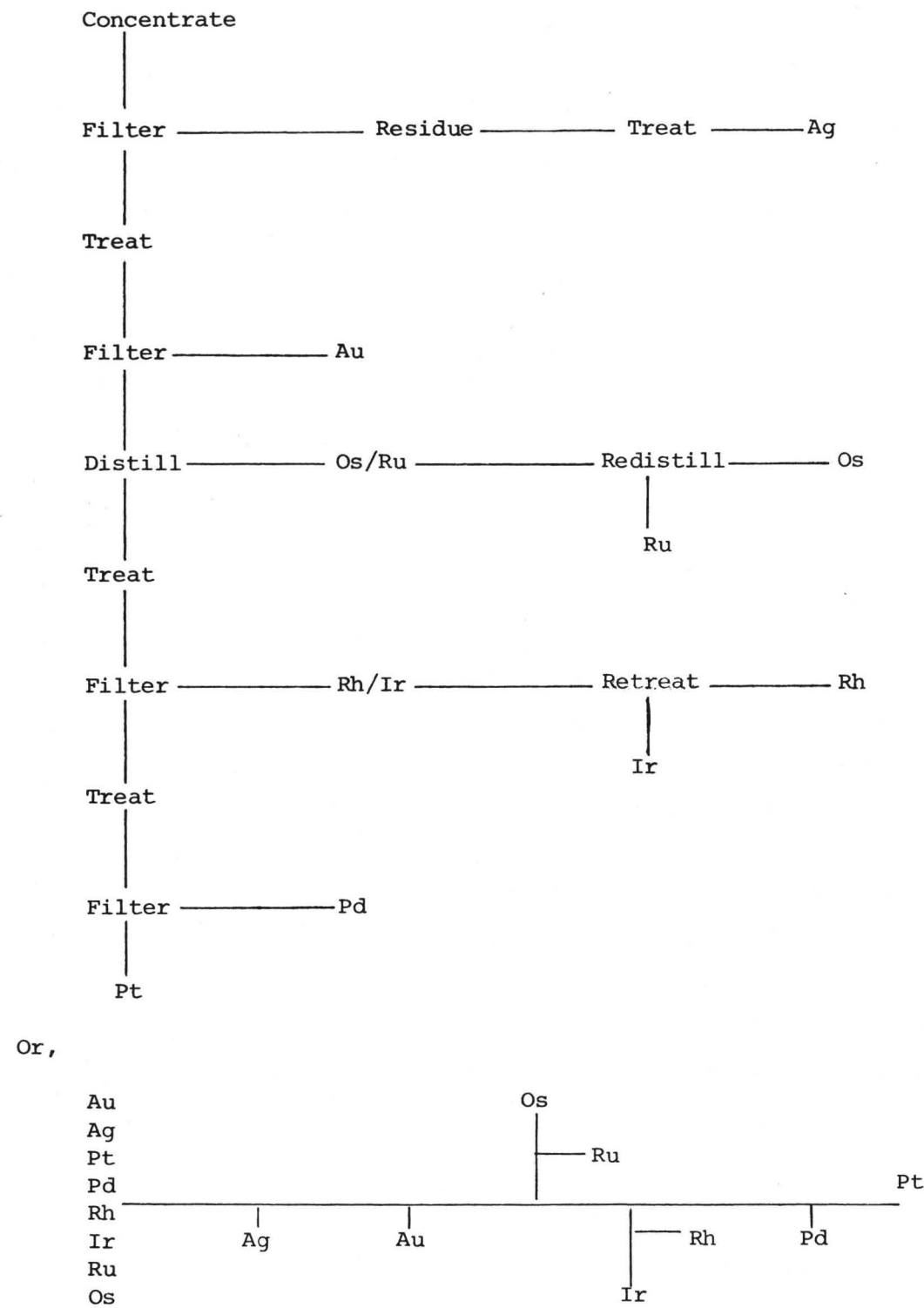
and 3, and subsequently divided until pure metal streams are obtained. The latter method is the basis of the classical separation of the platinum group metals. (The concentrate of platinum group metals plus gold and silver is treated with dilute aqua regia. Gold, platinum and palladium are generally soluble, and silver and the remaining four platinum group metals are generally insoluble. Thus, rhodium, iridium, ruthenium and osmium acquired the term "insoluble metals" of the platinum group. The method then proceeds to separate the soluble constituents of the treatment, to render the undissolved portion soluble, and then to separate the "insoluble" metals in this stream.

The disadvantage of this method, and of all precious metals separation processes, is that the split of "soluble" and "insoluble" metals is incomplete. For example, some platinum may remain undissolved and report in the insoluble stream, and some ruthenium may dissolve and report in the soluble stream. Secondary treatment is then required to recover the misdirected metal and recycle it. The extent to which this happens is dependent on the chemical and metallurgical form of the metals in the original concentrate, and will differ according to the mineral source and the manner of primary concentration. Precious metal refiners who employ this approach go to considerable lengths in the pre-treatment of the concentrate to ensure the soluble metals stay soluble, and most particularly, the insoluble metals remain insoluble, at the primary dissolution stage. An alternative approach was developed by Matthey Rustenburg Refiners (UK) Ltd. during the early 1970's to improve chemical refining efficiencies. A new metallurgical process was developed to produce a primary concentrate in which the platinum group metals and gold were substantially soluble. The subsequent chemical refining scheme could then be of a "straight chain" type. Though many alternative sequences of separation could be proposed, a system in which all metals are recovered with minimum overall time and cost is the optimum. Even so, advantages can be shown to sequences in which the more readily marketable metals (gold, platinum, rhodium for example) are refined early. Alternatively, those present in greater proportion, (platinum, palladium and ruthenium in the concentrates refined from the Rustenburg Platinum Mines) should be separated.

Another factor of which there has been increasing awareness during the 1970's is the allergenic properties of certain halogenated platinum radicals (2,3). The early removal of platinum in the refining sequence is therefore desirable. To all these considerations must be added the ultimate limitation: though platinum group metals chemistry is complex, it does not allow a practical scheme to be proposed for every alternative metal removal sequence.

One sequence currently used in our refineries is shown in figure 1. Problems still remain in this and other similar schemes. The principal cause of process inefficiency is the incomplete separation at each stage, and most particularly, the contamination of the precipitate containing the metal whose separation is desired by those we wish to leave in solution. It is almost impossible to irradicate this problem. For this reason, and because it was felt that a solvent extraction based process could achieve a cleaner separation, higher product purities and more rapid overall processing, work started in the early 1970's in the Johnson Matthey Group Research Laboratories on the development of a process for platinum group metals separation based on solvent extraction.

FIG. 1: CHEMICAL SEQUENCE (Simplified)



3. PROCESS CHEMISTRY

The process chemistry of Platinum Group Metals as applied to refining technology, and particularly to solvent extraction separations has been extensively reviewed (4) and is not therefore reproduced here.

In summary, PGM's form co-ordination complexes, the most important of which are the chloro-complexes. This is due to the fact that the most effective medium for PGM dissolution is the chloride system, usually chlorine saturated hydrochloric acid.

The PGM species normally encountered are given in table 1.

Table 1

<u>Element</u>	<u>Chloro Species</u>	<u>Oxidation State</u>
Gold	$(\text{AuCl}_4)^-$	Au III
Platinum	$(\text{PtCl}_4)^{2-}$	Pt II
Platinum	$(\text{PtCl}_6)^{2-}$	Pt IV
Palladium	$(\text{PdCl}_4)^{2-}$	Pd II
Palladium	$(\text{PdCl}_6)^{2-}$	Pd IV
Iridium	$(\text{IrCl}_6)^{2-}$	Ir IV
Iridium	$(\text{IrCl}_6)^{3-}$	Ir III
Rhodium	$(\text{RhCl}_6)^{3-}$	Rh III
Osmium	$(\text{OsCl}_6)^{2-}$	Os IV
Ruthenium	$(\text{RuCl}_6)^{2-}$	Ru IV
Ruthenium	$(\text{Ru}_2\text{OCl}_{10})^{4-}$	Ru IV
Ruthenium	$(\text{RuCl}_6)^{3-}$	Ru III
Ruthenium	$(\text{RuCl}_5\text{H}_2\text{O})^{2-}$	Ru III

4. THE PROCESS REQUIRED

A refining process for separation of PGM's from primary and secondary feedstocks must have specified characteristics. Particular advantages of a solvent extraction route are summarised as follows :

- increased operational safety to overcome allergenic problems associated with some Pt compounds.
- reduced overall processing time, particularly for the major elements, e.g. platinum.
- improved primary yields of each element.
- total recovery of all elements present in the feed.

- Reduced process recycles/reverts.
- Flexibility and versatility.
- Low solvent poisoning.
- Preferably (although this is not critical) it should employ commercially available reagents.

Each of these factors is successfully accommodated by the process operated by MRR. Of particular importance is the ability to separate PGM's from untreated primary PGM concentrates containing high levels of base metals. A typical feed analysis is given:

Au	5-7 gm/litre
Pt	80-130 gm/litre
Pd	45-65 gm/litre
Ru	10-20 gm/litre
Rh	10-20 gm/litre
Os	0.1 - 1 gm/litre
Ir	1-5 gm/litre
Base	50-200 gm/litre
Metals	
(e.g. Fe,	
Cu, Ni, Fe,	
Se, As, Bi,	
Pb, Sn, Sb)	

The base metal tolerance is particularly important not only for primary feedstocks derived from South Africa, but also for treatment of secondary materials, for example, recycled catalyst scrap, often encountered in the North American and European market.

5. PROCESS SEQUENCE

The sequence of separation of the precious metals is as indicated in figure 2. The system is orientated about the total solubilisation of the primary concentrate. The philosophy is the "straight chain" approach. Those who attended ISEC 77, or who have studied papers on the process developed by the National Institute of Metallurgy (NIM), (5) will note that the NIM process follows a different refining sequence. This may be due to its having been developed from a "branched chain" chemical refining system.

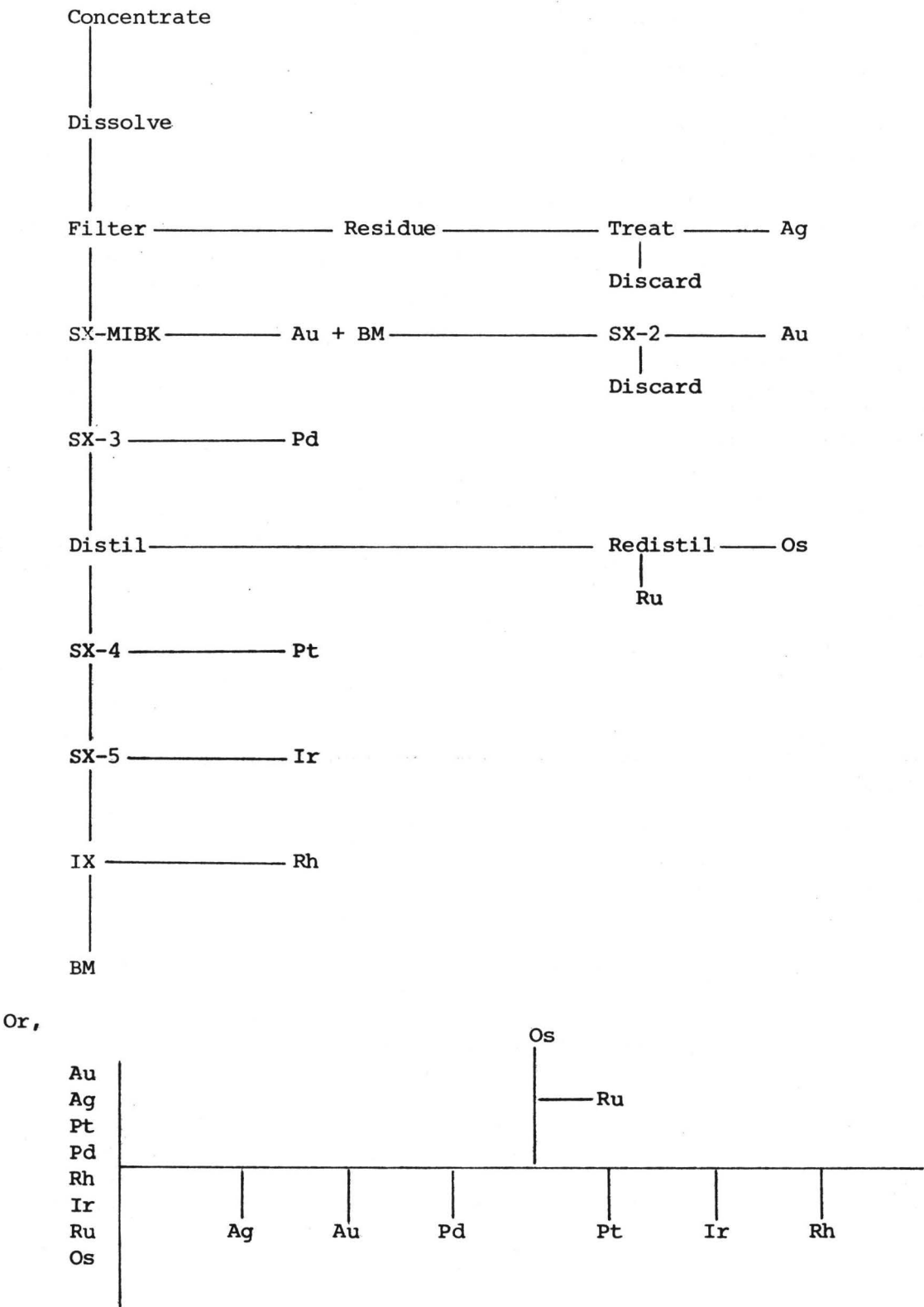
6. THE PROCESS

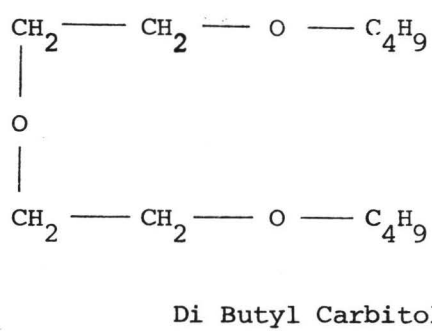
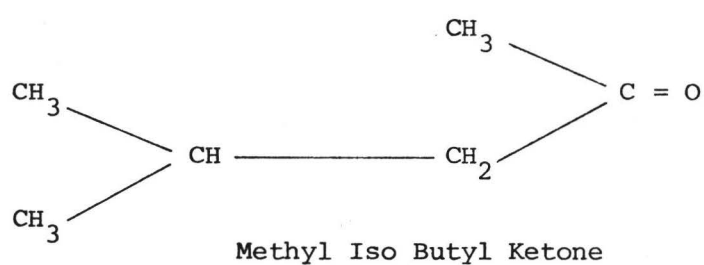
An extensive research and development effort examined possible alternative flow sheet configurations and modules; ultimately an oxime/amine processing route was chosen as having an optimum balance of the previously listed advantages.

6.1. Gold

Solvent Extraction for gold is well known and developed and has been operated commercially for a number of years. Ion exchange solvents extracting the $(AuCl_4)^{2-}$ ion including solvating reagents such as dibutyl carbitol or methyl-isobutyl ketone can be used.

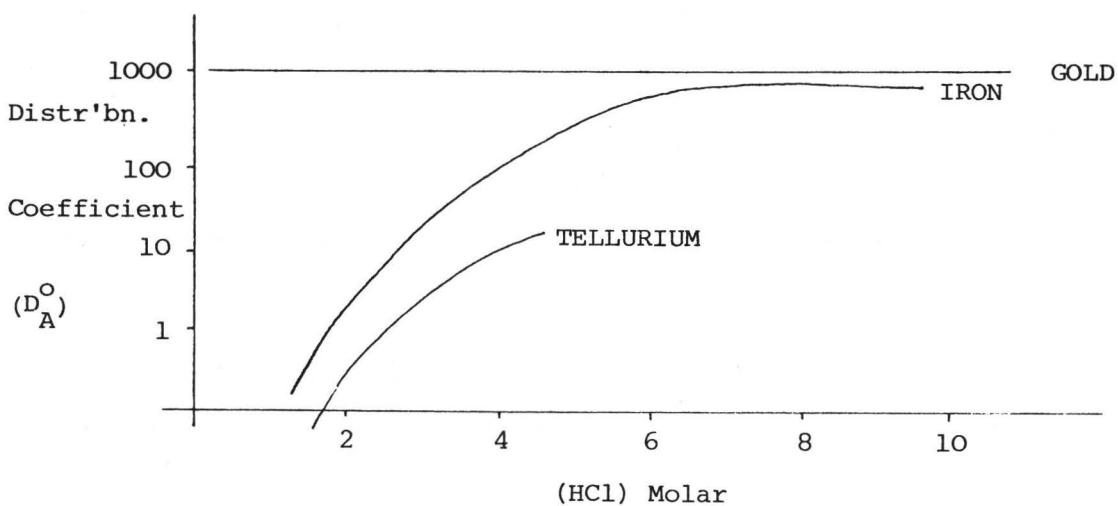
FIG. 2: MRR SOLVEX PROCESS SEQUENCE (Simplified)





Extraction of Au by MIBK can be operated in two modes, depending on feedstock. This is illustrated in figure 3.

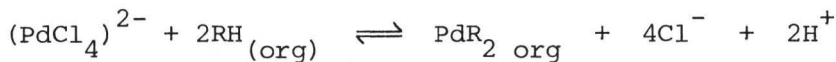
Figure 3



By operating in low acid media (<1N), Au is extracted, but not Fe, Te, Pt, the major contaminants. However, at high acidity, Au can be extracted with such contaminants at high efficiency. This can be particularly significant in the reduction of solvent poisoning and crud formation at later process stages.

6.2. Palladium

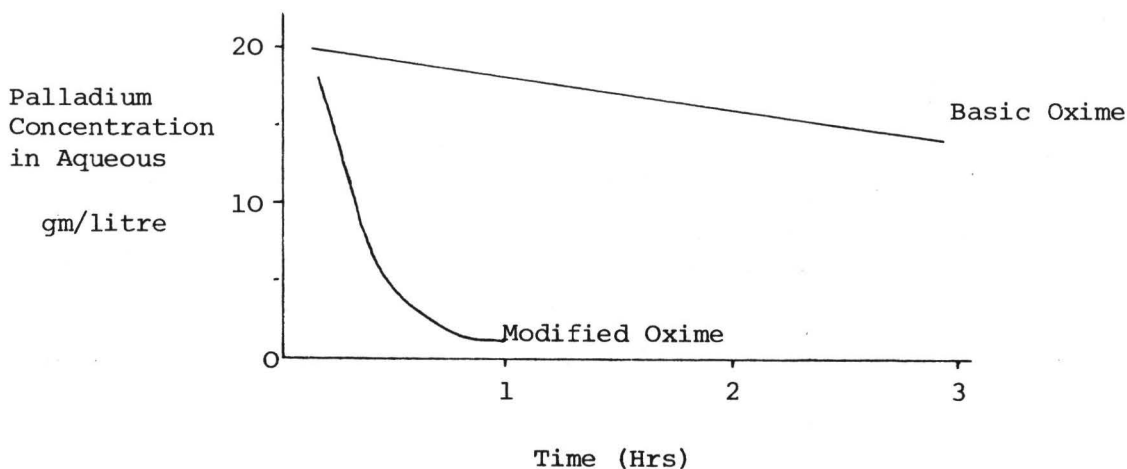
Two systems reported in recent years for palladium separation are based on oximes or alkyl sulphides. Both systems are kinetically slower than, for example, amine extraction and rely on kinetic differences to achieve separation. The basic reaction employed is, for a β hydroxy oxime:



Although the kinetics of most oxime systems are too slow for continuous mixer-settler operation, accelerating additives can be used to modify the kinetics sufficiently for realistic operation.

These modifiers, organic amines, decrease selectivity slightly, but this is perfectly acceptable to the final refining route used, Fig. 4.

Figure 4



Palladium Purity

Accelerator	99.5+%
Non Accelerator	99.9+%

Copper can be removed by selective stripping from palladium.

Oxime Extractants

Advantages

Commercially available.
Good selectivity for Pd.
Strip into HCl.
Production fully compatible with refinery intermediates.
High distribution coefficient for Pd.
High recovery efficiency.

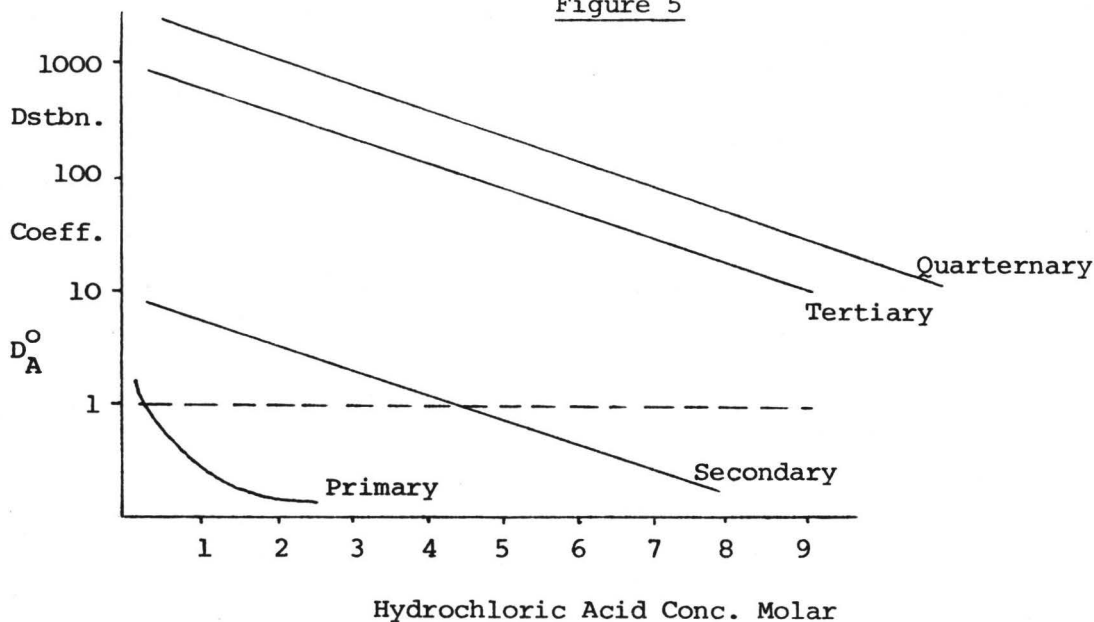
Disadvantages

Commercial reagents contain impurities.
Slow kinetics.

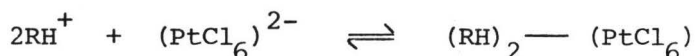
6.3. Platinum

Platinum can be removed selectively by ion exchange using amines, provided palladium has been removed first. Secondary, tertiary and quaternary systems have acceptable distribution characteristics.

Figure 5



The equilibrium lies well to the right in the equation, consequently stripping is not difficult.



It can, however, be accomplished by both acid or alkali.

From a refining viewpoint, acid is advantageous. However, strong acid is needed to break the ion pair with consequent engineering and solvent degradation problems. 10-12M hydrochloric acid is required.

Alkali, such as sodium carbonate or sodium hydroxide solutions, can also be used to break the ion pair. These systems however, are complicated by crud formation. Many commercial amines will, under operating conditions, extract a range of base metals. If these are not removed by washing circuits, a reaction can occur with formation of carbonate/hydroxyde precipitates in the settlers. Under such conditions phase separation is problematic and large gravity settlers are required. Alternatively a thickener/settler has been developed which improves settling rates.

A further disadvantage of alkali stripping is that subsequent reaction to recover Pt yields sodium chloride effluent, which is increasingly unacceptable as an effluent at any location away from the sea.

6.4. Ruthenium

Solvent extraction routes for ruthenium separation have been reported via a nitrosyl complex (6). At present, the conventional separation technique of distillation of ruthenium and osmium, as the tetroxide is preferred. This gives the desired intermediate in both high yield and purity.

6.5. Iridium

Having removed Au, Pt, Pd and Ru, the iridium can be extracted with amine solvents as the oxidised $(IrCl_6)^{2-}$ species.

The extraction of iridium very clearly illustrates the advantage of highly efficient stage separations achieved with solvent extraction.

Iridium is present in small quantity relative to platinum. In a conventional operation as much as 5% of the input platinum can report to the iridium intermediate giving a purity at intermediate of significantly less than 50% iridium, when other PGM's are taken into account. In Solvex separation giving 99.99% removal of Pt, the comparable intermediate is 99%+ pure having regard to other metals.

6.6. Rhodium

Rhodium finally remaining can be separated from residual base metals, mainly nickel and sodium chlorides, by a variety of techniques, such as :

- ion exchange of base metals.
- ion exchange of rhodium.
- chemical refining.

7. PILOT OPERATION AND DEVELOPMENT

The main flowsheet options identified at laboratory scale were examined at pilot scale in order to :

- generate design data.
- prove the flowsheets and equipment at a substantial operating scale.
- examine long term operational effect, e.g.
 - safety
 - reagent degradation.
- demonstrate the acceptability of new technology to production personnel.
- examine operating yields, recovery, pipeline, costs, etc.

A pilot plant facility with a capacity of processing 80,000 to 100,000 Troy oz of Pt from a variety of feedstocks was established in 1975 adjacent to an existing MRR refinery at Royston. For the last two years, the plant has operated at full capacity, of 80000-100000 Troy oz. Pt and various standard primary and secondary feedstocks have been processed on a routine basis to give separate metal streams which are processed via the existing refinery for sale.

The input materials, though standard, vary considerably in precious metals content. For example, feedstocks with Pt:Pd ratios of 10:1 to 1:1 and Pt:Ru ratios of 6:1 to 100:1 have been processed satisfactorily. In all, some 5 tons of precious metal have been processed to high grade intermediates. Examples of purity achieved are Pt at 99.9%, Pd at 99%. MRR is currently designing larger scale production plant for construction in 1981 and commissioning in 1983.

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EXTRACTION OF THE PLATINUM METALS WITH 2-OCTYLAMINO-
PYRIDINE AND SOME SELECTIVITY PROBLEMS OF METAL
EXTRACTION.

O.M. Petrukhin, N.A. Borshch, Yu. A. Zolotov
Vernadsky Institute of Geochemistry
and Analytical Chemistry, Academy of
Sciences, Moscow 117334, USSR.

ABSTRACT 2-Octylaminopyridine (OAP) has been proposed as an extractant for the platinum group metals. Some constants have been determined which describe the behaviour of OAP in solvent extraction systems and conditions for extraction of the noble metals. The compositions and properties of the compounds extracted have been investigated. The reasons, responsible for the selectivity of OAP and other aromatic amines with regard to the platinum metals, are discussed.

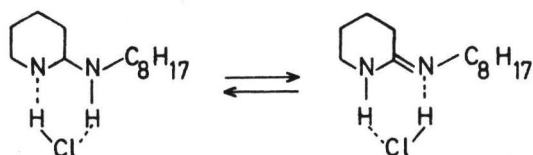
Solvent extraction is widely used for the isolation and separation of the noble metals (1,2). Aromatic amines are particularly promising extractants for this purpose: p-octylamine (3) and a copolymer based on 3(5)-methylpyrazol and styrene (4) have been used for group extraction of the noble metals, and we have proposed 2-octylaminopyridine as a reagent for the extraction of indium and rhodium from solutions containing large amounts of copper, iron and other metals (5). So far 2-octylaminopyridine had not yet been used for extraction purposes.

Properties of OAP. OAP was synthesized by condensation of 2-aminopyridine Na-derivative with octylbromide in dry toluene (6). OAP is readily dissolved in various organic solvents, e.g. CCl_4 , CHCl_3 , dichloroethane, benzene, ethanol, acetone. After recrystallization from acetone, OAP is recovered as needle-shaped crystals (melting point $43 \pm 0.5^\circ\text{C}$). The substance was identified by elemental analysis, infrared and PMR studies.

OAP is a rather strong organic base due to the heterocyclic nitrogen ($\text{pK}_a = 7.35 \pm 0.02$ at $\mu = 0.1$ and 20°C). Its partition constant in the chloroform-water system is high ($\log K_D = 5.94 \pm 0.04$ at $\mu = 0.1$ and 20°C). OAP forms well extracted ion associates with mineral acid anions: e.g. it quantitatively extracts hydrochloric acid over a wide range of concentrations owing to neutralization reaction ($\log K_{\text{ex}} = 4.13 \pm 0.03$; $\log K_D = 2.49 \pm 0.03$ at $\mu = 0.03-0.1$, 20°C and CHCl_3). An amine

salt, containing one acid molecule, is extracted. Insignificant overstoichiometric extraction is observed only from solutions with HCl concentration above 8 M (6).

The spatial position of the α -amine group relative to the heterocycle nitrogen in an OAP molecule can result in the formation of an intramolecular hydrogen bond in the ion associates $\text{OAPH}^+ \cdot \text{X}^-$ ($\text{X}^- = \text{Cl}, \text{Br}, \text{I}$). For instance, a six-membered ring forms in the case of octylaminopyridine chloride :



The infrared spectrum of $\text{OAPH}^+ \cdot \text{Cl}^-$ confirms the cycle formation. The infrared spectrum of the extract resembles the octylaminopyridinium chloride spectrum. Thus, a salt with an intramolecular hydrogen bond is extracted and this salt does not practically involve any water molecule. This accounts for the high constant of HCl extraction via neutralization chemism. The PMR studies of $\text{OAPH}^+ \cdot \text{X}^-$ salts ($\text{X} = \text{GaCl}_4^-, \text{Cl}^-, \text{Br}^-, \text{I}^-$) have shown that the chemical shifts due to heterocyclic (δ_1) and amine (δ_2) protons change with the nature of the ion associate and increase with the polarizability of the anion. The degree of charge delocalization (α) in a 2-octylaminopyridinium cation for different anions can be expressed, in %, by the formula

$$\alpha = -\left(1 - \frac{\delta_1 - \delta_2}{\delta_1 - \delta_2 - 2\delta}\right) \cdot 100$$

where δ denotes the chemical shift of the OAP amine nitrogen. The calculated results are given in Table 1, all the shifts being reported p.p.m. as relative to tetramethylsilane as internal standard.

Table 1.

The degree of delocalization (α) in 2-octylaminopyridine cation for different anions.

Anion (X^-)	δ_1 p.p.m.	δ_2	α , %	Polarizability (cm^3)
GaCl_4^-	11.9	6.9	48	-
Cl^-	15.1	8.7	54	6.7
Br^-	14.1	8.5	60	9.6
I^-	19.2	8.4	90	13.7

Therefore, OAP is a readily polarized ligand having a generalized π -electron cloud involving an undivided electron pair of the amine nitrogen. According to Pearson's classification, free OAP should be assigned to soft bases, protonated one to soft acids.

Extraction of the noble metals. The metals were extracted by an OAP solution in chloroform, either directly (procedure A) or after a pretreatment with stannous chloride (procedure B). In the former case, after the usual extraction procedure, metal concentrations in both phases were measured spectrophotometrically or radiometrically. In the latter case, a SnCl_2 solution was added to the metal solution before adding an OAP² solution in acetone and the mixture was boiled for 40 minutes. The solution was then cooled, chloroform was added and after shaking the mixture, procedure A was applied.

By using procedure A, all the metals studied are extracted from hydrochloric acid solutions. High distribution coefficients are obtained if free OAP is present in the organic phase (0.1 M OAP, 10^{-4} - 10^{-5} M Me, CHCl_3 , 30 minutes contact time) :

$C_{\text{HCl}}(\text{pH}_{\text{eqw}})$, M	3.0	0.2(1.25)	0.08(1.58)	0.01(3.35)
	2.50	20	-	86
	2.10	-	13	-
	-	0.9	-	205
	3.0	150	180	160

The distribution coefficients for iridium increase with the contact time up to 50 hrs and even more in the extraction from 1-6 M HCl.

By using procedure B, the percentage of noble metal extraction decreases in the order $\text{Ir} \gg \text{Rh} > \text{Pt} \gg \text{Ru} > \text{Pd} \gg \text{Au}, \text{Ag}$ (with HCl concentration between 1 and 6 M and OAP concentration 0.1 M). The distribution coefficient for iridium is very high ($D_c = 300$ -1000) while these for platinum and rhodium are an order of magnitude lower. Ruthenium and palladium partially, gold and silver quantitatively, float at the interface as chloroform-insoluble species. Iron and common nonferrous metals are extracted with low distribution coefficients under the conditions studied ($\text{Fe}, \text{Ni}, \text{Co} \approx 0.001$; $\text{Cu} \approx 0.4$). The extraction of Ir, Rh and Pt with OAP can be used for a preconcentration of these metals (5).

Composition of the extracted compounds. The studies of the composition of the extracted compounds by physicochemical methods and elemental analysis have shown the following. In the extraction procedure A, palladium at HCl concentration ≤ 3 M and platinum at $\text{pH} \geq 1.5$ are extracted as coordinatively solvated complexes MCC_2L_2 . At HCl concentration > 3 M platinum is also extracted, first as a mixed complex $\text{LH}^+[\text{PtCl}_3\text{L}]^-$ and then as an ion associate $(\text{LH}^+)_2[\text{PtCl}_4]^{2-}$. Iridium is extracted by an OAP chloroform solution from 1-6 M HCl as ion associates $(\text{LH}^+)_n[\text{IrCl}_6]^{-n}$ ($n = 2.3$). These data were obtained for the extraction of Pd, Pt and Ir by 0.1 M OAP solution in CHCl_3 , with initial metal concentrations of 10^{-5} - 10^{-3} M and a shaking time of 30 min.

If the extraction is performed following procedure B, palladium complexes are mainly formed which float at the interface. Ruthenium, gold, and silver behave in a similar way. When the mixture is not boiled after the addition of the SnCl_2 solution, palladium is extracted as mixed complexes of variable composition. In the extraction of iridium following procedure B, ion associate type species are extracted, which involve anionic complexes of iridium. The anionic complexes involve neutral OAP molecules and negatively charged ligands SnCl_3^- and Cl^- . The brutto formula of the iridium complexes extracted is $(\text{LH}^+)^{3-x} [\text{IrL}_x(\text{SnCl}_3)_{m-x} \text{Cl}_{6-m}]^{x-3}$ ($x = 0.2$; $m = 1-6$).

Studies of the MCC_2L_2 ($\text{M} = \text{Pt}, \text{Pd}, \text{Ni}$) extracted species. Specific properties of aromatic amines with regard to the noble metals, compared with these of aliphatic amines, are mainly related to the formation of coordinatively solvated compounds, even in the extraction from acid solutions. The formation of such compounds results in high selectivity of the extraction of the noble metals compared with that of common nonferrous metals such as nickel. To elucidate the factors responsible for this selectivity, we synthesized and studied the compounds of isovalent and isoelectronic metals MCl_2L_2 ($\text{M} = \text{Pt}, \text{Pd}, \text{Ni}$). The compounds were identified by elemental analysis and examined by infrared, PMR, ultraviolet, and ESCA-studies. The MCl_2L_2 complexes are coordination compounds. The central metal atom forms bonds with chloride ions and the heterocyclic nitrogen atom of OAP. The amine group hydrogen forms a hydrogen bond with the metal-coordinated chlorine atom. This is promoted by the amino group spatial position and the fact that the coordinated chlorine atom possesses an excess negative charge.

The extraction of coordinatively solvated species can be considered from the viewpoint of formation of electronic donor-acceptor complexes by neutral complexes MCl_2 and OAP molecules (7). Generally, OAP is first of all an electron donor. This follows from the fact that the energy level of 1 s nitrogen electrons is lower from free OAP than for the complexes of all the metals studied (Table 2).

Table 2.

The ionization energies (eV+0.1) for electrons from inner ligand levels in the complexes of the platinum group metals with 2-octylaminopyridine.

Compound	N 1s	Cl 2p 3/2
1	2	3
OAP	399.2	-
OAP.HCl	399.9 ; 401.0	197.7

1	2	3
$\text{Ni}(\text{OAP})_2\text{Cl}_2$	400.0	198.4
$\text{Pd}(\text{OAP})_2\text{Cl}_2$	399.7	198.4
$\text{Pt}(\text{OAP})_2\text{Cl}_2$	399.6	198.5
$\text{Pd}(\text{NH}_3)_2\text{Cl}_2^*$	400.4	199.1
$\text{Pt}(\text{NH}_3)_2\text{Cl}_2^*$	400.2	196.9

*for 8.

From the change of the energy of 1 s-level related to the complex formation, it may be concluded that the acceptor ability of nickel is higher than that of palladium and platinum in the corresponding halides. It is of interest that the energy of $2p_{2/3}$ -level is much lower if the central atom forms a bond with an aromatic nitrogen but not with an ammonia nitrogen (nitrogen of most "hard" aliphatic amines). Hence, the electron density, localized at the OAP donor atom, redistributes not only directly to the acceptor atom, but also further along the N-Me-Cl-chain. A change in this very ability of the donor nitrogen atom from aliphatic to aromatic amines is probably responsible for the increased selectivity of aromatic amines as extractants for coordinatively solvated species.

This ability correlates with the orbital electronegativity of unpaired nitrogen electrons and seems to increase with the fraction of π -electron density of the hybrid orbital (9).

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SOLVENT EXTRACTION BEHAVIOUR OF NICKEL(II), COBALT(II) AND
COPPER(II) WITH 1-PHENYL-3-METHYL-4-BENZOYLPYRAZOL-5-ONE

Amrit N. Patel

Department of Chemistry
University of Nigeria

Nsukka, Anambra State, Nigeria

The extraction behaviour of nickel(II), cobalt(II) and copper(II) with 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (PMBPOH) dissolved in carbon tetrachloride from the aqueous chloride and thiocyanate systems, in the range of hydrochloric acid concentration between 0.1 M and 5.0 M in the aqueous phase, has been studied. The extraction of nickel(II) with PMBPOH has been found to be higher compared with that of cobalt(II) and copper(II). Also, the presence of thiocyanate ions in the aqueous phase leads to enhanced extraction of nickel(II). The composition of the extracted species has been studied. The infrared bands for the reagent and the extracted species are reported. The mechanism of the extractions and structures of the extracted species are discussed.

INTRODUCTION

The separation study of nickel(II), cobalt(II), copper(II), zinc(II) and manganese(II) by the solvent extraction method using various extraction reagents (1-5) including β -diketones (5-8) is receiving greater attention from several research workers in view of the industrial importance of these metals. 1-Phenyl-3-methyl-4-acylpyrazol-5-one as β -diketones has been employed in a number of solvent extraction studies of metals (9-15) since they were first reported for such uses by Jensen (16) in 1959. In continuation of the solvent extraction studies of various metals with PMBPOH, the present paper attempts to report the extraction behaviour of divalent nickel, cobalt and copper with PMBPOH dissolved in carbon tetrachloride from the aqueous chloride and thiocyanate systems in the range of hydrochloric acid concentration between 0.1 M and 5.0 M in the aqueous phase.

EXPERIMENTAL

All chemicals used in this study were of standard reagent quality. The reagent, PMBPOH, was synthesized as reported in the literature (16). A 0.08 M solution of PMBPOH in carbon tetrachloride served as organic phase. The stock solutions of 0.04 M metal ion concentration of divalent nickel, cobalt, and copper were prepared by dissolving their chlorides ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$) in aqueous hydrochloric acid solutions of the required molarity.

Two equal volumes (25 mL) of the organic and aqueous phases were shaken for about forty minutes at 25°C, although the equilibrium was attained more rapidly. The metal ion concentrations in the aqueous phase were determined by the complexometric titration with EDTA (17) and those in the organic phases were calculated by difference between the initial and final values. The metal ions concentrations in the organic phases were also checked by a method where a known volume (20 mL) of the organic phase was evaporated to dryness, followed by addition of concentrated hydrochloric acid (about 5 mL) and evaporation to dryness again. The residue was dissolved in dilute hydrochloric acid and made up to 25 mL. The concentrations of the metal ions were then determined as in the case of the aqueous phase. For the extraction study from the thiocyanate system, 5 mL of potassium thiocyanate solution of 0.5 M was added to the aqueous phase and the resultant aqueous mixture was then extracted with 30 mL of the organic phase. The concentrations of nickel(II), and cobalt(II) in the aqueous phases were determined by complexometric titration with EDTA, and that of copper(II) by iodometric titration (17). Concentrations of the metal ions in the organic phases were also checked using the method described above.

The complexes of nickel(II), cobalt(II) and copper(II) with PMBPOH from the aqueous chloride and thiocyanate systems were obtained by evaporating the respective organic phases under reduced pressure to a small volume and then adding an approximately equal volume of petroleum ether. The solid complexes thus obtained were filtered off and dried in a vacuum desiccator. Analysis of the metal complexes from the aqueous chloride system indicated a stoichiometric ratio of 1:2 for M:OPBMP (M = Ni(II), Co(II) and Cu(II); PMBPO = anion of 1-phenyl-3-methyl-4-benzoylpyrazol-5-one). Similarly, the metal complexes from the thiocyanate system gave the stoichiometric ratio of 1:3:1 for M:SCN:OPBMP.

The infrared spectra of the metal complexes, along with the PMBPOH, were recorded using the Nujol mull technique on a Perkin Elmer Infra-red Model 257 spectrophotometer.

RESULTS AND DISCUSSION

1-Phenyl-3-methyl-4-benzoylpyrazol-5-one, like other β -diketones, exhibits a keto-enol tautomerism and exists in the following two stable tautomeric forms (Fig.1), although four tautomeric forms are possible. This is explained by conjunctive effects in the molecule. The PMBPOH being acidic in nature also exists in an anionic form. For instance, at pH < 2 it is in the molecular form with an absorption peak at 252 nm (ϵ_m 1.695×10^4), and at pH > 3 the anionic form exists which shows an absorption maximum at 260 nm (ϵ_a 1.556×10^4) (15).

The maximum absorption thus undergoes a bathochromic shift in an alkaline solution. 1-Phenyl-3-methyl-4-benzoylpyrazol-5-one is a stronger acid ($pK = 3.95 - 4.15$) (15) than thenoyltrifluoroacetone (TTAH, $pK = 6.28$) (18) as well as other analogous β -diketones (13,18).

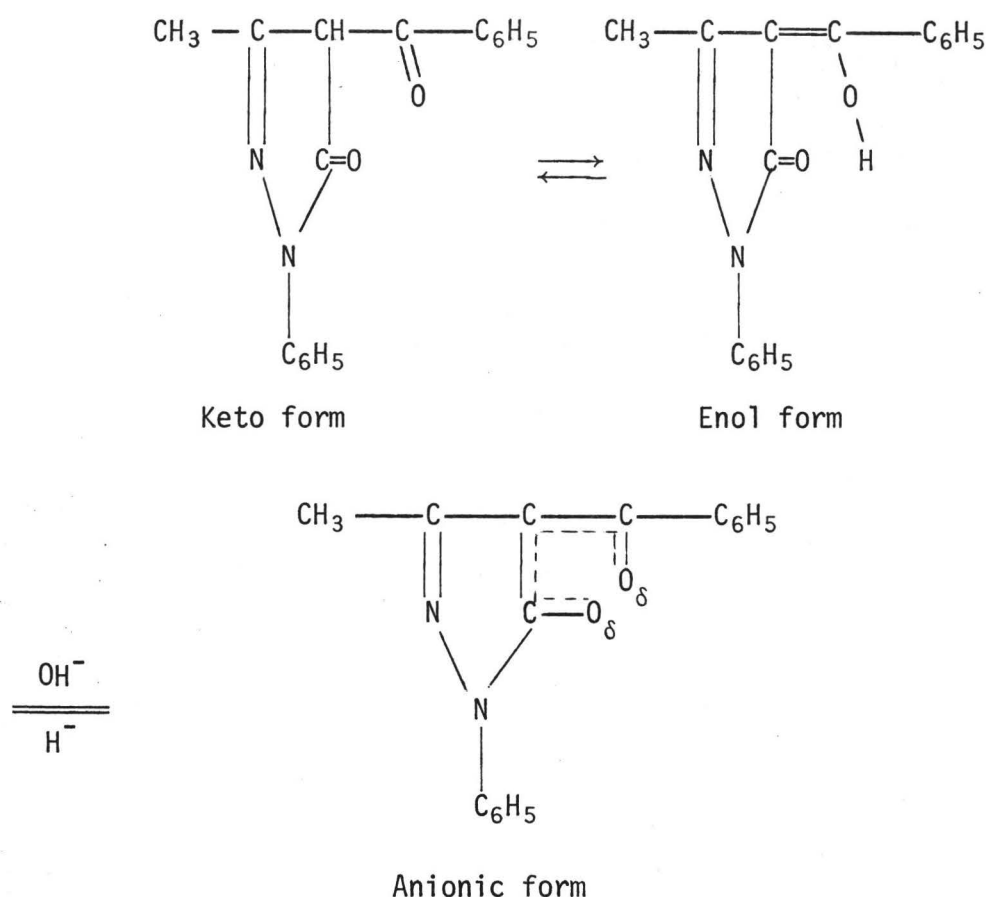


Fig. 1. Keto, enol and anionic forms of 1-phenyl-3-methyl-4-benzoylpyrazol-5-one.

Numerous investigators (19,20) have demonstrated the influence of diluents on the extraction of a large number of metals and extractants. And as far as the so called "inert" diluents are concerned, the synergic effect increases in the order cyclohexane > hexane > carbon tetrachloride > benzene > chloroform (21,22). Furthermore, diluent influence is very large for tetra- and trivalent metals and less pronounced for di- and monovalent metals. Several factors such as dielectric constant, interactions of diluents with ligands and solubility of water in diluents have been advanced to explain the influence of the diluents. Carbon tetrachloride, being in the middle of the order and having a large density difference with water as compared to other solvents, was selected as a solvent for the present study. The large density difference between water and carbon tetrachloride will obviously enhance the rate of separation of aqueous and organic layers.

Since nonpolar solvents usually extract nonpolar or neutral species from polar media, the extraction of metal chelates from highly polar aqueous media with carbon tetrachloride postulates the formation of a neutral complex. The extraction reaction of 1-phenyl-3-methyl-4-benzoylpyrazol-5-one dissolved in carbon tetrachloride for the divalent metal ions may be represented as:



where, M = Ni(II), Co(II) and Cu(II).

The distribution ratio, D, expressed as:

$$D = \frac{[M(PMBPO)_2]_{org}}{[M^{2+}]_{aq}} \quad \text{.....(2)}$$

is related to the per cent extraction, E:

$$D = \frac{E}{100 - E} \quad \text{.....(3)}$$

The results of the extraction studies of the three metals with 1-phenyl-3-methyl-4-benzoylpyrazol-5-one dissolved in carbon tetrachloride are summarized in Tables 1 and 2.

Table 1. Per cent extraction of metal ions.
Metal ions concentrations in the aqueous acid phase, 0.04 M
PMBPOH concentration in the organic phase, 0.08 M.

HCl, M Initial	Per cent extraction, E		
	Ni(II)	Co(II)	Cu(II)
0.5	24.25	1.77	5.50
1.0	56.04	5.17	9.90
2.0	66.65	13.76	13.02
4.0	70.58	20.26	14.72
5.0	69.20	19.50	12.50

Table 2. Per cent extraction of metal ions in the presence of thiocyanate ions.
Metal ions concentrations in the aqueous phase, 0.04 M and PMBPOH concentration in the organic phase, 0.08 M.

HCl, M Initial	Per cent extraction, E		
	Ni(II)	Co(II)	Cu(II)
0.10	80.49	5.03	35.00
0.50	79.10	6.20	38.10
1.00	80.85	7.41	37.50
2.00	80.05	10.52	35.15
3.00	79.07	10.31	30.05
4.00	77.15	10.25	22.25
5.00	75.75	9.85	15.15

The extraction of nickel(II) with PMBPOH is found to be much better compared with that of cobalt(II) and copper(II) and increased with an increase in the acid concentration in the aqueous phase up to 4 M. It also decreased at very high concentration of acid in the aqueous phase. The method of slope analysis as well as the analysis of the composition of the extracted species, indicated the stoichiometric ratio of 1:2 between the metal ions and PMBPOH. The extracted complexes therefore can be written as $M(OPBMP)_2$. This agrees well with the extraction equilibrium represented by extraction reaction Eq.1.

The I.R. spectra of the reagent PMBPOH and its complexes with the metal ions are quite complex. The complexities can be attributed to the presence of a number of functional groups, viz: $C=O$, $C=C$, $C=N$, $=N--N=$ and C_6H_5- due to their conjunctive effects. The I.R. spectrum of the enol form of the free ligand has a band around $3380 - 3200\text{ cm}^{-1}$ corresponding to the presence of the hydrogen bonded hydroxyl group. However, this band disappeared in the I.R. spectra of the complexes, thereby indicating the removal of hydrogen of the hydroxyl group in the formation of the complexes via the hydroxyl oxygen atom. The carbonyl band at 1635 cm^{-1} in the complexes occurs at a lower frequency as compared with 1645 cm^{-1} of the parent ligand, which gives support for coordination of metal ions via carbonyl oxygen. The $C=O$ band at 1195 cm^{-1} in the free ligand is also shifted to a lower frequency at 1180 cm^{-1} in the metal complexes, which also suggests the formation of the metal complexes via the hydroxyl oxygen atom.

The presence of thiocyanate ions in the aqueous phase considerably improves the extraction of nickel(II) with PMBPOH (see Table 2).

It is presumably due to the formation of thiocyanate complexes leading to peeling off the aquo-shell of the nickel(II) ion, which in turn may have contributed in the formation of extractable species and thereby enhancing the extraction rate of nickel(II). The extraction of nickel(II), cobalt(II) and copper(II) shows a decrease with increase in the acid concentration above 2 M. However, the decrease is small for nickel(II) and cobalt(II) but is pronounced for copper(II). It appears that, in the case of copper(II) at higher acid concentration, the thiocyanate complexes of copper(II) may have become unstable and copper(II) reduced to copper(I), thereby adversely affecting the extraction of copper(II). The analysis of the composition of the extracted species of the three metal complexes from the thiocyanate system suggests a stoichiometric ratio of 1:3:1 for the metal ion:thiocyanate ion:PMBPO in the extracted species. It appears from the stoichiometric ratio that the extractable species are likely to be of the type $[M(SCN)_3 \cdot OPBMP]^{2-}$, although a definite conclusion could not be drawn at this stage. The infrared spectra of the extracted species have a sharp band at 2140 cm^{-1} which implies that the thiocyanate group may have coordinated to divalent metals through sulphur atom (23), although the thiocyanate group bonded to a metal forms either $M-N$ or $M-S$ bonds, depending on the nature of metals.

The preliminary separation study of nickel(II) and cobalt(II) was carried out by equilibrating 200 mL of an aqueous phase containing Ni(II) (12.00 g/L, 75%) and Co(II) (4.00 g/L, 25%) in 1 M HCl solution with 0.08 M solution of PMBPOH in carbon tetrachloride. The aqueous phase was equilibrated three times with the organic phase, first with 200 mL, the second and third times with 100 mL only. Analysis of the aqueous phase after the third equilibration indicated a change in the percentage ratio of nickel(II) and cobalt(II), from 75:25 in the pre-equilibrated aqueous phase to 22:77 in the equilibrated aqueous phase, thereby showing a transfer of about 91.5 per cent of nickel(II) and 12.5 per cent of cobalt(II) of the organic phase. The metal

ions from the combined extract were stripped by boiling with ammonia solution followed by an addition of dilute hydrochloric acid solution. The metal ions were dissolved in the aqueous phase as an amino complex while the PMBPOH remains in the organic phase. The infrared spectrum of the recovered PMBPOH was superimposed on that of the original. The results of the preliminary study are encouraging. However, a definite conclusion could not be reached without a more detailed investigation.

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SEPARATION AND RECOVERY OF VANADIUM AND CHROMIUM
FROM SOLUTIONS BY SOLVENT EXTRACTION WITH
PRIMARY AMINES AS SOLVENT*

Shu-chiou Yu, Shiang-sheng Meng,
and Chia-yung Chen

Institute of Chemical Metallurgy,
Academia Sinica

Beijing (Peking), China

It has been found in the present research program that vanadate can be extracted quantitatively by primary amines from nearly neutral chromium(VI)-containing solution. Studies were made on the conditions of extraction and separation of vanadate and chromate from aqueous solution with primary amines as diluent, as well as the conditions of scrubbing and stripping the loaded solvent. A flowsheet is proposed to extract and separate vanadium and chromium from a solution derived from chromium- and vanadium-containing titaniferous iron ore. Satisfactory results were obtained in bench scale tests using solution from the leaching of sodium salt-roasted titaniferous iron ore.

INTRODUCTION

Vanadium-containing titaniferous iron ore is one of the important iron ore resources of China and many other countries. Some orebodies of this type have a rather high content of chromium, titanium and vanadium. Processes such as smelting in a blast furnace, or direct reduction, can be developed to make iron from the concentrate of this type of iron ore. But no matter what process is used to make iron, the vanadium and chromium in the concentrate will finally go into a process by-product such as slag. This by-product can be roasted with the addition of sodium salts, followed by water leaching, to dissolve vanadium and chromium. Vanadium and chromium are then in the alkaline leaching solution in the form of vanadate and chromate, respectively.

A number of studies have been reported on the separation and recovery of vanadium and chromium from such aqueous solutions by solvent extraction. Swanson et al (1) studied the extraction of vanadium by Aliquat 336 and separation of vanadium and chromium in the alkaline solution. Deptula (2) used tri-n-octyl amine as solvent to extract chromium(VI) from solutions containing sulphuric acid. TBP was used as the extractant by Tuck et al (3) to extract chromium(VI) from solution. The equilibria between Aliquat 336 and various metal anions involving chromium, vanadium, and the chloride and hydroxide anions were investigated by Hughes et al (4). Rothmann et al (5) considered the different methods such as precipitation, ion exchange and

*Patent applied for, China Patent Bureau

solvent extraction to recover V and Cr. Ritcey (6) studied the separation of V(V) and Cr(VI) by solvent extraction with Adogen 464 from a solution derived from titaniferous iron ore. Seven stages were required to extract vanadium, with the raffinate containing vanadium at about 50 mg/L.

Solvent extraction can be considered as an efficient method to recover and separate chromium and vanadium from the solution. In the present research program, it has been found in the early stage of screening extractants that V(V) can be extracted quantitatively by primary amines from the nearly neutral solution. A flowsheet was designed and tested based on this discovery to recover and separate vanadium and chromium in the solution derived from the titaniferous iron ore.

EXPERIMENTAL RESULTS

An electric stirrer or shaker was used to mix the organic and aqueous phases. Chromium and vanadium in aqueous solution were determined by volumetric titration or by colorimetry. The metallic contents of the organic phase were calculated by difference and agreed, within experimental error, with the values determined by stripping the metallic values into the aqueous phase followed by analyzing its metallic contents.

The primary amine used was N-1923 provided by the experimental plant of the Institute of Organic Chemistry, Academia Sinica, Shanghai, China. Its primary amine content was above 95%, its average molecular weight 312, with the following physical constants D_{25}^{25} 1.4530; d_4^{25} 0.8154; n_D^{25} 1.4773; b.p. 146-202°C (5 mm). The diluent used was lamp grade kerosene without any additional treatment. The other chemicals used were of either chemical pure or analytical pure grade. In this paper, n stands for gram equivalents, m gram atoms, A aqueous phase and O organic phase.

Extraction of Vanadium from Solutions Containing Vanadium and Chromium

Two series of experiments were carried out to study the effect of pH on the extraction of V(V) from solution. In the first series, acid was added to the stock solution (pH 8-9) to the required pH and then the solution was mixed with primary amine in kerosene. Results are indicated in Table 1. In the other series, stock solution was mixed with solvent and then the calculated amount of sulphuric acid, based on gram atoms of V(V) in solution, was added to the mixture. Results are given in Fig. 1. Within a certain range of the ratio of V(V) to Cr(VI) in the aqueous solution results of these two experimental series are about the same, with the latter giving better separation of V(V) to Cr(VI).

It can be seen from Table 1 and Fig. 1 that pH is an important variable for V(V) extraction. When the ratio of gram equivalents of H^+ added to gram atoms of vanadium in the solution is equal to or higher than 1, good extraction of vanadium, and separation of vanadium from chromium, will be obtained. Experiments were also carried out with liquor obtained from leaching sodium salt-roasted titaniferous iron ore as shown in Fig. 2.

When extraction is carried out by first adjusting the aqueous solution pH, the presence of a certain amount of Cr(VI) in the solution is a necessary condition for highly efficient vanadium extraction. Table 2 shows the experimental results obtained with different ratios of vanadium to chromium in

the solution. When acid is added during extraction, based on the amount of vanadium in the aqueous solution, the degree of vanadium extraction depends on the amount of acid added with more acid being required for higher Cr(VI) concentrations in aqueous solution, as indicated in Table 3.

Table 1. Effect of solution pH on vanadium and chromium separation.

Org: 10 vol% N-1923 in kerosene, O/A = 1, 16°C, 5 min.
Aq: V(V) 6.33, Cr(VI) 11.05 g/l.

Solution pH	At Equilibrium					Percent	
	Aqueous Phase			Organic Phase		Extraction	
	pH	V g/l	Cr g/l	V g/l	Cr g/l	V	Cr
4.36	7.38	0.025	7.50	6.31	3.55	99.7	32.2
4.77	7.40	0.032	7.64	6.30	3.41	99.4	30.9
5.33	7.49	0.025	7.96	6.31	3.09	99.7	28.0
6.08	7.88	0.139	10.05	6.19	1.00	97.8	9.05
6.61	-	0.279	10.07	6.05	0.98	95.5	8.83
6.91	8.29	2.27	10.90	4.06	0.15	64.1	1.36
7.08	8.35	3.67	10.90	2.66	0.15	42.0	1.36
7.40	8.48	5.20	10.96	1.13	0.09	17.9	0.82

Table 2. Effect of vanadium to chromium ratio in aqueous solution on vanadium extraction by primary amine.

Time: 10 min, O/A = 1, 12 to 14°C

pH	Aqueous Solution			Amine Conc. %	Aqueous Phase at Equilibrium			Percent Extraction	
	V g/l	Cr g/l	V/Cr by wt.		pH	V g/l	Cr g/l	V	Cr
6.50	0.891	9.75	0.091	10	8.42	0.078	7.76	91.0	19.4
7.0	0.891	9.75	0.091	5	8.27	0.040	8.81	94.8	9.65
7.0	0.891	9.75	0.091	2.5	7.93	0.112	9.02	87.5	7.5
6.55	7.33	12.15	0.60	10	8.33	0.085	11.68	98.7	3.87
6.50	6.14	6.90	0.89	10	8.75	0.68	6.73	89.0	2.46
6.52	6.17	3.73	1.67	10	8.98	2.66	3.58	56.8	3.90
5.88	6.17	3.73	1.67	10	8.79	0.88	3.42	85.8	8.07
5.46	2.07	1.23	1.64	10	-	0.049	1.21	97.5	1.64
6.70	10.92	0	-	10	9.0	9.37	0	14.3	-
3.10	10.92	0	-	10	-	6.77	0	38.0	-
6.70	7.05	1.79	3.93	10	-	4.21	1.67	40.3	6.58
3.00	7.05	1.79	3.93	10	7.76	1.75	1.33	75.2	25.6

Temperature has a rather remarkable influence on vanadium separation from chromium as indicated in Table 4. The percent vanadium extracted decreases as temperature increases. It can be considered that the tendency of H-bond formation for solvation mechanism of V(V) extraction by primary amines decreases

as the temperature increases (7). Extraction time has some effect on vanadium and chromium separation, with best results at about five minutes. Some chromium extracted initially will exchange with vanadium in the aqueous solution resulting in better separation.

Table 3. Effect of vanadium to chromium ratio in aqueous solution on vanadium extraction.

Time: 5 min, O/A = 1, 20°C.

Aqueous Feed				H ₂ SO ₄ Added n _H ⁺ /m _V	Amine Conc. %	Aqueous Phase at Equilibrium			% Ext.	
pH	V g/l	Cr g/l	V/Cr by wt.			pH	Vg/l	Cr g/l	V	Cr
8.16	6.44	1.0	6.44	1.0	10	8.21	0.31	0.74	95.1	35.6
8.40	6.44	5.0	1.3	1.0	10	8.25	0.36	4.67	94.5	7.08
8.45	6.44	7.0	0.92	1.0	10	8.20	0.286	6.89	95.5	1.60
8.20	2.10	10.21	0.21	0.5	2.5	7.80	1.47	10.20	30.0	-
8.20	2.10	10.21	0.21	1.0	2.5	7.60	1.04	10.10	50.5	0.98
8.20	2.10	10.21	0.21	1.5	2.5	7.42	0.79	9.68	62.4	5.10
8.20	2.10	10.21	0.21	2.0	2.5	7.40	0.413	9.74	80.5	5.07
8.20	2.10	10.21	0.21	2.0	5	7.85	0.103	9.88	95.2	3.23
8.20	2.10	10.21	0.21	3.0	5	7.62	0.080	8.06	96.2	21.5
9.27	0.70	9.27	0.021	2.0	2.5	7.85	0.187	9.14	73.3	1.40
9.27	0.70	9.27	0.021	3.0	2.5	7.70	0.104	8.67	85.0	6.47
9.27	0.70	9.27	0.021	4.0	2.5	7.60	0.080	8.25	88.5	11.0

Table 4. Effect of temperature on vanadium extraction and vanadium to chromium separation.

Aqueous phase: pH 8.55, V(V) 6.64 g/l, Cr(VI) 13.5 g/l;
H₂SO₄ added during extraction: n_H⁺/m_V = 1
Organic phase: 10% N-1923 in kerosene; O/A = 1; 5 min

Temp °C	Aqueous phase			Org. phase		% Ext.		Separation factor (V/Cr)	
	pH	V g/l	Cr g/l	V g/l	Cr g/l	V	Cr		
5	8.70	0.169	13.50	6.47	0.01	97.5	0	5.2	x 10 ⁴
10	8.54	0.193	13.40	6.45	0.10	97.0	0.74	4.5	x 10 ³
15	8.47	0.221	13.28	6.42	0.22	96.7	1.63	1.74	x 10 ²
20	8.20	0.48	13.13	6.16	0.37	93.0	2.74	4.55	x 10 ²
30	8.10	0.578	13.0	6.06	0.50	91.4	3.70	2.75	x 10 ²
40	7.82	1.77	12.88	4.87	0.62	73.5	4.60	57	

Extraction of Chromium

Cr(VI) in the raffinate from vanadium extraction can be extracted with primary amines, while V(V) remaining in the raffinate will also be extracted at the same time. Experiments were carried out with acid addition during extraction. Table 5 shows the variation of percent Cr(VI) extraction with the amount of acid added during extraction. It was found that the ratio of gram ions of H⁺ added to the gram atoms of Cr(VI) in aqueous solution was about

three, Cr(VI) extraction was a maximum. Temperature has not much effect on the percent chromium extracted. However, the time required to reach extraction equilibrium is less than one minute.

Table 5. Extraction of chromium by primary amine.

Aqueous solution: Sodium chromate 10.02 g/l of Cr(VI), pH 8.28, 20°C, O/A = 1, 3 min, with 10% N-1923 in kerosene

H ₂ SO ₄ added n _{H⁺} /m _{Cr}	At Equilibrium			% Cr extracted
	Aqueous pH	Cr g/l	Org. phase Cr g/l	
0.5	7.9	7.85	2.17	21.6
1.0	7.7	5.58	4.44	44.2
1.5	7.4	3.50	6.52	65.0
2.0	7.0	1.50	8.52	84.9
2.5	6.1	0.645	9.38	93.6
2.8	2.5	0.478	9.54	95.4
3.0	2.2	0.132	9.90	98.5
3.5	1.87	0.167	9.85	98.3
4.0	1.6	0.210	9.81	97.8
5.0	1.4	0.280	9.74	97.1

Scrubbing and Stripping of Vanadium and Chromium in the Organic Phase

In order to decrease the vanadium in the raffinate from vanadium extraction, the amount of acid added during extraction must be more than the stoichiometric value, i.e., gram ions of H⁺ added equal to gram atoms of vanadium in aqueous solution. This takes some Cr(VI) into the organic phase with vanadium. Chromium in the organic phase can be scrubbed out by using sodium vanadate solution. It is thus assumed that dichromate in the organic phase will change into chromate and give H⁺ to the vanadate ion with the result of extraction of polyvanadic acid in the organic phase (7). Results are shown in Table 6.

When the V(V) content in the scrub solution is about twice the amount of Cr(VI) in the organic phase, Cr(VI) left in the organic phase after scrubbing will be less than 0.1 g/L. After scrubbing, the aqueous solution can be combined with the raffinate from vanadium extraction to further extract Cr(VI).

Sodium carbonate is a very effective stripping agent to recover vanadium from the organic phase. With the ratio of gram mols of sodium carbonate in aqueous solution to gram atoms of vanadium in the organic phase approximately equal to 1, vanadium can be quantitatively stripped in one stage as shown in Table 7.

To obtain vanadium pentoxide as the final product, ammonium carbonate has to be used as the stripping agent instead of sodium carbonate. When the ratio of gram equivalents of ammonium carbonate to the gram atoms of vanadium in the organic phase is above 2.34, with an O:A ratio of 20, the percent of vanadium precipitated during stripping is close to completion as shown in

Table 8.

Either sodium or ammonium carbonate can be used as the stripping agent for the recovery of chromium in the organic phase. Ammonium carbonate can be converted into chromium oxide by thermal decomposition. Chromium can be stripped in one stage with results shown in Table 9.

Table 6. Scrubbing of organic phase containing vanadium and chromium.
Scrubbing solution: sodium meta-vanadate, 10 g/L V(V), pH 7-8,
13°C, 10 minutes.

Loaded org. phase V g/l Cr g/l		Scrubbing phase ratio O/A	After scrubbing				% of Cr scrubbed
			Aq. phase V g/l Cr g/l		Org. phase V g/l Cr g/l		
6.74	0.82	5	-	-	8.15	0.119	85.5
6.74	0.48	10	0.155	4.70	7.60	0.155	80.0
6.94	0.48	10	-	-	7.58	0.064	87.0
6.94	0.48	8	0.091	4.22	7.62	0.032	93.3
7.53	0.49	10	0.455	4.47	8.36	0.019	96.0
7.65	0.34	12	0.162	4.55	8.82	0.071	79.0

Table 7. Stripping of vanadium in the organic phase with sodium carbonate.
Temp: 45°C, time: 10 minutes.

Loaded org. phase g/l V(V) Cr(VI)		Stripping phase ratio O/A	Na ₂ CO ₃ M	After stripping org. phase g/l V(V)	% stripped	
					V(V)	Cr(VI)
6.92	0.48	5	0.5	0.018	~100	100
6.92	0.48	6	1.0	0.009	"	"
6.92	0.48	7	1.0	0.007	"	"
6.92	0.48	7	0.75	0.01	"	"
6.75	0.82	8	1.0	0.109	98.5	"
6.75	0.82	10	1.0	2.82	58.5	"
6.75	0.82	10	1.5	2.34	65.3	"

Table 8. Stripping of vanadium with ammonium carbonate.
Organic phase: V(V) 6.30 g/L; time: 10 minutes.

Stripping Condition Temp °C O/A		(NH ₄) ₂ CO ₃ nNH ₄ ⁺ /mV	V(V) g/l in stripping soln.	Stripping %	% of V ppted.
25	4	2.0	3.30	~100	87.0
25	4	4.0	3.00	"	88.0
25	4	8.0	0.83	"	96.6
25	10	3.2	1.35	"	98.0
25	10	3.2	0.87	"	98.7
55	20	2.34	1.92	"	98.9
55	20	2.34	1.24	"	99.3

Table 9. Stripping of chromium by sodium carbonate or ammonium carbonate.

Stripping			Cr g/l in org. phase	$(\text{NH}_4)_2\text{CO}_3$ $n_{\text{NH}_4^+}/m_{\text{Cr}}$	Na_2CO_3 $n_{\text{CO}_3}/m_{\text{Cr}}$	Cr remained in organic phase g/l	% Cr stripped
Temp °C	time min	O/A					
30	10	3	10.91	0	3.0	<0.010	~100
30	10	4	"	0	2.4	0.032	99.5
30	10	7	"	0	2.7	0.055	99.4
30	10	8	"	0	2.4	0.010	100
30	5	4	"	0	3.0	0.010	100
23	10	5.22	10.00	1.0	0	7.59	24.1
23	10	5.22	"	2.0	0	3.06	69.4
23	10	5.22	"	3.0	0	0.52	94.8
23	10	"	"	8.0	0	0.056	99.4
42	10	"	"	1.0	0	7.05	29.5
42	10	"	"	2.0	0	1.65	83.5
42	10	"	"	3.0	0	0.004	99.7
42	10	8	"	3.5	0	~0	100
42	10	10.4	"	4.0	0	~0	100

Flowsheet for Separation and Recovery of Vanadium and Chromium

Based on the results of laboratory tests, a flowsheet as shown in Fig.3 is proposed for the separation and recovery of vanadium and chromium from alkaline liquor of leaching, say, sodium salt-roasted titaniferous iron ore. Silicate in the liquor is removed first by acidification. Then the purified solution is mixed with primary amine-kerosene mixture at room temperature for 5-10 minutes to transfer vanadium into the organic phase. Sulphuric acid is added during extraction based on the vanadium content ($n_{\text{H}^+}/m_{\text{V}} > 1.0$) in the aqueous solution. The organic liquor after separation is scrubbed with sodium vanadate solution to decrease its chromium content. The scrubbing solution and the raffinate from vanadium extraction are combined and extracted with a primary amine-kerosene mixture to remove chromium. Sulphuric acid is also added during extraction according to the chromium content in the aqueous solution ($n_{\text{H}^+}/m_{\text{Cr}} = 3$).

Both vanadium- and chromium-loaded organic solutions are stripped in one stage respectively with sodium carbonate or ammonium carbonate depending on whether sodium salts or oxides of the metals are the required products. The organic liquor from vanadium extraction after stripping can be recycled back for extraction again. The stripped organic solution from chromium extraction is contacted with raffinate from chromium extraction and sulphuric acid is added to maintain the acid concentration of organic phase at about 0.2 gram equivalent per litre. The raffinate from chromium extraction contains originally about 100 to 200 mg/L chromium at a pH of 3-4 and, after contacting with the organic solution, the total quantity of vanadium and chromium is reduced to less than 10 mg/L at a pH about 7.0. The organic solution is then recycled back for chromium extraction.

The ammonium metavanadate and ammonium dichromate (or chromate) are roasted to obtain vanadium pentoxide and chromium oxide respectively. Solubility of primary amine in the neutral or weakly basic solution is rather low. For the N-1923 used, it is about 14 ppm. Primary amine under the proposed extraction condition is rather stable to oxidation reactions of chromate and vanadate. The waste liquor of vanadium and chromium extraction contains V and Cr at a total of $[\text{V(V)} + \text{V(IV)} + \text{Cr(III)} + \text{Cr(VI)}]$ less than 10 mg/L only.

Bench Scale Test

In order to check the proposed flowsheet and the laboratory results, a bench scale test was carried out by using solution obtained by leaching the titaniferous iron ore after roasting with sodium sulphate at 1250-1280°C. This special kind of iron ore contains no chromium, so sodium chromate was added to the leaching solution. The resulting solution contained about 5-6 g/L vanadium and about 10 g/L chromium(VI), with impurities as shown in Table 10.

Table 10. Impurities of alkaline leaching liquor of roasted titaniferous iron ore (in mg/L).

	TFe	Al ₂ O ₃	SiO ₂	P ₂ O ₅	TiO ₂	CaO	MgO	MnO
A	0.40	1430	1250	130	0.08	7.1	3.8	0.36
B	0.77	930	10	0.27	0.08	2.6	1.0	0.17

A - Before purification

B - After purification

Extraction and stripping experiments were conducted in a 0.1 m³ stainless steel mechanically agitated tank with a conical bottom. The volume of aqueous leaching liquor used for each batch was 24-40 litres. The organic solution used throughout the tests was 10% N-1923 primary amine in kerosene. Sulphuric acid added during extraction was based on the ratio of gram ions of H⁺ added to the gram atoms of vanadium in aqueous solution. The ratio number was determined in the laboratory to be 1.5 for the leach liquor used. Effect of extraction time on vanadium and chromium separation is shown in Table 11.

Table 11. Bench scale test results - Effect of extraction time on vanadium to chromium separation.

Leach liquor: pH 8.6 V(V); Cr(VI) 9.86 g/L

Ext. time min	Aqueous phase			Org. phase		% Ext.		Separation factor α (V/Cr)
	pH	V g/l	Cr g/l	V g/l	Cr g/l	V	Cr	
1	8.25	0.250	9.07	7.88	1.18	95.5	8.0	241
3	8.20	0.197	9.21	7.95	0.975	96.3	6.6	382
5	8.20	0.125	9.34	8.07	0.78	98.0	5.3	773
10	8.22	0.155	9.40	8.02	0.69	97.4	4.7	705
15	8.25	0.174	9.27	8.00	0.886	97.0	6.0	480

It can be seen from Table 11 that for an extraction of five minutes, vanadium extracted in one stage is about 98% and the separation factor of vanadium from chromium is about 770. Raffinates from vanadium extraction with different vanadium contents were mixed with 10% N-1923 in kerosene to extract chromium. Sulphuric acid was added during extraction at a ratio of gram ions of H⁺ added to gram atoms of chromium in solution equal to three. Results agree well with those of laboratory tests (with 97.6-99.0% chromium extraction). The raffinate from chromium extraction was contacted for 2 to 3 minutes with the lean organic solution with addition of sulphuric acid to give an organic liquor of 0.2 gram equivalent of acid per litre. The

aqueous solution thus treated contained a total amount of V 2, Cr 7 mg/L; Na^+ 21 and SO_4^{2-} 50 g/L at a pH of about 7.0. It may be economical to recover sodium sulphate from this waste liquor for roasting titaniferous iron ore or for some other purposes.

Ammonium carbonate was used for stripping vanadium and chromium respectively. The ratio of gram equivalents of NH_4^+ in the strip solution to gram atoms of vanadium and chromium in the organic phase was kept at 2.34 and 3.0 respectively. Typical analysis of metallic oxides obtained by roasting of the ammonium salts is shown in Table 12.

Table 12. Typical analysis of V_2O_5 and Cr_2O_3 obtained in the bench tests (%).

(1) V_2O_5 ; (2) Cr_2O_3 .

	Na_2O	Mn	S	CaO	MgO	P	Si@	Al@	K_2O	V_2O_5	Cr_2O_3
(1)	0.012	.002	.045	.024	.011	0	.057	.003	.002	-	0.17
(2)	0.051	.002	1.11	.028	.020	.002	.035	.003	.005	0.36	-

(@ Semi-quantitative analysis)

The CaO and MgO in the products were introduced from the tap water used in the bench test. The sodium and sulphur contents in the Cr_2O_3 may be decreased by washing the organic phase with water to remove contamination by the aqueous phase.

CONCLUSIONS

A flowsheet is proposed, and has been tested on the bench scale, to separate and recover vanadium and chromium by solvent extraction with primary amines from solutions obtained by leaching either sodium salt-roasted titaniferous iron ore or a by-product of iron-making with titaniferous iron ore as a raw material. It could be considered that the process reported in this paper is much better than those previously reported. Work is in progress to further improve the process.

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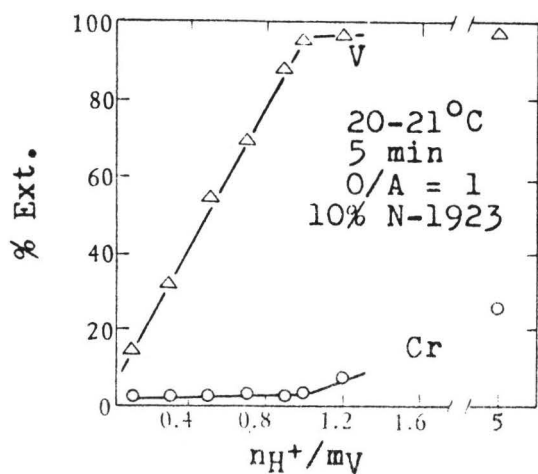


Fig. 1 Acid Addition on V/Cr Separation

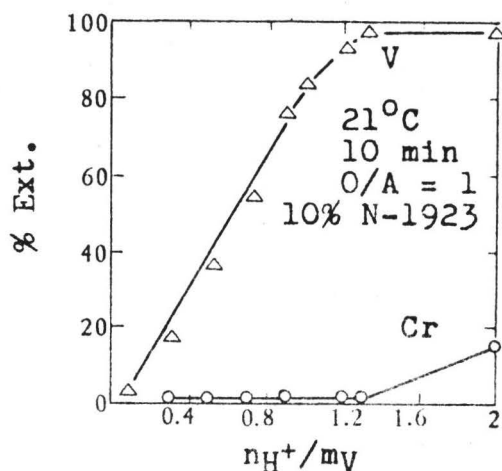


Fig. 2 Acid Addition on V/Cr Separation from Liquor of Leaching Na-salt Roasted Titaniferous Iron Ore

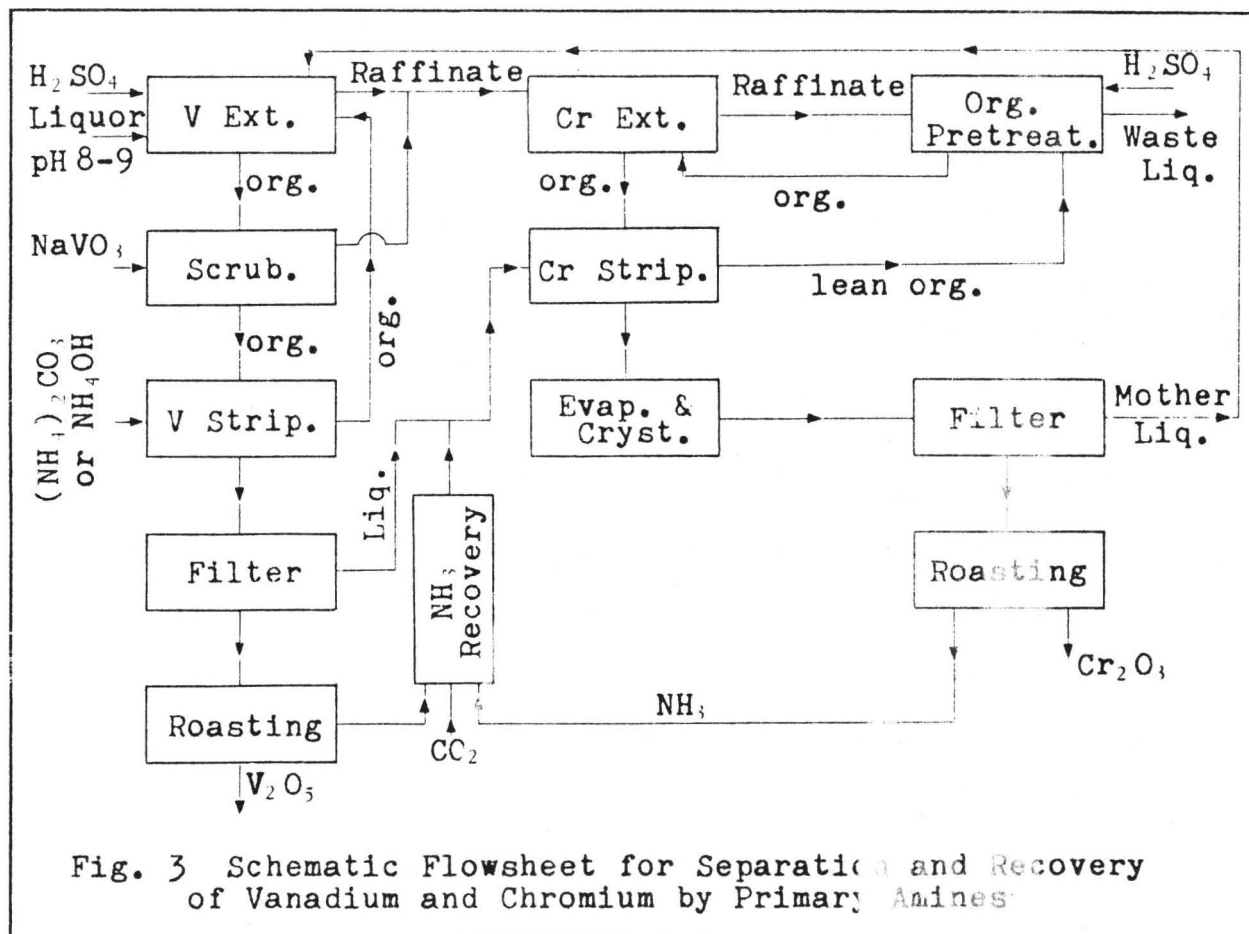


Fig. 3 Schematic Flowsheet for Separation and Recovery of Vanadium and Chromium by Primary Amines

THE EXTRACTION BEHAVIOUR OF ZIRCONIUM
POLYNUCLEAR COMPOUNDS
WITH CERTAIN TETRAVALENT ELEMENTS

O.A. Sinegribova, G.A. Yagodin,
S.V. Chizhevskaya, A. Sarsenov,
E.G. Kudryavtsev & A.A. Gurov

Mendeleev Institute of Chemical Technology

Moscow, U.S.S.R.

Zirconium is able to form in nitric acid solutions extractable and unextractable polynuclear compounds (PC's) with hafnium and cerium(IV). Polynuclear compounds with titanium are decomposed when extracted by TBP. There are no mixed compounds of zirconium with thorium. The presence of soluble silica compounds affects the zirconium chemical and extraction behaviour.

PC's are able to concentrate at the interface forming stable adsorption structures.

A characteristic feature of the chemical behaviour of zirconium in aqueous solutions is its intensive inclination towards hydrolysis and hydrolytic polymerization. The presence of polymerized forms affects zirconium extractability, the behaviour of the zirconium compounds at the interface, and the extraction separation of zirconium and the elements which are capable of forming copolymeric compounds with zirconium.

Hydrolyzed zirconium compounds are present in solutions of high acidity (for example, up to 4 M HNO_3 or 2 M H_2SO_4), whereas polymerization initiates even with a 10^{-1} M concentration of metal. A fragment of hydrolytic polymers is a tetrameric cycle of zirconium atoms linked by hydroxyl bridges (the so-called α -form) which, under certain conditions, are partially (β -form) or completely (γ -form) converted into oxo-bridges. The degree of oxolation of the bonds affects the extraction behaviour of the zirconium compounds.

Polymeric zirconium compounds with oxolation bridges are polymerized to a greater extent in weakly acid solutions of HNO_3 than are the β - and γ -forms (Fig.1). However, these compounds easily decompose with higher acidity and are in a state of moveable equilibrium with monomeric forms readily extractable by neutral organic phosphorous compounds. The extractability of the α -form polymers proper is low, and is observed only under conditions of a low acidity and a large amounts of salting-out agent. Thus the extraction has been established of polymerized zirconium hydroxonitrates into TBP from a solution containing 7 M LiNO_3 (1), or of polymerized zirconium hydroxothiocyanates from solutions containing zirconium sulphate and NH_4SCN (2). Since zirconium and hafnium replace each other isomorphously during the formation

of polymerized compounds, in the case of copolymer extraction zirconium and hafnium are almost inseparable. Table 1 presents the results of extraction and separation of Zr, and Hf concentration in the initial solution (Fig.2) is explained, evidently, by the extraction of copolymeric forms.

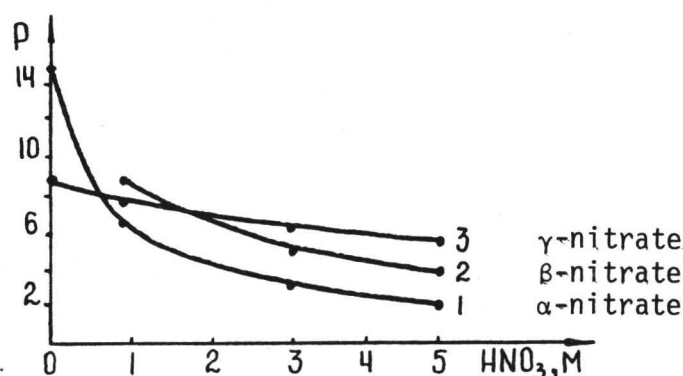


Fig. 1. The polymerization factor of zirconium nitrate various forms as a function of acidity. Zr = 0.1 M

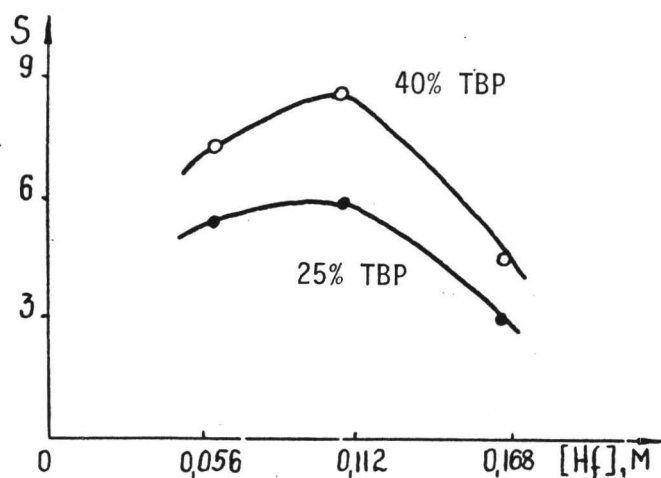


Fig. 2. Coefficient of zirconium and hafnium separation during extraction into TBP as a function of the hafnium content in the mixture Zr, Hf = 0.25 M.

As a result of the "aging" processes the hydroxyl bridges in the zirconium hydrolyzed compounds, having split off the water, are converted to oxygen bridges which cause hardening of the zirconium compounds and variations in their properties. Thus, when heating weakly acid solutions of hydroxonitrate, we may obtain γ -compounds, the so-called stable polynuclear compounds (SPC's), which do not decompose in HNO_3 up to 6 to 8 M concentration, are not in a transient equilibrium with the monomeric forms, and are not extractable by neutral organic phosphorus compounds under any conditions.

Table 1. Separation and distribution of Zr and Hf when extracted into TBP.

Initial Aqueous Solution	MeO ₂ Aqueous Phase g/L	MeO ₂ Organic Phase g/L	D _{Zr}	D _{Hf}	$S = \frac{D_{Zr}}{D_{Hf}}$	Number of Contacts
1, 6 M (Zr + Hf)	174.1	171.7	0.99	1.00	0.99	1
	145.1	177.1	1.22	1.08	1.13	2
	126.9	182.5	1.44	1.14	1.35	3
	102.3	188.3	1.84	1.61	1.14	4
7 M LiNO ₃ ·3H ₂ O	83.5	208.6	2.47	1.83	1.35	5
	70.3	131.2	1.86	2.52	0.74	6
	60.5	78.3	1.29	1.24	1.04	7
	58.7	59.7	1.01	0.86	1.17	8

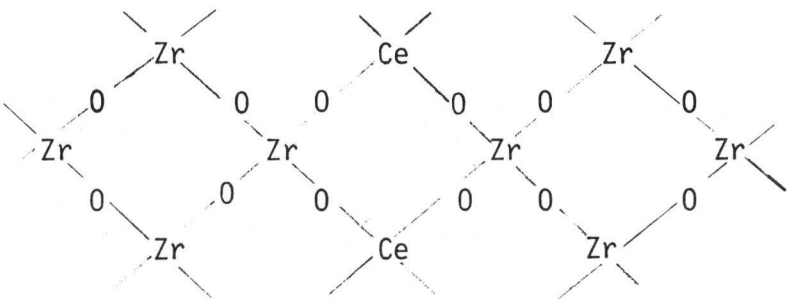
2, 2 M (Zr + Hf)	258.5	194.0	0.75	0.59	1.27	1
	246.2	184.6	0.75	0.70	1.06	2
	223.2	177.6	0.79	0.53	1.44	3
5 M Ca(NO ₃)·4H ₂ O	210.4	165.1	0.71	0.57	1.47	4
	200.3	141.4	0.57	0.52	1.09	5
	199.8	113.3	0.42	0.39	1.07	6
	191.4	81.0				7

It is possible to destroy compounds of this type by concentrated nitric acid only by continuous heating.

Zirconium in the form of SPC, even in a multi-step extraction process, remains completely in the aqueous phase. In the presence of monomeric forms of zirconium nitrate the stable polynuclear compounds react as salting-out agents (3).

Hafnium forms similar SPC's, therefore, in the case of their formation no separation of zirconium and hafnium occurs.

Cerium(IV), titanium(IV) and thorium, under conditions similar to those of the zirconium SPC production, would not polymerize in the same way. Zirconium, for instance, under conditions for forming stable polynuclear compounds with cerium(IV) would form compounds of the following structure:



Cerium present in the polymeric compound also is not extractable into the neutral organic phosphorous compounds, is not in equilibrium with the monomeric forms, and is not reducible to the trivalent state.

Unlike cerium(IV), titanium(IV) under conditions for producing stable polynuclear compounds forms copolymers with zirconium in which, although the ratio of $\text{Zr}:\text{Ti} = 4:1$ is observed, the hydroxyl-bridges dominate.

These mixed compounds have no enhanced stability and are in equilibrium with the monomeric forms: when contacted with TBP zirconium is transferred into the organic phase, whereas titanium remains in the aqueous phase and, after some time, precipitates in the form of hydrated oxides. The zirconium-titanium polymers also decompose when brought into contact with nitric acid and sulphuric acid.

Thorium, under conditions for producing SPC's does not form mixed polymeric compounds with zirconium.

Zirconium too, does not form polynuclear compounds with silicon, but the presence of soluble silica compounds in a zirconium solution affects the zirconium behaviour. The reaction of zirconium with soluble silica compounds prevents the formation of zirconium SPC's: in a weakly acid medium no polynuclear forms of zirconium are produced during heating owing to zirconium adsorption on polysilicon acids. In an alkali medium the silicate ion is adsorbed on the zirconium hydroxide, displacing the OH-group from the latter. The subsequent heating of such a hydroxide precipitate in a mother solution at a ratio of $\text{SiO}_2:\text{Zr} = 0.5:1$ does not result in the hydroxide aging; being dissolved in nitric acid the zirconium is completely extractable by TBP (Fig.3).

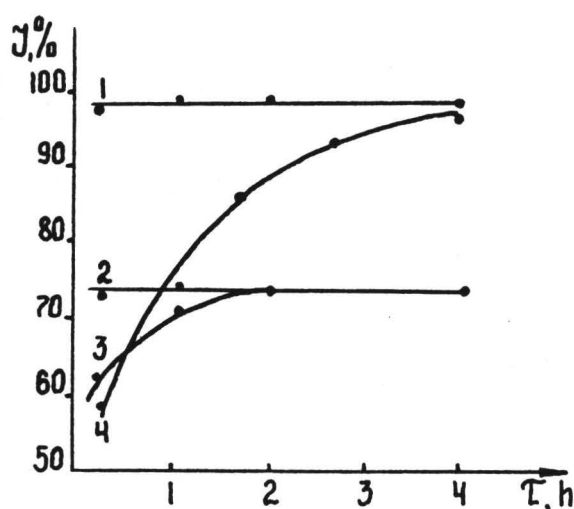


Fig. 3. The degree of zirconium extraction (in % of the equilibrium one) following the hydroxide dissolving in 5 M HNO_3 .

T - the time of the hydroxide dissolving. The precipitate composition: 1 - $\text{SiO}_2:\text{ZrO}_2$ 1:2; 2 - $\text{SiO}_2:\text{ZrO}_2 = 1:4$; 3 - without SiO_2 ; 4 - without SiO_2 , dissolving during heating.

The presence of polynuclear hydrolyzed compounds of zirconium affects not only the equilibrium of the extraction processes, but also the hydrodynamic and kinetic characteristics. Thus, when operating with nitric acid solutions a considerable excess of zirconium is present in the surface layer at the boundary with the monomolecular TBP layer, as compared to its content

in the bulk solution, the maximum concentration being observed at 1M HNO₃ (Table 2). Stable polynuclear compounds are concentrated to a greater extent than is the α-form.

Table 2. Effect of zirconium concentration and solution acidity on zirconium content in surface layer and on adsorption value.

Zr _{in} = 0,1M				
HNO ₃ M	Solution - air		Solution - TBP film	
	Zr g/l	$\Gamma \cdot 10^{-11}$ mol/cm ²	Zr g/l	$\Gamma \cdot 10^{-11}$ mol/cm ²
α - form				
-	11,2	0,74	12,9	1,78
1,0	11,9	1,17	16,4	3,93
3,0	11,7	1,04	14,2	2,58
5,0	10,6	0,37	11,3	0,80
γ - form				
-	13,3	3,56	16,0	5,22
1,0	13,8	3,87	16,8	5,71
3,0	11,4	2,39	13,2	3,50
5,0	9,1	0,98	10,2	1,66

As a result of the zirconium concentration at the interface we observe the formation of stable interfacial adsorption structures. Fig. 4 presents the relationship of the tensile strength (F) of the interfacial films (as determined by the method described in (4)) as a function of the solution hold-up time.

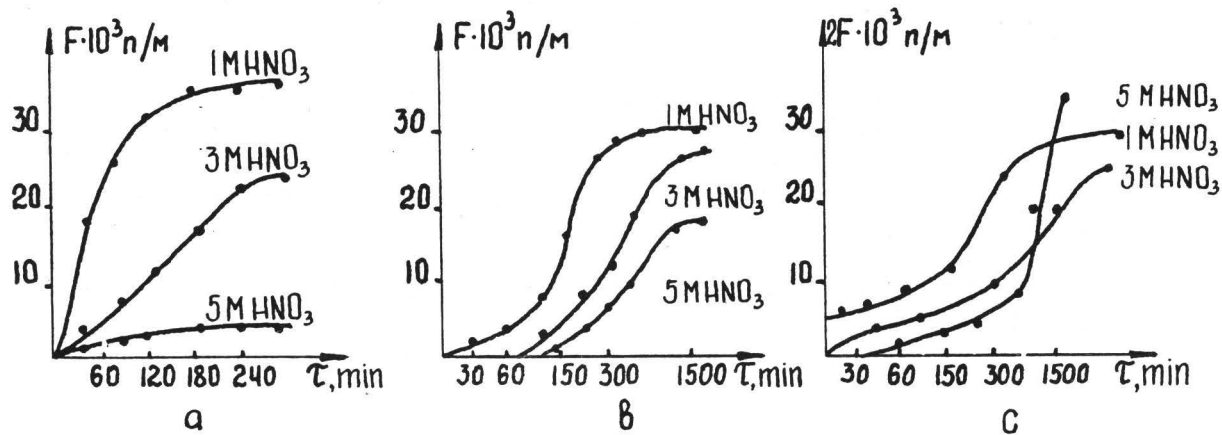


Fig. 4. Kinetics of the interfacial film strength increase in the system: 0.1 M Zr - HNO₃ - decane. a - α-form, b - β-form, c - SPC.

The highest rate of crosslinking is observed in the case where zirconium hydroxonitrates are present in the solution. The availability of rather

stable structures formed by the zirconium polymers at the interface could be one of the reasons of poor lamination of extraction emulsions when operating with weakly acid solutions.

Table 3 contains data on the lamination rate of the extraction systems: nitric acid-solution of zirconium-nitrate-decane, where $T_{\frac{1}{2}}$ - the half-life of lamination.

Table 3. The lamination rate of the extraction system with zirconium.

Zr, g/l	$T_{\frac{1}{2}}$, sec			
	HNO ₃ concentration, M			
	-	0,1	3,0	5,0
60,0	600	600	45	36
29,8	390	600	45	36
10,0	230	600	39	35

We can see that the rate of lamination is also in good correlation with the strength of the films formed at the interface.

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CERTAIN EXTRACTION PROCESSES FOR SEPARATION OF THE
RARE EARTH ELEMENTS.

G.V. Korpusov and Yu. S. Krylov

Institute of Physical Chemistry,
USSR Academy of Sciences, Moscow
USSR.

Extraction separation of rare earth elements (RE) is performed by various methods and techniques. The most frequent use is made of countercurrent multi-stage separation methods, while semicountercurrent and other nonstationary process, such as "Reflux" process, "Three fraction" extraction method, Kreig's distribution and "Total reflux" process have found much less application. The latter method is of particular interest, because it permits the highly efficient separation of multi-component mixtures. The potentialities of this method are far from being exhausted.

The basic idea of the "Total reflux" process is that the multi-stage extractor (of the mixer-settler type and having a large volume) is filled with the components of the extraction system, including the mixture of metals to be separated. The separation process is conducted so as to ensure that all the components of the raffinate are returned into the process together with the organic phase, while the components of the extract are reextracted and returned into the system together with the washing solution. In a certain period of time a sequence of transient zones and zones of pure components, from which pure products are extracted, is established in the cascade.

There is a general demand for all the extraction systems in which the "Total reflux" process can be used. The system should be applicable on the isotherm plateau or when the system is saturated in extractants or in complexon and in the presence of an excess of the separable components in the other phase. A disadvantage of the "Total reflux" process is due to the low extraction in the cycle, because a major part of the cascade is taken up by the transient zones. For this reason, the extraction of rare earth elements should be conducted in the extraction cascades having a great number of extraction stages. In the course of RE separation the separation coefficients do not exceed 2-4.

In the present paper the authors consider a number of techniques which make possible to markedly increase the extraction of pure components during the cycle and to decrease the number of extraction stages.

The principle of the new method consists in the fact that the chain unit of extraction cells at the formation point of pure components is supplemented with additional mixers or extraction reactors, the effective volume being many times larger than that of the standard countercurrent cell. In this case, the number of extraction stages can be reduced to the theoretical value which is calculated to be sufficient for the formation of transient zones, while the pure product is extracted from an additional mixer, or extraction reactor. The yield of the pure product will be determined only by the difference between the effective volumes of the mixer and of the extractor of the operating cascade.

Another advantage of similar systems is that the cells of the mixer-settler type with a big effective volume can be replaced by centrifugal cells with a small retaining effective volume. The application of extractors of the latter type leads to a yield of each component which is as high as 95-98 % due to the minimum retaining effective volume of the centrifugal cells in the transient zones.

Both the standard applications of the "Total reflux" process and the new modifications of the method can be based on calculations carried out with the necessary accuracy. On the ground of the obtained working formulas one can substantiate in advance the choice of the technique and the organization of the process.

The present paper is dealing with various versions of the "Total reflux" process for the RE separation used in combined installations equipped with reactors. The authors have discussed the purification of one component, separation of binary, triple and multi-component mixtures. The findings are supported by examples of purification of the valuable component from the impurities (separation of praseodymium, neodymium and rare earth elements of the cerium sub-group). Various techniques of separation processes by the "Total reflux" method have been comparatively estimated.

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SOLVENT EXTRACTION OF HAFNIUM(IV) BY 3-HYDROXY-2-
-METHYL-1-PHENYL-4-PYRIDONE

B.Tamhina, V.Vojković and M.J.Herak

Laboratory of Analytical Chemistry,
Faculty of Science, University of
Zagreb

Strossmayerov trg 14, 41000 Zagreb,
Yugoslavia

This paper deals with the application of 3-hydroxy-2-methyl-1-phenyl-4-pyridone (HX) to the extraction of hafnium(IV). Distribution of hafnium was determined radiometrically. The degree of extraction of hafnium(IV) with HX dissolved in chloroform, as a function of the hydrochloric, perchloric or sulphuric acid concentration was investigated. Hafnium(IV) is quantitatively extracted at pH values higher than 1.2 independently of the mineral acid used in the aqueous phase. Increased acid concentration decreases the extraction of hafnium and at the 1 M hydrogen ion concentration practically all hafnium remains in the aqueous phase. Hafnium can be stripped quantitatively with a concentration of hydrochloric, perchloric or sulphuric acid of 1 M or higher. Distribution studies show that distribution ratio is inversely third-power dependent upon the hydrogen ion concentration from the varying hydrochloric, perchloric or sulphuric acid solutions and third-power dependent upon HX concentration in the organic phase from all mineral acids used. These results indicate that three molecules of the reagent are bonded to one atom of hafnium and that three protons are released on the formation of an extractable complex.

Although hafnium thiocyanate alone is insoluble in chloroform, thiocyanate shows a moderate synergistic effect on hafnium extraction with HX. Hafnium(IV) can be quantitatively extracted with HX from more acidic solutions if the extraction is carried out from a hydrochloric, perchloric or sulphuric acid solution containing an excess of thiocyanate ions. Hafnium(IV) is quantitatively extracted at pH values higher than 0.6 if the concentration of thiocyanate ions is in the range 0.2 - 1.0 M. All experiments show that in the presence of an excess of thiocyanate hafnium(IV) is extracted as a mixed thiocyanate - HX complex which is formed at higher acidity. The relationship between log D and log conc. HX, determined from the aqueous phases at constant acidity and optimal concentration of thiocyanate shows that two molecules of HX are bonded to one atom of hafnium in the mixed complex.

Opposite to the effect of thiocyanate, oxalate ions completely mask hafnium(IV). In the presence of oxalate (studied range 0.05 - 2.5 M $\text{Na}_2\text{C}_2\text{O}_4$) all hafnium remains in the aqueous phase regardless of the acidity of the phase, the mineral acid present and the concentration of thiocyanate.

MUTUAL INFLUENCE OF IRON (III) AND GOLD (III) AS MACRO-CONSTITUENTS IN THE EXTRACTION SYSTEMS FORMING THREE LIQUID PHASES

Da. Maljković, Du. Maljković and
M. Branica*

Faculty of Metallurgy, Univ. Zagreb
and * "Rudjer Boskovic" Institute
Sisak and * Zagreb, Yugoslavia

Due to their importance in the development of new separation procedures it was interesting to study three-phase systems and the mutual influence of elements in such a more complex partition. The system FeCl_3 - AuCl_3 - HCl - H_2O -Diisopropyl ether (IPE)-Benzene as model was studied. Previous investigations of the extraction of either iron (III) or gold (III) by pure and diluted IPE from hydrochloric acid solution showed a striking difference in the behaviour of above mentioned metals ¹⁻³. In this paper the dependence of gold (III) and iron (III) distribution on the initial concentration of hydrochloric acid, iron (III) and IPE was studied under conditions of third phase formation.

It was found that the volume of the heavy organic phase in the extraction of both metals together was larger than the sum of the heavy organic phase volumes obtained in the extraction of the single elements under the same conditions. The increase in the initial concentration of iron (III) increases the distribution ratio of gold (III) as well as increasing the partial separation factor gold (III)/iron (III) between the heavy organic phase and the light organic phase. The influence of initial hydrochloric acid concentration was investigated with pure and diluted IPE (benzene as diluent). When diluted IPE was used the similarity of the curves describing the changes of metal concentration in the organic phase was very definite. There is a strong agreement between the initial metal molar ratio and the metal molar ratio in the equilibrate organic phase. Such behaviour confirms a mechanism of mixed ion associations formation probably of type $\text{H}^+\text{FeCl}_4^-$ - $\text{H}^+\text{AuCl}_4^-$ similar to the ion associations proposed in the case of the coextraction of indium (III) in the presence of iron (III) ⁴.

One can conclude that gold (III) is coextracted in the presence of iron (III) when both of them are in the macro-amounts, and that the coextraction is independent of the initial molar ratio of the metals in the investigated range.

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THE EXTRACTION OF HAFNIUM(IV) BY SOME ORGANOPHOSPHORUS
COMPOUNDS IN THE PRESENCE OF TWO MINERAL ACIDS

O. Navrátil

Department of Inorganic Chemistry
Purkyně University

611 37 Brno, Kotlářská 2
Czechoslovakia

In the course of a systematic study of Zr and Hf extraction by some neutral organophosphorus agents, such as TBP, it has been found that the synergic effect (SE) occurred in the presence of two convenient mineral acids as a mixture in the aqueous phase. In this paper, results of the extraction of Hf by some neutral and also acidic organophosphorus agents, i.e. di-n-octyl- (HDOP), di-n-amyl- (HDAP), di-n-butylphosphoric acid (HDBP), and n-decylphenylphosphonic acid (HDPP) in benzene, chloroform and n-octane from aqueous solutions of the total acidity of 2, 4, 6 and 8M $\text{HClO}_4\text{-HNO}_3$ and $\text{HClO}_4\text{-HCl}$ are presented; $c_{\text{Hf}} = 1 \times 10^{-6}$ to $4 \times 10^{-4}\text{M}$.

It has been shown that

(1) using the same analytical concentration of organophosphorus agents and acidity of the aqueous phase, the extractability of hafnium increases in the series $\text{TBP} < \text{triphenylphosphineoxide} < \text{HDBP} = \text{HDAP} = \text{HDOP} < \text{TOPO} < \text{HDPP}$.

(2) when using HA, the SE increases with the increasing acidity of the aqueous phase; it was found that SE occurred only when $c_{\text{H}^+} \geq 3.5\text{M HClO}_4\text{-HNO}_3$ or $c_{\text{H}^+} \geq 5\text{M HClO}_4\text{-HCl}$.

(3) the SE is more pronounced with the lowering of the initial concentration of HA.

(4) the maximum of the SE is shown when the concentration of HNO_3 or HCl in the mixture of two mineral acids is $1.0 \pm 0.5\text{M}$.

(5) When other chelating agents - not containing phosphorus - are used, such as HTTA, N-benzoyl-N-phenylhydroxylamine or 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone, the SE does not occur.

(6) The main motive for the described SE is not the anomalous value of hydrogen ion activity in the aqueous phase, but the salting out effect of perchloric acid in the mixture of both mineral acids. This fact is supported by conductometric measurements and potentiometric determinations of the Hammett function H_0 in the mixture $\text{HClO}_4\text{-HNO}_3$ and $\text{HClO}_4\text{-HCl}$.

Even though we do not demonstrate directly the existence of extractable mixed complexes of the type $\text{HfY}_x(\text{ClO}_4)_y(\text{HA})_z$, where $\text{Y} = \text{Cl}, \text{NO}_3$, HA = acidic organophosphorus agent, their existence is supposed.

EXTRACTION OF RUTHENIUM AND RHODIUM SULPHATE
COMPLEXES WITH AMINES

A.M.Orlov, Yu.S.Shorikov,
 N.N.Chalissova, I.V.Kunaeva,
 I.P.Ryzhova, T.A.Fomina, M.I.Yuzko
 Institute of Rare Metals, Giredmet

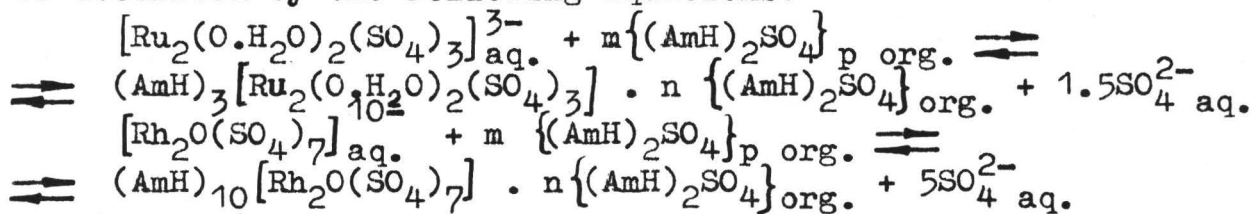
Moscow, USSR

The present report deals with the main laws observed in the extraction of rhodium trisulphate (III) - $[\text{Rh}_2\text{O}(\text{SO}_4)_7]^{10-}$ and ruthenium sulphate (III, IV) - $[\text{Ru}_2(\text{O} \cdot \text{H}_2\text{O})_2(\text{SO}_4)_3]^{3-}$ from sulphuric-acid solutions with aliphatic amines. These complexes were prepared in the form of equilibrium compounds, in the systems "platinum metal hydroxide - concentrated sulphuric acid", at a temperature of $280 \pm 50^\circ\text{C}$.

The recovery of ruthenium and rhodium into the organic phase during the extraction decreases as the concentration of sulphuric acid and sulphate ions in the aqueous phase increases. The maximum recoveries (Rh - 89% and Ru - 100%), were obtained from 0.1-0.5 M H_2SO_4 , at an amine concentration of 0.05 to 0.1 mole/l, the phases being taken in equal volumes and brought to contact for several seconds. The starting complex sulphates in aqueous sulphuric - acid solutions are unstable and subjected to equation which results, ultimately, in the formation of highly aggregated cations and neutral particles which cannot be extracted with amines. An increase in the temperature of solutions of ruthenium and rhodium sulphates accelerates to a significant extent the hydrolytical processes.

The extractive capacity of amines in the systems investigated increases in the following sequential order: tertiary < secondary < primary amines. An increase in the amine concentration in the organic phase (with decane as a diluent) improves the extraction of ruthenium and rhodium.

There were synthesized and investigated Ru and Rh sulphate complexes with primary amines which pass into the organic phase during the extraction. As shown by the chemical analysis, thermogravimetry electronic and IR-Spectroscopy, in the process of extraction, the structure of the internal sphere of the starting complexes is preserved. In general terms, the complex formation reaction from freshly prepared solutions can be described by the following Equations:



CHEMISTRY OF THE EXTRACTION OF ZIRCONIUM FLUORIDE
COMPLEXES BY NEUTRAL AND ACIDIC ORGANIC
PHOSPHORUS COMPOUNDS

Chekmarev A.M., Strashnov V.I.,
Yagodin V.G., Sinegribova O.A.
Mendeleev Institute of
Chemical Technology
Moscow, USSR

Phosphine oxide extracts Zr from the K_2ZrF_6 solutions as compounds with the ratio F : Zr 4. Since phosphine oxide is a neutral compound, it is natural to suggest that Zr passes into the organic phase in the form of fluorometallate acids. We used the chemical analysis of the extracts and raffinates, the solvation number determination by the dilution method, and the determination of the distribution coefficient dependence on the hydrogen ion concentration. The relationship of the components in the organic phase is H : Me : F : E = 1:1:5:2 (E = phosphine oxide). In the organic phase IR spectra the absorption band of a free P=O group disappears, two absorption bands, shifted relatively the initial one, appearing in its stead. The nuclear magnetic resonance spectrum of the extract (F19) also confirms the presence of two different compounds containing zirconium fluoride. The integral intensities of both signals are unequal their ratio being about 2:3. The possible mechanism is:

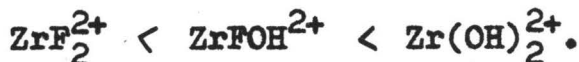
1. $HMeF_5 + 2E \rightleftharpoons HMeF_5 \cdot 2E$
2. $2HMeF_5 \rightleftharpoons H_2MeF_6 \cdot 2E + MeF_4 \cdot 2E$

When extracting Zr from the K_2ZrF_6 solutions by di-2-ethylhexylphosphoric acid (HA) the extraction mechanism has been studied by the method of IR spectroscopy, organic phase saturation, determination of the Zr and F reciprocal rate of transfer into the organic phase, the distribution coefficient dependence on the aqueous phase acidity. The following mechanism of extraction has been suggested:

1. $K_2ZrF_4(OH)_2 + 2(HA)_2 \rightleftharpoons Zr(OH)_2(HA_2)_2 + 2KF + 2HF$
2. $K_2ZrF_5OH + 2(HA)_2 \rightleftharpoons ZrF(OH)(HA_2)_2 + 2KF + 2HF$
3. $K_2ZrF_6 + 2(HA)_2 \rightleftharpoons ZrF_2(HA_2)_2 + 2KF + 2HF$

The dominating occurrence of one of the reactions is controlled by the fluorezirconate concentration and by the aqueous phase acidity.

The rate of transfer into the organic phase for various complexes increases in the following series:



THE MECHANISM OF THE ZIRCONIUM AND HAFNIUM
SULFATES EXTRACTION BY ALIPHATIC AMINES

Yagodin G.A., Chekmarev A.M.
Mendeleev Institute of Chemical
Technology
Moscow, USSR

Investigation into the equilibrium of the extraction of non-hydrolyzed Zr and Hf sulfates complexes permitted to suggest a summarized extraction reaction:



The apparent extraction constants proved to be equal to

$$K_{\text{Zr}} = 500, K_{\text{Hf}} = 47.$$

The above equation has been confirmed by the value of maximum separation coefficient, by the ratio of components, by the quantity of the acid released. But the variation of the tangent of the dilution technique curve from 1 to 2 in the presence of octanol, the data obtained on the SO_4 exchange kinetics, and the data on the composition of Zr complexes in sulfate media, permitted to describe the procedure as follows:

1. $\text{Zr}(\text{SO}_4)_3^{2-} + 2(\text{NR}_3\text{H})\text{HSO}_4 \rightleftharpoons \text{Zr}(\text{SO}_4)_3(\text{NR}_3\text{H})_2 + 2\text{HSO}_4^-$
2. $2(\text{NR}_3\text{H})\text{HSO}_4 \rightleftharpoons (\text{NR}_3\text{H})_2\text{SO}_4 + \text{H}_2\text{SO}_4$
3. $\text{Zr}(\text{SO}_4)_3(\text{NR}_3\text{H})_2 + (\text{NR}_3\text{H})_2\text{SO}_4 \rightleftharpoons \text{Zr}(\text{SO}_4)_4(\text{NR}_3\text{H})_4$

In extraction of hydrolyzed complexes the amine salt addition has a more important role. The phenomenon of the organic phase anomalous saturation under condition of the interface surface contact limitation, gave evidence of coordinately unsaturated compounds formation during extraction:

1. $\text{Zr}(\text{OH})_2(\text{SO}_4\text{H})_2 + (\text{NR}_3\text{H})_2\text{SO}_4 \rightleftharpoons \text{Zr}(\text{OH})_2(\text{SO}_4\text{H})(\text{SO}_4)(\text{NR}_3\text{H})_2$
2. $\text{Zr}(\text{OH})_2(\text{SO}_4\text{H})_2(\text{SO}_4)(\text{NR}_3\text{H}) \rightleftharpoons \text{Zr}(\text{SO}_4)(\text{NR}_3\text{H})_2 + 2\text{H}_2\text{O}$
3. $\text{Zr}(\text{SO}_4)_3(\text{NR}_3\text{H})_2 + (\text{NR}_3\text{H})_2\text{SO}_4 \rightleftharpoons \text{Zr}(\text{SO}_4)_4(\text{NR}_3\text{H})_4$

An anomalous isotherm obtained in the process of the $\text{Zr}(\text{SO}_4)_2$ aqueous solution exhaustion with fresh portions of the amine sulfate give evidence of hydrolyzed sulfate polymers extraction.

A series of sulfate complexes of Zr(Hf) has been established in the order of the extractability diminishing: non-hydrolyzed monomers hydrolyzed monomers hydrolyzed polymers.

IRIDIUM EXTRACTION FROM SULPHATE SOLUTIONS
AT ELEVATED TEMPERATURES

A.M. Orlov, Yu. Shorikov, M.A. Meretukov
 L.G. Anoshechkina, M.V. Polyakov
 Institute of Rare Metals, Giredmet

Moscow, USSR

In the equilibrium sulphuric-acid solutions iridium occurs in the form of polymeric aquohydroxosulphates (III), which are non-extractable into organic phase under conventional extraction conditions.

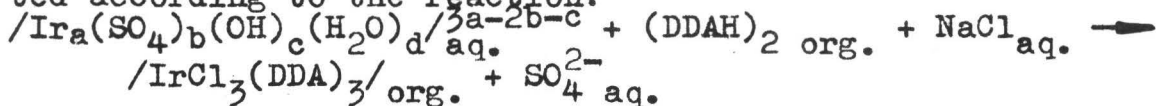
The main laws underlying the iridium extraction from aquohydroxosulphate solutions $\text{Ir (III)-/Ir}_a(\text{SO}_4)_b(\text{OH})_c(\text{H}_2\text{O})_d/$ with amines in the presence of chloride-ions at elevated temperatures have been studied. The effect of temperature, phase ratio, sulphuric acid, chloride- and sulphate-ion contents in the aqueous phase, as well as the amine and solvent nature on the extraction process, has been discussed.

It has been shown that the maximum iridium recovery (95-98%) is observed when extracting from 0.1M H_2SO_4 at 160°, sodium chloride concentration of 30-40 g/l and sulphate concentration of 200 g/l.

With acid concentration increase up to 1.0M the iridium recovery declines to 20%, which fact is probably brought about by the competing action of the sulphate ion relative to the amine.

The position of amines as per their extractive capacity depends on the solvent nature. Thus, at a high-molecular alcohol content in an inert diluent of above 4 vol.% there is observed a recovery increase when passing from the tertiary alkylamines to the secondary and, further, to the primary ones, the last having extraction maximum at an alcohol content of 6 to 7 vol.%. With an increase in the number of carbon atoms in the primary amines from 6 to 9 the iridium recovery increases, which is consistent with the fact of the amine solubility decline in sulphuric-acid solutions. The extractive capacity of nonylamine is higher than that of decylamine, which fact can be explained by steric hinderance with an increasing length of the alkyl radical.

The iridium compound passing into the organic phase has been synthesized and studied by various physico-chemical methods. It has been established that in the system under study the chemical processes are brought about by conversion of the iridium sulphate complexes into chloride ones, as well as to amine incorporation into the inner sphere of a complex being extracted according to the reaction:



MOLYBDENUM EXTRACTION BY MIXTURES OF EXTRACTANTS.

Frolov, Yu.G.; Morgunov, A.F.;
Nasonova, G.I., Budanov, A.G.

Moskovskij Khimiko-Tekhnologicheskij
Institute after D.I. Mendeleev
Moscow, U.S.S.R.

The paper has studied the main regularities in molybdenum extraction from sulfuric acid solutions by mixtures of di-2-ethyl-hexylphosphoric acid (HDEHP) with neutral extractants: tri-n-butyl phosphate (TBP) and petroleum sulfoxides (PSO).

The extraction by a mixture of HDEHP and TBP in the region of low molybdenum concentrations (below 6 g/l) is accompanied with the antagonistic effect of TBP, which is related to the decrease of the active concentration of the extractant.

The same mixture extracts molybdenum more efficiently, provided the metal concentration exceeds 6 g/l. The synergistic effect in this case is stipulated by the extraction of molybdenum polymeric forms.

The extraction by a mixture of HDEHP and PSO in a wide range of molybdenum concentration is accompanied with the synergistic effect, it is most evidently exhibited at the molar ratio of HDEHP : PSO = 2 : 1.

In the cases considered for the mixture of the extractants the molar ratio of HDEHP : Mo_{org} is by far below the ultimate possible, equal to 2.00, if we predict the MoO_2A_2 compound formation. The absence of the sulfate-ion coextraction with Mo has been established. A considerable increase in the molybdenum concentration in the organic phase is stipulated by the extraction of isopolymolybdic acids.

The formation of complex polymeric compounds, when extracting molybdenum by a mixture of extractants, has been confirmed by the cryoscopic method and the investigation of the IR spectra of the extracts.

HOMOGENEOUS LIQUID - LIQUID EXTRACTION

Chia-Swee Ting, Evan T. Williams and
Harmon L. Finston

Department of Chemistry,
City University of New York
Brooklyn College
Brooklyn, New York 11210

Homogeneous liquid-liquid extraction has been applied to the extraction of TTA complexes of many metal cations and a variety of chelate and ion association complexes of iron. The extraction rate was, in all cases, very rapid (less than five minutes) compared to the slow rate of conventional extraction methods.

The efficiency arises from both inherent characteristics of propylene carbonate, e.g., formation of a single homogeneous phase at temperatures above 71°C, and in the case of TTA the higher percentage in the enolate form, and also from the fact that the extraction occurs at higher temperature with its concomitant more rapid mass transfer. The low vapor pressure of propylene carbonate makes it feasible to perform these extractions at high temperatures, and the formation of the single homogeneous phase eliminates the slow step in conventional chelate extractions. It is also noteworthy that in this uniform medium consisting of water and organic solvent, the activity of water is lowered, therefore the hydration sphere of the metal cation is affected somewhat (becoming smaller or broken) and the substitution reaction of the metal ion-aquocomplex with complexing agent is consequently expedited.

Phase diagrams were determined for the system water-propylene carbonate and also for the system water-ethanol propylene carbonate which give the compositions of the respective phases as a function of temperature.

A convenient technique for atomic absorption analysis of the respective phases has been developed based on the fact that water-ethanol-propylene carbonate forms a single homogeneous phase at room temperature. This enables direct comparison of aqueous and organic phases with an aqueous standard that has been diluted with ethanol and propylene carbonate.

Base Metals

Session 18

Co-chairmen : H. Reinhardt (Mx-Processor, Molndal, Sweden)
A. De Schepper (Metallurgie Hoboken-Overpelt, Olen, Belgium)

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- 80-146 A case study - optimizing the performance of the uranium S.X. plant at Rossing Uranium Limited in Namibia.
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- 80-184 The extraction of aluminium (III) from carboxylic acid solutions by di-(2-ethylhexyl)-phosphoric acid.
T. Sato, T. Nakamura, T. Yoshino and T. Kudo, Shizuoka University, Hamamatsu, Japan.

APPLICATION OF LIQUID EXTRACTION FOR ANTIMONY AND
BISMUTH SEPARATION.

V. Bumbalek^a, K. Cermak^a, J. Haman^b

^aOre Research Institute, Praha

^bResearch Institute of Chemical
Equipment, Praha

Praha, Czechoslovakia.

ABSTRACT

The development of a procedure for antimony and bismuth separation from a chloride solution by means of liquid extraction is shortly reviewed. A 40 % solution of tri-n-butylphosphate in white spirit is used as the extractant.

The laboratory-scale equipment consisted of a cascade, whereas RDC columns were used for model-scale testing of the process. The pilot-scale equipment for antimony and bismuth separation using liquid extraction consisted of two packed columns.

Siderite-sulphide ores are treated by flottation in order to recover polymetallic sulphide concentrate containing mainly tetrahedrite and chalcopyrite. This concentrate contains 1-3 % Hg, 5-15 % Sb, 20 % Cu, 1.2 % As, 0.3 % Bi, 0.08-0.3 % Ag and 18-20 % Fe.

Mercury of commercial grade and the roasted product - CuSbAsBi - which cannot be treated by conventional metallurgical methods are recovered from this concentrate by oxidative roasting. Therefore, a process was developed enabling to produce a copper concentrate having less than 1 % Sb and to separate a mixture of antimony and bismuth. The process allows the recovery of antimony trioxide having a Bi content of less than 0.01%, max. 0.2 % Fe and max. 0.01 % Cu, and a high-grade bismuth concentrate with a Bi content of at least 75 %.

The roasted product is treated following a combined pyrometallurgical and hydrometallurgical process, schematically shown in the flowsheet (Fig. 1). It is roasted in a counter-current flow of ammonium chloride. A CuAg concentrate is recovered and a flue dust containing Sb, Bi and As is obtained by filtration of flue gases.

The antimony-containing flue dust is leached in a hydrochloric acid solution. The residual mercury is reduced by metallic antimony. From this solution, antimony is extracted by a 40 % solution of tributylphosphate in white spirit and stripped with a weak acid solution of ammonium chloride. Antimony is precipitated from the strip solution with ammonia and filtered off. The filtrate is re-used for stripping after acidity control.

Bismuth is precipitated with ammonia from the raffinate after antimony extraction and, after re-dissolution of the Bi-precipitate in hydrochloric acid, bismuth is recovered from the solution by the same extraction process.

Tri-n-butylphosphate, diluted up to 40 % in white spirit, seemed to be the most suitable extraction as was indicated by laboratory-scale experiments. The distribution coefficients of the main elements of this multicomponent system using a 40 % TBP-solution were determined and are illustrated in Fig. 2. The curves in Fig. 2 present the relationship between the distribution coefficients and the hydrochloric acid concentration in the aqueous phase. The results are obtained after a single stage contact and a volumetric ratio $O/A = 1$.

Also was found that the selectivity of the solvent to antimony-bismuth separation rises from 3 up to 100 ($KD_{Sb}/KD_{Bi} = 120$ at 8-m HCl) when increasing the concentration of chloride ions in the aqueous phase.

The distribution coefficients in a multicomponent system is not always predictable. While the distribution coefficients of the components which are present in low concentrations (max. 1-5 g/dm³) in the feed do not vary with respect to the concentrations in this range, the presence of antimony in much higher concentrations reduces considerably the distribution coefficient of the other components as well as that of its own. In Fig. 3, the curve a illustrates the reduction of the distribution coefficient of antimony in 4-m HCl when increasing antimony concentration in the organic phase. A similarly significant decrease of the distribution coefficient has been observed for the other components of the mixture when the concentration ion of the component which takes part in the solvation reaction is increased.

This phenomenon appears also with ammonium ions, as may be seen from the curve c. If two moles of hydrogen ions are replaced by ammonium ions, the distribution coefficient decreases from the level of the curve a to the level of the curve c. Even in this case, the decrease is considerable for the considered components as the curve b shows for the distribution coefficients of Fe in a mixture with Sb. For instance, if the aqueous phase consisting of 6-m HCl is replaced by a phase consisting of 5.75-m $NH_4Cl + 0.75\text{-m HCl}$, KD_{Sb} is reduced 8-times and KD_{Bi} 3-times (within the range of low concentrations).

This effect is utilized in the stripping. A high concentration of ammonium chloride is acidified to such extent that no hydrolysis of metallic components takes place.

A basic layout of the section for extraction and stripping of antimony and bismuth is based on the laboratory-scale cascade experiments, whereas continuous countercurrent tests were performed using RDC columns. RDC glass columns with a diameter of 50 mm and a total height of the working part of 2 were used. Specific throughput of 5 to 40 m³/m² per hour of both liquid phases were used. The aqueous phases were continuous, the number of revolutions of a disc impeller varied between 500 and 1000 r.p.m. Typical average analysis of the individual streams - feeds and raffinates of extraction and stripping stages are summarized in Table 1.

The recovery of antimony by extraction ranged between 99.8 and 99.9 % and that of bismuth between 98.92 and 99.90 %. The efficiency of the columns was evaluated by comparison of the separation attained with that achieved in cascade. Two meters' height of the column should have the efficiency equivalent to 5.6 to 6.1 theoretical stages for antimony extraction and 3 to 11.5 theoretical stages for bismuth extraction.

Since a very pure strip solution of antimony is required, especially with respect to the bismuth content, in addition to a high recovery yield, the effect of refluxing the antimony extract was experimentally investigated. Two stages for extract washing were added to the five-stage countercurrent cascade for antimony extraction and various alternative of refluxing with solutions having a low content of accompanying metals, especially bismuth, were investigated using the reflux-to-feed ratio 1 : 10. We have been able to reduce the bismuth content in the antimony strip solution from approx. 0.02 g/dm³ to concentrations ranging between 0.002 and 0.005 g/dm³. The content of other impurities decreased considerably as well.

The development of the new process resulted in a complete line for treatment of the roasted product - CuSbBiAg - with a throughput of 600 kg of feed per hour. In the hydrometallurgical part of the line, main attention was paid to the extraction section. When the extraction unit was build there appears severe problems regarding the construction materials because of the high aggressivity of the medium caused by the combined influence of concentrated hydrochloric acid and chlorides and an organic phase. The results of material tests did show that only one glass, glass-reinforced plastics, branched polyethylene, teflon and some few non-conventional materials, less suitable for construction purpose, resist to the combined influence of the medium. This has been confirmed by operational experience.

With respect to a quick realization, glass columns with diameter of 300 mm, assembled of 1 m high glass cylinders packed with glass Raschig rings, were used for extraction and stripping operations. The height of the working part is 9 m, total height of the column is 12 m. Also other parts of the line such as pumps, pipes, fittings are made of glass ; glass-reinforced plastics were used for bins.

In order to ensure the safety of the operations, electric parts such as lighting fittings, pumps and agitators, fans of heaters, ect. were of the explosion-proof type and measuring and control systems were pneumatic-driven. The extraction shop was ventilated while the sewage system from the shop was attached to a separated sump.

The extraction column load was approx. $16 \text{ m}^3/\text{m}^2$ for both phases when extracting antimony. The antimony strip-solution was partially used as reflux. The stripping column was loaded with approx. $20 \text{ m}^3/\text{m}^2$. The working temperature was 20°C . Typical analysis of the individual streams for antimony extraction are also given in Table 1.

Although the results of the extraction section meet the technological requirements, low efficiency of the packed columns is evident when comparing the separation effect of both column types. The packed columns will be replaced by rotating disc contactors made from plastics. When comparing the extraction efficiency with the stagewise process, it has been established that almost 2.2 to 3 m height of Raschig rings packing is necessary in order to obtain an antimony and bismuth extraction effect of 1 theoretical stage.

The extraction system presents good physical properties. There is no formation of emulsions, no entrainment of phases while there were no regulation and process control problems.

High economic efficiency is obtained by creating a closed circuit for the organic phase and a closed circuit for the stripping agent. The latter is easily obtained by ammonia precipitation of the extracted components out of the strip solution. The excessive ammonium chloride is separated after re-crystallization which is used as the chloridizing agent during roasting at the head of the process.

Bismuth middlings are treated by the same process but since the bismuth content in the feed is 20-times lower than that of antimony, no proper equipment for bismuth recovery has been built. Bismuth middlings are stored and treated per campaign, when antimony recovery is stopped, in the same equipment. Therefore, the data on bismuth production could not yet be included into this paper.

Conclusion

The results of the tests have shown that an antimony product of the required quality can be obtained at an industrial scale

with a high recovery yield when using RDC extractors under the presumption that the conditions established in model and pilot scale will be kept.

(For Fig. 1 and Table 1, see later on).

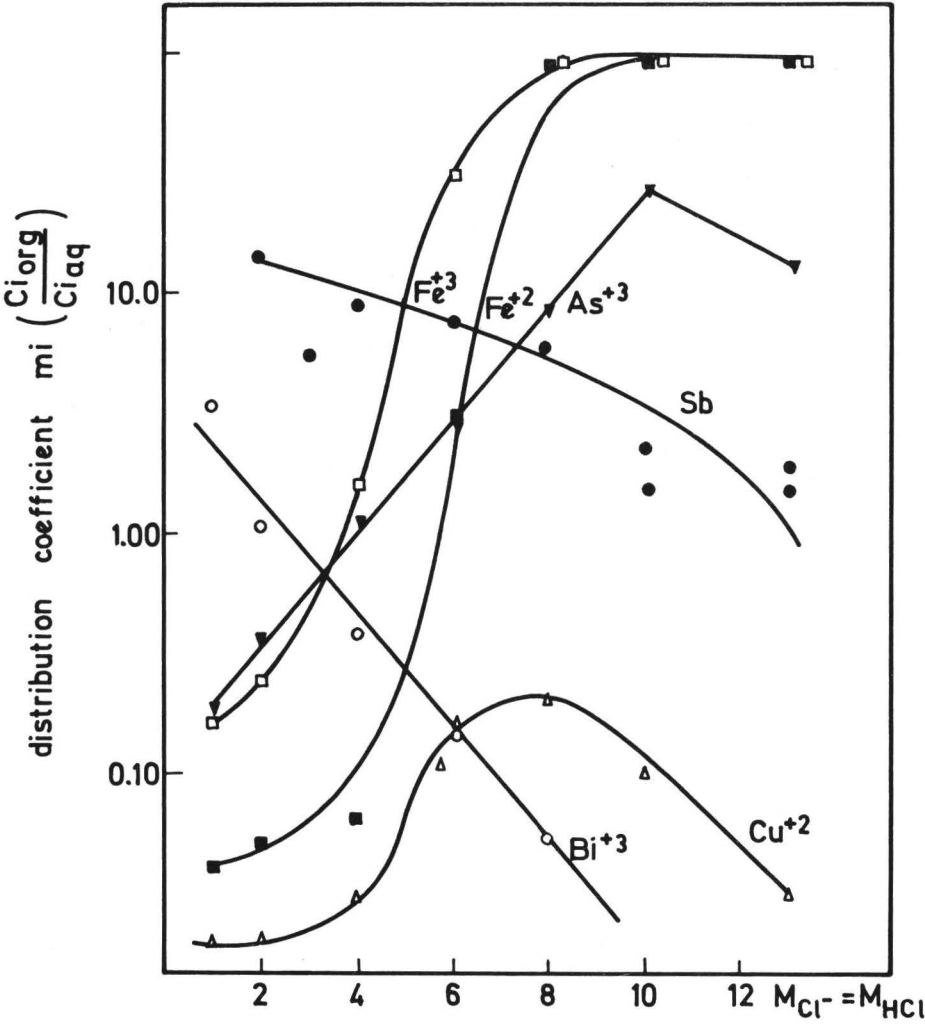


FIG. 2

Dependence of distribution coefficients on concentration of hydrochloric acid.
 Solvent : 40 % TBP
 60 % white spirit

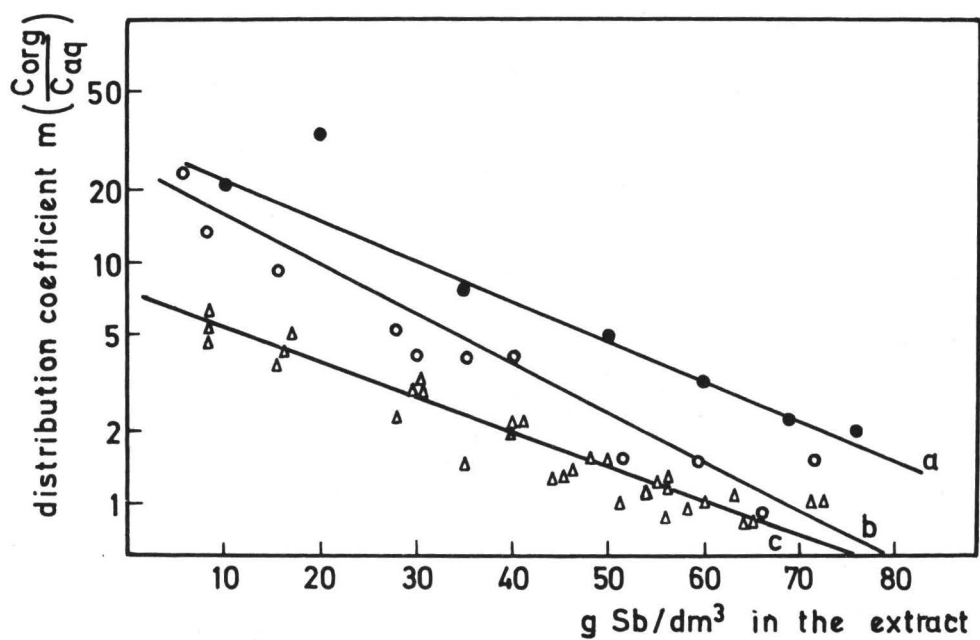


FIG. 3

Dependence of distribution coefficients on Sb concentration in the extract.

a) system Sb-4-M HCl

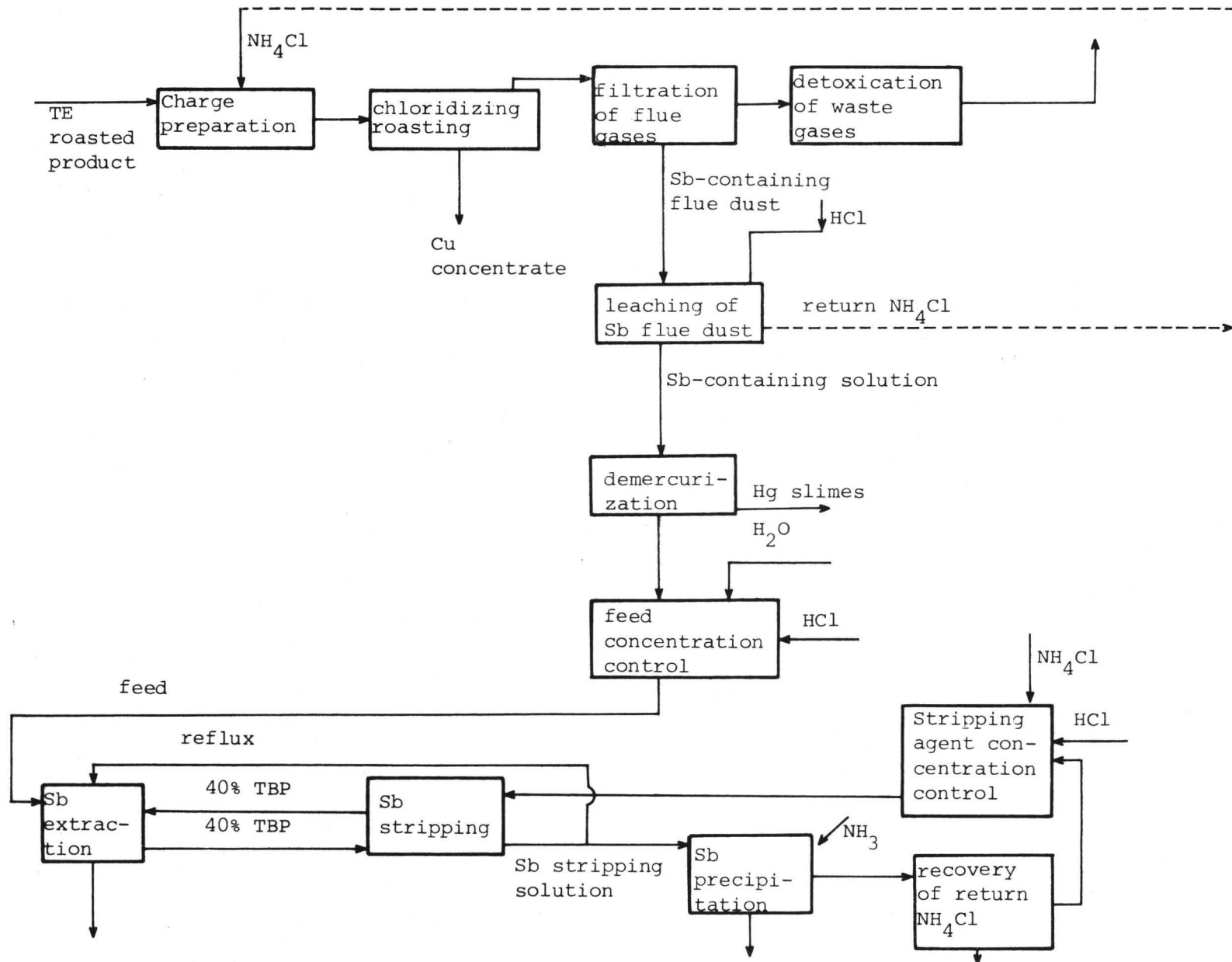
b) system Fe-2-M HCl - 1.9-M NH_4Cl

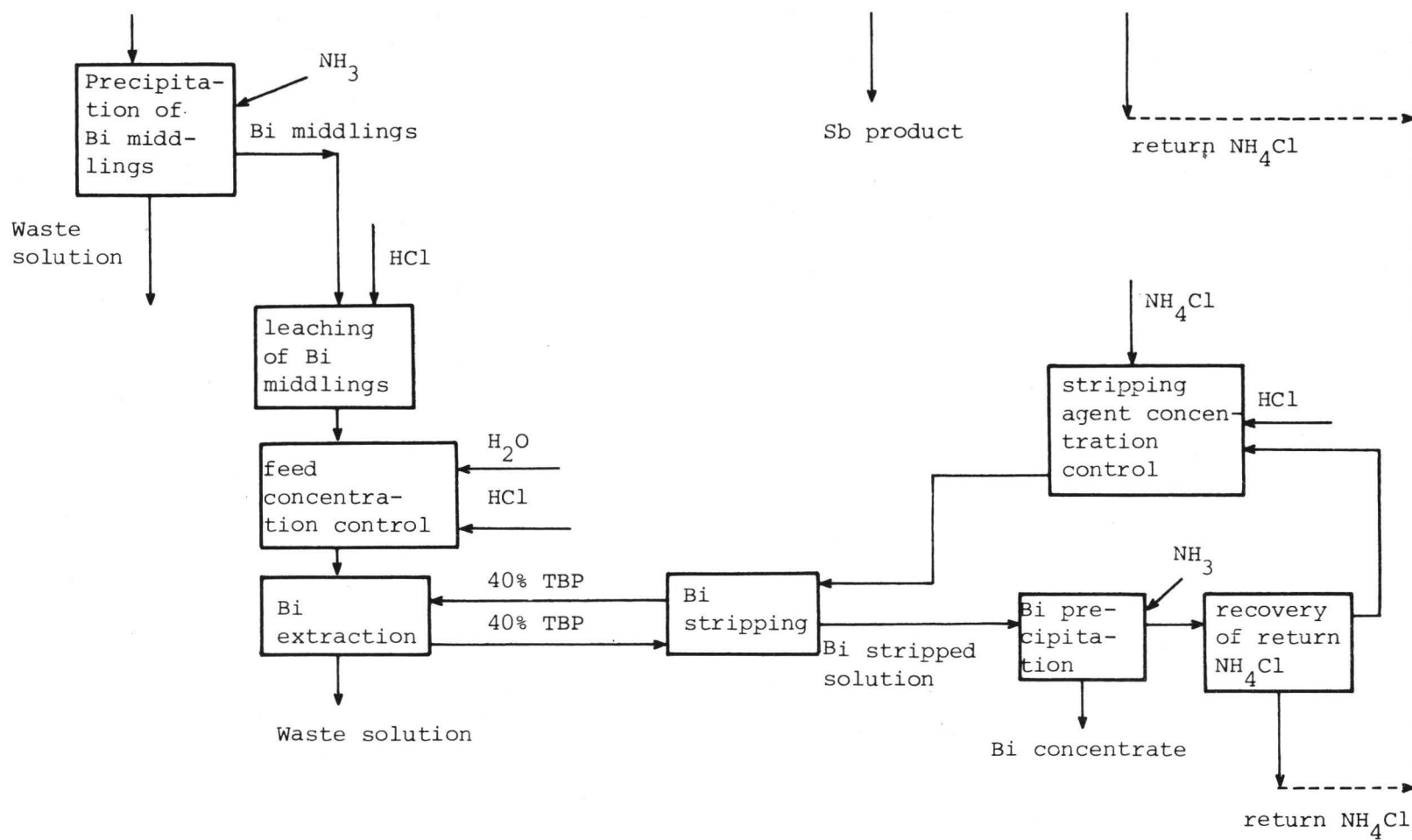
c) system Sb-2-M HCl - 1.9 M NH_4Cl

Table 1. Analysis of the streams in antimony extraction (g/dm^3)

Component	Laboratory-scale countercurrent cascade: 5 extraction stages + 5 stripping stages			Laboratory-scale countercurrent cascade: 5 extraction stages + 2 stages of extract washing with reflux + 5 stripping stages			RDC 50 mm diameter			packed columns 300 mm diameter		
	feed	raffinate	stripped product	feed	raffinate	stripped product	feed	raffinate	stripped product	feed	raffinate	stripped product
Sb	75.0-80.0	1.75-4.85	35.10-41.30	7.33-80.2	1.675-13.0	34.26-38.0	75	0.06-0.15	36.0-44.0	71.8-86.4	0.9-2.9	32-49
Bi	1.84-2.64	1.8-2.65	0.02-0.06	1.84-2.65	1.96-2.205	0.0017-0.0047	2.3	2.27-2.3	0.008-0.012	3.08-3.36	2.9-3.3	0.01-0.03
Ag	0.102-0.112	0.090-0.110	0.004-0.03	0.112-0.138	0.11-0.130	0.002-0.003	0.102	0.096-0.101	0.0008-0.0021	0.019-0.031	0.021-0.036	0.001-0.0015
Cu	0.85-1.05	0.74-1.01	0.008-0.096	0.533-0.85	0.53-0.89	0.0005-0.002	1.05	0.34-0.50	0.25-0.40	1.02-1.63	0.19-0.45	0.37-0.56
Fe	1.7-2.51	0.017-0.24	0.26-0.611	2.28-2.51	0.055-0.835	0.0497-0.889	1.5	0.02-0.38	0.43-1.06	5.1-5.6	3.9-5.0	0.49-0.84
As	1.75-3.60	0.275-3.05	0.35-1.78	3.11-3.60	2.33-3.21	0.047-0.254	1.5	1.25-1.30	0.28-0.29	3.1-3.8	1.9-2.66	0.45-0.7
Hg	0.70-0.856	0.325-0.77	0.174-0.31	0.857	0.594-0.774	0.07-0.1	0.71	0.03-0.08	0.14-0.40	0.04-0.16	0.008-0.1	0.012-0.023
Cl^-	214.5-218.0	151.3-154.6	217.8-223.2	215.1-217.5	149.9-153.8	220.4-226.2	215.3	146.8-159.5	221-230.1	206-228	153-157	219-274
NH_4^+	40.8-41.5	42.3-43.8	87.9-92.1	41.2-43.0	42.9-44.7	88.3-91.8	41.20	43.1-46.3	88.4-91.3	46-50	49-53	87-106

FIG. 1 : Technological flowsheet.





SEPARATION OF SECONDARY BASE METALS BY SOLVENT EXTRACTION

J. R. Harlamovs, G. Harrison and
G. J. Lawson

Department of Minerals Engineering,
University of Birmingham.

Birmingham, U.K.

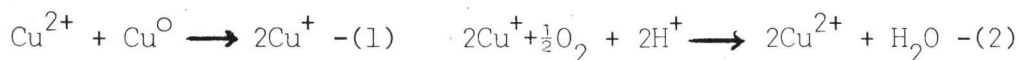
ABSTRACT

The separation of values from 'black metal' alloys, produced from low-grade copper-bearing scrap, has been investigated using hydrometallurgical methods. Leaching of the alloy is rapid in acid or ammoniacal chloride media, the latter giving some selectivity of dissolution. Recovery of the metals Cu, Ni, Sn and Zn from the leach solution has been examined by solvent extraction with several commercial reagents; a separation procedure can be devised involving successive extraction from an acid chloride solution with TBP, an amine, and a copper-selective extractant such as LIX64N.

INTRODUCTION

For several years, with increasing primary metal prices, the importance has been recognised of the recovery of base metals from secondary sources. Particularly, low-grade copper-containing scrap is smelted to produce a 'black metal' which usually contains 70-80% copper, combined with iron, zinc, nickel and tin as minor constituents. This alloy requires further pyrometallurgical treatment followed by electrowinning to produce pure copper; a continuous smelting furnace has been described(1) which allows the production of an alloy containing a greater proportion of copper (~90%) but this still contains appreciable amounts of other non-ferrous metals, and requires further refining. An alternative approach is to use hydrometallurgical techniques, particularly leaching and solvent extraction, to process these alloys, whereby the recovery of the more valuable minor components may be feasible.

Leaching studies have shown that the presence of cupric ions in the initial leach liquor is beneficial, and that the leaching of the 'black metal' is controlled by the leaching of the copper content (2). The leaching of metallic copper proceeds as shown in equations 1 and 2.



Initially, equation 1 is rate-determining and the overall reaction shows first order dependence upon cupric ion concentration, but as the cuprous ion accumulates the rate is governed by the oxidation of cuprous ion, so that equation 2 becomes rate-determining, and the leaching rate consequently becomes independent of cupric ion concentration⁽³⁾. It has been shown that ammonia/ammonium salt mixtures are good leaching reagents for copper and that the rate of leaching is still governed by equations 1 and 2⁽³⁾; for leaching, ammoniacal solutions should have an advantage over acidic media in exhibiting a degree of selectivity, tending to dissolve only those metals which form aqueous-soluble ammine complexes.

Although considerable research has been applied to various metals and metal combinations, few solvent extraction studies have been directed towards 'black metal' leach liquors, and these are limited to the use of commercially available chelating extractants for the recovery of copper from acid leach solutions (4,5,6). In this paper the feasibility of recovering not only the copper, but also the other non-ferrous metals present in these alloys, from acid or ammoniacal leach solutions is investigated, using chelating, solvating and amine type extractants.

EXPERIMENTAL

All experiments were carried out at 25°C. Extraction reagents were obtained from the manufacturers, and were used without further purification: LIX64N, Alamine 336 and Aliquat 336 from General Mills Inc.; SME529 from Shell Chemicals Ltd.; P17 from Acorga Ltd.; and tributyl phosphate from Union Carbide Ltd. Working organic solutions were prepared by dissolving weighed amounts of extractant in either 'kerosene white' (Hopkin and Williams Ltd.) or the aromatic diluent Shellsolve (Shell Chemicals Ltd.). Other reagents were of A R grade. Before use, Alamine 336 was equilibrated with 1.0M hydrochloric acid to convert the amine to the chloride form, thus preventing uptake of acid during extraction experiments. Metal concentrations were determined by atomic absorption using an IL Model 751 spectrophotometer and pH values were measured with a Radiometer combined glass electrode attached to a Radiometer Digital pH meter, Model M63.

The specifically designed cylindrical leach vessel was equipped with four perspex baffles to prevent formation of a vortex. The solution (500ml) was stirred by a perspex stirrer driven by a variable speed electric motor. Calibration showed that a stirrer speed of ~ 750 rpm was adequate to produce uniform dispersion of the metal sample (5g of fine shavings). Aeration was provided by two sintered glass distributors attached to two small constant speed pumps. The appropriate copper salt was added to give an initial cupric ion concentration of approximately 2g l⁻¹. Samples were withdrawn at regular intervals; after appropriate dilution their metal contents were determined. The following systems were investigated: 1.0M HCl, 1.0M H₂SO₄, 1.0M NH₃/1.0M NH₄Cl, 1.0M NH₃/0.5M (NH₄)₂SO₄ and 1.0M NH₃/0.5M (NH₄)₂CO₃.

Solvent extraction experiments on the 'black metal' leach solutions were carried out using a combined mixer-settler⁽⁷⁾ (PMA), with 250ml phase volumes. Those with the simulated leach liquor were carried out by 'shake flask' techniques, using 20ml phase volumes in 100ml stoppered conical flasks which were shaken for 16h; the phases were allowed to disengage, and separated with Whatman 1PS phase separating papers. The simulated leach

liquor was prepared by dissolving appropriate metal chlorides in 0.4M and had the following composition: 5.60gl⁻¹ Cu, 0.24gl⁻¹ Ni, 0.48gl⁻¹ Zn, 0.72gl⁻¹ Fe, 0.40gl⁻¹ Sn, and 0.56gl⁻¹ Pb (total concentration of black metal 8gl⁻¹). Complete dissolution of 5g of black metal in 1.0M HCl gave a solution of composition 9.1gl⁻¹ Ca, 0.32gl⁻¹ Ni, 0.02gl⁻¹ An, 0.07gl⁻¹ Fe, 0.31gl⁻¹ Sn, and 0.30gl⁻¹ Pb.

RESULTS AND DISCUSSION

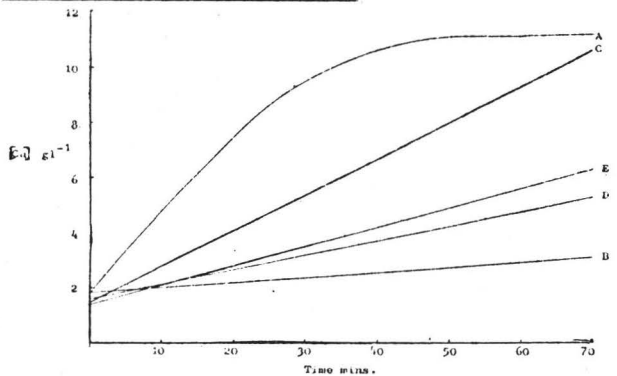


Fig. 1. Leaching of 'black metal' shavings - copper leached versus time

Metal	Recoveries after 65 min.(%)				
	A	B	C	D	E
Cu	100	13	89	39	50
Ni	100	12	74	44	50
Zn	100	0	73	37	37
Fe	100	31	0	0	0
Sn	100	5	0	0	0
Pb	100	33	0	0	0

Table 1 - Metal Recoveries after 65 min. of leaching

A, 1.0M HCl- B, 1.0M H₂SO₄; C, 1.0M NH₃/1.0M NH₄Cl; D, 1.0M NH₃/0.5M(NH₄)₂SO₄; E, 1.0M NH₃/0.5M (NH₄)₂CO₃

The relation of copper leached to time for the five systems investigated is shown in FIG. 1; all the copper is leached by 1.0M HCl within 45 min., but dissolution is incomplete with all the other systems even after 65 minutes. The gradients of the lines are A, 0.25, B, 0.02, C, 0.13, D, 0.05, and E, 0.07 gl⁻¹ min⁻¹; this shows dissolution by hydrochloric acid to be an order of magnitude faster than by sulphuric acid, while for the ammoniacal systems, chloride is nearly twice as fast as carbonate, which is faster than the sulphate system. The linearity indicates that the rate of reaction is independent of cupric ion concentration, and the differences between the gradients probably reflect the relative stabilities of cuprous ions in the different solutions, choride ions providing greater stability in both acidic and ammoniacal media.

Table 1 shows the relative dissolutions of the black metal components for the five systems after 65 min. Hydrochloric acid dissolves all the sample completely, while sulphuric acid reacts more slowly but with some preferential dissolution of iron and lead. As expected the ammoniacal systems show a degree of selectivity tending to dissolve only copper, nickel and zinc, the percentages of the last two tending to reflect the extent of copper dissolution. Leach liquors from the two chloride systems and the ammoniacal sulphate system were filtered prior to examination by solvent extraction.

At the initial pH value of the leach solution, a 40% solution of LIX64N in kerosene extracted all the copper from an ammoniacal chloride (pH 9.4) or an ammoniacal sulphate(pH 9.7) solution, but only 35% and 87% respectively of the nickel and none of the zinc. As the pH value was decreased the extraction of nickel and zinc increased to some extent, presumably due to the breakdown of aqueous ammine complexes, while at low pH values (<3) the extraction of all metals decreased with some separation

between copper and zinc appearing (FIG. 2a, b). With a 20% solution of LIX64N, approximately the stoichiometric equivalent of all the metals in an equal volume of ammonia/ammonium chloride leach solution, a better separation was achieved, only 2.5% of nickel being extracted at the starting pH. In this respect LIX64N was superior to the hydroxyoxime extractants SME 529 and P17, which under the same conditions extracted 38% and 83% of nickel respectively, but these extractants may have a larger capacity than LIX64N. Extraction of the hydrochloric acid leach liquor with 40% LIX64N in kerosene is illustrated as a function of pH in FIG. 2c. As expected, copper is extracted preferentially, but only 75% extraction is reached before significant extraction of iron occurs. As the pH is increased, the remaining metals are extracted, except for tin which precipitates before extraction can occur. Better copper/iron separations should be possible by optimising the conditions, but extraction with LIX64N from acidic solutions still has the potential disadvantages that relatively large amounts would be needed to remove all the copper and iron, the latter being of negligible value, before the remaining non-ferrous metals could be recovered, and moreover the most valuable constituent, tin, could not be extracted.

FIG. 3a, b, c shows the effect of increasing sodium chloride concentration on the extraction of a simulated leach liquor by various concentrations of tributyl phosphate (TBP) in kerosene. Tin was extracted well, while extraction of zinc became significant only at higher extractant concentrations and of iron only at high chloride concentrations. The behaviour of tin is such that at relatively low TBP concentration (160 gl^{-1}) and in the presence of 200 gl^{-1} sodium chloride, good recovery with separation from other values can be obtained; however, with more concentrated TBP, similar performance is possible at smaller salt concentrations, although the co-extraction of zinc and copper may become significant. TBP thus has the advantage that a valuable minor constituent, tin, can be recovered without the necessity of extracting the major component, copper. Tin was readily recovered from the TBP extract, ~90% recovery being effected by two contacts with 1M hydrochloric acid and without phase disengagement problems.

The extraction behaviour of the various metals with different concentrations of Alamine 336 in Shellsolve ($40, 80$ and 160 gl^{-1}), for simulated leach solutions containing increasing concentrations of sodium chloride, is shown in FIG. 4a, b, c. Tin, zinc and iron were all well extracted but nickel not at all. Copper showed a small initial extraction which increased with increasing extractant and sodium chloride concentrations; the extraction of lead was good initially, decreasing with increasing sodium chloride concentration but still increasing with extractant concentration. Stripping the organic phase with dilute hydrochloric acid proved difficult due to emulsification caused by the precipitation of a complex tin salt; consequently the use of amines would probably require prior removal of tin.

Aliquat 336 extracted slightly less iron than Alamine 336 from the same leach liquor, though extraction of the other metals was as good if not better (FIG. 5a, b, c). In general separations of 'black metal' components could be achieved similar to those with Alamine 336, but phase separation was improved with Aliquat 336. The pattern of lead extraction with the two amine extractants is difficult to explain. Abbruzzese⁽⁸⁾ found similar extraction curves for lead with a tertiary amine and a quaternary salt when

varying the concentration of hydrochloric acid and, from slope analysis data, postulated the extraction of a complex of the type $\text{HNR}_3\text{PbCl}_3$. It would seem therefore that, since the species PbCl_4^{2-} would become predominant at high chloride concentrations, the reduction in lead extraction is probably associated with the corresponding reduction in the concentration of PbCl_3^- .

The amine systems are of particular interest in that, with suitable choice of conditions, most of the minor components can be extracted from a 'black metal' leach solution, leaving only copper and nickel. As with TBP, amine systems require relatively high chloride concentrations to be useful but this would not be a disadvantage in the leaching operation as increased chloride concentrations accelerate the dissolution rate. A complex separation scheme can be envisaged using all three types of extractant; this would involve the prior removal of tin with TBP, followed by amine extraction, which could leave the copper and nickel in aqueous solution from which copper could easily be extracted selectively, e.g. with LIX64N, and returned to a sulphuric acid electrolyte.

CONCLUSIONS

Leaching studies have shown that chloride systems are superior to sulphate systems for the leaching of 'black metal'. Ammoniacal systems show selectivity but do not dissolve the tin content, and thus the residue would need further treatment if the tin were to be recovered. Hydrochloric acid dissolves all of the 'black metal' and produces a leach solution from which the more valuable metal components can be recovered by using a combination of the three extraction systems studied.

ACKNOWLEDGEMENTS

Grateful acknowledgement is made to Professor N. A. Warner, Head of the Department of Minerals Engineering, for his interest; to Mr. M. A. Cabezas for experimental assistance; to the Science Research Council and the Wolfson Foundation for generous support; and to Acorga Ltd., General Mills Inc., and Shell Chemicals Ltd. for samples of reagents.

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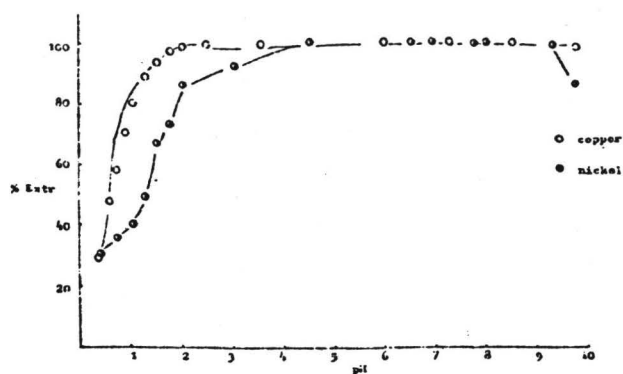


FIG. 2a

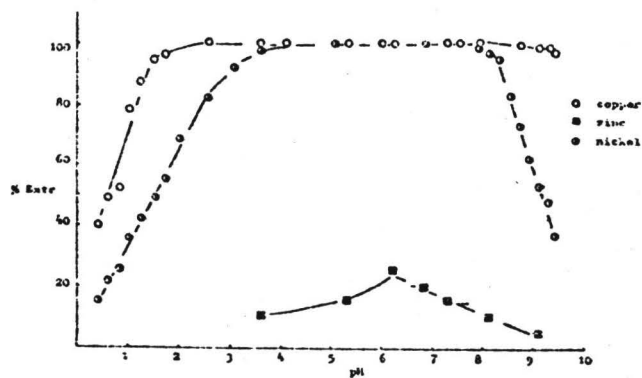


FIG. 2b

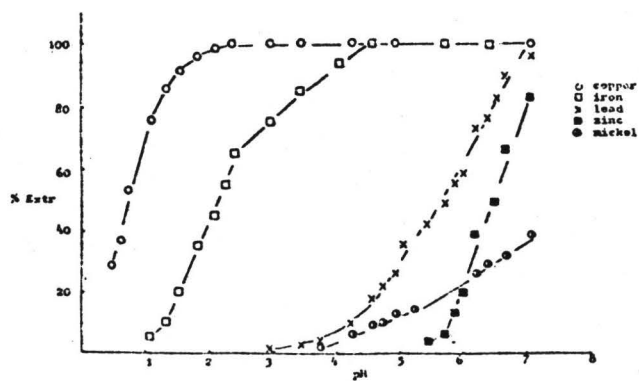


FIG. 2c

FIG. 2

Extraction of metals from 'black metal' leach liquors by 40% LIX64N in kerosene:

(a), $\text{NH}_3/\text{NH}_4\text{Cl}$; (b), $\text{NH}_3/(\text{NH}_4)_2\text{SO}_4$; (c), HCl

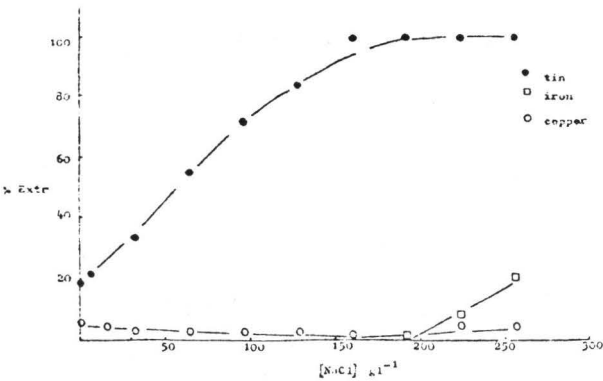


FIG. 3a

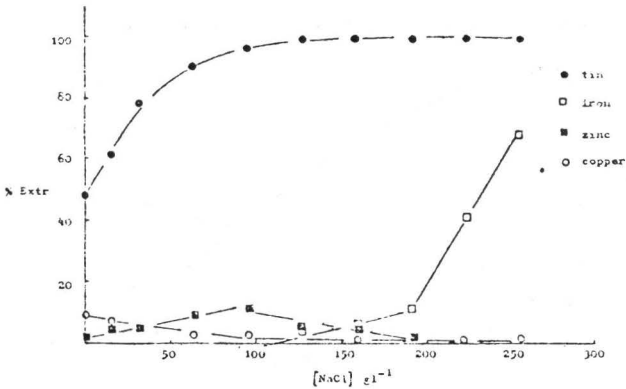


FIG. 3b

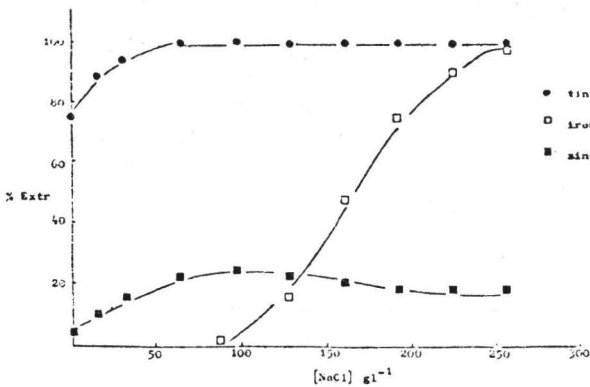


FIG. 3c

FIG. 3

Extraction of metals from a simulated chloride leach liquor by TBP in kerosene with 16% v/v n-dodecanol. TBP concentration: (a), 160g l⁻¹; (b), 240g l⁻¹; (c), 320g l⁻¹

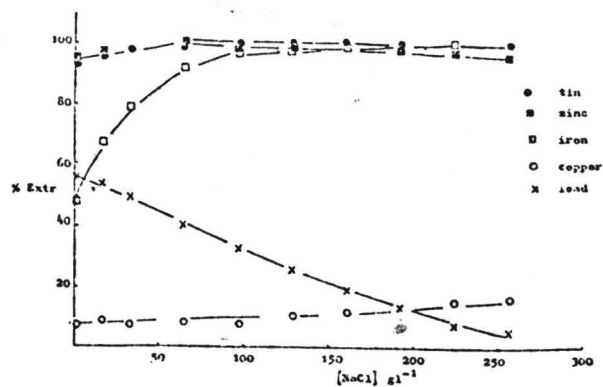


FIG. 4a

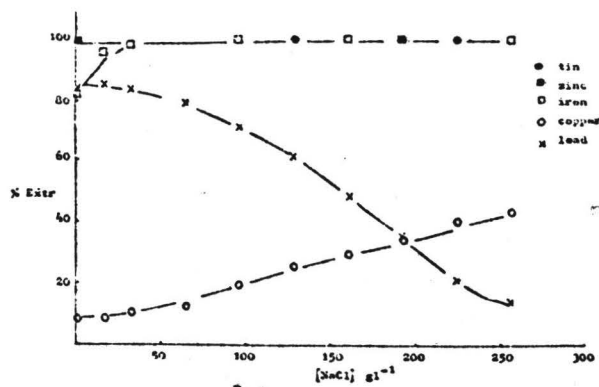


FIG. 4b

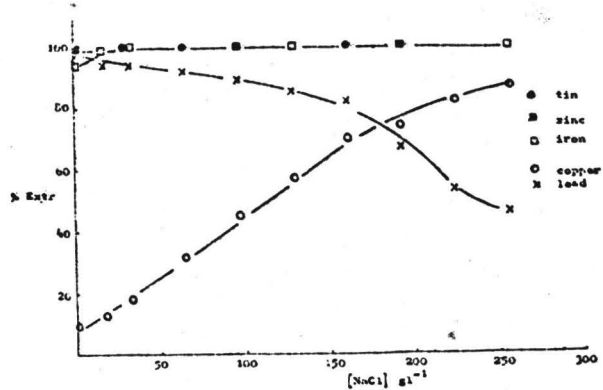


FIG. 4c

FIG. 4

Extraction of metals from a simulated leach liquor by Alamine 336 in Shell-solve. Alamine concentration:

(a), 40g l⁻¹; (b), 80g l⁻¹; (c), 160g l⁻¹

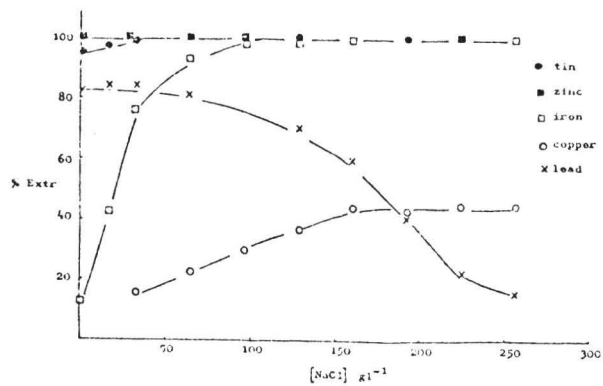


FIG. 5a

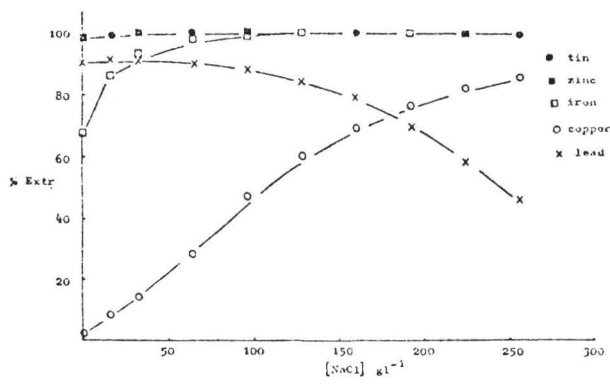


FIG. 5b

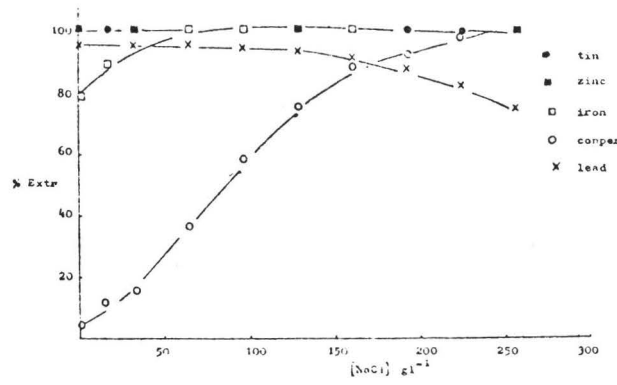


FIG. 5c

FIG. 5

Extraction of metals from a simulated leach liquor by Aliquat 336 in Shell-solve. Aliquat concentration:

(a), 50g l⁻¹; (b), 100g l⁻¹; (c), 200g l⁻¹

EXTRACTION OF COPPER AND ZINC FROM CHLORIDE LEACH LIQUORS RESULTING
FROM CHLORINATION ROAST-LEACH OF FINE-GRAINED SULPHIDES

G.M. Ritcey, B.H. Lucas, K.T. Price

CANMET, Dept. Energy, Mines and Resources
555 Booth Street

Ottawa, Canada
K1A 0G1

ABSTRACT

The paper describes the solvent extraction separation and recovery of copper and zinc from chloride leach liquors resulting from the low temperature chlorination of a lead-zinc sulphide concentrate. The results of bench studies are summarized for the selection of the extractants, the effect of total chloride and equilibrium pH on extraction and discrimination, scrubbing and stripping. Acorpa P5300 was the most suitable extractant for copper, and TBP was selected for zinc. High purity copper sulphate and zinc chloride electrolytes were produced for subsequent direct electrowinning.

Based on the bench data, small-scale continuous tests were run in mixer-settlers to define the required stages. Continual recycling showed no evidence of solvent degradation.

A detailed economic evaluation of the process is described.

INTRODUCTION

The conventional refining of zinc usually comprises a hydrometallurgical route, alone or in combination with pyrometallurgy. Roasted concentrates are dissolved with dilute sulphuric acid to produce a solution containing zinc sulphate plus impurities. After a series of process steps to remove the impurities, the zinc is recovered by electrolysis, and the depleted zinc sulphate solution and regenerated sulphuric acid are returned to the leaching step. However, due to their mineralogy, some of the fine-grained, complex, zinc-bearing ores do not respond to the production of concentrates. Such complex sphalerite ores are to be found in large quantity in countries such as Canada, Australia and Norway. Differential flotation is relatively unsuccessful, and only at considerable loss of values.

At CANMET, the problem of treating such ores was recognized, and a comprehensive R&D program commenced late in 1975. After examination of the problem, one of the approaches selected was that of producing a bulk concentrate which would be chlorinated and brine leached, and the metals subsequently separated and recovered from the solution by solvent extraction. Such a process would provide high metal recoveries, eliminate the environmental problem of sulphides in the tailings, and produce metals of high purity. Any chloride process would also have to provide for recycle of chlorine in order to make the process economically feasible.

Previous investigators have reported on the solvent extraction of metals from chloride solutions containing metals such as copper, lead and zinc (1). The use of TBP has been proposed for the extraction and separation of zinc from cadmium (2,3,4). The best separation of zinc from cadmium

utilized 100% TBP (2,4), with the zinc recovered by stripping with sulphuric acid. The use of TOPO for zinc extraction from chloride liquors showed an increase in the E values compared to TBP (3). Extraction data for the use of naphthenic acid (2,5,7) or Versatic 911 (4,5,6,7) have been reported for the extraction and separation of zinc from cadmium showing that extraction was pH-dependent and reached a maximum at pH 6. With respect to amines, although the primary amines preferentially extract zinc, the secondary, tertiary and quaternary amines were selective for cadmium (4). The Espindesa process uses a secondary amine for zinc extraction, followed by scrubbing and then water stripping the zinc which is subsequently extracted with D2EHPA (1). The extraction and separation of zinc from cadmium with D2EHPA is accomplished best in the pH range 0.5 to 1.0 (4). Mixed extraction systems of Kelex 100 and Versatic 911 showed an increase separation factor for zinc over cadmium (5,6).

The literature contains considerable information on the extraction of copper from chloride liquors. LIX 64N has been used in a pilot process by NIM in Johannesburg (8). Others have demonstrated that chloride ion concentrations up to 4M for LIX 64N and 3M for Kelex 100 do not hinder the extraction of copper in the presence of ferric iron (9,10) because the kinetics favour copper over iron. The same authors reported that small amounts of chloride were extracted by LIX 64N but that no chloride was extracted by LIX 65N, due to the presence of LIX 63 in the LIX 64N (11). In the Minimet process (13) (a cupric chloride leach) copper is extracted with LIX 65N, chloride is removed by scrubbing with water or copper sulphate solution, and stripping is accomplished with spent electrolyte from conventional electro-winning of copper sulphate solution.

Although much data are already available on chloride systems, the type of solution that would result from the chlorination-leach of the complex galena-sphalerite-chalcopryrite could differ in extraction and separation characteristics. Also, the objective at CANMET was to produce high purity zinc by electrowinning of zinc chloride solutions, thereby returning chlorine to the circuit. The results of the initial screening tests on many possible extractants and subsequent research (14,15) indicated the best reagents to achieve the overall objectives of providing high purity electrolytes for copper and zinc electrowinning were the Acorga P5300 for the extraction of copper and tri-butyl phosphate (TBP) for the extraction of zinc. Because of the length restrictions of this paper, the results of basic work are summarized briefly. This paper deals then with the continuous testing in a small pilot operation, the description of a flowsheet and an economic appraisal.

GENERAL OVERALL PROCESS DESCRIPTION

Ore, or concentrate, containing the copper and zinc is fed to a furnace where the material is chlorinated at a temperature of less than 500°C. The chlorinated material is transported to a second furnace where, under an oxidizing atmosphere at 450°C, some iron is volatilized as gaseous FeCl_3 , while the remainder is converted to Fe_2O_3 . In the subsequent brine leaching stage essentially all the iron remains insoluble with the process residue. Following hot filtration, the liquor is allowed to cool to crystallize the PbCl_2 from solution. The resultant supernatant liquor, which is fed to solvent extraction, contains approximately, in g/L, 30 Zn, 0.4 Cu, 0.4 Pb, 0.1 Fe (or less), in 3M NaCl and in a pH range of 2-4. The copper and zinc are recovered by solvent extraction-electrowinning and the final raffinate is returned to the leach circuit after removing and treating a small bleed stream for impurity build-up. The lead chloride is further treated to produce high purity lead. A typical analysis of the feed concentrate to chlorination is shown in Table 1. The schematic of the overall process is shown in Figure 1.

TABLE 1 - ANALYSIS OF ORE AND CONCENTRATE (%)

ANALYSIS	ORE	CONCENTRATE
ZN	9.02	29.9
CU	0.42	0.74
PB	3.15	9.48
FE	31.7	19.9
S	37.9	36.6
SiO		0.22
Ag+2	118*	270*

*G/TONNE

RESULTS

Bench Scale Results

The preliminary bench studies (in which all the possible copper extractants were examined and evaluated on the chloride liquor containing copper, zinc, lead and sodium chloride) indicated the following:

1. Copper was extracted best with one of the following reagents: Acorga P5100, P5300 or Shell SME 529, and stripped with copper sulphate return electrolyte;
2. Zinc was extracted with TBP, and was water stripped to produce $ZnCl_2$;
3. Lead would be crystallized from the brine leach solution for subsequent electrolysis and chlorine recycle, with the remaining lead in the supernatant recycled back to leaching.

The subsequent research on the copper system was devoted to a comparison of the three possible copper extractants with respect to equilibrium, kinetics, metal discrimination, scrubbing and stripping. For zinc, the possibility of using mixed extractants for synergism was investigated as to extraction and stripping.

The results of those tests, leading up to continuous testing in mixer settlers, were as follows: (14)

Copper Circuit

1. The Acorga P5300 was ultimately selected because of its superior performance in the important aspects of scrubbing and stripping. The Acorga P5100 had much in its favour for extraction (equilibrium, phase separation and kinetics). The SME 529 was superior only in being slightly better for discrimination over zinc.
2. Water or Na_2SO_4 appeared to be suitable as a scrub solution for the removal of chloride from the loaded Acorga P5300 solvent. Room temperature was more effective than $50^\circ C$ for scrubbing chloride.
3. The loaded solvent was readily stripped with a solution of 30 g Cu/L containing 150 g H_2SO_4/L , producing a strip electrolyte feed to electro-winning containing about 50 g Cu/L.
4. After stripping, any sulphate on the solvent was removed by water scrubbing prior to recycling the solvent to extraction.

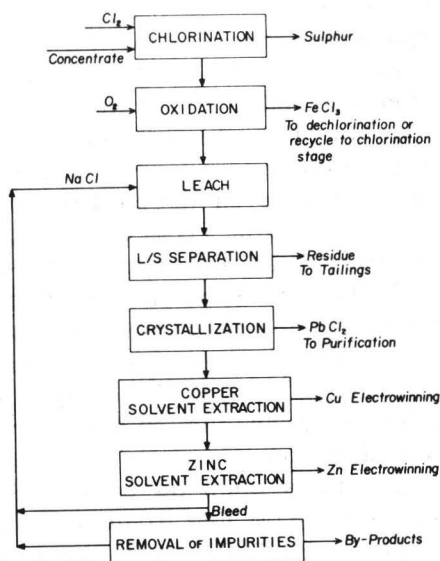


Figure 1. SCHEMATIC OF OVERALL PROCESS FOR TREATMENT OF Pb/Zn CONCENTRATES

Zinc Circuit

1. The mixed extractant systems could be effective (Adogen 464-TBP, Adogen 381-TBP or TOPO-TBP), in that the extraction equilibria for the three mixed extractants were favourable and complete extraction was completed in less than 30 seconds. However, all three solvents were difficult to strip compared to the TBP system.
2. An increase in extraction of zinc resulted from an increase in the NaCl concentration from 0 to 3M; if the extraction was carried out from a 3M NaCl feed solution, pre-equilibration could be with acid or salt, and the equilibrium pH in the range 1-4 had no effect on zinc extraction. Pre-equilibration could be accomplished with 50 g HCl/L.
3. A solvent concentration above 20% TBP is required, with 60% more effective in the loading-stripping stages with respect to discrimination over Pb and Fe as compared to 75% TBP. Six stages with 60% TBP would be used.
4. Impurities such as Cu and Pb, that are co-extracted with Zn, could be removed from the loaded solvent by scrubbing with a solution of 25 g Zn/L in 3M NaCl in 3 stages.
5. Although water could be used for stripping zinc from TBP, subsequent evaluation of this electrolyte for electrowinning indicated that such an electrolyte would not be satisfactory. The medium chosen was 15 g Zn/L at pH 1.0 in HCl (16).

Continuous Testing

As a result of the bench-work, and the sequence of extraction and separation stages that were indicated, subsequent work was directed towards continuous testing in stage-wise mixer settlers. The mixer settlers used in the investigation had 620 mL mixer capacity, obtained from Bell Engineering in Tucson, Arizona. In the initial runs, synthetic solutions were used as the chlorination-roast-leach portion of the flowsheet had not been optimized. Later tests employed process liquor to substantiate the work. All tests were run with aqueous the continuous phase in each circuit.

Copper Circuit

Extraction

Feed to the extraction of copper at pH 4.0 contained, in g/L: 0.4 Cu, 0.4 Pb, 28.5 Zn, 0.003 Fe^{+3} in 3.0M NaCl. The extractant was 5% by volume of Acorga P5300 in Shell 140.

The residence time in each mixer was 0.5 minutes and an A/O ratio of 3.5 was used (311 mL aqueous, 89 mL organic). Typical results for a 2 to 4-stage run are shown in Table 2, indicating good extraction of copper and increasing discrimination over zinc, lead and iron with an increasing number of stages.

Scrubbing and Stripping

Because the major impurity of concern for the subsequent copper electrowinning circuit would possibly be chloride ion, scrubbing was investigated at room temperature using both Na_2SO_4 and water as the scrub solutions, as indicated by the earlier bench-scale tests. Scrubbing was performed at an O/A of 5/1, (300 mL organic, 60 mL aqueous) in 6 stages. The scrubbed solvent was stripped in 3 stages, O/A 6/1, using a strip solution containing 28.7 g Cu/L in 150 g H_2SO_4 /L. The results of scrubbing and subsequent stripping at room temperature, shown in Table 3, indicate that water is as effective as Na_2SO_4 for scrubbing of chloride, and that a relatively high purity of copper strip feed to electrowinning results. Narrower dispersion

TABLE 2 - COPPER EXTRACTION CIRCUIT - EXTRACTANT 5% P5300 IN SHELL 140

STAGE NO.	EQUIL. PH	EXTRACTION			DISCRIMINATION IN LOADING		
		RAFFINATE Cu	SOLVENT Cu	% Cu EXT'D	Cu/Zn	Cu/Pb	Cu/Fe
2	1.29	0.013	1.33	96.3	1700	1320	1500
3	1.30	0.004	1.36	98.8	2300	1360	1900
4	1.29	0.002	1.40	99.8	3500	1400	2300

TABLE 3 - SCRUBBING OF ACORGA FOR CHLORIDE REMOVAL (6 STAGES)

SCRUB SOLUTION	EQUIL. PH	SCRUB SOLUTION ANALYSIS CL ⁻	STRIPPED SOLVENT		STRIP SOLUTION						PURITY IN STRIP		
			Cu (G/L)	CL ⁻ PPM	Cu G/L	FREE ACID G/L	CL PPM	Zn PPM	Pb PPM	Fe PPM	Cu/Zn	Cu/Pb	Cu/Fe
50 G/L Na ₂ SO ₄ WATER	4.2	44 PPM	0.73	10	39.3	129	12.4	6	1	60	6550	39000	5500
	4.17	33	0.67	10	40.3	129	16	5	5	95	8000	8000	425

bands and therefore better coalescence rates were achieved with the water scrub solution. Again, as in the bench tests, a residual amount of approximately 0.7 g Cu/L remains on the stripped solvent in equilibrium with the stripping copper sulphate solution. This residual amount could be removed, if desired, by stripping with a solution containing 150 g H₂SO₄/L, to produce a stripped solvent containing about 0.01 g Cu/L, but at an extra cost. Prior to recycling the stripped solvent to extraction, the solvent is scrubbed with water to remove any sulphate present.

Degradation Tests and Solvent Losses of Acorga

Degradation tests were performed on the solvent to determine whether continual cycling would result in a break-down of the Acorga copper extractant. The test involved recycling Acorga P5300 in a Shell 140 diluent, through the 3 stages of extraction and 3 stripping stages using 15.9 g Cu/L in 150 g H₂SO₄/L. The duration of the test was for 500 cycles of the solvent. The aqueous feed solution contained 4 g Cu/L and 3M NaCl at a feed pH 2.2.

Over the 24 hour period of the run, constant extraction and stripping results were achieved. Various bench tests were performed on the solvent after 500 cycles in order to obtain a plot of an equilibrium isotherm for comparison with that obtained on a fresh solvent in earlier bench studies (14). The data indicated that no change of solvent performance occurred with repeated cycling. Analyses of the solvent for P5300 molarity also indicated no change. Solvent losses reported in the raffinates at <1 ppm of Acorga P5300. Thus the Acorga P5300 appears suitable for extraction of copper from such a chloride medium.

Zinc Circuit

Extraction

The raffinate from the copper circuit, fed to a six-stage zinc extraction circuit, contained 28.5 g Zn/L, 0.016 g Cu/L, 0.40 g Pb/L, 0.003 g Fe Fe⁺³/L, 3.0M NaCl at pH 1.39. The extractant was 60% TBP in Solvesso 150 diluent, pre-equilibrated with 50 g HCl/L at O/A 5/1. Extraction was at ambient temperature at an O/A 2.1/1 (237 mL/min solvent, 113 mL/min aqueous) in 6 stages to obtain a loading of 13.6 g Zn/L. The retention time in each mixer was 1.8 minutes. Following extraction, the loaded solvent was stripped in 6 stages at ambient temperature and O/A 2.5/1 using 15 g Zn/L at pH 1.0 (HCl). No scrubbing was attempted in the initial zinc circuits, but subsequently, following a series of electrowinning studies, scrubbing stages were added. The results for the extraction and stripping circuits are shown

in Tables 4 and 5. As in the bench tests, a residual value of about 2.4 g Zn/L remains in the solvent after stripping. In spite of the fact that no scrub stages were included the purity of the aqueous strip solution with respect to Pb, Fe and Cu was reasonably good as is shown in Table 6.

TABLE 4 - ZINC EXTRACTION CIRCUIT - 60% TBP IN SOLVESSO 150

FEED		RAFFINATE		LOADED SOLVENT (G/L)				EXTRACTION (%)
ZN (G/L)	PH	ZN (G/L)	PH	ZN	PB	FE	CU	ZN
28.5	1.39	2.05	1.0	12.6	.005	.0005	.0002	92.8

TABLE 5 - ZINC STRIPPING CIRCUIT

STRIP FEED			STRIPPED SOLVENT (G/L)			LOADED STRIP (G/L)		
ZN (G/L)	PH	FEED EQUIL.	ZN	PB	FE	ZN	PB	FE
15	1.0	0.83	2.35	.001	.0009	39.5	0.010	0.0007

TABLE 6 - PURITY IN EXTRACTION AND STRIPPING CIRCUITS

	ZN/PB	ZN/FE	ZN/CU
LOADED SOLVENT	2.480	24.800	62.000
LOADED STRIP	3.950	56.400	

Degradation Tests and Solvent Losses of TBP

The solvent losses in the extraction circuit were analyzed at 1-3 ppm. Degradation tests, similar to those for the Acorga P5300, were performed on the TBP, that is, the solvent containing 60% TBP in Solvesso 150 was cycled through the extraction and stripping stages to determine whether any degradation of the TBP occurs after 500 cycles. The aqueous feed and the strip solutions were of the same composition as were used in the continuous testing above. After cycling for 500 cycles, the analysis of the extraction and stripping circuits showed no change. Data from subsequent bench scale verification tests indicated that, in extraction, a slightly lower loading of zinc occurred with used solvent compared to fresh solvent, and that there was no change or build-up of Pb or Fe impurities on the solvent with continual use. As for the stripping circuit, the recycled solvent appeared to be slightly more effective than did the fresh solvent. Chemical analyses of the TBP indicated no change in molarity. Thus there was no evidence of degradation of the TBP with continual use.

Copper and Zinc Electrowinning

Smooth, compact copper deposits were electrowon at 35°C and 269 A/m² (25 A/ft²) current density from the strip electrolytes (Table 3) using 10 mg/L Jaguar C13 as the addition agent. The current efficiency for the 26 h deposits was 98-99%. These results are in good agreement with those obtained for copper electrowinning from simulated electrolytes using a small pilot-scale electrowinning cell (17).

Smooth, compact, dendrite-free, 24 h zinc deposits were electrowon at 35°C and 323 A/m² (30 A/ft²) from a zinc strip electrolyte (38.7 g Zn/L and impurities, in ppm, of 10 Pb, 0.5 Cu, 0.06 Cd, 0.1 Co, 0.6 Fe, 0.1 Ni, <0.1 As, <5 Sb) using a diaphragm cell with electrolyte circulation (by air-sparging) and with 15 mg/L tetrabutyl-ammonium chloride as the addition agent. The current efficiency of 88.9% was improved to 96.2% when the electrolyte was treated with activated carbon prior to electrowinning the zinc. The activated carbon treatment which removed entrained organic matter from the electrolyte, also improved the quality of the zinc deposits. These results are in good agreement with those obtained from zinc electrowinning tests using synthetic electrolytes (16).

Flowsheet

The solvent extraction flowsheets shown in Figures 2 and 3 are the results of testwork in the laboratory and in pilot plant operations. The

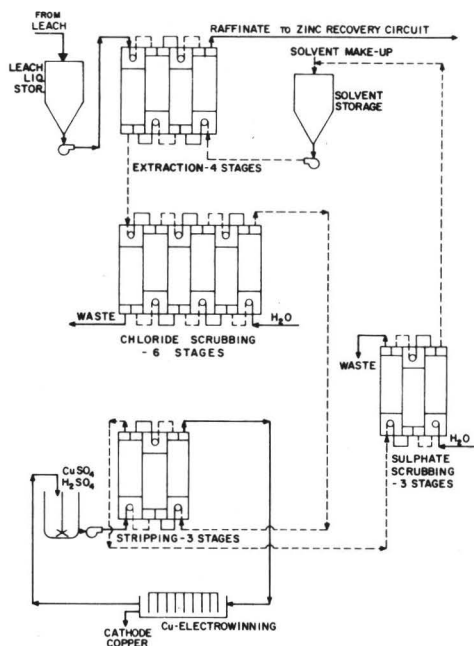


Figure 2 COPPER RECOVERY CIRCUIT

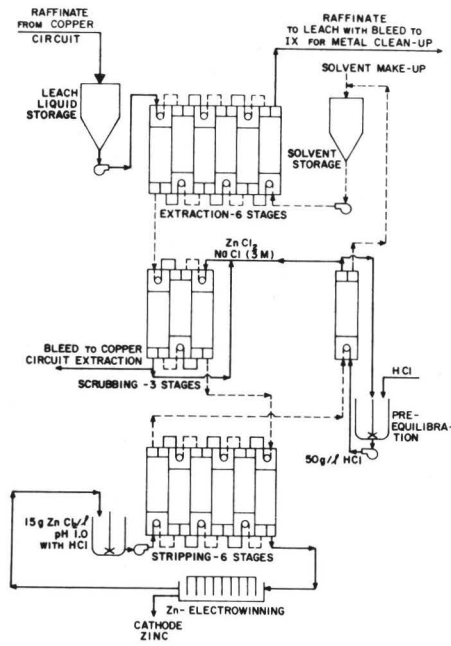


Figure 3 ZINC RECOVERY CIRCUIT

metallurgical balance and the sizing of the equipment are based on an assumed daily feed of 909.8 tonnes (1003 tons) of concentrate to chlorination roasting. Assuming 95% overall recovery in the chlorination-leaching-purification stages, the production will be 259.2 tonnes (285.8 tons) of zinc per day. For a 350 day operation, this is equivalent to 90,703 tonnes (100,000 tons) of zinc annually, corresponding to an hourly solution feed to solvent extraction of 6013 L/min (1323 gal/min) based on a leach solution feed, in g/L, of 30 Zn, 0.4 Cu, 0.4 Pb, 0.002 Fe, in 3.0M NaCl at pH 4.0. These rates and concentrations were used in the sizing of the plant.

Copper Circuit

Extraction of copper is in 4 stages of mixer-settlers, using 5% Acorga P5300 in an aliphatic kerosene diluent such as Shellsol LX 154. At an A/O ratio of 3.5/1, 6013 L/min aqueous (1323 gal/min) and 1718 L/min solvent (378 gal/min), the solvent will load to 1.4 g Cu/L. The retention time in the mixer is 0.5 min. Following extraction, the solvent is scrubbed with water in 6 stages, at an O/A ratio of 5, to remove chloride from the solvent. The mixing time is 1 min. The copper is recovered from the solvent by stripping in 3 stages with return electrolyte from electrowinning, containing 30 g Cu/L and 150 g H₂SO₄/L, at an O/A ratio of 6 and with a retention time in the mixer of 1 min. Sulphate remaining on the solvent after stripping is removed in 3 stages of water scrubbing at an O/A of 8 for 1 min. All settlers were designed on a basis of 73.4 L/min/m² (1.5 gal/min/ft²) settler area.

Zinc Circuit

Zinc extraction is accomplished in 6 stages at an O/A ratio of 2.2 and a flow of 13,225 L/min (2910 gpm) of 60% TBP in Shell Solvesso 150 aromatic diluent. A retention time of 1.8 minutes is used in the mixer. The solvent is scrubbed in 3 stages at an O/A of 3, for 1 minute, with a solution consisting of 25 g ZnCl₂/L in 3M NaCl. Zinc was recovered from the solvent by 6 stages of stripping using return electrolyte containing 15 g Zn/L at pH 1.0 in HCl at an O/A of 2.5 for 1.8 minutes. Prior to recycling the stripped solvent to extraction, the solvent was acid equilibrated with 50 g HCl/L at an O/A of 5 for 1.8 minutes.

Estimated Costs

The estimated plant costs are based on December 1979 prices for an assumed production of 90,703 tonnes (100,000 tons) zinc per year for the two circuits as described. The construction material selected for the two circuits was fibreglass reinforced polyester.

Capital Costs

The estimated capital purchase requirements for the copper and zinc circuits, respectively, are \$1,141,400 and \$3,469,400 resulting in a total estimated purchase cost of \$4,610,800 plus an additional amount of \$9,242,000 for the combined solvent inventories of the two circuits, amounting to \$293,000 and \$8,949,000 for copper and zinc respectively. The total solvent extraction plants fixed capital costs are shown in Table 7 as \$25,438,831.

Based on an amortization of that total, on a 10-year straight line depreciation and 350 days per year, the capital cost for the recovery of copper and zinc by solvent extraction is \$6.53/tonne (\$7.20/ton) concentrate fed to the chlorination stage. This equates to 2.80¢/kg (1.27¢/lb) Zn produced. To that cost must be added the cost of electrowinning. The cost of the copper circuit must be borne by the zinc recovery circuit.

Operating Costs

The total operating costs for such a plant are estimated at \$22.46/tonne (\$20.37/ton) concentrate treated (Table 8). The estimated labor rates were arbitrarily taken as \$10 and \$18 per hour respectively for hourly and staff, resulting in a total labor cost of \$11.61/tonne (\$10.53/ton) concentrate treated. Solvent losses were assumed to be high, 30 ppm for each of TBP and Acorga P5300 and 10 ppm for the diluents. Based on a cost/tonne concentrate treated, the total individual operating costs are \$9.63 and \$12.89 respectively for the copper and zinc. Obviously, at this high cost for copper (with a value of only about \$7.25/tonne (\$8/ton) of the concentrate) the copper must be considered as a by-product, the processing cost of which must be borne by the zinc circuit. On that basis, the cost of Zn produced is \$3.37¢/kg (1.53¢/lb) and 4.50¢/kg (2.04¢/lb) respectively for copper and zinc.

Income

Table 9 shows the daily production value for copper and zinc as \$255,160 or \$280.40/tonne (\$254.40/ton) concentrate treated. No credits have been given for other by-products that will be recovered by other means.

Discussion and Conclusion

This paper has been limited to the solvent extraction, separation and recovery of high purity copper and zinc from the chloride solutions resulting from the chlorination-leach-solvent extraction-electrowinning of complex fine-grained zinc-lead-copper sulphide concentrates. The data presented here have demonstrated the technical and economic feasibility of recovery of copper and zinc from such chloride liquors, using Acorga P5300 and TBP respectively. Also no evident degradation of the two solvents was detected by recycling. Because the copper is present as a minor quantity in the predominantly zinc concentrate, copper recovery should be considered as a necessary step in the purification of a solution for the eventual recovery of zinc. The copper is considered a by-product, with the total costs of copper and zinc being charged to the zinc circuit. Other metal values such as silver, cadmium, lead and sulphur can be considered as potential by-products in the circuit. The cost of recovery of those by-products will probably be more than met by the values recovered.

TABLE 7 - TOTAL SOLVENT EXTRACTION PLANTS FIXED CAPITAL COSTS FOR CU AND ZN CIRCUITS

TOTAL ESTIMATED PURCHASE COSTS	\$4,610,800
INSTALLED EQUIPMENT COST (x 1.43)	\$ 6,593,000
PIPING (20% OF INSTALLED COST)	1,319,000
INSTRUMENTATION (10% OF INSTALLED COST)	659,000
BUILDINGS AND SITE (15% OF TEPC)	692,000
AUXILLIARIES (E.G., ELECTRIC POWER)(10% OF IEC)	132,000
OUTSIDE LINES (10%)	132,000
TOTAL PHYSICAL PLANT COSTS	\$ 9,527,000
ENGINEERING AND CONSTRUCTION (55% OF TOTAL PHYS. PLANT COSTS)	5,240,000
CONTINGENCIES (15% OF PPC)	1,429,000
TOTAL SOLVENT INVENTORY COST	9,242,000
TOTAL PLANT FIXED CAPITAL COSTS	\$25,438,000

TABLE 8 - OPERATING COSTS FOR SOLVENT EXTRACTION CIRCUITS (Cu & Zn)

	¢/TONNE CONC. TREATED	¢/KG ZN PRODUCED
LABOUR, MAINTENANCE AND ADMINISTRATION	11.61	4.08
DEPRECIATION	7.94	2.78
REAGENTS (INCL. SOLVENT LOSS)	2.72	0.95
POWER (3.0¢/KWH)	0.19	0.07
	22.46	7.88

TABLE 9 - DAILY PRODUCTION AND VALUE

	PRODUCTION LBS/DAY	DAILY VALUE	\$/TONNE CONC. TREATED
CU AT \$1.23/LB	7,620	\$ 9,372	
ZN AT \$0.43/LB	571,600	245,788	
		\$255,160	
CU + ZN			\$280.46

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ALUMINUM-IRON SEPARATION FROM HYDROCHLORIC SOLUTIONS
OF ACID LEACHED ALUMINO-SILICATE ROCKS

A. Cocco; I. Colussi; I. Kikic; S.
Meriani

Applied and Industrial Chemistry Ins-
titute - University of Trieste -
Via Valerio, 2 - 34127- Trieste, Italy

ABSTRACT

The extraction of iron (III) from a hydrochloric solution containing aluminum and potassium ions was examined. The solution was obtained through a leaching procedure developed for the production of alumina from alumino-silicate rocks, in particular leucite-bearing rocks.

After an outline of the flow-sheet applied in a preliminary stage of the research for the separation of iron, aluminum and potassium ions from the acid solution with classic methods based on well-known chemical reactions, the present paper discusses a modified application based on the experimental results obtained by introducing solvent extraction techniques.

INTRODUCTION

The object of the present study is the behaviour of iron, aluminum and potassium ions in a solvent extraction system involving hydrochloric solutions and different extractants, in order to assess the feasibility of a process for the recovery of aluminum from alumino-silicate rocks.

The investigation is carried out on a hydrochloric solution obtained through a leaching procedure applied to leucite-bearing rocks. This process is based on three main operations: firing of the as-mined raw material, acid leaching of the ground glassy mass with consequent silica separation, iron and aluminum hydroxides step separation followed by potassium chloride recovery. The main new feature of this procedure is that it is possible, and even best, to treat the rock as-mined directly. The same procedure may be successfully applied also to other alumina-bearing rocks (e.g., some types of clay).

In a previous communication (1), the separation of iron, aluminum and potassium from the hydrochloric solution was performed applying precipitation techniques.

In the present paper, this section of the process is reinvestigated in order to disclose a feasible route to separate iron and aluminum using solvent extraction methods.

FLOW-SHEET OUTLINE

The formerly proposed process is outlined in FIG.1. The rock was ground and milled down to a 250 microns size; the resulting powder was pressed into pellets to be easily handled and brought to the firing kiln where they went through a firing cycle which was formerly tested and reported (1). With a heating rate of about 250 °C/h up to a 1200 °C peak temperature and a soaking period lasting about one hour, the fired mass could be water-quenched to deliver an easily friable material. To assure for a rapid chemical attack, this prefired material was milled down to 100 microns and then mixed with hydrochloric acid solution 4.6 N concentration.

The chemical reaction was carried out at boiling-simmering temperature. After one hour, heating was closed down and the mixture left to settle out the silica residue. The solution was made free of the solid residue, which was stored after washing for further treatment and analysis.

The composition of the leucite-bearing rock, of the acid solution after the leaching step and of the dried amorphous silica is reported in TABLE 1.

TABLE 1

	Feed rock wt%	Acid solution wt%	Residue wt%
SiO ₂	52.2	-	99.7
Al ₂ O ₃	18.7	18.6	0.03
K ₂ O	10.0	9.9	0.07
Fe ₂ O ₃	7.0	6.7	0.05
Na ₂ O	2.9	2.3	0.07

Adding a certain amount of KOH 3 N concentration to the solution (containing iron, aluminum, potassium and other minor amounts of other metal chlorides) to reach a pH value of about 13, resulted in the precipitation of the iron hydroxide, maintaining the aluminate ion in solution.

Aluminum hydroxide was precipitated by the well-known carbonation method, which consisted in allowing a stream of CO₂ to bubble through the strong alkaline solution. The pH was lowered at a 6.7 value at which the Al(OH)₃ was considered quantitatively separated.

Potassium was recovered as the chloride by the addition of small amounts of HCl; in this manner the mother liquor from KCl separation was recycled to the leucite-bearing rock leaching step. Other details of this process are reported in the previously mentioned paper (1). The recovered aluminum oxide scored a 99% purity and above 91% recovery.

With this procedure, the rock as-mined can be treated. The enrichment operations (selective crushing and magnetic separation) considerably raised the cost of the concentrate material, which amounted 20-25% of the whole rock only, and the enrichment resulted in a higher K₂O content of the concentrate, leaving the

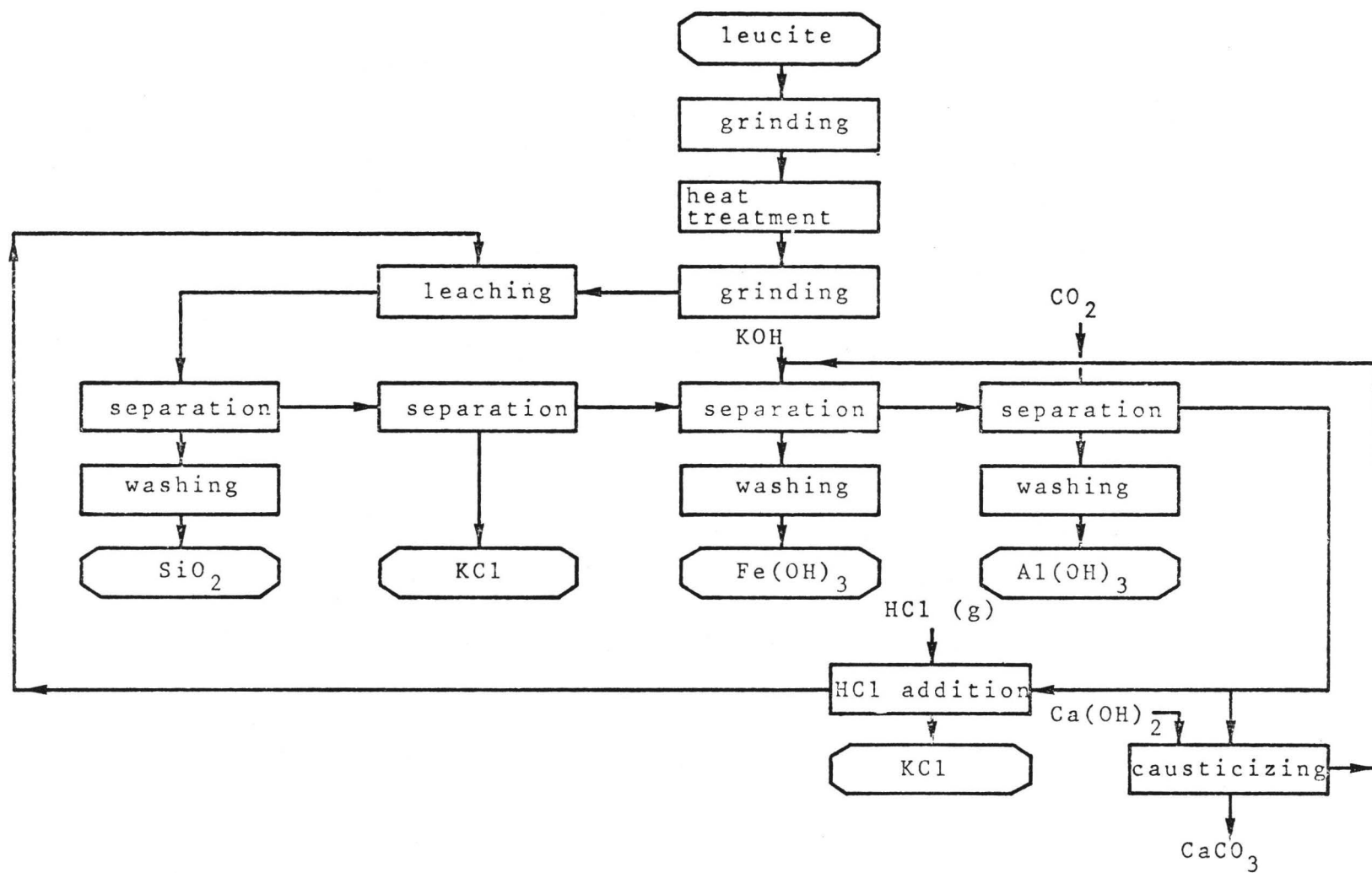


FIG. 1

Al_2O_3 content practically unaltered; in other words this means high percents of Al_2O_3 in the left-over raw material.

As a matter of fact, some of the magnetic silicate rocks which accompany leucite mineral do contain as much aluminum as leucite does. Their participation to the leaching process greatly influences the recovery figures, because some of them are not soluble in the dilute solution of hydrochloric acid by which the pure leucite mineral is rapidly dissolved. In order to make the raw material prompt for being processed by chemical means, they should be either freed of insoluble matter or treated to be transformed into a less resisting phase composition. Any enrichment operation acts accordingly these needs; however sometimes up to 75% of the original rock is left over as a waste by-product. In order to reduce this limiting feature, the thermal treatment was conceived and applied to the rock as-mined.

In the present paper, the separation section is reinvestigated. The separation of iron hydroxide was said to be performed with a solution of KOH 3 N concentration. In this way volumes are greatly increased; however, in this way the heat output was limited to the neutralization, avoiding the heat of hydration of solid potassium hydroxide. Better results could be obtained applying solvent extraction procedures. For this reason, many extractants have been taken into consideration in order to make the whole process studied more economic.

EXPERIMENTAL SECTION

The extractants used are:

methyl isobutyl ketone	MIBK
tri ethyl phosphate	TEP
tri butyl phosphate	TBP
tri 2 ethyl hexyl phosphate	T2EHP
isodecyl diphenyl phosphate	IDDP
bis 2 ethyl hexyl sebacate	B2EHS
bis 2 ethyl hexyl phthalate	B2EHP
di hydroxi ethyl formate	DHEF
N-ethyl o,p-toluene sulfonamide	NETSA

The composition of the initial aqueous hydrochloric solution after silica separation was:

Al^{3+}	1.94×10^{-2} g/cc	Ca^{2+}	0.54×10^{-2} g/cc
K^{+}	1.59×10^{-2} g/cc	Na^{+}	0.41×10^{-2} g/cc
Fe^{3+}	0.94×10^{-2} g/cc	Mg^{2+}	0.19×10^{-2} g/cc

Tests were carried out using various extractants and different concentrations. Working solutions of the extractants were made up by volumetric dilution with Solvesso 100, as indicated in TABLE 2. All extractants were analytical grade.

Equal volumes (50 ml, if not differently indicated) of organic and aqueous phases were added into 100 ml glass-stoppered conical flasks and shaken for 30 seconds. After shaking, the phases were allowed to disengage; the extraction equilibrium was obtained in a thermostated chamber maintained at a temperature of $25 \pm 0.5^\circ\text{C}$. Portions of the aqueous solution were then diluted, and their metal contents determined using a Perkin-Elmer model 300 atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

The experimental results are listed in TABLE 2.

A comparison of the different extractants can be made on the basis of the results obtained in the tests carried out with out the diluent. It clearly appears that the best results are given by the phosphates and by methyl-isobutyl-ketone (2)(3). The latter, like triethyl-phosphate, is highly soluble in water; it is known that the solubility is an important criterion in the choice of an extractant, as the economic feasibility of a solvent extraction process depends on the small losses of extractant during the production cycle. On the other hand, phosphate esters obtained from long-chain alcohols give rise to serious problems because of their high viscosity. For the further tests, therefore, the low-cost and easily available tributyl-phosphate was chosen, which has already found widespread applications in many industrial extraction cycles (4)(5). This extractant is effective in the extraction of iron even if it is diluted in Solvesso 100 and its ratio to the feed is 1:3.

The flow-sheet of FIG.1 can be modified looking at a solvent extraction system, avoiding the previously mentioned steps of iron and aluminum separation by means of precipitation techniques which are more difficult and more expensive in respect to solvent extraction methods.

The system TBP-Solvesso 100 in proper proportions gives a quantitative separation of iron from aluminum with small losses of potassium.

CONCLUSIONS

The possibility of a quantitative separation of iron (III) from aluminum in hydrochloric solutions was tested. The best extractants are phosphates, in particular tributyl-phosphate, as it is a low-cost extractant and its recovery from the extract can be performed with methods already tested in industrial plants. The introduction of this solvent extraction technique in the formerly studied process for the recovery of alumina from alumino-silicate rocks can give rise to many advantages in the chemical plant, as the neutralization step for iron hydroxide precipitation is avoided and also losses of aluminum in this step are reduced.

At present, the modelling of the extraction process is examined in order to study the influence of different factors on the degree of extraction and to optimize the whole process.

TABLE 2

	Extractant (E)	Diluent (D)	Ratio Feed/(E+D)	Extraction %		
				Fe ³⁺	Al ³⁺	K ⁺
MIBK	100 %	0 %	1:1	99.95	0.00	31.03
MIBK	80 %	20 %	1:1	99.69	0.00	11.11
MIBK	15 %	85 %	1:1	4.26	0.00	16.67
TEP	60 %	40 %	1:1	99.36	0.00	1.02
TEP	15 %	85 %	1:1	76.60	0.00	11.11
TBP	100 %	0 %	1:1	99.96	0.00	23.07
TBP	80 %	20 %	1:1	99.97	0.00	11.11
TBP	60 %	40 %	1:1	99.98	0.00	16.67
TBP	80 %	20 %	1:3	99.99	0.00	1.15
TBP	80 %	20 %	3:1	99.97	0.00	16.67
T2EHP	100 %	0 %	1:1	99.99	0.00	24.87
IDDP	100 %	0 %	1:1	99.87	0.00	5.56
IDDP	15 %	85 %	1:1	4.26	0.00	11.11
B2EHS	100 %	0 %	1:1	53.18	80.00	2.06
B2EHP	100 %	0 %	1:1	53.18	67.00	1.88
DHEF	100 %	0 %	1:1	78.72	0.00	11.11
DHEF	15 %	85 %	1:1	4.26	0.00	11.11
NETSA	80 %	20 %	1:1	99.99	0.00	33.33
NETSA	15 %	85 %	1:1	4.44	0.00	11.11

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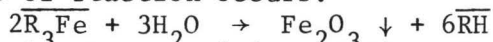
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THE APPLICATION OF HYDROLYTIC STRIPPING
TO THE IRON PROBLEM IN HYDROMETALLURGY

A.J. MONHEMIUS and G. THORSEN
 Dept. of Metallurgy Dept. of Chem. Engng.,
 & Materials Science, Norwegian Institute
 Royal School of Mines, of Technology,
 Imperial College, 7034 Trondheim-NTH,
 London SW7 2BP, U.K. Norway.

ABSTRACT

The problems encountered in the production of environmentally safe iron residues by current aqueous phase hydrolysis methods are discussed. The technique called hydrolytic stripping is described. This involves reacting an iron-loaded carboxylic acid solution with water at 150-200°C, whereupon the following type of reaction occurs:



Iron is thus precipitated directly as hematite and the carboxylic acid is regenerated and can be recycled to extraction. The advantages of this technique compared with conventional iron precipitation processes are outlined. An alternative technique, called precipitation stripping, is also described. In this, the iron-loaded carboxylic acid is heated with dilute mineral acid solutions at 100°C at atmospheric pressure, with the result that iron precipitates from the mixed system, normally as a hydrated oxide. The application of solvent extraction and hydrolytic stripping to iron removal in the electrolytic zinc process is outlined.

INTRODUCTION.

"The problem of iron in hydrometallurgical processes, both in solution and in residues, has not yet been resolved to the satisfaction of either metallurgists or environmentalists."

This statement, which was made five years ago (1), is still an accurate assessment of the current situation with respect to the iron problem in hydrometallurgy. There are various facets to the overall problem, but one of the most pressing is the removal of iron from acidic leach liquors which has yet to be resolved in a fully satisfactory manner.

Over the past fifteen years, great progress has been made in the application of hydrolysis methods to the precipitation of iron from such liquors. The most important development was the introduction of the Jarosite process, whereby iron can be precipitated from acidic sulphate liquors as crystalline, easily filterable, basic sulphates known as jarosites $MFe_3(SO_4)_2(OH)_6$. This process has been adopted in particular by a large number of electrolytic zinc plants and this has led to a very significant increase in the overall recovery of zinc that can be achieved by the electrolytic route. More recently, the Goethite and Hematite processes have been developed, both designed to do much the same as the Jarosite process.

All three processes can achieve their primary objective, namely the removal of iron from acidic leach liquors, in a technically successful manner. However the outstanding problem, which is growing more acute in certain parts of the world, is the disposal of the iron residues generated by these processes in an environmentally acceptable manner. The problems involved are illustrated by the data given in Table 1, where it may be seen that the iron products are contaminated by significant quantities of zinc and sulphur. The former arises principally from zinc calcine, which is added during the precipitation of iron to neutralise the acid produced by the hydrolysis reactions, while the latter is due either to the incorporation of sulphate in the crystal lattice of the iron product or to the co-precipitation of basic sulphates. Furthermore, the iron precipitates are prone to further contamination by small but significant amounts of other heavy metals which may be present in the leach liquors due to secondary effects such as adsorption, occlusion or co-precipitation.

TABLE 1. Compositions and quantities of iron residues (2)

<u>Process</u>	<u>Jarosite</u>	<u>Goethite</u>	<u>Hematite</u>
Wt. residue/wt.			
Zn concentrate	0.4	0.25	0.18
Fe wt. %	25-28	40-45	58-60
Zn wt. %	4-6	5-8	0.5-1.0
Total S wt. %	10-12	2.5-5	3

This contamination of the iron residues makes them unacceptable for further uses such as iron-making and the only remedy is to dispose of the residues by dumping. However, weathering of the dumps leads to leaching of the contaminating elements and this effect can create serious problems of containment and treatment of the run-off effluents from the dumps.

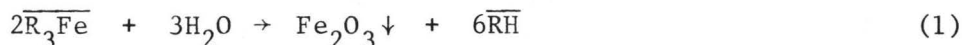
At the present time, these difficulties are most evident in the electrolytic zinc industry, but similar problems arise in other hydrometallurgical processes, particularly those designed to treat sulphide concentrates by acid leaching.

The obvious solution to this situation would be to devise a method for precipitating iron from solution as a clean, uncontaminated solid, preferably an oxide, which could be utilised as feed to an iron-making process, thereby obviating the need for dumping. However, judging by the results of the considerable amount of research and development effort expended over the past decade or so, this goal does not appear to be achievable if precipitation of iron is carried out from an aqueous phase. Even if the iron solution is highly purified prior to precipitation, contamination of the precipitate with the anion present in solution is almost inevitable.

In spite of the fact that ferric iron can be readily removed from aqueous solutions by solvent extraction, by organic acids for example, or amines in the case of chloride solutions, very few applications of this process for iron extraction are in commercial use. One of the reasons for this is that solvent extraction as currently practised does not solve the fundamental iron problem - it merely transfers iron from one aqueous solution to another. The iron will finally report in an aqueous strip liquor from which it still has to be precipitated for ultimate disposal. However, the new technique of hydrolytic stripping (3), by which iron oxides can be precipitated directly from organic phases, offers an alternative approach to the iron problem,

which shows promise of overcoming the difficulties associated with aqueous phase precipitation outlined above.

Hydrolytic stripping, which has been shown to be applicable in particular to organic phases containing alkyl carboxylic acids, involves heating an iron-loaded carboxylic acid solution with water to temperatures in the region of 150-200°C, whereupon the following type of reaction occurs:-



where a bar over a species indicates that it is in the organic phase and R represents the alkyl carboxylic radicle. Thus by this simple procedure, iron is precipitated directly from the organic phase as an oxide and the carboxylic acid is regenerated in the acid form for recycle to extraction. At the elevated temperatures required for the process, thermal stability is a primary requisite of the organic acid utilised to carry the iron. In addition to alkyl carboxylic acids, alkyl phosphoric and alkyl sulphonic acids have been examined, but neither of these has shown the necessary thermal stability. In all the experimental work reported below, Versatic acids, commercially available, tertiary alkyl carboxylic acids, produced by Shell, have been used.

EXPERIMENTAL

Solutions of 33% by volume Versatic 10 in Escaid 110 were used. Iron was loaded into the organic phase by first dissolving solid CaO into the Versatic acid solution by heating and stirring and then vigorously shaking the calcium-loaded organic solution with aqueous ferric chloride solution. After iron loading, the organic solutions were washed with acidified water to remove residual calcium and then filtered through phase-separation paper to remove entrained water.

Kinetic studies on the rates of hydrolytic stripping at elevated temperatures were carried out in a stainless-steel autoclave of 300 ml internal volume, equipped with an efficient stirrer and a sampling system. The required volume of iron-loaded organic phase (usually 120 to 200 ml) was heated to the reaction temperature in the sealed autoclave, usually under a nitrogen atmosphere. After temperature stabilisation, a sample of the organic phase was taken and then the required volume of water (usually 10 ml) was injected into the autoclave from a reservoir. Samples of the organic phase were then taken periodically, via the sampling system, immediately filtered, and stored for later analysis by atomic absorption.

Experiments on precipitation stripping at the boiling point were carried out in a stirred glass reaction vessel of 250 ml volume, heated by an electric mantle. The required volume of iron-loaded organic phase (usually 100 ml) was put in the reaction vessel and heated with stirring to 100°C. The required volume of aqueous phase (usually 100 ml), containing the appropriate concentration of acid, was heated to the boiling point and then added to the hot organic phase in the reaction vessel to start the reaction. The rate of reaction was followed by periodically withdrawing samples of the mixed phases from the vessel by pipette. These were allowed to separate, any solids were filtered off, and then the iron contents of each phase were determined.

The acid values of the organic phases before and after stripping were determined by potentiometric titration. Residual iron was first removed from the organic phase by mineral acid stripping followed by water washing.

Weighed amounts of organic phase were then dissolved in ethanol and titrated with standard aqueous sodium hydroxide solutions.

RESULTS

1) Hydrolytic Stripping.

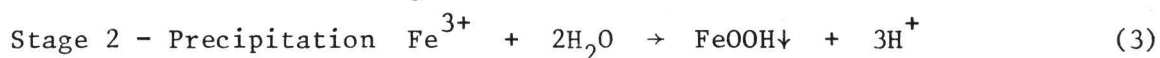
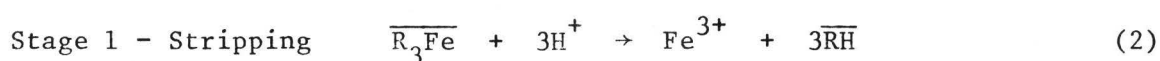
The effect of temperature on the rate of precipitation of ferric iron from solutions of Versatic 10 reacted with water is shown in Figure 1. It may be seen that the rate of precipitation is strongly influenced by temperature. At 150°C only approximately 15% of the iron had been precipitated after 2 hours, whereas at 185°C virtually total precipitation had occurred within 20 minutes. At temperatures below 200°C the iron oxide product was usually hematite and the overall reaction may be represented by Equation (1). The particle size range of the precipitates generally increased with temperature - the d_{50} (particle size at 50% cumulative weight) rising from 20 μ at 170°C to 40 μ at 215°C. No major difficulties were experienced with filtration of the organic/oxide slurries and simple acetone washing reduced levels of adsorbed organic to less than 1% by weight of the solid products.

At reaction temperatures of 200°C and below, there was no observable change in the acid value of the organic phase after hydrolytic stripping and it was concluded that Versatic acid was stable under the reaction conditions at least up to 200°C.

The rate data shown in Figure 1 strongly suggest that the precipitation of hematite in this system occurs by a nucleation and growth mechanism. Further evidence of this is provided by the effect of "seeding" shown in Figure 2. These data were obtained by adding to the system iron oxide precipitated in a previous experiment. The presence of the solid particles in the system at the beginning of the reaction provided growth sites and reduced the nucleation period, with the result that the time required for total precipitation was substantially reduced. This procedure also increased the mean particle diameter of the oxide product.

2) Precipitation Stripping.

Although hydrolytic stripping, using water as the stripping agent, has a number of advantages as outlined in the following discussion, pressurised equipment is necessary to contain the water vapour pressures at the elevated temperatures required for the process. It is however possible to carry out similar reactions at temperatures close to the boiling point at atmospheric pressure. In order to do this it is necessary to change the stripping agent from pure water to a dilute mineral acid solution. The presence of acid in the aqueous phase is required to initiate stripping of iron from the organic phase. Thereafter the reaction is self-sustaining due to the production of hydrogen ions during the hydrolysis and precipitation of iron. Experimental evidence suggests that, under these conditions, the overall reaction occurs in two stages:-



The hydrogen ions formed in Stage 2 are then available to continue the Stage 1 reaction. Thus the metal is precipitated from the aqueous phase, and stripping is a separate, albeit interrelated, process. For this reason

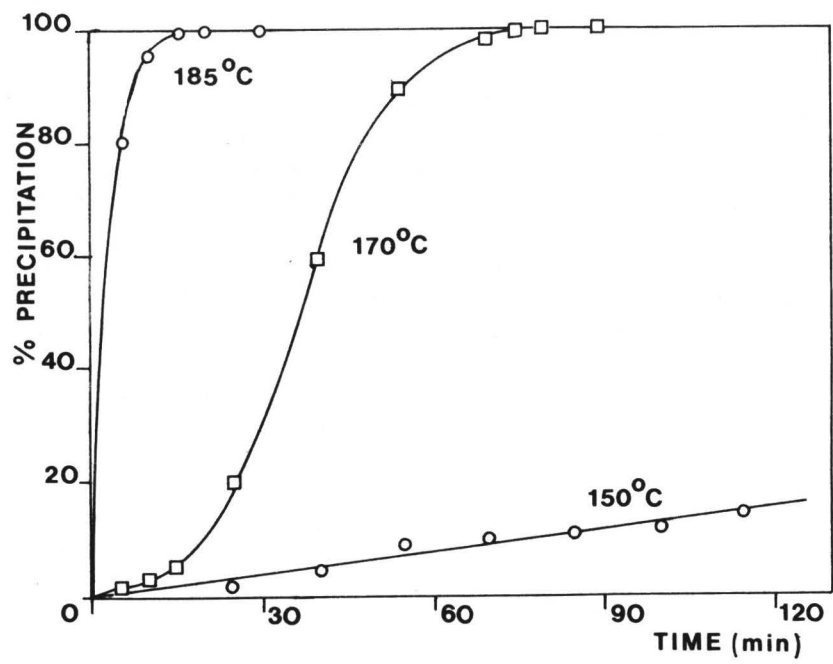


FIG 1.

Hydrolytic stripping: effect of temperature on rate of precipitation.
Organic phase: 120 ml 33% Versatic 10 containing 10.5 g/l Fe^{3+} . Aqueous phase: 10 ml H_2O .

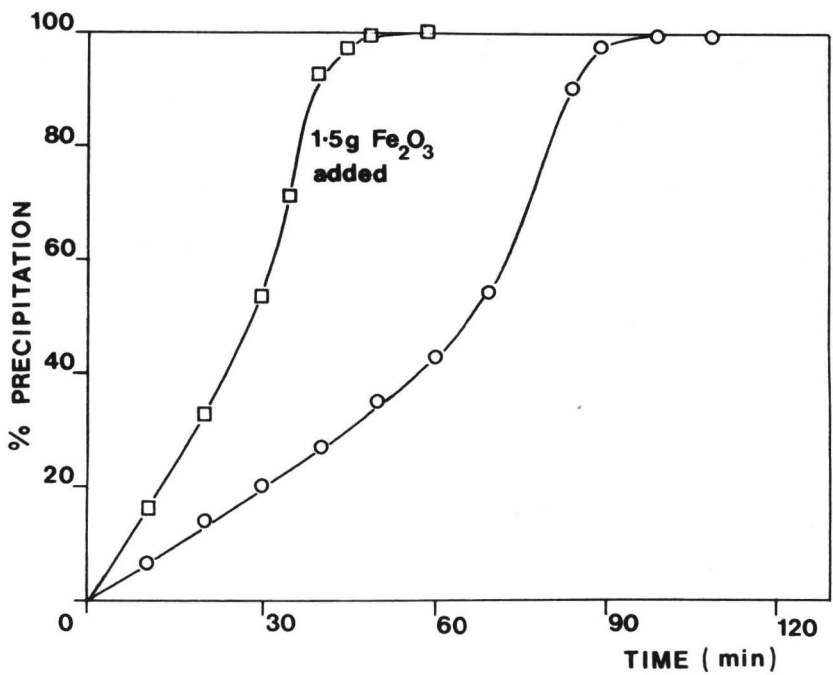


FIG 2.

Hydrolytic stripping: effect of recycled solids on rate of precipitation.
Temperature: 170°C. Organic phase: 200 ml 33% Versatic 10 containing 21.5 g/l Fe^{3+} . Aqueous phase: 10ml H_2O .

this type of reaction at the normal boiling point has been named "precipitation stripping" to distinguish it from hydrolytic stripping, where pure water and elevated temperatures are used.

As can be seen from equations (2) and (3), unlike conventional aqueous hydrolytic precipitation there is no necessity to add a neutralising agent during the reaction. The system is self-buffering, with the basic organic acid radicle consuming the hydrogen ions produced by the hydrolysis of iron.

Sulphuric acid can be used to initiate the reaction. Figure 3 illustrates results obtained when solutions of Versatic 10 containing about 25 g/l Fe^{3+} were reacted at 100°C with equal volumes of dilute sulphuric acid, containing from 5 to 40 g/l H_2SO_4 . The results show the concentrations of iron in the organic and aqueous phases as a function of reaction time, together with the percentage of iron precipitated as a solid product and the changes in pH of the aqueous phases.

It may be seen that with an aqueous phase containing 5 g/l H_2SO_4 , no reaction occurred and all the iron remained in the organic phase. This was because the pH of the aqueous phase was about 5 and was too high to cause stripping. However at 10 g/l H_2SO_4 the aqueous phase was sufficiently acidic for stripping and subsequent precipitation to occur and, after 6 hours, over 95% of the iron had been removed from the organic phase and precipitated from solution. At an initial acidity of 20 g/l H_2SO_4 the stripping rate was considerably faster, with over 95% of the iron removed from the organic phase in 2 hours. However, the percentage of iron precipitated was reduced due to the lower pH of the aqueous phase and the consequent higher solubility of iron in this phase. This effect was accentuated with an initial acidity of 40 g/l H_2SO_4 .

The form in which iron is precipitated depends on the composition of the aqueous phase and the concentration of iron in the organic phase. For sulphuric acid stripping, the iron product is usually goethite, FeOOH , except when the initial sulphate/iron ratio in the system is high, i.e. when the sulphuric acid concentration of the aqueous phase is high or the iron concentration in the organic phase is low. Under these conditions, basic sulphates such as glockerite, $\text{Fe}_4\text{SO}_4(\text{OH})_{10}$, or jarosite, $\text{H}_3\text{OFe}_3(\text{SO}_4)_2(\text{OH})_6$, may be formed. If hydrochloric acid is used in place of sulphuric acid, then the iron product is normally hematite, Fe_2O_3 .

As in the case of hydrolytic stripping, the rate of precipitation stripping can be considerably increased by "seeding" with solids recycled from previous runs. A comparison of runs (c) and (e), shown in Figure 3, illustrates this effect. Furthermore, this procedure promotes particle growth and greatly improves the solid/liquid separation characteristics of the precipitates.

DISCUSSION.

The unique characteristic of hydrolytic stripping is that iron is precipitated directly from loaded carboxylic acid solutions by reaction with pure water. Because of the strong affinity of carboxylic acids for iron, the organic phase can be purified to any desired degree by standard solvent extraction techniques prior to stripping. Therefore there need be no inorganic ions in the system, except iron and those derived from water itself, with the result that the product of the process is pure iron oxide, uncontaminated

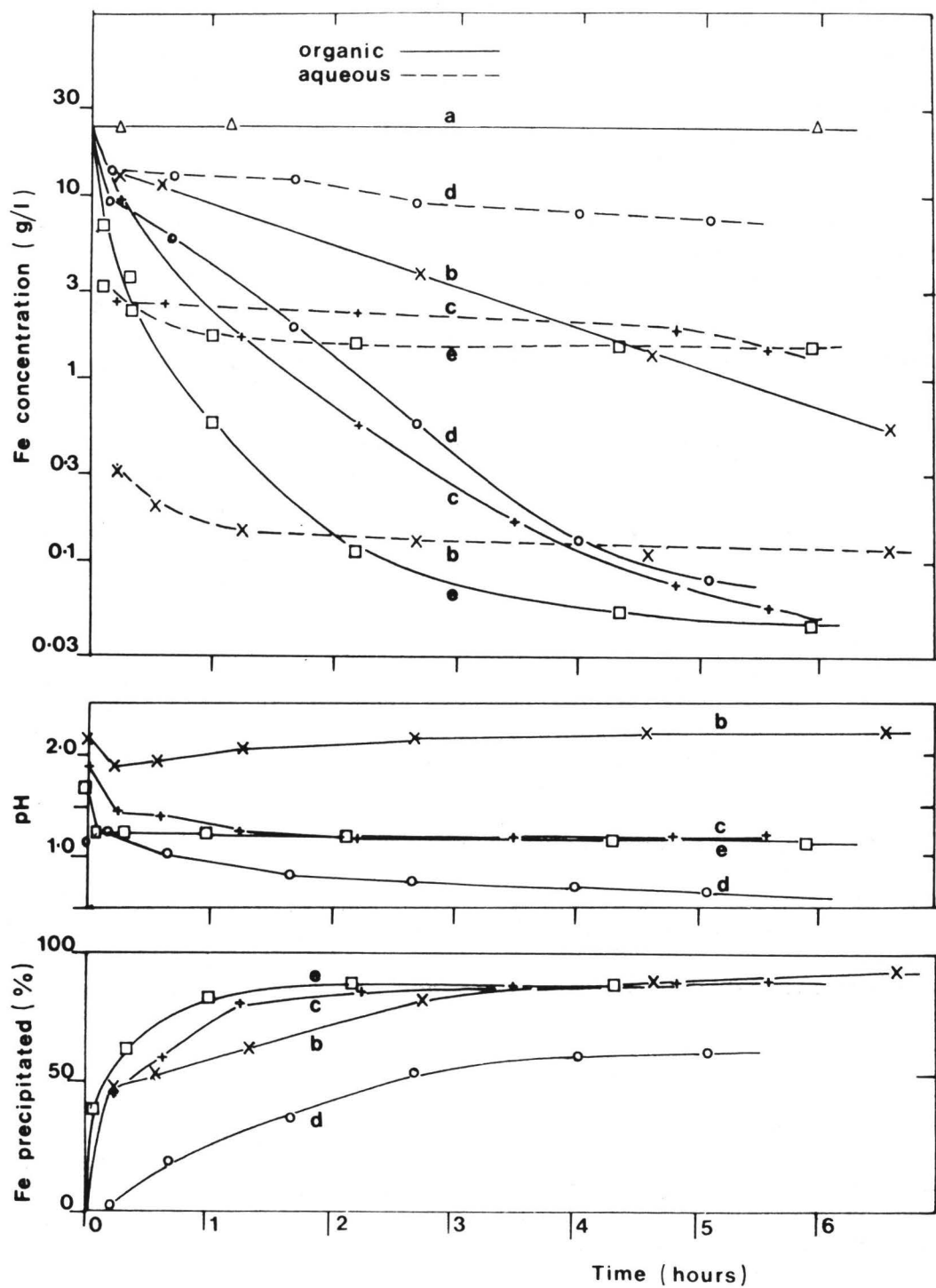


FIG 3.

Precipitation stripping: Rate of change in organic and aqueous iron concentrations, aqueous pH and percent precipitation.
Temperature: 100°C. Organic phase: 100 ml 33% Versatic 10 containing 25 g/l Fe³⁺. Aqueous phase: 100 ml containing H₂SO₄ at (a) 5 g/l, (b) 10 g/l, (c) 20 g/l, (d) 40 g/l and (e) 20 g/l, plus 3.5 g recycled FeOOH.

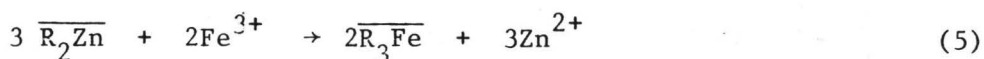
by inorganic anions or cations. This is the key difference and major advantage of hydrolytic stripping compared with conventional aqueous phase hydrolytic precipitation. The iron oxides from hydrolytic stripping should therefore be suitable for further use, particularly in iron-making processes. It is likely, of course, that the oxide will be contaminated by some adsorbed organic phase, but this will merely act as "free" reducing agent during iron-making.

A secondary advantage of the process is that it reduces the number of unit operations required to produce a solid product via solvent extraction, since the conventional stripping stages are eliminated. Pressurised equipment will be necessary because of the elevated temperature required. However, as illustrated in Figure 1, reaction rates can be made to be very rapid and therefore throughputs in the pressurised equipment will be high - a simple pipeline reactor may suffice.

Although hydrolytic stripping offers considerable potential advantages over current processes used for iron removal from process liquors, the major economic problem is likely to be the cost of loading iron into the carboxylic acid in the first place. Because extraction occurs by a cation exchange mechanism, the protons produced during the reaction have to be neutralised in order to bring about full metal loading in the organic phase. For a low-value product like iron, direct neutralisation with an alkali will often not be economically viable and an alternative method has to be sought. In the case of iron removal from zinc process liquors, the alkaline property of zinc calcine, ZnO, can be used to overcome this problem, as discussed in a recent paper by Thorsen and Grislingas (4). Briefly, the technique is to react the carboxylic acid solution directly with the zinc calcine to produce an organic solution containing zinc carboxylate:-



This step is termed organic leaching. The zinc carboxylate solution is then contacted in a conventional solvent extraction system with the main iron-bearing aqueous zinc leach liquor, where an exchange extraction mechanism occurs, with iron entering the organic phase and being replaced in the aqueous phase by zinc:-



Thus the combination of organic leaching and exchange extraction enables iron to be removed from the main leach liquor into the organic phase without any extraneous alkali requirement. The overall organic cycle can then be completed by utilising hydrolytic stripping for iron removal. A conceptual flowsheet of the integrated process is shown in Figure 4.

The main practical difference between hydrolytic stripping and the alternative technique discussed in this paper, namely precipitation stripping, is that in the latter method pressurised equipment is not necessary. However, this apparent advantage is offset by the fact that it is necessary for the aqueous phase to contain mineral acid. This of course introduces a source of inorganic anions into the system and therefore anion contamination of the iron product must be expected. Nevertheless the iron product from precipitation stripping is still likely to be purer than those produced by current aqueous phase hydrolytic processes, for the following reasons.

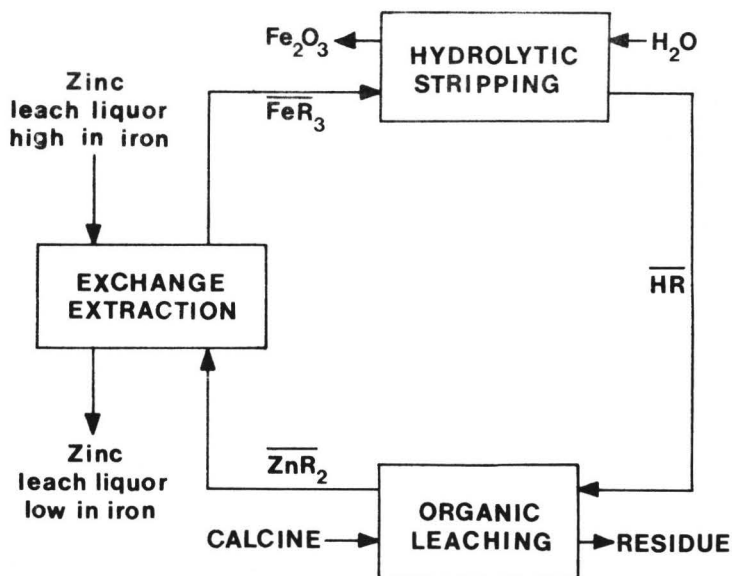


FIG 4.

Conceptual flowsheet for integrated zinc-iron exchange extraction process.

Firstly, traces of contaminating cations can be eliminated from the organic phase prior to precipitation and, secondly, no neutralising agent has to be added during precipitation because of the self-buffering property of the precipitation stripping system.

CONCLUSION

The techniques outlined in this paper are clearly not a panacea for all aspects of the iron problem in hydrometallurgy. Nevertheless, it is believed that the basic concept of direct hydrolytic reaction with iron contained in an organic phase, where it is chemically isolated from the usual sources of contamination, is one which may help to overcome some of the problems encountered when dealing with aqueous solutions containing this ubiquitous element.

ACKNOWLEDGEMENTS.

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NEW PROCESS FOR THE RECOVERY OF URANIUM
FROM PHOSPHORIC ACID

P. MICHEL*, G. RANGER*, P. COROMPT*,

P. BON**

* COGEMA

** APC

Branche Uranium

Département

La Boursidière

Procédés B

92357 - Le Plessis

31053 - Toulouse

Robinson Cedex

Cedex

ABSTRACT

A process for the recovery of uranium from wet-process phosphoric acid has been perfected by COGEMA and APC using tests from laboratory up to semi-industrial pilot scale.

In laboratory and small pilot unit, the process was defined mainly from a physico-chemical point of view. In the last step the phosphoric acid preparation before uranium solvent extraction and entrained solvent elimination were particularly investigated. Several extraction equipments were also tested. The whole of the achieved results have allowed to reach the decision of undertaking an industrial operation.

INTRODUCTION

The increasing uranium price rates since 1975 have given a new interest to uranium recovery from wet process phosphoric acid. Several industrial scale units are now working (or about to start) in U.S.A.

Taking into account the available amounts of uranium in phosphate rocks processed in France or in countries other than the U.S.A., it appeared that uranium recovery ought to be studied. C.E.A. specialists had a large experience in uranium chemistry and solvent extraction, but needed information on phosphate industry. So C.E.A. associated with A.P.C. who operates several phosphoric acid plants, particularly in Grand Couronne, and was experienced in solvent extraction too. Later C.E.A. transferred its industrial activities to a subsidiary Company called COGEMA. When A.P.C. was integrated in the CdF-Chimie group, collaboration then went on between COGEMA and CdF-Chimie.

The purpose of the program, the experiments effected and the main results achieved are dealt with in the present paper.

I) PREVIOUS SITUATION

At the start-up of the studies program, three processes (patented in U.S.A.), the aim of which was uranium solvent extraction from 30 % P_2O_5 phosphoric acid, were known.

I.1. - Two cycle processes using TOPO-D₂EHPA (1)

Uranium + 6 is extracted using a synergistic mixture of 0.125 M TOPO - 0.5 M D₂EHPA (optimum composition). Stripping is carried out using uranium reduction with ferrous iron in phosphoric acid. This first cycle achieves a first purification step and a concentration factor of 80. The second cycle after uranium reoxidation, is quite similar but from a phosphoric solution more concentrated in uranium, a high uranium saturation of the solvent is achieved and therefore the extraction is better. Uranium is stripped using ammonium carbonate and ammonia, generally as crystallized AUTC. The two main criticisms which can be passed on that process are :

- Stripping using uranium reduction is actually possible but rather difficult to carry out. Particular precautions have to be taken to prevent a fast reoxidation of iron and uranium.
- It requires two cycles which is acceptable if a second cycle central unit is connected to several first cycle units but is expensive for a medium size isolated phosphoric acid plant.

I.2. - Two cycle processes using MOPPA-DOPPA (2)

Uranium + 4 is extracted with a mixture of MOPPA and DOPPA at a 0.3 M concentration. The concentration factor U in loaded solvent is about 6 to 7. U in aqueous feed
Uranium is stripped using an oxidizing agent in phosphoric acid medium. The second cycle carried out using TOPO-D₂EHPA mixture is the same one described in 1.1.

The criticisms which can be passed on this process are similar to the ones passed on the process (I.1.), i.e. :

- Uranium must be reduced before extraction and similar precautions must be taken as the previous process but applied to larger volumes.
- It requires a second cycle (see 1.1.)
- It requires two kinds of solvents
- When TOPO and D₂EHPA diluted in hydrocarbons are insoluble in phosphoric acid and are stable, the MOPPA and DOPPA solubility is low but not equal to zero and moreover they are sensitive to hydrolysis.

I.3. - Process using OPFA (3)

The OPFA extracts U (IV) which is then stripped as insoluble UF₄ using hydrofluoric acid. At the moment this process is the only one which had been used at an industrial scale. Nevertheless it shows the following disadvantages :

- Uranium reduction prior to extraction
- The OPFA is not very selective.

Out of uranium many other cations such as iron and aluminum are extracted. The fluoride thus obtained contains many impurities and is accepted by refiners only with penalties or requires a purification cycle.

- The OPFA is not stable and its consumption rate is rather high. This may be considered less as a disadvantage because the solvent is not very expensive and because its instability may destroy partly the amount entrained in phosphoric acid after extraction.

This critical survey did not lead to reject the said processes but brought us to the conclusion that it was possible to imagine a simpler process even without looking for new solvents.

II) PROCESS PRINCIPLES

To design a new process, two aims were assigned :

- only one purification cycle
- no-uranium reduction.

As far as no new solvent was used for these purposes, the first consequences were :

- The solvent is necessarily the TOPO-D₂BHPA mixture
- Uranium reduction is not used for stripping

The stripping method chosen uses solvent chemical neutralization with ammonia and ammonium carbonate. A similar stripping method is actually used in the second cycle of the process described in 1.1., but using process conditions which are not applicable to a first cycle stripping.

The basic flowsheet thus achieved is represented in figure 1.

The expected difficulties, from a physico-chemical point-of-view, were as follows :

a) During stripping, extracted cations are precipitated as hydroxides, particularly iron as $\text{Fe}(\text{OH})_3$. In the settlers there are three phases : one solid phase and two liquid phases. That fact could have three consequences :

- A poor phase disengagement
- Some difficulties to discharge hydroxides out of settlers
- Poor settling or filtering rates for eluate-hydroxides separation.

Actually no serious difficulties were encountered as far as the process conditions were respected.

- Phase disengagement is rather good
- Hydroxides are only in the aqueous phase and get out easily of the settlers
- Hydroxides easily filtered : using a rotary drum filter with precoat the specific rate is $1 \text{ m}^3 \cdot \text{h}^{-1} \text{ m}^{-2}$.

b) Should ammonium be acceptable in the phosphoric acid, then the solvent can be regenerated by using a large excess of barren phosphoric acid. If not, acidification is carried out with the minimum volume of phosphoric acid in order to obtain a concentrated solution of MAP. In that case this operation is just a little more difficult to carry out, the MAP solution being sent to a fertilizer or MAP unit.

III) DEVELOPMENT WORK

III.1. - Scope of the work

Studies have consisted of 4 steps

- a) Tests to define the chemical bases of the process such as distribution isotherms, chemical factors for uranium stripping and solvent regeneration, mass transfer kinetics.
- b) Tests of the whole process flowsheet in a laboratory set of mixer-settlers operating counter-currently.

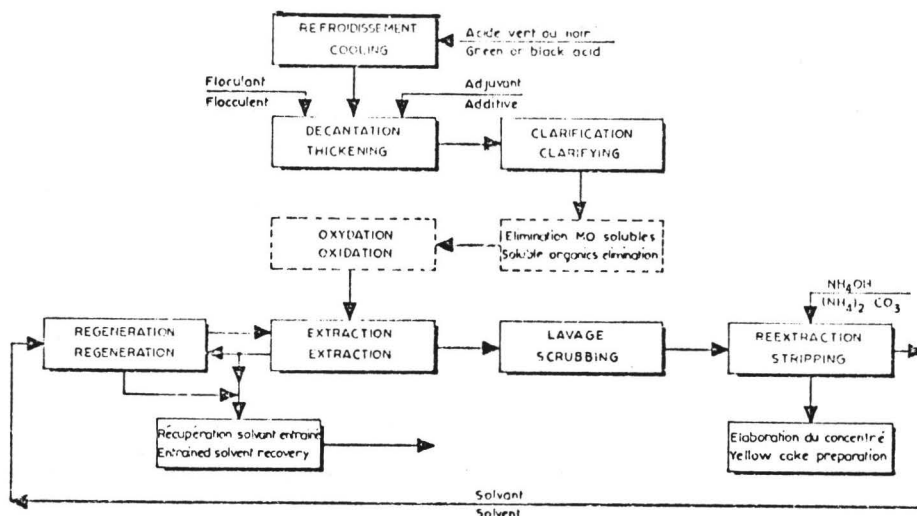


FIG. 1

SCHEMA DE PRINCIPE
BASIC FLOWSHEET

c) Tests of the whole process flowsheet in a pilot scale set of mixer-settlers (feed flowrate $25-30 \text{ l.h}^{-1}$). During this step the stripping chemical conditions were completely defined and when they were completed a common patent was taken out by COGEMA and A.P.C. (4)

During these first three steps, tests were done with industrial phosphoric acid which had rested several weeks before using it for tests. Under these conditions the problems relating to instability of the phosphoric phase (gypsum and fluosilicate precipitation), to the solid materials content of the phase and to the presence of natural organic materials could not be investigated.

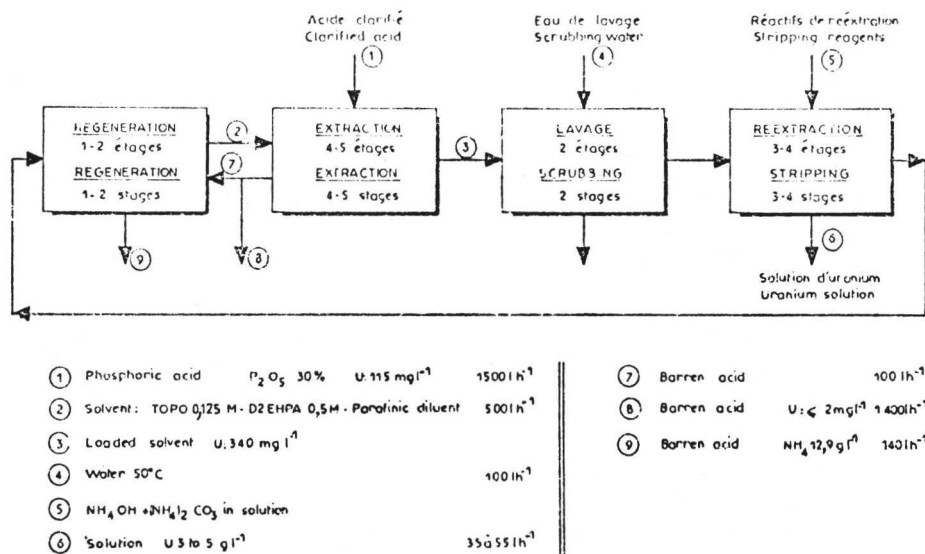
Therefore it was decided to test the process on a semi-industrial scale (1/50) on line with wet-process phosphoric acid plant. A large pilot unit was accordingly erected in Grand Couronne on the CdF-A.P.C. site. The aims of this pilot unit processing were as follows :

- Prove with an actual phosphoric feed the validity of the operating conditions determined in the course of the three previous steps.
- To experiment and perfect 1) the preparation of the phosphoric feed before extraction operation and 2) the recovery of organic solvent entrained by the barren phosphoric acid.
- Compare operation of various types of extractors to carry out extraction cycle.
- Determine with more accuracy the investment and operating costs for an industrial plant.

III.2. - Results achieved in semi-industrial unit

1) From a physico-chemical point of view results achieved during the first three steps were fully confirmed (see flowsheet on figure 2. that is to say :

- Extraction recovery of about 99 %
- Solvent uranium load of 300 mg.l^{-1} from a feed of 100 mg.l^{-1}
- Solution from stripping containing 3 to 6 g.l^{-1} in U
- Production of a yellow cake meeting the commercial specifications.



PILOTE INDUSTRIEL : SCHEMA EXPERIMENTE

FIG.2 SEMI-INDUSTRIAL SCALE PILOT: TESTED FLOWSHEET

2) Connected operations

It is well known that two kinds of difficulties are met when phosphoric acid comes into contact with an organic solvent :

a) Difficulties due to the presence of suspended solids and mainly to the crystallization of gypsum and alkaline fluosilicate, which is able to plug in pipes and to induce scaling in tanks and processing equipments.

This type of difficulty has been overcome by cooling phosphoric acid to a temperature a little lower than needed for extraction. On the other hand, and as it will be explained later, solids are separated along with organics.

b) Difficulties due to the presence of organics in the phosphoric acid after phosphate rocks leaching and solution filtering. Strictly speaking it may be useful to distinguish suspended organics and soluble organics (or behaving like soluble organics). The acid produced from Morocco or Togo phosphate rocks contains rather few soluble organics. Several methods were tested. The most efficient ones were flotation and quickened settling. The last one has been chosen. To carry out this settling successfully, a conventional flocculant and an additive adsorbing qualities are added to the liquor. Thus all the solids, organics and additives are quickly settling together. The phosphoric acid in the overflow needs only to be clarified which is easily carried out, using filtration for instance.

The phosphoric acid produced from Florida phosphate rocks may contain some soluble organics species. In some cases after the previous treatment, acid can be contacted with solvent any trouble. In some other cases the content of soluble species is higher and it may be necessary to add a purification stage using active carbon or washing with hydrocarbons.

3) Solvent elimination

Solvent carried along with barren phosphoric acid ought to be eliminated for two reasons :

a) Phosphoric acid after uranium extraction is sent to the main plant to be submitted to the following treatment which includes concentration and conversion in various products (fertilizers, MAP, tripolyphosphates, ...). Solvent damaging of the concentrators linings and of some gaskets is the main hazard.

b) Solvent entrainments must be considered as expensive losses. For instance for a feed flowrate of $100 \text{ m}^3 \cdot \text{h}^{-1}$ and an entrainment of $300 \text{ mg} \cdot \text{l}^{-1}$ the loss would be 720 liters per day which means more than 115 kg D₂EHPA and about 35 kg TOPO, and an expense of more than 6 000 FF per day. Therefore it is preferable to use a method allowing solvent recovery and recycling. Several methods have been tested ; among them the most efficient ones were flottation methods which decrease the content of entrained solvent largely under 50 ppm.

Other tests on resistance of the various linings to solvent have shown that for solvent content less than 50 ppm no hazard seems to be feared.

4) Extraction equipment

The steps of the extraction process were experimented using several types of mixer-settlers and pulse columns.

From a general point of view all the equipments tested were satisfactory as for efficiency of extraction and scrubbing.

Moreover the following observations were made :

- The mixer-settlers, mainly the most compact types, are sensitive to the presence of solids and to scaling.
 - Solvent entrainments in the aqueous phase vary between 50 and some hundreds ppm from the less to the most compacts models.
 - Pulse columns are not troubled by solids.
- Some of the devices which can be used for interphase control would seem a little sensitive to the presence of organics.
- Stripping which needs a good pH control in any part of the equipment, appears for the moment as more easy to carry out in mixer-settlers than in pulse columns. Nevertheless tests are continued to have a more sure opinion on that point.
 - Solvent entrainment when using pulse columns is largely less than 50 ppm (10 to 25 ppm).

IV) CONCLUSIONS

The different investigation steps described in the present paper have given all informations necessary to appreciate correctly process availability and economy.

The results achieved on uranium extraction itself and also on connected operations are satisfactory and may be scaled-up due to the pilot scale chosen (1/50) and to the connexion of the pilot unit to an industrial phosphoric acid plant.

These results, and the economic studies based on them, have allowed the decision to build an industrial unit. The engineering studies are presently in progress.

ABREVIATIONS USED

C.E.A.	Commissariat à l'Energie Atomique
A.P.C.	Azote et Produits Chimiques (French Company)
COGEMA	Cie Générale des Matières Nucléaires (Subsidiary of C.E.A. - France)
CdF-Chimie	Charbonnages de France - Chimie (French Company)
TOPO	Trioctylphosphine oxide
D ₂ EHPA	Di 2 Ethyl hexylphosphoric acid
AUTC	Ammonium uranyl tricarbonat
MOPPA	Mono octylphenyl phosphoric acid
DOPPA	Di Octylphenyl phosphoric acid
OPPA	Octyl pyrophosphoric acid
MAP	Mono ammonium phosphate

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A CASE STUDY - OPTIMIZING THE PERFORMANCE OF THE URANIUM
S.X. PLANT AT ROSSING URANIUM LIMITED IN NAMIBIA.

Co-authors :

Dr. I.E. Lewis⁽¹⁾ & Dr. S. Kesler⁽²⁾

(1) C.R.A. Services Limited

(2) Rossing Uranium Limited.

Rossing Uranium Ltd., a company within the R.T.Z. group, operates the world's largest uranium oxide production facility near Swakopmund in Namibia (South West Africa). Some of the processes, many of the techniques, and certainly the scale of the operation, are unique to Rossing. The plant processes include four stage closed circuit crushing, grinding, leaching, sand washing, C.C.D., continuous ion exchange followed by solvent extraction, precipitation and roasting.

The solvent extraction plant consisted of two parallel lines, each line consisting of twelve identical mixer-settler stages plus a raffinate coalescer. There were five extraction stages, two wash stages, four strip stages and a regeneration stage.

Feed for the S.X. plants comes from the elution stages of a continuous ion exchange plant and has a U_3O_8 content of between 2 - 5 gram/litre and a H_2SO_4 level of 80 - 110 gram/litre. Wash water from the two washing stages of the S.X. plant was mixed with the loaded stream from the C.I.X. plant. pH control in strip was by injection of anhydrous NH_3 in to three of the strip stages. The strip liquor was 90 - 120 gram/litre $(NH_4)_2SO_4$.

The stripped organic flowed to the regeneration stage where the organic was contacted with a $NaOH/Na_2CO_3$ solution.

Plant throughput at design capacity is 7500 kg/day of U_3O_8 and the normal plant flow rates are:

pregnant feed	1600 litres/minute
organic	1200 litres/minute
wash water	200 litres/minute

$(\text{NH}_4)_2\text{SO}_4$
 $\text{NaOH}/\text{Na}_2\text{CO}_3$

600 litres/minute
Recycled, batch feed.

In May 1978 a fire destroyed one line of the S.X. plant and it became imperative to attempt to raise the capacity of the remaining line and to optimize its performance. Dr. I. Lewis, a Principal Research Metallurgist with C.R.A. Services Ltd. subsequently joined with Dr. S. Kesler to work on optimizing plant performance. The steps taken to improve the plant performance were:

1. Settler capacities were increased by 10 - 20% by removing solids build-up. A vacuum cleaner system was designed for cleaning on a routine basis. The buildup consisted of precipitated silica and ion exchange resin.
2. Organic and aqueous entrainment losses were reduced by installation of the C.R.A. Services Ltd. patented baffled settler system. This resulted in physical organic entrainment levels in raffinate being reduced from the range 600 - 1200 p.p.m. to less than 5 p.p.m. Monthly organic makeup dropped from approximately $100 \text{ m}^3/\text{month}$ (prior to the fire) to an estimated 10 - 15 m^3/month . The baffle installation also enabled the extraction section to operate at higher flowrates and in some tests flowrates were increased by 35% with physical organic entrainment in raffinate still being less than 5 p.p.m.
3. Phase continuity. The extraction stage of the S.X. plant was operating on organic continuous by recycle of organic to give an O:A ratio of 1.2:1. It was demonstrated that with the pregnant feed containing approximately 100 gram/litre H_2SO_4 , much better performance could be obtained by running aqueous continuous. Phase break times were up to 25% less than for organic continuous. As the settlers were under-designed for the design flowrate (settlers 3 metres wide x 10 metres long for a total organic plus aqueous flow of 3520 litres/minute) this change to aqueous continuous operation with no recycles had a major effect in allowing operation at higher throughput rates, in fact the suction limitation of the pump-mixers became the limiting factor.

4. Wash stage performance was improved by the C.R.A. baffle installation in extraction as the physical aqueous entrainment levels in loaded organic were reduced from a before baffles figure of 400 - 600 p.p.m. to less than 1 p.p.m. Wash water flow to wash was reduced by 50% and the interface lowered resulting in very little entrained aqueous transfer to strip, thus reducing ammonia consumption.
5. Crud problems caused by colloidal silica were severe and high losses of organic in crud were being experienced (crud removed and dumped contained up to 80% organic when separated in a centrifuge). As wash water was recycled to pregnant feed the crud could not get out of the system and severe coalescence problems and flooding often occurred in the first extraction stage. A new C.R.A. in-line crud treatment technique was installed between extraction and wash stages. Crud now passes through this "crud breaker", is transferred to the wash stage where it disperses in the wash water phase. The wash water is removed from the circuit and returned to leach. The installation of this crud process has contributed to lower organic losses and eliminated the flooding problems in extraction.
6. Variations in extraction efficiency were occurring and the reason was not clear. On analysis of the plant data over a few months it became obvious that acid level in pregnant feed was affecting extraction. This was studied more closely over all extraction stages and it was soon concluded that acid level should be less than 100 gram/litre. Values in excess of 110 g/litre definitely led to poor extraction efficiency. The control of acid levels in the elution section of the C.I.X. plant was improved so that acid could be maintained at the 90 - 100 g/litre level.
7. Regeneration of the organic was examined and found to be causing considerable trouble in extraction because of entrained $\text{NaOH}/\text{Na}_2\text{CO}_3$ aqueous phase. Regeneration was stopped completely and regeneration will now only be carried out when necessary, perhaps every six months, and using a 3 - 5% solution of Na_2CO_3 for regeneration. This change resulted in a large reduction in plant operating cost and improved extraction performance.

8. Strip stages were operating with organic feed of 1200 litres/minute and aqueous feed of 600 litres/minute plus organic recycle. There was no need for organic recycle so these lines were shut off with an improvement in performance.

9. Ammonia requirements in the plant had been high and prior to May 1978 had been approximately 1 kg NH_3 per kg of U_3O_8 produced. Ammonia gas was added to three strip stages and pH control had been poor. During May 1978 the pH control was improved and this reduced the plant NH_3 usage to approximately 0.5 kg of U_3O_8 produced. At the start of July a NH_3 sparge ring was installed at the base of the mixer in the draft tube of one strip stage. This was shown to be inefficient with much NH_3 ending up in the organic phase and gassing off in the settler. This sparge ring was disconnected and NH_3 added at the base of the overflow weir as in the past and as existed in the other two strip stages. There was still precipitation occurring in the third strip stage because of the difficult control and low NH_3 required. At this stage, 70% of the NH_3 went to S1, 28% to S2 and 2% to S3.

It was decided to add NH_3 to only S1 and S2 in the ratio of approximately 85% to S1 and 15% to S2. Better control was achieved, no NH_3 smell was evident, and no precipitation of U_3O_8 or crud formation was observed. Ammonia requirement dropped after these changes to a figure of approximately 0.36 kg per kg U_3O_8 produced.

10. Diluent in the plant had been a low flashpoint paraffin. A recommendation was made to change to a Shell high flashpoint diluent, Shellsol 2325. This change was made at the end of 1979 and should result in lower evaporative organic losses. It was also noticed that with the installation of the C.R.A. baffles and the C.R.A. crud treatment technique and the consequent very high reduction in organic loss, that the flashpoint of the organic in the circuit rose significantly over a fairly short period (approximately 10°C in two months) reducing the fire risk problems.

At the end of 1979 the new S.X. line to replace the destroyed line came on stream. Details of the startup problems and the performance of this line are described.

THE IMC/PRAYON URANIUM RECOVERY FROM PHOSPHORIC ACID PROCESS

W. W. Berry, New Wales Chemicals, Inc.*
P. O. Box 1035, Mulberry, Florida 33860
*Subsidiary of International Minerals &
Chemical Corporation
A. Dubreucq, Societe de Prayon
B-4130, Engis, Belgium

ABSTRACT

International Minerals & Chemical Corporation, Societe de Prayon and Metallurgie Hoboken-Overpelt have combined their experiences to develop a uranium recovery process for wet process phosphoric acid.

The process is based on the two-cycle Oak Ridge National Laboratory reductive strip, DEPA/TOPO extraction technique suitably modified for the variety of phosphoric acid production conditions encountered around the world. Extensive acid clean-up results in the production of green phosphoric acid.

The uranium product produced is uranyl peroxide of exceptional purity.

International Minerals & Chemical Corporation, Societe de Prayon and Metallurgie Hoboken-Overpelt have entered into a joint venture to combine their respective technologies in uranium phosphoric acid processing and general extractive metallurgy; the result being a uranium recovery from phosphoric acid technology applicable to a wide range of phosphoric acids produced around the world.

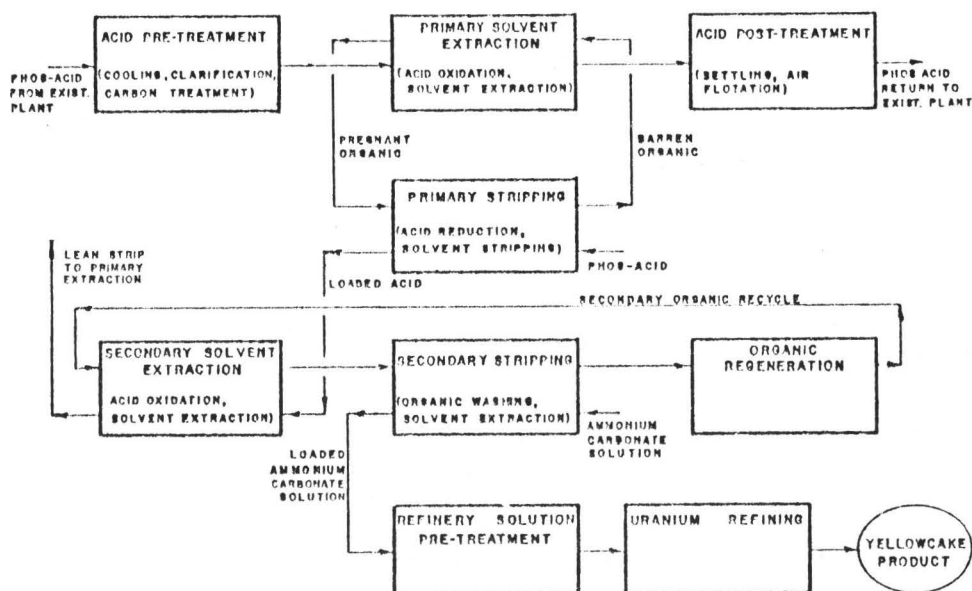
These combined technologies and the breadth of experience possessed by the companies allows this technology to be applied to phosphoric acids ranging from Florida material; which, as you know, is extremely dark in color and contains substantial quantities of humics; to low color acids such as those made from North American rock; that is lower humic levels and lighter in color.

Until recently, the uranium, which occurs naturally in the phosphate rock, has stayed with the phosphoric products produced from the rock. IMC/Prayon technology is now being employed to recover this valuable commodity.

Figure 1 shows a basic block diagram of the IMC/Prayon process. The first phase of this presentation will involve a general "walk-through" of the process, followed by a more detailed discussion of the individual processing blocks.

FIG. 1

IMC/PRAYON URANIUM RECOVERY PROCESS OVERALL BLOCK DIAGRAM



GENERAL PROCESS OVERVIEW

Acid is received as primary or "number one" filtrate from the existing phosphoric acid facility. In the "Acid Clean-Up" operation, the acid is cooled in spiral heat exchangers, pretreated, clarified, then passed through activated carbon columns. It is in this step that the solids and humic materials are removed from the acid, resulting in a clean, green phosphoric material.

In order to minimize confusion, the bulk of this discussion will be geared towards Florida phosphoric acid since, in most cases, this is the most difficult material to work with. It normally contains a substantial amount of humic material and, for the most part, is produced from uncalcined rock.

The green acid is pumped to the Primary Solvent Extraction System. The first phase of this operation involves oxidation of the acid in order to convert all of the uranium to the U^{+6} valance state.

The acid is next contacted with a solvent, composed of DEPA/TOPO; (di-2-ethyl hexyl phosphoric acid and tri-n-octyl phosphine oxide), dissolved in a diluent consisting of Ashland 460. A counter-current mixer settler system, modified to accommodate phosphoric acid, is utilized for this step.

Pregnant organic from the solvent extraction step is then stripped with a small stream of phosphoric acid which has been reduced with iron. Uranium transfers from the pregnant organic to the reduced acid. A substantial concentration increase is accomplished utilizing this technique, which is based on work conducted by the Oak Ridge National Laboratory.

Raffinate phosphoric acid, leaving the Primary Extraction Circuit, is then treated to remove any entrained organic and returned to the phosphoric acid plant. Treatment consists of a settling step, followed by air flotation.

Loaded strip acid is again oxidized and treated in a Secondary Extraction Circuit with DEPA/TOPO. At this stage of the process, the liquid volumes involved are considerably smaller due to the concentration increase of uranium in the strip acid. The raffinate strip acid, leaving the Secondary Extraction Circuit, is returned to the front end of the Primary Circuit.

Secondary pregnant organic is first washed with water to remove any entrained P_2O_5 , then stripped with a solution of ammonium carbonate. The DEPA is converted to the ammonium form and the uranium transfers to the carbonate solution. Barren organic is regenerated, then returned to the Secondary Extraction System.

The secondary loaded strip solution, that is, the ammonium carbonate material, is then prepared for uranium precipitation in a proprietary pretreatment technique. The prepared solution is pumped to the Refinery Circuit.

In the Refinery, uranium is precipitated from the prepared secondary strip solution as uranyl peroxide. The precipitated peroxide is thickened, washed, centrifuged, then dried in a multiple hearth-type drier. Calcination is not necessary due to the purity of the yellowcake produced.

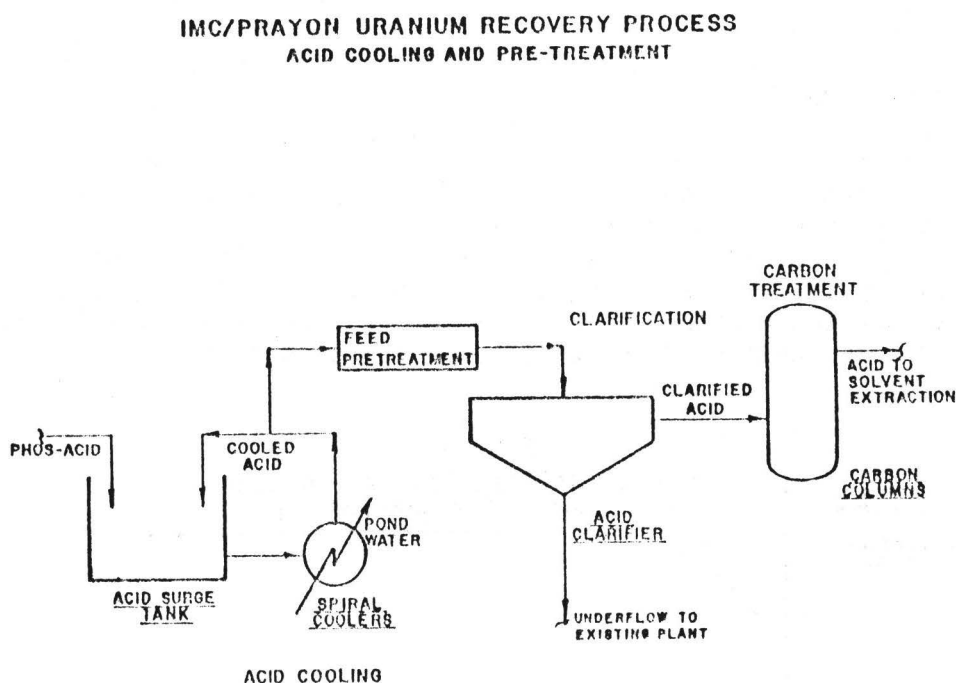
The discussion will now center on the individual processing blocks and review certain aspects of the major processing sections.

PROCESS DISCUSSION

ACID COOLING AND PRETREATMENT

A basic diagram of the Acid Cooling and Clean-Up System is shown in Figure 2.

FIG. 2



As indicated earlier, phosphoric acid received from the existing P_2O_5 facility is first cooled to about $120^{\circ}F$ in order to increase the extraction coefficient, minimize diluent evaporation, and precipitate additional solids from the acid. Since recirculated, acidic gypsum pond water is available for cooling, spiral coolers have been utilized for this task.

Periodically, the cooler is "rotated", i.e., the acid flow is switched to the water side and vice versa. Rotation of the coolers results in acidic pond water being circulated through the previous acid side. The acidic water then removes any scale precipitated during the acid side cycle.

If existing plant conditions will not accommodate this type of cooling system, vacuum coolers may be effectively utilized.

Cooled acid then enters the clarifier feed pretreatment section. It is important to note that the basic concept behind the combined technology is the use of extensive acid clean up in order to minimize problems in the Solvent Extraction Circuit, such as crud formation and phase separation.

The clarified acid is fed to the activated carbon columns where it is contacted with granular activated carbon. Humic material from the phosphoric acid is absorbed by the carbon, resulting in a green phosphoric material. In addition, due to the design nature of the carbon system, additional solids removal is accomplished. Clarifier underflow is recycled to the existing phosphoric acid facility.

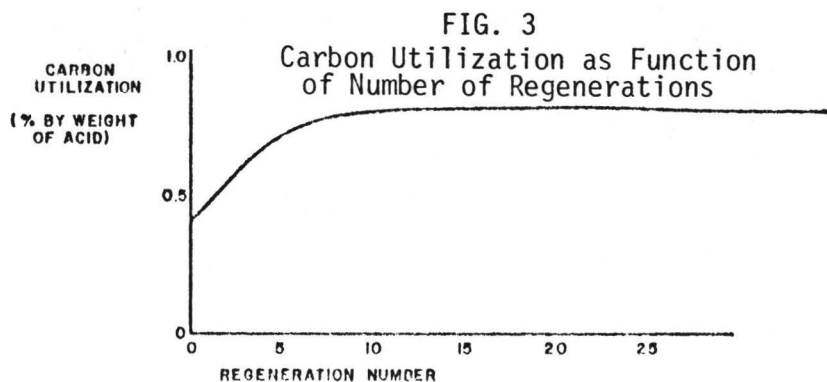
That activated carbon can be used to remove humics is well known and standard procedures are available for carbon evaluation and applicability (1,2,3). The key to the IMC/Prayon Process, however, is the economical use of carbon and the basic system design required to accommodate phosphoric acid.

Phosphoric acid is a high scaling material and post-precipitation of solids presents a major design problem. Consequently, design of any commercial installation must consider these important aspects in order to function properly.

From an economic and operability standpoint, the carbon must be utilized many times before it is disposed of. For this reason, not only the initial carbon column response, but the long term performance of the carbon must be considered.

To date, the carbon column system has operated according to earlier design estimates. As expected, after several regenerations, the carbon does lose some surface area and the amount of carbon required to treat a given quantity of phosphoric acid increases.

It has been observed, however, that once the initial "run-in" has been completed, typically five to ten cycles, the rate of surface area loss decreases, and the carbon appears to reach a steady-state level. Carbon utilization, per unit of P_2O_5 , also tends to reach a steady value as shown in Figure 3.

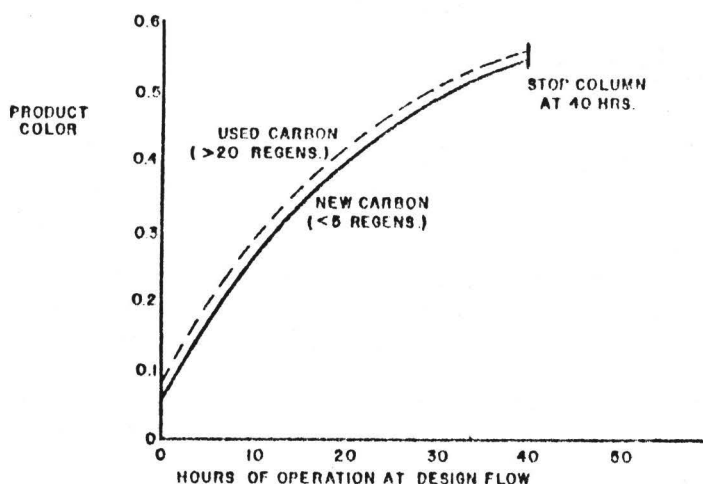


Our definition of carbon utilization is the weight of carbon which must be regenerated per unit weight of phosphoric acid solution treated and should not be confused with carbon make-up, i.e., the amount of new carbon which must be purchased due to the various carbon losses.

Obviously, one of the key parameters in this operation is the regeneration technique. It is advantageous to have carbon which can be utilized for a number of cycles and which maintains its adsorptive capacity throughout its useful life. Figure 4 compares product column breakthrough curves for new carbon, that is, material that has had less than five regenerations, and used carbon, defined as material with more than twenty regenerations.

FIG. 4

PRODUCT COLUMN BREAKTHROUGH CURVES



Under normal conditions, we stop the columns for rotation at forty hours. Comparing the product acid colors during the forty-hour run, it is seen that the used material has maintained a high degree of its original adsorptive capacity. For reference purposes, an acid color of 0.5 would be a bright green material. Normal brown Florida acid typically has an acid color of 3 - 4, on our particular color scale.

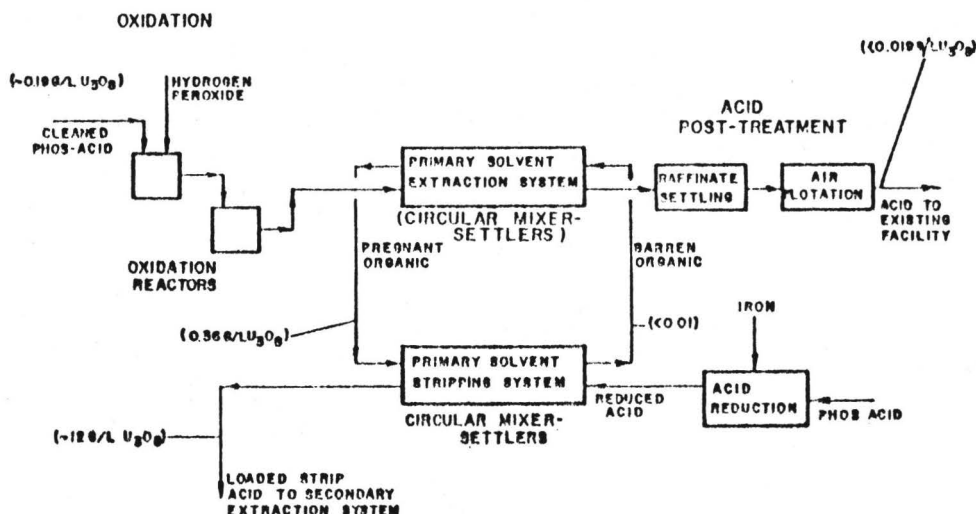
The cleaned acid is then pumped to the Primary Solvent Extraction System. Figure 5 shows a block diagram of the Oxidation, Extraction, Stripping and Acid Post-Treatment steps. Design U_3O_8 concentrations are also shown for the major streams.

ACID OXIDATION

In the oxidation step, the valance of the uranium is adjusted using an oxidizer. In order to be extracted by the DEPA/TOPO solvent, uranium must exist in the U^{+6} valance state. Due to the iron-uranium redox couple, however, it is essential that most of the iron present in the phosphoric acid be in the Fe^{+3} state.

FIG. 5

**IMC/PRAYON URANIUM RECOVERY PROCESS
ACID OXIDATION, PRIMARY SOLVENT EXTRACTION/
STRIP AND ACID POST-TREATMENT**



In our process, we are using hydrogen peroxide for the initial operation due to the ease of operation, simple equipment design and so forth. A continuing program is underway, however, to determine alternate techniques.

It was recognized in the early development phases that various chemical oxidants were available and several are less expensive than hydrogen peroxide. It must be kept in mind, however, that as a phosphoric acid producer, the addition of new ions to the acid is considered undesirable.

Thus, an oxidizer, such as sodium chlorate, is not an acceptable alternate due to the chlorine. Nitric acid, while producing acceptable oxidation, results in the addition of nitrates to the acid. While techniques are available to destroy the nitrate, additional processing steps are involved and a large flow of acid must be treated.

PRIMARY SOLVENT EXTRACTION AND STRIP

Oxidized phosphoric acid is contacted with a solvent mixture consisting of DEPA/TOPO, dissolved in a diluent. A 4-stage counter-current extraction technique is utilized, although, more or less stages can be used depending on specific process requirements. The addition of TOPO to the conventional DEPA material produces a synergistic combination which greatly increases the extraction ability of the solvent system.

The DEPA/TOPO concentration is normally 0.5 molar DEPA and 0.125 molar TOPO. The overall system, as indicated, is based on work conducted at Oak Ridge National Laboratories (4, 5, 6).

The contacting of an aqueous and organic system is a standard practice in a number of metallurgical recovery operations. In a similar manner, phos-acid and organic contacting can be accomplished in fairly conventional equipment. We have taken care, however, to incorporate phosphoric acid design considerations into the plant equipment. Unfortunately, even though the phosphoric acid has been cooled, clarified, etc., it still has a tendency to scale and precipitate to some extent. It is, therefore, necessary to accommodate this factor into the overall process package.

Rectangular pumper mixer and/or circular mixer-settler units can be employed for the contacting steps. At New Wales and at the CF Modules, circular mixer-settlers, utilizing gravity flow for the phosphoric acid, are employed. This design was chosen due to the magnitude of the flows involved and was considered the most conservative approach at the time.

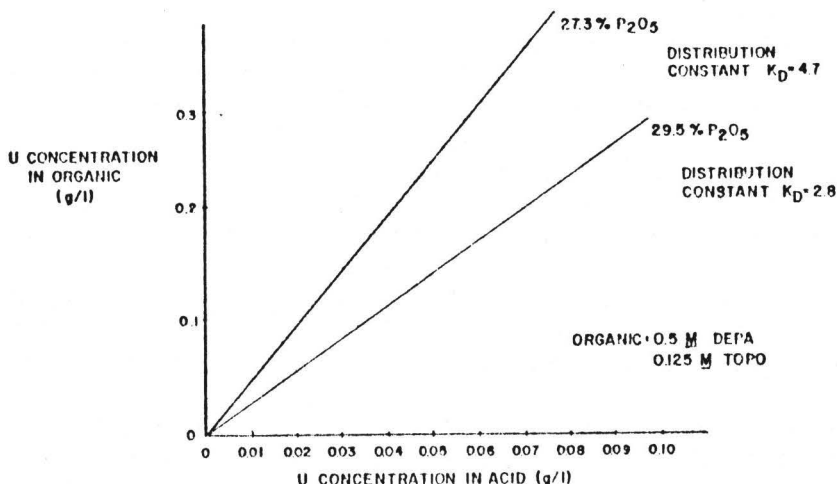
In the extraction system, the aqueous to organic ratio is typically maintained at about 2:1 in all but the last mixer-settler unit. The last unit can be operated organic continuous in order to minimize organic entrainment in the acid. With green phosphoric acid, organic continuous operation has a pronounced effect on the degree of entrainment in the acid exiting the Solvent Extraction Circuit.

The raffinate acid exiting the last mixer-settler flows to the Acid Post-Treatment System.

DEPA/TOPO, in a conventional sulfuric acid leach operation, would have an extremely large extraction coefficient. Due to the nature of the uranium phosphate complex, the coefficient is not nearly as great. The extraction coefficient of uranium in the DEPA/TOPO system is, first of all, sensitive to the P_2O_5 concentration in the acid. Figure 6 shows isotherms for two different strengths of acid. As seen, higher acid strengths detrimentally effect the value of K_D .

FIG. 6

URANIUM DISTRIBUTION ISOTHERMS
FOR IMC PHOSPHORIC ACID
(IMPACT OF ACID CONCENTRATION)

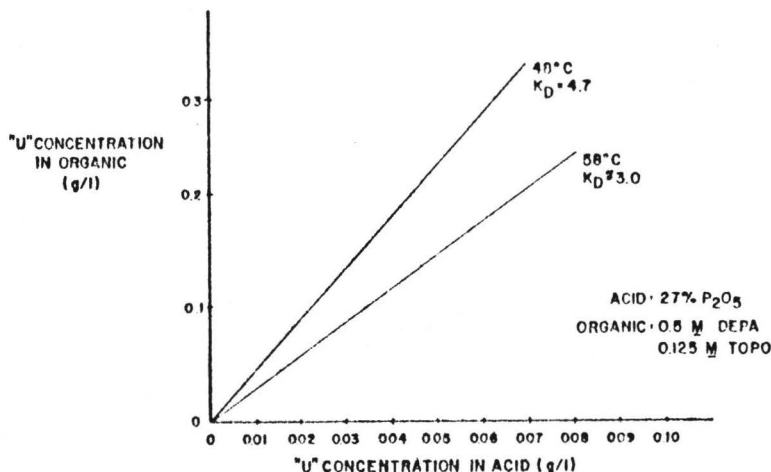


The impact of acid temperature on K_D is shown in Figure 7. As indicated earlier, acid cooling is utilized, in part, to improve K_D , thus reducing the organic flow rate and decreasing the number of extraction stages required.

Next, pregnant organic is stripped with a small stream of phosphoric acid which has been reduced with iron. Approximately 1.5 percent of the main acid stream is treated with iron to provide the proper amount of Fe^{+2} throughout the strip system.

Since DEPA/TOPO has little affinity for U^{+4} , the presence of Fe^{+2} in the strip acid reverses the extraction reaction, provides efficient stripping of the uranium from the organic and results in a substantial uranium concentration increase. Under normal conditions, a 65-70 fold increase in U concentration is observed in the strip acid, relative to the main phosphoric acid stream, that is, the loaded strip acid will typically contain 10-12 g/l of U.

FIG. 7
URANIUM DISTRIBUTION ISOTHERMS
FOR IMC PHOSPHORIC ACID
(IMPACT OF TEMPERATURE)



Since the stripping operation is an extremely critical step, several techniques are employed in the IMC/Prayon process to insure proper Fe^{+2} concentration. As expected, two of the most important factors for good operation are; 1) close monitoring of the system and 2) achievement of steady-state operation.

As indicated in the earlier discussion on acid clean-up, a basic philosophy has been to minimize solvent extraction related problems by going to extreme lengths in the pretreatment system to remove potential crud forming materials. This has been accomplished by the use of the clarification and activated carbon adsorption systems.

As a result of our clean-up system, the amount of crud formed in the circuit is minimal. Typically, the values observed are similar to those encountered in more conventional processes.

Higher humic acids can be treated in the Solvent Extraction Circuit if the proper processing steps are employed. The amount of crud formed, however, can be significantly greater than that produced in the green acid circuit.

Various techniques are employed, to both remove and treat, the crud material formed in the Solvent Extraction Circuit. In our system, minimal crud treating facilities are required due to the low potential for crud formation.

ACID POST-TREATMENT

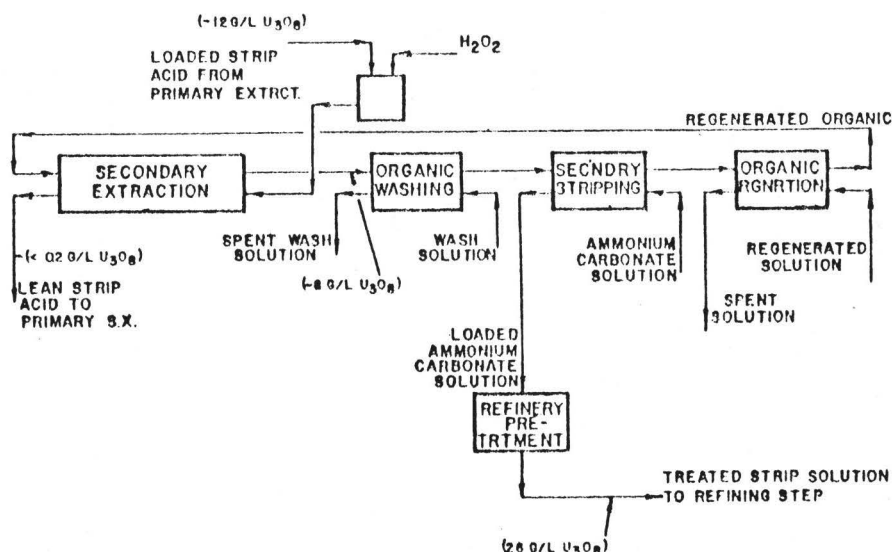
It is extremely important that organic entrainment be minimized in the phosphoric acid returning to the existing plant. Since the bulk of the down-stream equipment is rubberlined, excessive organic could result in substantial damage. In addition, solvent losses must be minimized in order to contain operating costs.

Acid from the last mixer-settler first enters the raffinate settler, which is essentially a large de-entrainment vessel designed to remove the bulk of the organic material. From the raffinate settler, the acid enters modified flotation cells for final entrainment removal. Typically, acid leaving the post-treatment system contains less than 30 parts per million by volume. After post-treatment, the acid is returned to the P_2O_5 Facility.

Loaded strip acid then enters the secondary circuit. The basic components of this system are shown in Figure 8. The design uranium concentrations of primary streams are also shown.

FIG. 8

**IMC/PRAYON URANIUM RECOVERY PROCESS
SECONDARY EXTRACTION/STRIP SYSTEM**



SECONDARY EXTRACTION AND STRIP

Loaded strip acid is first oxidized, then sent through a second DEPA/TOPO extraction circuit. Rectangular mixer-settlers are used and again uranium is transferred from the acid to the organic phase.

Lean strip acid is returned to the primary extraction circuit. Pregnant organic is sent through a water wash to remove any entrained P_2O_5 , then enters a secondary stripping circuit. The water washing step is employed to remove any entrained and/or dissolved phosphoric acid from the pregnant secondary organic. This insures that P_2O_5 contamination in the final product is minimized.

In the strip circuit, the pregnant organic is mixed with a dilute ammonium carbonate solution, the uranium is stripped from the organic and the DEPA is converted to its ammonium form. A weak ammonium carbonate solution is used in order to avoid uranium precipitation in this circuit.

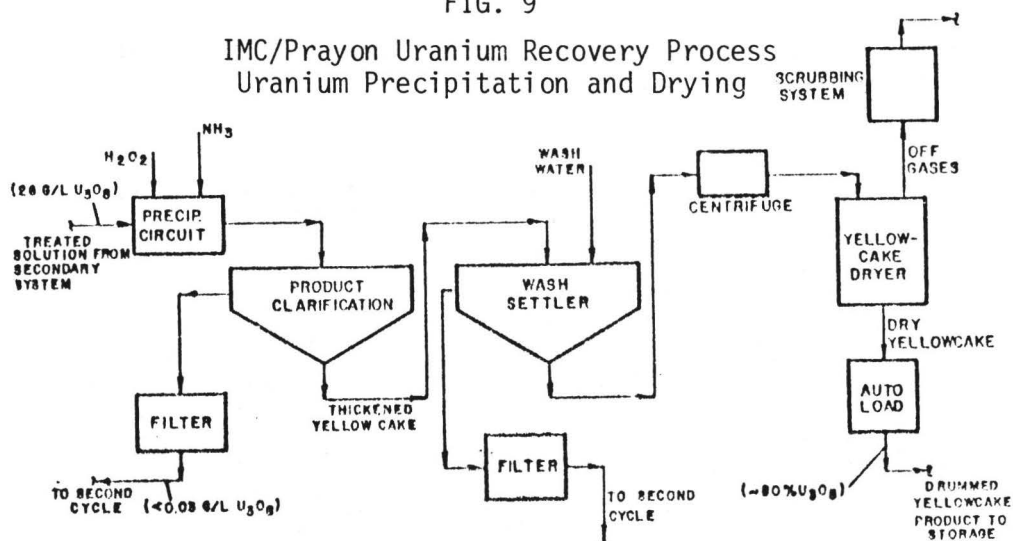
Barren organic is regenerated, then returned to the secondary extraction circuit. Regeneration is accomplished using a mineral acid to reconvert the DEPA to its acid form.

Loaded alkaline strip solution is next treated in a proprietary preparation step in order to reduce the pH, remove CO_2 and prepare the solution for uranium precipitation. This step is extremely critical to the operation.

URANIUM PRECIPITATION AND DRYING

At New Wales, a modification of the United States Bureau of Mines Peroxide Precipitation Technique is utilized. The use of hydrogen peroxide has been discussed in various publications and is in use in some conventional uranium operations (7,8). Figure 9 shows the primary steps involved in this system, which is generally referred to as the Refining Operation.

FIG. 9



A continuous precipitation circuit is utilized in this proprietary system. Hydrogen peroxide is added to the prepared strip solution, the pH is adjusted and uranium is precipitated as uranyl peroxide ($\text{UO}_4 : 2 \text{H}_2\text{O}$).

The uranium slurry is clarified, washed, centrifuged, then dried. This technique results in uranyl peroxide product of exceptional purity, since the peroxide route is quite selective for uranium under the conditions employed. As a general rule, the concentration of various contaminants in the final product is significantly below allowable limits established by the UF₆ up-graders. The joint IMC/Prayon technology, however, allows the use of other precipitation methods, depending on Client requirements. The Prayon Plant (located in Belgium) utilizes a slightly different technique, in which a uranyl hydrate compound is precipitated. Again, a high purity product is produced.

The IMC/Prayon Process offers a proven route for uranium recovery from phosphoric. In addition, the resulting clean, green acid provides an ideal feed for other processing techniques, such as tech-grade acid, fluorine recovery, magnesium removal, etc.

As a result of the foundation developed, it is felt that solvent extraction will play an over increasing role in future phosphoric acid processing technology.

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SOME ASPECTS ON LEAD EXTRACTION AND STRIPPING BY LIX-34

Ying-Chu Hoh and Wei-Ko Wang

Institute of Nuclear Energy Research, CAEC

P.O. Box 3, Lung-Tan, Taiwan, China.

ABSTRACT

LIX 34 liquid ion exchange reagent, one of a new class of metal extractants, was introduced for commercial application by General Mills in 1976. This paper studied some aspects on lead extraction and stripping in acetic medium by using LIX 34 diluted with Kermac 470B as the organic extractant. Equilibrium and pH isotherms, temperature effect and the rates of extraction and stripping of the system Pb^{++} - HAc - LIX 34 - Kermac 470B are reported. The experimental results indicated (1) the optimum extraction pH is 10. At this pH value, 15.5 g/l out of 21.3 g/l of lead were extracted into an organic extractant comprising 14% by volume of LIX 34 balanced with Kermac 470B. (2) A linear relation between the loading capacity and the organic extractant concentration was obtained. Numerically, one percent per unit volume of LIX 34 extractant solution extracted approximately one gram of lead. (3) The extracted lead in the organic phase was stripped effectively by dilute acetic acid solution. A linear relation between the concentrations of the acetic acid and the stripped lead was obtained. 14.5 g/l out of 16.3 g/l of lead can be stripped by 1 v/v% of acetic acid solution. (4) The extraction and stripping processes were not sensitive to temperature. The calculated ΔH° for extraction and stripping were equal to $-4.679 \text{ (cal)/(g-mole)(K)}$ and $5.395 \text{ (cal)/(g-mole)(K)}$ respectively, and (5) both the rates of extraction and stripping were less than one minute. Kordosky's, et al.⁽¹⁾ preliminary data indicated that the loading limit for each percent per unit volume of LIX 34 toward copper was 0.19 g/l. Chou and Hoh's⁽²⁾ results indicated that the loading limit for each percent per unit volume of LIX 34 toward zinc in nitrate medium is 0.34 g/l. Hence, regardless of the aqueous media, the loading capacity of LIX 34 toward lead is much higher than copper and zinc. These data are very important in designing a solvent extract circuit for related metals.

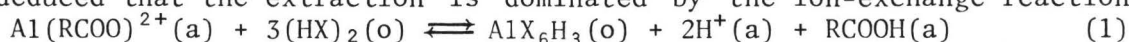
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THE EXTRACTION OF ALUMINIUM(III) FROM CARBOXYLIC ACID SOLUTIONS BY
DI-(2-ETHYLHEXYL)-PHOSPHORIC ACID

Taichi SATO, Takato NAKAMURA, Takashi YOSHINO
and Tomoya KUDO
Department of Applied Chemistry,
Faculty of Engineering,
Shizuoka University
Hamamatsu, Japan

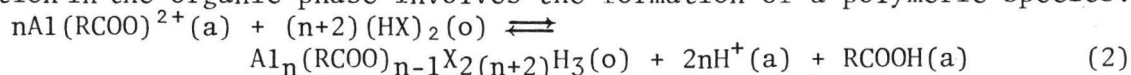
The distribution of aluminium(III) between aqueous carboxylic (formic or acetic) acid solutions and solutions of di-(2-ethylhexyl)-phosphoric acid (DEHPA, HX) has been investigated under different conditions. The infrared spectral study has been carried out for the organic extracts.

When aluminium(III) is extracted into DEHPA solutions from aqueous carboxylic acid solutions of varying acidity, the distribution coefficient decreases with aqueous acidity. In contrast, the extraction from mixed carboxylic acid/sodium carboxylate solutions shows that the distribution coefficient is not appreciably influenced by the carboxylate ion concentration. From the dependencies of distribution coefficient on the aqueous acidity and DEHPA concentration, it is deduced that the extraction is dominated by the ion-exchange reaction



in which R = H or CH₃, (HX)₂ refers to the dimeric solvent, and (a) and (o) are aqueous and organic phases, respectively.

Furthermore the molar ratio of dimeric DEHPA concentration to the aluminium concentration in the organic phase approaches a limiting value of unity with increasing the initial aqueous aluminium concentration. This is also supported by the continuous variation method for the aluminium concentration in the organic phase at a fixed total concentration of initial aqueous aluminium and DEHPA. Hence it is postulated that the monomeric species is formed when the DEHPA is present in excess, and the increase of the aluminium concentration in the organic phase involves the formation of a polymeric species:



where $n \geq 1$.

These facts consist with the infrared results for the organic extracts: With increasing the aluminium concentration in the organic phase, the intensities of the OH stretching and bending bands which arise from the hydrogen bond in the dimer of DEHPA decrease, while the P→O stretching band shifts to lower frequencies; the C-O stretching bands ascribed to carboxylate group coordinated to aluminium ion appear; the absorptions due to the coordination of DEHPA and carboxylate group coordinated to aluminium ion are observed in a region of far-infrared; a significant change in the [P-O]-C stretching vibration results from the effect of the interaction between the oxygen atom and the extracted aluminium ion on the formation of the polymeric species.

Additionally the rate of the extraction has been surveyed under non-equilibrium conditions. As the change in entropy of activation is negative¹⁾, it is expected that the extraction process is governed by the S_N2 mechanism. Further the observed rate constant is larger than the rate constant for water exchange²⁾, suggesting that the aqueous species exists as $\text{Al}(\text{RCOO})(\text{H}_2\text{O})_5^{2+}$ rather than $\text{Al}(\text{H}_2\text{O})_6^{3+}$.

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