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Inorganic processes
Session 7

Co-chairmen : L.G. Sherrington (Wokhingham, U.K.)
C. Ek (University of Liège, Belgium)

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SEPARATION OF MIXTURES OF INORGANIC ACIDS (NITRIC/PHOSPHORIC AND NITRIC/SULPHURIC) BY AMINE SALT EXTRACTANTS

I. A. Khan and M. W. T. Pratt

Schools of Chemical Engineering,
University of Bradford,

BRADFORD,
England.

ABSTRACT

Separation processes for mixtures of inorganic acids may be based on the use of the salts of long-chain organic amines as extractants. They extract preferentially one acid from an aqueous feed mixture to form a weakly bound complex in the organic phase, which may be stripped simply by contact with water.

Processes for the partial or complete separation of the acid mixtures nitric/phosphoric and nitric/sulphuric are described, which use as extractant the salt tri-n-octylamine nitrate in kerosene diluent, with 12% v/v n-decanol as modifier. In some experiments, the alternative amine extractants Adogen 363 and 382 have been used. Equilibrium distribution isotherms at 25°C are given and the processes have been modelled using a multi-stage mixer-settler.

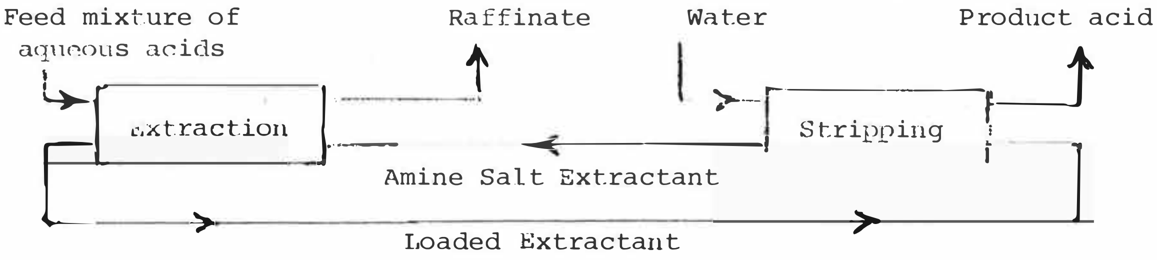
INTRODUCTION

The separation of mixtures of inorganic acids is of actual or potential importance in several industrial chemical processes and, in recent years, solvent extraction techniques have started to be used for this purpose. An important application is a solvent extraction process for the manufacture of phosphoric acid, pioneered by Israeli Mining Industries (IMI). In the traditional 'wet' process for phosphoric acid production in the fertiliser industry, phosphate rock is acidified with sulphuric acid and the impure product phosphoric acid is separated from calcium sulphate by filtration. In Israel, sulphuric acid is relatively expensive, but cheap hydrochloric acid is available. However, treatment of phosphate rock with hydrochloric instead of sulphuric acid does not form a precipitate, as calcium chloride is soluble. IMI found that a $C_4 - C_5$ industrial alcohol solvent will extract preferentially phosphoric acid from the aqueous product mixture, together with a proportion of hydrochloric acid. A process was developed (1) which includes four solvent extraction stages, the acid extraction being followed by purification, washing and raffinate stripping stages. The aqueous phosphoric acid from the washing stage is concentrated thermally, with evaporation of both water and hydrochloric acid, to yield 95% phosphoric acid of high purity. In later developments, 'wet' process phosphoric acid is purified by simple extraction with di-isopropyl ether so that it can be used to make detergent and food chemicals (2).

Recently, processes have been introduced in the fertiliser industry in which phosphate rock is acidified with concentrated nitric acid. In the Typpi-Oy process (3), the resulting mixture of phosphoric and nitric acids is extracted by tertiary amyl alcohol and reacts with ammonia to form the ammonium nitrate and phosphate components of a compound fertiliser. Different biological crops require fertilisers of various ratios of nitrogen and phosphate content, and in order to produce these, there is a need for a means to separate mixtures of nitric and phosphoric acids, either completely or partially, so that the concentration ratio of the two acids may be adjusted.

Aromatic nitration is commonly carried out by mixed nitric and sulphuric acids and processes for the separation of these two acids could also be beneficial.

Organic solvents, such as TBP or MIBK, may be used to extract inorganic acids and a process for the separation of nitric and phosphoric acids by MIBK has been patented (4). Although the use of amines to extract single acids has frequently been reported, little attention has been given to the potentialities of amine salts as alternative reagents for the separation of acid mixtures. However, the salts of long chain organic amines are capable of reacting preferentially with one inorganic acid in an aqueous mixture to form a complex in the organic phase. This complex is weakly bound and may be stripped by contact of the loaded organic phase with water to yield an aqueous solution of the purified acid. At the same time, the uncomplexed amine salt is regenerated for recycle. The combination of a highly selective extraction coupled with a simple water strip forms the basis of practical separation processes for mixtures of acids:



The initial reaction of a long chain organic amine with an aqueous acid, HA, is to form a salt, soluble in the organic phase; e.g. for a tertiary amine:

$$R_3N_{org} + HA_{aq} = R_3N\ HA_{org} \tag{1}$$

Smith and Page (5) in 1948, reported the ability of long chain organic amines to form salts with inorganic acids and found that a strong mineral acid, such as hydrochloric, was extracted with high selectivity from a mixture containing a weak organic acid such as amino-acetic or glutamic. Quaternary and tertiary amines are better acid extractants than secondary and primary amines, the ability improving as the carbon chain length increases. Extractant power, therefore, increases with increase in the nucleophilic character of the anion of the amine salt.

Kertes and Platzner (6), Bertocci and Rolandi (7), Shmidt (8), Sato (9) and other workers showed that amine salts may themselves act as extractants because they can form addition complexes with further molecules of acid, e.g.

$$R_3N\ HA_{org} + HA_{aq} = R_3N\ HA.HA_{org} \tag{2}$$

There is evidence from infra-red and proton magnetic resonance spectra that the excess acid molecules above the requirement for salt formation are hydrogen bonded to the amine salt so that a definite complex is formed and it is not just a physical distribution of the extra acid dissolving in the organic phase. Several investigators found that the graphs of equilibrium concentrations of organic phase total nitric acid versus aqueous nitric acid are linear, at least at low amine concentrations, the intercept on the organic phase axis corresponding closely with the amount of acid required to form the amine salt in that phase. Following this, Mason (10) proposed a simple equilibrium model: $\alpha = [HNO_3\ \text{excess}]_{org}/[\text{Amine}]_{org}\cdot[HNO_3]_{aq}$, where $[HNO_3\ \text{excess}]$ represents the concentration of nitric acid in the organic phase above that required to form the amine salt, and α is approximately constant, having a value between 0.16 and 0.18 for tertiary amines. Kertes and Platzner (6) developed the model to include the concentration of undissociated mineral acid in the aqueous phase, as this is thought to be the species reacting to form the complex. Using the data on the dissociation of nitric acid given by Krawetz, they obtained good experimental justification for their model.

The extraction of acids by amine salts has been considered by Shmidt and Rybakov (11), who distinguished between (a) the extraction of an aqueous acid by an amine salt of the same acid, as in equation (2), and (b) the case where a different acid is extracted by anion exchange: i.e. the salt amine HX reacts with aqueous acid HA to form salt amine HA in the organic phase, and a third type (c) in which the anion of an amine salt having nucleophilic properties adds a molecule of any electrophilic compound; e.g. the salt amine HX reacts with aqueous acid HA to form the complex amine HX.HA. Examples of reaction type (c) studied were the extraction of oxalic, formic, acetic and chloracetic acids from aqueous hydrochloric and hydrobromic acids by the corresponding tri-n-octylamine halides.

The separation of 5 N HCℓ and 1 N HNO_3 by 0.6 M Alamine 336 in diethyl benzene in a 10 stage mixer-settler was achieved by Baybarz and Weaver (12); the raffinate concentration of nitric acid being non-detectable.

Described in this paper is the use of the tertiary amine salt, tri-n-octylamine nitrate, as extractant to separate mixtures of nitric and phosphoric acids, and also nitric and sulphuric acids. In both cases, nitric acid is preferentially extracted. Two other amine reagents, Adogens 363 and 382, have also been assessed as alternatives to tri-octylamine (TOA) for the nitric /phosphoric acid separation. Distribution equilibria for nitric acid alone and for the mixed acids between the organic and aqueous phases have been measured at 25°C. The separation process was then modelled, using a laboratory multi-stage mixer-settler apparatus, to confirm theoretical predictions of performance, to study the effect of changes in process variables such as the flow ratio of the two phases, and to assess the long-term performance of the extractant.

EXPERIMENTAL

Tri-n-octylamine and the Adogen amines were used as a solution in kerosene as diluent, with 12% v/v n-decanol as a modifier to prevent third-phase formation.

To determine distribution equilibrium isotherms, a 15 ml sample of the organic extractant was shaken in a conical flask with an equal volume of an aqueous phase of known acid concentrations. The time of shaking was 30 minutes, which was shown to be more than adequate to achieve equilibrium. Experiments were performed in a thermostated room, maintained at a temperature of 25°C ± 1°C. After equilibration, the two phases were separated, centrifuged, and then the aqueous phase, and sometimes the organic phase also, was analysed to determine the equilibrium acid concentrations. In some experiments, equilibrium was approached, as in stripping, by shaking the loaded extractant with an equal volume of pure water. Before contact, the loaded extractant was filtered through phase separation paper, which retained any free aqueous acid.

The analytical techniques varied with the system:
NITRIC ACID ALONE The aqueous phase nitric acid concentration was determined, before and after equilibration with the extractant, by titration with standard sodium hydroxide to the phenol-phthalein end point. The equilibrium nitric acid content of the extractant could be found from the difference in aqueous phase concentrations before and after contact, but it was occasionally confirmed by direct measurement: an organic phase sample was neutralised with excess sodium hydroxide, the released TOA was separated, and the unreacted alkali back titrated with hydrochloric acid.
NITRIC/PHOSPHORIC ACID MIXTURES Potentiometric titration of aqueous mixtures of the acids with standard caustic soda gave two end points: the first, at pH 4.5, corresponding to the neutralisation of nitric acid and the first ionisation of phosphoric acid; the second, at pH 9.2, representing the second phosphoric acid ionisation. The concentrations of the two acids could therefore be determined separately, and analyses of the aqueous phase concentrations before and after contact with extractant allowed the organic phase concentrations to be found by difference. Checks were made on the organic phase concentration of phosphoric acid by gravimetric analysis based on the precipitation of ammonium phosphomolybdate: the agreement with the volumetric analysis results was always within 0.02 M.
NITRIC/SULPHURIC ACID MIXTURES Total acidity was determined by titration with caustic soda. The concentration of sulphate was then measured by precipitation as barium sulphate following the addition of excess barium chloride solution. The unreacted barium was estimated by titration with potassium sulphate in the presence of the sodium salt of rhodizonic acid, which gives a pink colour in the presence of barium ions in solution, changing to colourless as the barium is precipitated. Organic phase equilibrium acid concentrations were found from the difference in aqueous phase concentrations, before and after contact with the extractant.

Equilibrium concentrations of acids were calculated after making a correction for the change in phase volume which occurs because the extractant takes up water. The volume change was proportional to TOA concentration and was 1% for 0.45 M TOA extractant. Acid concentrations were shown by repeated measurements to be reproducible within an error of ± 0.01 M for nitric acid, but ± 0.02 M for phosphoric or sulphuric acids. In separate experiments, it was established that the equilibrium concentrations of acids are stable for times up to 12 days, that the presence or absence of light has no appreciable effect, and that increase in temperature over the range 5°-40°C causes only a 5% decrease in equilibrium acid concentrations. The extractant is not attacked by nitric acid up to 10 M, but is not stable in contact with 12 M acid. In the distribution measurements, total acidity was therefore kept below 10 M.
MULTI-STAGE EXTRACTION AND STRIPPING A laboratory scale multi-stage glass mixer-settler (13) was used to model the separation process for nitric/phosphoric acid mixtures with the same TOA extractants. In general, two stages were used for both extraction and stripping. At total flow rates up to 6 ℓ/h each stage was equivalent, within experimental error, to an equilibrium stage. The two phases were fed by a calibrated Watson-Marlow multi-channel peristaltic metering pump with Neoprene pumping tubes. The aqueous phase flow rate was in the range 0.3 to 0.5 ℓ/h and to achieve organic/aqueous phase flow ratios up to 5:1, extra organic phase pumping tubes were attached. A fine adjustment could be made to the flow rate in each line by a screw clip, which

partially constricted the tube.

The equipment was left running for an adequate time (more than 15 mins) to achieve constant concentrations in each stage and then samples were taken from both phases in each stage for analysis to find the equilibrium acid concentrations.

RESULTS AND DISCUSSION

NITRIC ACID Equilibrium isotherms at 25°C for the distribution of nitric acid alone between an aqueous phase and TOA extractant at seven different amine concentrations from 0.11 M to 1.13 M (i.e. 5% - 50% v/v TOA) in kerosene with 12% v/v n-decanol are shown in Figure 1. There is little acid concentration in the aqueous phase until the organic phase contains enough acid to form the 1:1 molecular salt with the amine. For TOA concentrations from 0.11 M to 0.68 M, the isotherms are essentially straight lines with intercepts on the vertical axis corresponding to an organic nitric acid molarity nearly equal to the amine molarity. At higher TOA concentrations, the equilibrium isotherms curve in the direction of decreasing gradient as nitric acid concentration increases. Values of α in Mason's relation were found to be in the range 0.13 - 0.20 and considering the simplicity of this model, it was a reasonable fit of the data. However, the experimental results when fitted to the Kertes and Platzner model did not give a constant, probably due to the difficulty in finding accurately the concentration of undissociated nitric acid from the graph given by Krawetz.

NITRIC/PHOSPHORIC ACID MIXTURES Equilibrium distributions for nitric/phosphoric acid mixtures for four different TOA concentrations are given in Figures 2-4. The organic phase concentrations of both acids are plotted against the aqueous phase nitric acid concentration. In each figure the pre-contact phosphoric acid concentration in the aqueous phase is constant: 2 M in Figure 2, 4 M in Figure 3 and 6 M in Figure 4. The range of acid concentrations examined was 0.5 - 9 M for nitric acid and 0.5 - 8 M for phosphoric acid. As the figures show, the concentration of phosphoric acid in the organic phase is always low, and so the equilibrium aqueous concentrations of phosphoric acid are approximately equal to the initial pre-contact concentrations.

For TOA concentrations below 0.68 M, the distributions of nitric acid are again linear, and the concentration of phosphoric acid in the aqueous phase affects the nitric acid distribution only slightly. Up to 0.45 M TOA, organic nitric acid concentration increases a little with increase in the aqueous phosphoric acid concentration, but at low concentrations of aqueous nitric acid (below 2 M), the organic phase nitric acid concentration is relatively lower at the high phosphoric levels.

The separation factor for the two acids is always high, but is subject to a large experimental error, as the organic phase phosphoric acid concentration is often low and of the same order as the experimental error in its measurement.

As so little phosphoric acid is in the organic phase (0.01 M to 0.14 M for 0.45 M or 20% TOA) the stripping equilibrium obtained by contact of the loaded extractant with water is, within experimental error, identical with the pure nitric acid distribution given in Figure 1. On stripping, essentially all the excess nitric acid, above the requirement for amine salt formation, is transferred back to the aqueous phase, together with the small amount of phosphoric acid extracted.

Equilibrium distribution isotherms were measured for the tertiary amine extractants Adogen 363 and 382 (supplied by Ashland Chemicals) as alternatives to TOA. They were used as 0.45 M solutions, again in kerosene diluent with 12% v/v n-decanol. The distributions (Figure 5) were very similar to those for TOA: for example, for 0.45 M extractant contacted with an equal volume of 5 M nitric acid and 0.5 M phosphoric acid, the equilibrium organic phase concentrations of nitric acid were: TOA, 0.78 M; Adogen 363, 0.68 M; Adogen 382, 0.74 M.

NITRIC/SULPHURIC ACID MIXTURES Figures 6-8 show distribution equilibria for mixtures of nitric acid (1 - 3 M) with pre-contact sulphuric acid concentrations of 2 M (Figure 6), 4 M (Figure 7) and 6 M (Figure 8) with five different TOA concentrations from 0.22 to 1.13 M. Organic phase equilibrium concentrations of both acids are given. At TOA strengths up to 0.68 M, the nitric acid equilibria remain as straight lines, within experimental error. The effect of increase in sulphuric acid concentration up to 4 M is to increase somewhat the organic phase nitric acid concentration. The proportion of sulphuric acid extracted into the organic phase is low, and in the range 0.01 - 0.15 M for 0.45 M TOA. The stripping equilibrium may therefore be taken as the pure nitric acid distribution.

The nitric acid loading in the organic phase is greater in mixtures with sulphuric acid than with phosphoric acid, at corresponding pre-contact molarities and extractant concentrations.

MULTI-STAGE PROCESS The experimental measurements of equilibrium acid concentrations achieved in the multi-stage extraction and stripping process agreed well with the theoretical predictions made by construction of a McCabe-Thiele diagram. Further theoretical predictions were made of the performance of the process for a greater number of equilibrium stages and for higher organic/aqueous flow ratios than were used experimentally. For an aqueous feed mixture of 3 M nitric and 1 M phosphoric acids, the results of these predictions are shown in Table 1, together with experimental results, indicated by an asterisk.

TABLE 1

Theoretical Predictions and Experimental Results$^{(*)}$ for the Multi-Stage Separation of a Mixture of 3 M Nitric and 1 M Phosphoric Acids

$[\text{TOAHNO}_3]$ M	No. of Stages Extn. & Strip	Extraction			Stripping	
		Flow Ratio O/A	Raffinate $[\text{HNO}_3]_{aq}$	Loaded Extractant $[\text{HNO}_3]_{org}$	Flow Ratio O/A	Product $[\text{HNO}_3]_{aq}$ M
0.21	2	1.1	2.84	0.39	1.2	0.15
0.21	2	2.2	2.62	0.38	2.2	0.41
0.21	2	4.6	2.28	0.38	4.6	0.68
*0.20	2	1.25	2.78	0.39	1.0	0.19
*0.21	2	2.2	2.64	0.38	2.2	0.38
*0.21	2	4.6	2.24	0.38	4.6	0.78
0.43	2	17	0.80	0.56	5	0.74
0.43	6	10	0.68	0.64	10	2.10
0.43	10	11.5	0.46	0.65	11.5	2.50

For this feed mixture, it reasonably may be assumed that the same nitric acid distribution curve applies for both extraction and stripping and this was used in the McCabe-Thiele diagrams. On this assumption, the maximum concentration of the purified nitric acid product stream will be the same as the nitric acid concentration in the feed, but this would require infinite flow ratios. For a given number of stages, increase in organic/aqueous flow ratio during extraction reduces the nitric acid concentration in the aqueous raffinate, but lowers the concentration of nitric acid in the loaded extractant. During stripping, increase in flow ratio produces an increase in product acid concentration, but tends to prevent a complete strip of the complexed nitric acid. Increase in extractant concentration is beneficial both in increasing the proportion of nitric acid extracted, and also the concentration of product acid. Extra stages in extraction and stripping increase the separation efficiency, but this has to be balanced against the increased capital cost of the plant. The concentration of phosphoric acid in the product nitric acid stream would be expected to be always less than 7% of the total acid, for the process configurations considered in Table 1, which give possible arrangements for practical processes designed to separate partially the feed acids.

CONCLUSIONS

The results presented show that trioctylamine nitrate extractant may be effectively used to separate mixtures of nitric/phosphoric and nitric/sulphuric acids. Processes of the general type described, which include a simple water strip stage, are worthy of comparison with separation processes employing other organic solvents and may be capable of application to the separation of other mixtures of inorganic acids.

The processes described in this paper are covered by U.K. Provisional Patent Application 7911855.

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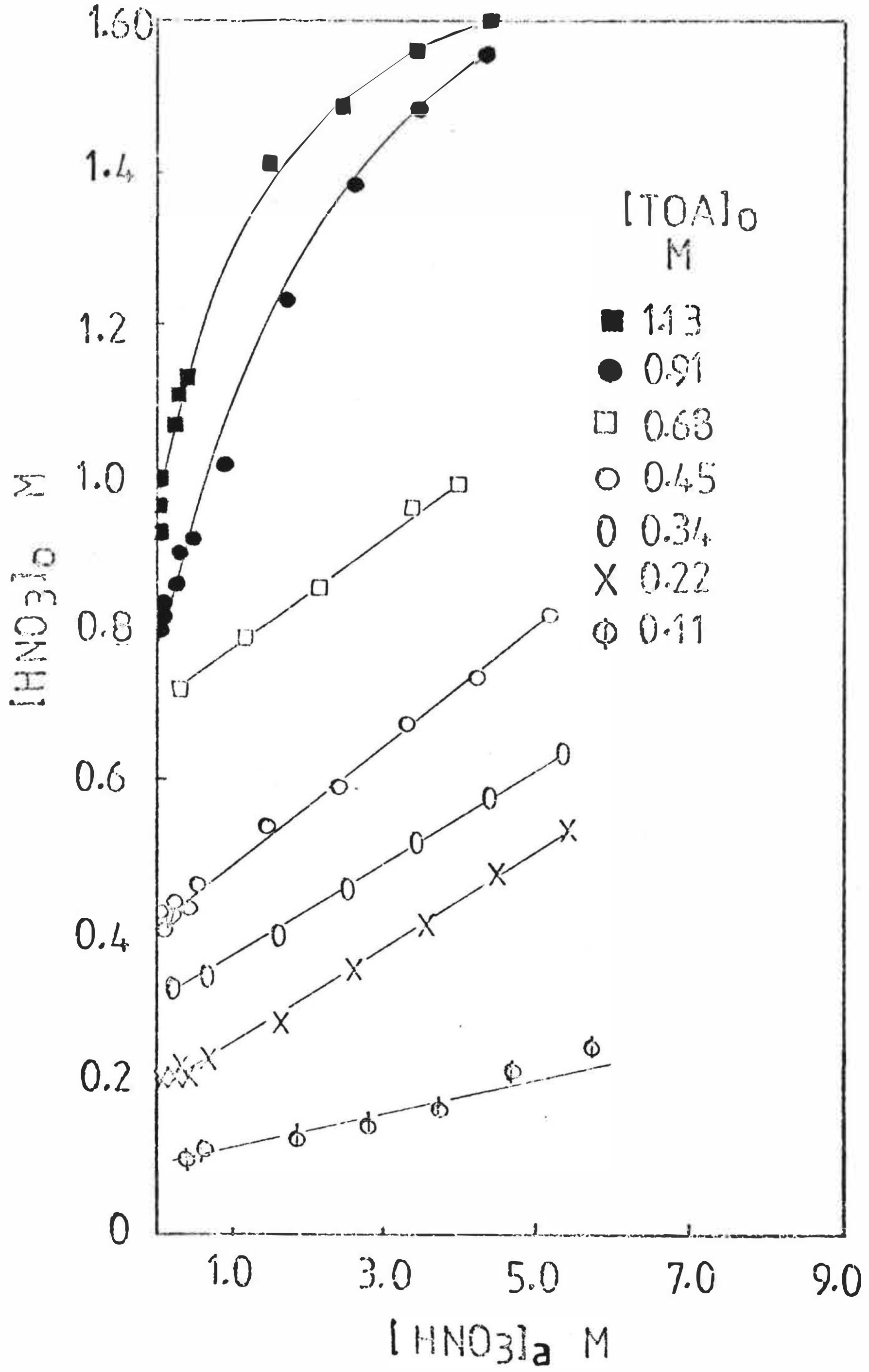

FIG. 1

Distribution for HNO_3 alone between TOA extractant and aqueous phase

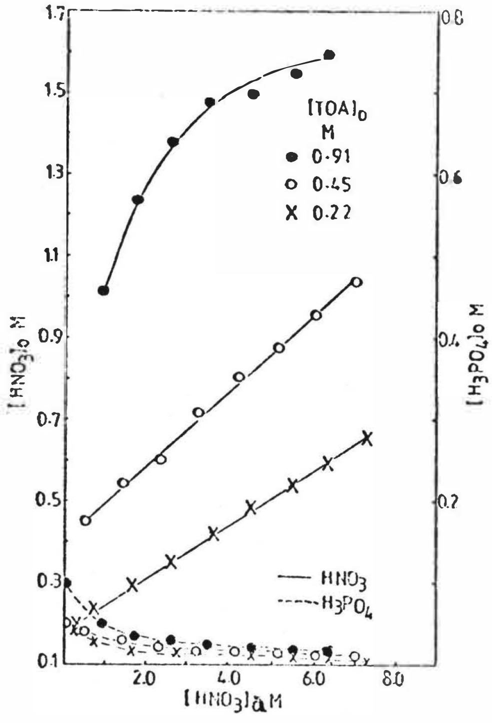

FIG. 2

Distribution of HNO_3/H_3PO_4 mixtures; $[H_3PO_4]_{aq}$ = 2 M

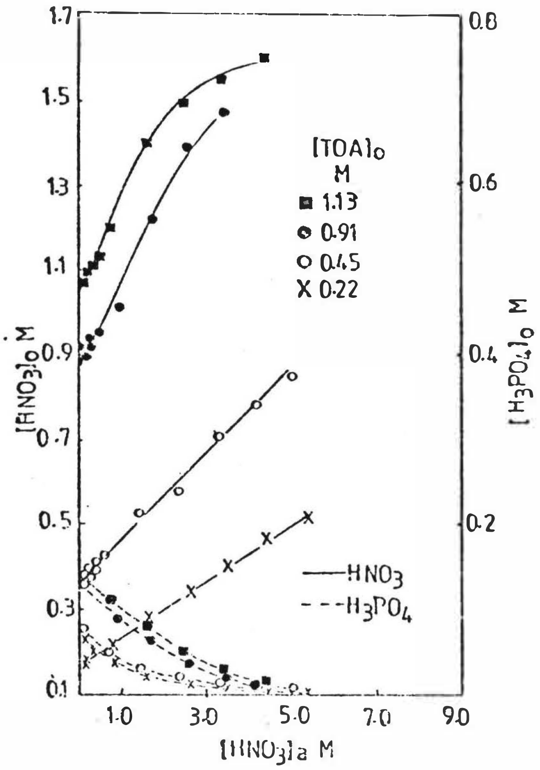

FIG. 3

Distribution of HNO_3/H_3PO_4 mixtures; $[H_3PO_4]_{aq}$ = 4 M

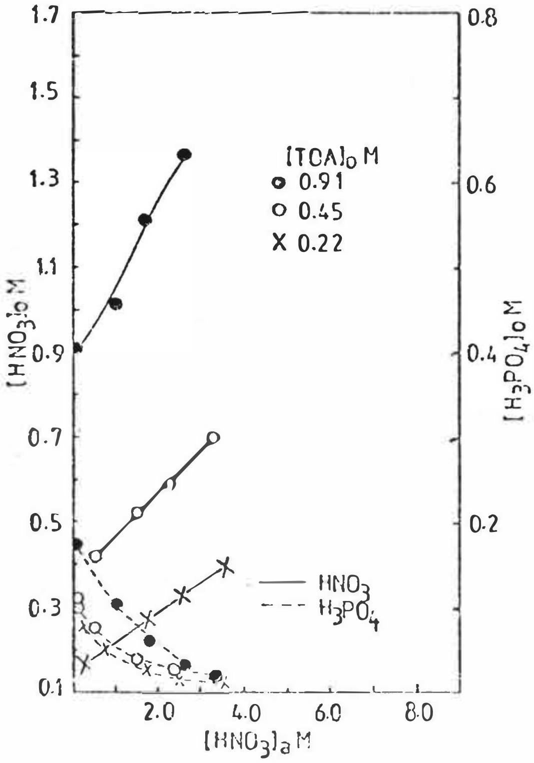

FIG. 4

Distribution of HNO_3/H_3PO_4 mixtures; $[H_3PO_4]_{aq}$ = 6 M

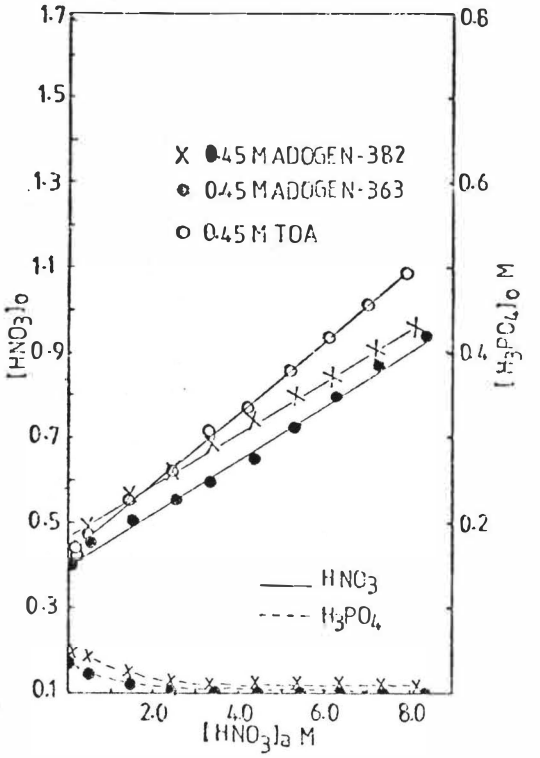

FIG. 5

Adogen Extractants and TOA; HNO_3/H_3PO_4 mixtures; $[H_3PO_4]_{aq}$ = 0.5M

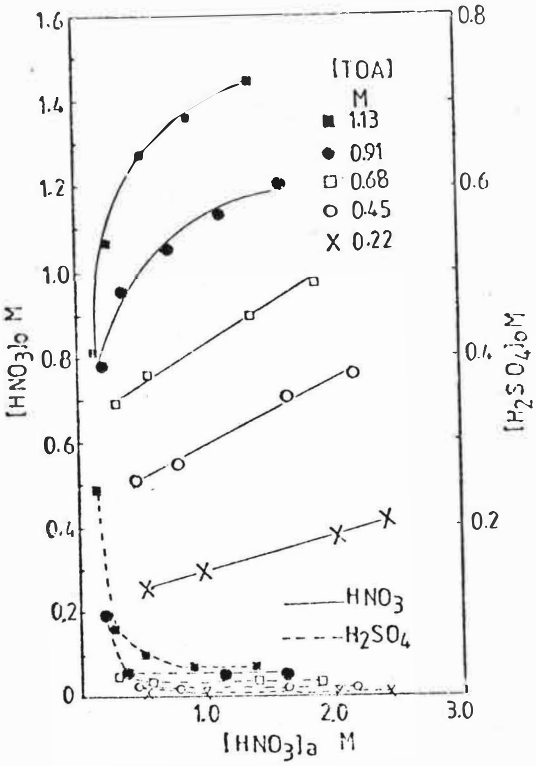

FIG. 6

Distribution for HNO_3/H_2SO_4 mixtures; $[H_2SO_4]_{aq}$ = 2 M

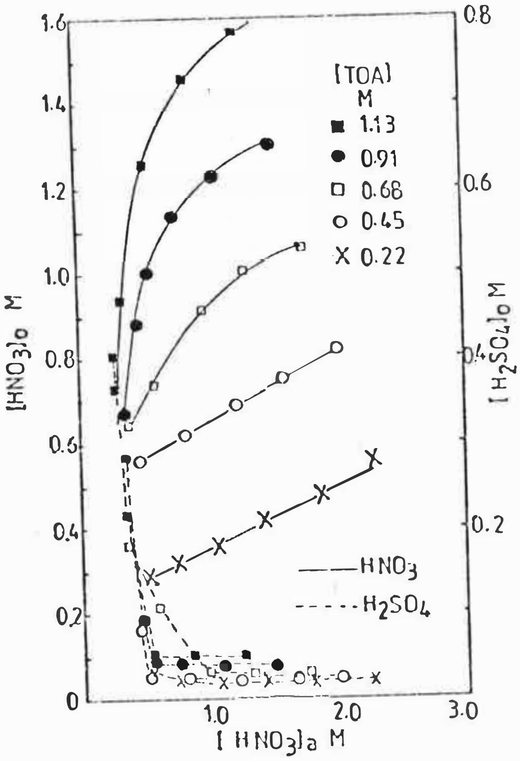

FIG. 7

Distribution for HNO_3/H_2SO_4 mixtures; $[H_2SO_4]_{aq}$ = 4 M

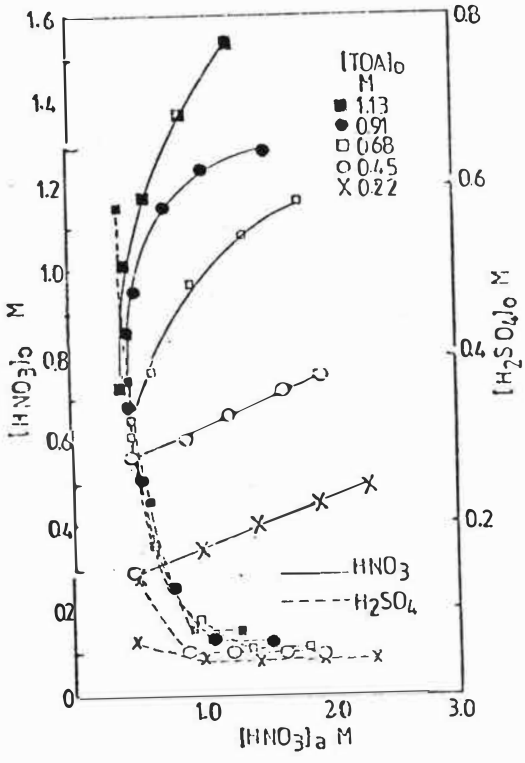

FIG. 8

Distribution for HNO_3/H_3PO_4 mixtures; $[H_2SO_4]_{aq}$ = 6 M

ACID EXTRACTION BY TERTIARY AMINES

Chekmarev A.M., Ochkin A.V.,
Sergievsky V.V., Tarasov V.V.,
Yagodin G.A.
Mendeleev Institute of
Chemical Technology
Moscow, USSR

ABSTRACT.

The thermodynamic description of acid extraction by tertiary amines is considered. The equations are deducted to compare the results of the different methods. The extraction kinetics is studied to clear up the mechanism of the process.

The acid extraction by tertiary amines can be represented by the equation

$$H^+ + A^- + \overline{R_3N} \rightleftharpoons \overline{R_3NHA} \qquad (1)$$

with the equilibrium constant

$$K = \frac{m_3 \gamma_3}{a_{HA} m_2 \gamma_2} \qquad (2)$$

where a_{HA} is the acid activity, m_i and γ_i are the molal concentrations and the concentration activity coefficients in the organic phase, the subscripts 1,2 and 3 refer respectively to solvent, amine and amine salt. Usually $\gamma_2 = 1$ whereas the values γ_3 often deviate from 1 owing to non-ideality of the organic phase. One of the reasons of this non-ideality is the association of ammonium salts but their hydration and solvation ought to be taken into account too.

The values can be calculated from solvent activities which are determined by the cryoscopic, ebulliometric or similar methods through the Gibbs-Duhem equation

$$\frac{10^3}{M_1} d\ln a_1 + m_3 d\ln a_3 = 0 \qquad (3)$$

where M_1 is the molecular mass of the solvent. Usually the osmotic coefficient φ is introduced

$$\varphi = -\frac{10^3}{m_3 M_1} \ln a_1 \tag{4}$$

Then integrating eq. (3) we find

$$\ln \gamma_3 = \varphi - 1 - \int_0^{m_3} \frac{1-\varphi}{m_3} \, dm_3 \tag{5}$$

Sometimes the non-ideality of alkylammonium salt solutions is treated through association equilibrium

$$p\overline{R_3NHA} \rightleftharpoons \overline{(R_3NHA)_p} \tag{6}$$

with the formation constant

$$\beta_p = \frac{m_3(p)}{m_3^p(1)} \tag{7}$$

where $m_3(1)$ and $m_3(p)$ are the molalities of monomer and p-mer respectively. Obviously

$$m_3 = \sum_p p\beta_p m_3^p(1) \tag{8}$$

The constants β_p can be calculated from data of cryoscopy, ebulliometry, vapour pressure, osmometry, etc. through the equation

$$-\frac{10^3}{M_1} \ln a_1 = \sum_p \beta_p m_3^p(1) = m_3\varphi = \frac{m_3}{\bar{n}} \tag{9}$$

where $\bar{n}$ is the average association degree. Using this equation we get after integration of eq. (5)

$$p\overline{R_3NHA} + q\bar{B} \rightleftharpoons \overline{(R_3NHA)_p \cdot B_q} \tag{10}$$

The eq. (10) can be expanded on the formation of solvates (hydrates)

$$\ln \gamma_3 = \ln \frac{m_3(1)}{m_3} \tag{11}$$

with the formation constant

$$\beta_{pq} = \frac{[(R_3NHA)_p \cdot B_q]}{m_3^p(1) \cdot m_4^q(1)} \tag{12}$$

where $m_4(1)$ is the concentration of monomer B. Apparently m_4 can be expressed similarly to (8) and instead (9) we have

$$-\frac{10^3}{M_1} \ln a_1 = \sum_{p,q} \beta_{pq} m_3^p(1)\, m_4^q(1) \tag{13}$$

Substituting this result into (3) we find that the eq. (10) is true for both the components 3 and 4. It is easy to show in this case that

$$\left(\frac{\partial \ln a_3}{\partial m_4}\right)_{m_3} = \left(\frac{\partial \ln a_4}{\partial m_3}\right)_{m_4} \tag{14}$$

The solvate formation can be treated as

$$pH^+ + pA^- + p\overline{R_3N} + q\bar{B} \rightleftharpoons \overline{(R_3NHA)_p \cdot B_q} \tag{15}$$

with the equilibrium constant

$$K_{pq} = \frac{[(R_3NHA)_p \cdot B_q]}{a_{HA}^p \cdot m_2^p \cdot m_4^q(1)} = K_{10}^p \cdot \beta_{pq} \tag{16}$$

where

$$K_{10} = \frac{m_3(1)}{a_{HA} \cdot m_2} \tag{17}$$

Substituting $m_3(1)$ from eq. (10) we find

$$K_{10} = K \tag{18}$$

The equations (10), (16) and (18) allow us to compare the results of the different methods. Kertes and Markovits (1) have investigated the association of some trilaurylammonium (TLA) salts in benzene, carbon tetrachloride and cyclohexane. They got after integration of the Gibbs-Duhem equation

$$\log \gamma_3 = A + Bm_3 + Cm_3^2 + Dm_3^3 \tag{19}$$

Obviously the coefficient A must be equal to zero because $\gamma_3 = 1$ at $m_3 = 0$. Unequality of A to zero means that eq. (19) is that of interpolation and may be only applied in the concentration range under the investigation. Simultaneously the authors (1) determined the constants β_p from the same data. Therefore it is possible to compare the values of log γ_3 calculated by two methods and to estimate the possible errors. The results presented in Table 1 show there is a small discrepancy between the two methods. Because the initial experimental data were the same this discrepancy is connected with the computation procedure. It was stated that the relatively long extrapolation to infinite dilution may be subject to a small constant error in the activity coefficients represented by

Table 1

LOG γ_3 FOR TRILAURYLAMMONIUM BROMIDE SOLUTIONS IN CYCLOHEXANE AT 25°C

$m_3 \cdot 10^3$	7	10	20	40	50
Eq. (19)	-0,533	-0,598	-0,778	-1,000	-1,064
Eq. (10) and (9)	-0,601	-0,684	-0,851	-1,057	-1,120
Eq. (21)	-0,400	-0,489	-0,680	-0,882	-0,949

the polynomial" (1). This extrapolation is especially difficult when the non-ideality is large. In order to avoid these difficulties we recommend to treat experimental data with the equation (2)

$$\frac{m_3}{\ln f_1} = A + Bm_3 \qquad (20)$$

where f_1 is the mole fraction activity coefficient of solvent. Substituting (20) into (3) and integrating we find :

$$\ln \gamma_3 = \left[-\frac{10^3}{M_1 B} \ln\left(1 + \frac{B}{A} m_3\right) + \frac{B m_3}{A + B m_3} \right] \qquad (21)$$

The suitability of eq. (20) has been demonstrated for a lot of systems (2-4). The scheme of the calculation will be considered here for trilaurylammonium bromide solutions in cyclohexane at 25°C. Experimental $\bar{n}$ were taken from (1) (benzene was mistakenly reported as a solvent in Table VII). At first molar concentrations were converted to molalities and eq. (9) was used to compute $\ln f_1$. Then we calculated $m_3^2/\ln f_1$ and determined A=0,101 and B=17,08 by the least-squares method. Intermediate results of the calculation are given in Table 2. The values of log γ_3 found according to eq. (21) are compared with the other results in Table 1. The maximum difference occurs at the lower concentration where the polynomial (19) does not already fit the experimental data. In other solutions where non-ideality is not so large as in the system under consideration the discrepancy between three methods are probably small or even negligible. For example, we found in TLA chloride solutions in CCl_4 at 51°C $\log \gamma_3$ =-0,263 (m_3= =0,01) and -0,569 (m_3=0,05) whereas the calculation on eq. (19) resulted in -0,319 and -0,662 respectively at 25°C.

The activity coefficients γ_3 determined from cryoscopic and similar data are strictly valid only for dry solutions. In some amine extraction systems the water concentration in the organic phase can exceed m_3 and therefore the effect of water on the activity coefficients should be investigated. Sometimes this effect is neglected (see, for example, (5)) but

Table 2

THE CALCULATION OF A AND B IN THE EQUATION (21) FOR TRILAURYLAMMONIUM BROMIDE SOLUTIONS IN CYCLOHEXANE AT 25°C

$C_3\cdot 10^3$ (1)	$\bar{n}$ (1)	$m_3\cdot 10^3$	$-10^4\cdot\ln x_1$	$10^4\cdot\ln f_1$	$\frac{m_3^2}{\ln f_1}$
6,6	1,83	8,6	7,23	3,28	0,225
8,6	1,91	11,2	9,42	4,49	0,279
13,3	2,04	17,3	14,55	7,42	0,403
19,9	2,19	26,1	21,94	11,92	0,571
33,3	2,50	44,0	36,96	22,18	0,873
46,6	2,76	62,1	52,12	33,24	1,160
53,3	2,78	71,3	59,83	38,31	1,327
66,6	2,98	89,8	75,29	50,02	1,612

no good reason of it has been offered. Now we suggest the thermodynamic description of the water effect on extraction equilibrium in amine systems.

The water concentration m_w has been proved to be expressed as

$$m_w = m_{wo}\cdot a_w + h\,m_3 \tag{22}$$

where m_{wo} is the water solubility in pure solvent at the water activity $a_w = 1$, h is the hydration degree. Usually

$$h = h_\infty\cdot a_w = m_{wo}\cdot k\cdot a_w \tag{23}$$

where h_∞ is the hydration degree at $a_w = 1$ and the constant k is equal $h/m_{wo}\cdot a_w$. Then

$$m_w = m_{wo}\cdot a_w\,(1 + k\,m_3) \tag{24}$$

It is necessary to change the standard state of water in eq. (24) so that its activity coefficient be equal to one in the infinitely diluted solution. We get

$$m_w = a_{w\infty}\,(1 + k\,m_3) \tag{25}$$

where $a_{w\infty} = m_{wo}\cdot a_w$. Using the equations (14) and (25) we find

$$\left(\frac{\partial \ln a_3}{\partial m_w}\right)_{m_3} = -\frac{k}{1 + k\,m_3} \tag{26}$$

Finally after integration we have

$$\ln\frac{a_3^0}{a_3} = h \tag{27}$$

where $a_3^\circ = a_3$ at $a_w = 0$. This expression was deduced by an other way in 1973 (6).

The eq. (27) shows that the amine salt activity decreases due to hydration. Similarly the activity coefficients γ_3 can be expressed through the activity coefficient in the dry solution γ_3°

$$\ln \gamma_3 = \ln \gamma_3^\circ - h \tag{28}$$

Apparently if h is constant the changes of do not depend on m_3 and they only affect the absolute value of K in (2). Furthermore the activity coefficients in eq. (2) ought to be choosen so that $\gamma_3 = 1$ in the infinitely diluted solutions saturated with water at corresponding a_w (usually $a_w = 1$). It is easily seen that

$$\gamma_{3,a_w} = \gamma_3^\circ \exp\left[h_\infty (a_w^\circ - a_w)\right] \tag{29}$$

where a_w° is the water activity in standard solution. Particularly at $a_w = a_w^\circ$ we might use the activity coefficients γ_3° in dry solutions in the calculations of K as it has been made in (5). But if a_w is less than a_w° the activity coefficient γ_{3,a_w} will be more than γ_3° and neglecting it results in the decrease of K (7).

Another important conclusion can be drawn from the Gibbs--Duhem equation

$$\frac{10^3}{M_1}\left(\frac{\partial \ln a_1}{\partial m_w}\right)_{m_3} dm_w + m_3\left(\frac{\partial \ln a_3}{\partial m_w}\right)_{m_3} dm_w + m_w\left(\frac{\partial \ln a_{w\infty}}{\partial m_w}\right)_{m_3} dm_w = 0 \tag{30}$$

Substituting (25) and (26) in (30) we find after integration

$$\frac{10^3}{M_1} \ln \frac{a_1}{a_1^\circ} = -\frac{m_w}{1 + k m_3} = -m_{wo} \tag{31}$$

where $a_1^\circ = a_1$ at $a_w = 0$ Thus the solvent activity decrease is determined only by "free soluted" water whereas water hydrating alkylammonium salt is osmotic inactive.

The hydration influences most strongly alkylammonium salt activity when there are deviations from eq. (24) and (25). Then instead eq. (25) we might apply

$$m_w = \sum_{n_1,n_2} A_{n_1 n_2}\, a_{w\infty}^{n_1}\, m_3^{n_2} \tag{32}$$

To determine the water effect on a_3 the relation suggested by McKay (8) can be used

$$\left(\frac{\partial \ln a_3}{\partial \ln a_4}\right)_{m_3} = -\left(\frac{\partial m_4}{\partial m_3}\right)_{a_4} \tag{33}$$

where in our case the subscript 4 refers to water. Substituting (32) into (33) and integrating we get instead (27)

$$\ln \frac{a_3}{a_3^\circ} = -\sum_{n_1,n_2} \frac{n_2}{n_1} A_{n_1 n_2}\, a_{w\infty}^{n_1}\, m_3^{n_2 - 1} \tag{34}$$

Similarly instead (31) we find from (30)

$$\frac{10^3}{M_1}\ln\frac{a_1}{a_1^o} = -\sum_{n_1}\frac{1}{n_1}A_{n_1 0}\,a_{w\infty}^{n_1} + \sum_{n_1,n_2}\frac{n_2-1}{n_1}A_{n_1 n_2}\,a_{w\infty}^{n_1}\,m_3^{n_2} \qquad (35)$$

where the first term in the right part shows solvent activity decrease due to the water solubility in pure solvent. If the terms with $n_1 > 1$ and $n_2 > 1$ can be neglected, eq. (34) and (35) transform to eq. (27) and (31) respectively. Due to these terms, $\ln a_3/a_3^o$ in eq. (34) depends on m_3. In practice this dependence can be mistakenly interpreted as the ammonium salt association. For example, Allen (9) investigated the sulphuric acid extraction by trioctylamine (TOA) and discovered sharp decrease of sulphate TOA activity when its concentration increased. He explained this with the association and even assumed formation of colloid solutions of sulphate TOA but afterwards he found only low association of this salt (10). This contradiction has been resolved recently (6) when the salt hydration was taken into account. The other example is the peculiar dependence of $\log c_3$ on $\log c_2 \cdot a_{HA}$ found by Muller and Diamond (11) for hydrohalic acid extraction by TLA. When c_3 increased the slope of the curve became infinitely large and even negative. This can't be explained by salt association and perhaps the salt hydration is the most probable reason. The dependence of water concentration on trilaurylammonium salt concentration in these systems seems to be non linear (11). On the other hand it is neccessary to point that the dependences of $\log c_3$ on $\log c_2 \cdot a_{HA}$ for hydrohalic acid extraction by TLA and for sulphuric acid extraction by TOA are similar.

Sometimes high-molecular weight alcohols are added to amine extraction systems to avoid third phase formation. This results in the increase of acid extraction due to solvatation of alkylammonium salts. Usually this solvation equilibrium is treated through eq. (11) and (12) but different approach is possible. As a matter of fact the solvation by alcohols is similar to the hydration of alkylammonium salts and may be described by equations analogous to (25) - (31):

$$m_{al} = a_{al}\,(1 + k'm_3)$$

$$\ln\frac{a_3}{a_3^o} = -\frac{k'}{1 + k'm_3}\cdot m_{al} \qquad (36)$$

$$\frac{10^3}{M_1}\ln\frac{a_1}{a_1^o} = -\frac{1}{1 + k'm_3}\cdot m_{al}$$

where m_{al} and a_{al} are the molality and the activity of alcohol.

In order to clear up the mechanism of acid extraction by tertiary amines we have studied the kinetics of hydrochloric acid extraction by TOA, TLA and tridecylamine (TDA). It has been shown by the short-time contact method (STCM) that all the reactions in the systems are fast and their rates are diffusion-controlled. The protonation reaction proceeds at the interface whereas the ionic association takes place in a very thin layer at the side of the organic phase.

Unexpectedly the hydrochloric acid extraction by TDA and TLA at the HCl concentrations in the aqueous phase below

10^{-3} mole/l has proven to be complicated by the formation at the interface of a thin layer of a new phase which sharply decreases the extraction rate. The new phase has a high viscosity which has been measured by an electromagnetic viscosimeter of the pendulum type. The new phase is supersaturated with water and the addition of high-molecular weight alcohol (2 + 5% vol.) to the organic phase decreases the supersaturation with water and destroys the film effect on the extraction kinetics.

The acid stripping is also complicated with the formation of interface layers supersaturated with water. This results in an unusual dependence of stripping rate on time or concentration. These effects are especially large for perchloric acid stripping (Fig.1).

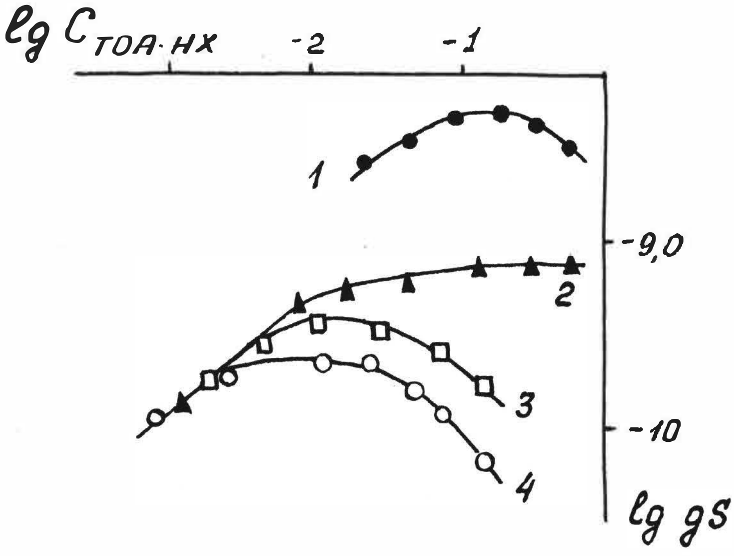

FIG. 1

Effect of ammonium salt concentration on the stripping rate of HCl and $HClO_4$. 1 - $TOA\cdot HCl$, $C_{TOA}=0$;2,3 and 4 - $TOA\cdot HClO_4$ at C_{TOA} = 0; 0,005 M and 0,02 M respectively.

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PROCESS DEVELOPMENT OF BORON RECOVERY FROM ASCHARITE

Y. F. SU and D. Y. YU
Shanghai Institute of Chemical Technology
Shanghai 201107, CHINA
S. D. CHEN
Shanghai Borax Works

ABSTRACT A process has been developed for converting the mineral ascharite (B_2O_3-$2MgO$-H_2O) into H_3BO_3 and MgO. Firstly, ascharite is decomposed by recovered HCl to give a solution containing > 95% B_2O_3 and 85% MgO of the ore. From the clarified solution H_3BO_3 is extracted by 2-ethylhexanol-kerosene mixture and is stripped by water and NaOH solution to produce boric acid and borax respectively. The raffinate is purified and concentrated; the magnesium chloride hydrate obtained is decomposed to give MgO and HCl which is recycled for the decomposition of ascharite.

This process may produce much less solid and liquid wastes and require less energy than the present production process.

INTRODUCTION

Extensive boron deposit available in the north-east of China exists as the mineral ascharite (B_2O_3-$2MgO$-H_2O). The present method for the recovery of its boron value in China has been confined to alkaline digestion, yielding borax as an immediate product and leaving a large amount of muddy waste consisting chiefly of magnesium compounds which has to be disposed. In order to lessen the trouble of waste disposal and recover the boron value partly as boric acid to meet the market demand, the acid treatment of the ore has been considered.

Literature survey has revealed that the use of mineral acids, such as nitric (1), sulphuric (2) (3) (4) (5) (6), hydrochloric (7) and phosphoric acids (8), as ore decomposing agents has been proposed by different authors. However, among these acidic agents only sulphuric acid has been ever used in industry. But due to the large amount of slimes and high concentration of magnesium sulphate in the recycled liquor, the loss of boric acid is appreciable and other problems arising can not be easily solved (4).

The present authors have attempted the use of hydrochloric acid and found that ascharite (40 mesh) can be easily decomposed by hydrochloric acid at 100° to 105° C. As the reaction is irreversible, it is not necessary to use concentrated acid, and in a reaction period of 30 to 40 minutes more than 95% of boron can be brought into solution. Besides, unlike sulphuric or phosphoric acid, hydrochloric acid does not produce any insoluble reaction product and leaves much smaller amount of residue from which any occluded but soluble boric acid can be easily washed. The result will be higher yield of boric acid.

The mineral obtained from the market is usually poor in boric anhydride and rich in magnesium (and calcium) oxide, as shown in Table 1. Because the ignition loss is high, it can be anticipated that besides ascharite there exists appreciable amount of carbonates. This fact has been confirmed by differential thermal analysis.

The ore analysis in Table 1 represents the average quality of the raw material used in our industry. Sometimes the boric anhydride content may drop to about 10%. Therefore, any process simply making use of its boron value is not profitable and process based upon the utilization of both magnesium and boron values must be developed.

TABLE 1

Ore Analysis	B_2O_3	MgO	CaO	Fe_2O_3	Al_2O_3	Acid Insoluble	Ignition Loss
%	13,13	36,48	9,16	0,64	0,21	7,26	33,12
Solution Composition	H_3BO_3	$MgCl_2$	$CaCl_2$	$FeCl_3$	HCl	Residue	
g/1	57	280	45	4,0	0,07N	20% of Ore	
Residue Analysis	B_2O_3	MgO	CaO	Fe_2O_3		Acid Insoluble	
%	1,1	29,0	0,4	0,4		35,0	

When for each ton of the ore 2,7 to 3 m^3 of hydrochloric acid (containing enough HCl to neutralize 85% of MgO and CaO in ore) and 1 m^3 of recycled mother liquor of $MgCl_2$ (see FIG. 8) are used, the compositions of the resulting solution and the residue after digestion are also shown in Table 1. The residue amounts to 20% of treated ore. From the Table one can see that the percentage decomposition of ascharite is about 98% (based upon boron).

The next step after removing the insoluble residue is the separation of boric acid from the mother liquor consisting chiefly of $MgCl_2$ and $CaCl_2$. Solvent extraction has been selected as a means of the separation.

Many patents (9) have revealed that aliphatic and aromatic polyols (e.g. diols) are good extractants for boron either from alkaline brine or acidic solutions. Unfortunately, many of these diols are fairly water-soluble and liable to be lost or require certain means for their recovery. Besides, it is also known that monohydric aliphatic alcohols (from butanol to dodecanol) can also be used to extract boric acid from acidic solution and the latter can be back-extracted into water or alkali. If the carbon chain of the alcohol is moderately long, the solubility loss in water will be very much lowered (10). This patent concerns the removal of micro-quantity of boron from concentrated $MgCl_2$ solutions, whereas we are interested in the separation of macro- as well as micro-quantities of boric acid.

Two octanols have been tested as solvent for the extraction of boric acid, octanol-2 gives only small distribution coefficient, whereas 2-ethylhexanol gives much higher values at different conditions and therefore has been used for further investigation.

EQUILIBRIUM RELATIONSHIPS

1. Effect of solvent composition The distribution coefficients of boric acid by using pure 2-ethylhexanol and its mixture with kerosene as diluent are shown in FIG. 1. It is apparent that with kerosene alone as solvent no boric acid is extracted. But a mixture of equal volumes of 2-ethylhexanol and kerosene may possess an extracting power as good as the pure alcohol. The use of a diluent such as kerosene has the advantage of reducing the solvent viscosity and solubility of the alcohol in aqueous phase, and the reduction of both is desirable in extraction and stripping operations. Therefore, this mixed solvent is employed throughout our work. The selectivity of this solvent is also very high, for Mg^{2+} and Ca^{2+} are not extracted and the separation factor of H_3BO_3 from Fe^{3+} is greater than ten.

2. Effect of pH of aqueous solution As boric acid is extracted from acidic solution into solvent and stripped from solvent into pure water or alkaline solution, the distribution coefficient depends strongly upon the pH value of aqueous solution (see FIG. 2). FIG. 2 indicates that within the range investigated, when pH value smaller than 3, the distribution coefficient is always greater than 2.

In general, the leaching liquor can be directed to the extraction equipment without any adjustment of pH.

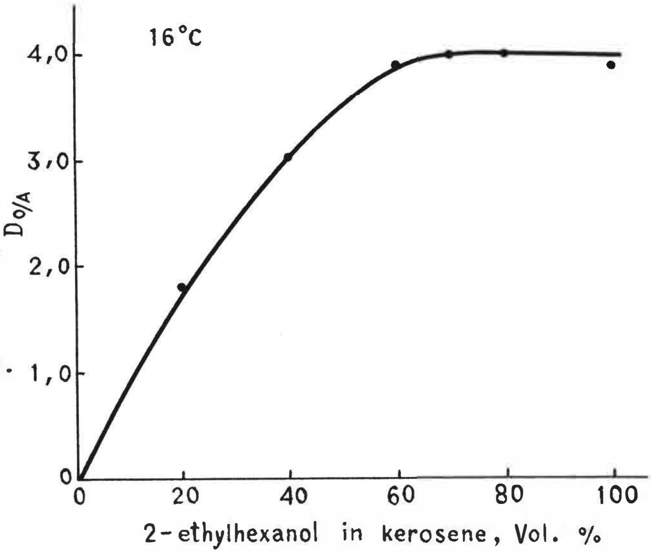

FIG. 1 Effect of solvent composition

Aqueous phase:

$MgCl_2$	282,83 g/l	$FeCl_3$	1,25 g/l
$CaCl_2$	31,43 g/l	HCl	0,13 N

3. Effect of salt concentration It is well known that the presence of unextractable salts in aqueous phase has generally salting-out effects on the extractable species. FIG. 3 reveals that the salting-out effect of $MgCl_2$ becomes more and more pronounced at increasing concentration.

The amount of recycled $MgCl_2$ solution stream (see FIG. 8) and the ratio of ore to total decomposing liquid must be properly chosen in order to obtain an ore-leaching liquor with high salt concentration, and consequently a high distribution coefficient can be secured.

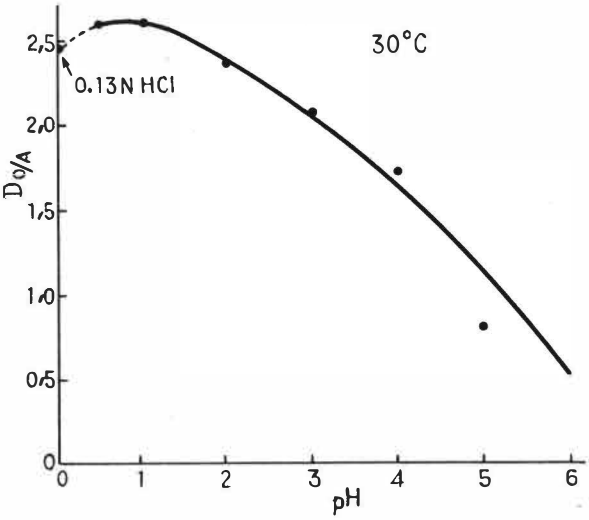

FIG. 2 Effect of pH of aq. soln.
Organic phase:
2-ethylhexanol : kerosene = 1:1
Aqueous phase: 280 g/l $MgCl_2$

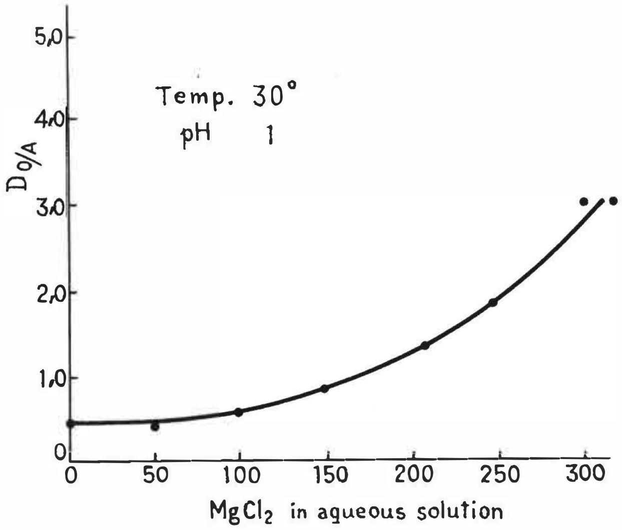

FIG. 3 Effect of $MgCl_2$ concentration

4. Effect of temperature of extraction As discussed in the preceding sections, it is desirable to extract boric acid from a leaching liquor containing possibly high concentrations of $MgCl_2$. At the same time, the

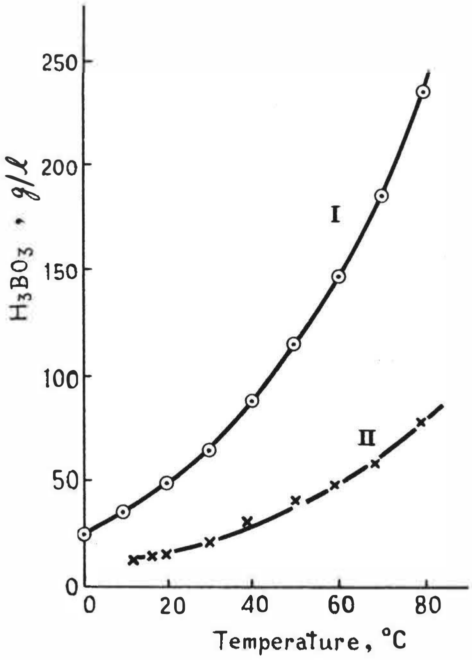

FIG. 4 Solubility curves of H_3BO_3
1. In water(I.C.T.,Vol.IV, p.226)
2. In salt solution:
$MgCl_2$ 293,8 g/l $FeCl_3$ 1,6 g/l
$CaCl_2$ 31,4 g/l HCl 0,12 N

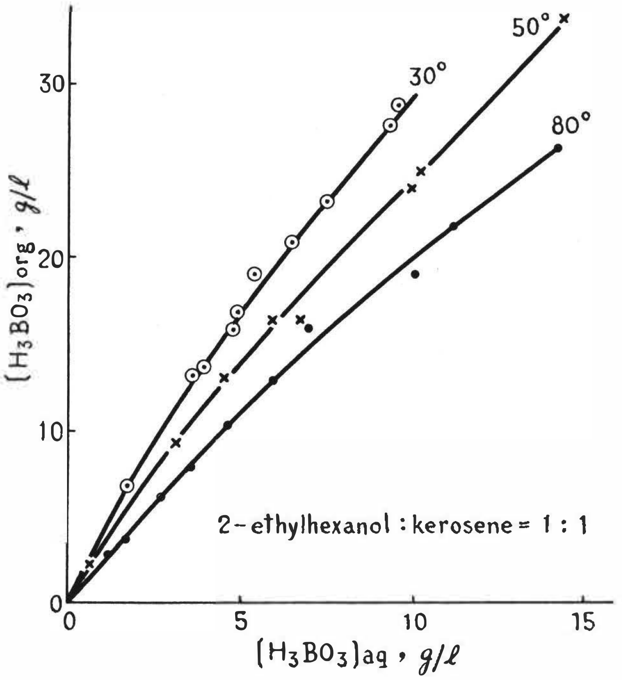

FIG. 5 Extraction isotherms
Aqueous phase:
$MgCl_2$ 286,3 g/l $FeCl_3$ 0,66 g/l
$CaCl_2$ 32,6 g/l $FeCl_2$ 0,47 g/l
HCl 0 42 N

solubility of boric acid is lowered. The solubility curve of boric acid in the leaching liquor (curve II) is compared with that in pure water (curve I) in FIG. 4.

At a temperature of 30°, only 20 g/l H_3BO_3 can be kept in solution (see FIG. 4, curve II), whereas at 80°, 80 g/l H_3BO_3 are soluble. Since our leaching liquor contains approximately 60 g/l H_3BO_3 it can not be cooled down below 70° without the precipitation of the solid. Therefore, the liquor is maintained at 80° so as to keep all boric acid in solution and is extracted at this same temperature. Alternatively, the hot clarified leaching liquor can be cooled down in a crystallizer to yield the first crop of boric acid crystals, and the remainder is recovered by extraction at a lower temperature.

For comparison, equilibrium relationships at 30°, 50° and 80° have been determined and are shown in FIG. 5. Extraction is favourable at low temperature, yet at 80° an average distribution coefficient has still a value of little more than 2 ($D_{o/A}$ at 50° is 2,6, at 30° is 3,2) which can be considered as sufficiently high from an engineering point of view.

5. Stripping with pure water The use of pure water to strip boric acid can produce directly the acid by subsequent cooling and crystallization. Equilibrium data are shown in Table 2, from which it is apparent that stripping is favourable at high temperatures. This is contrary to the fact revealed in extraction (see FIG. 5).

TABLE 2 Data of stripping with pure water

Temp. °C	Concentration, g/l		$D_{a/o}$	Temp. °C	Concentration, g/l		$D_{a/o}$
	(H_3BO_3)aq	(H_3BO_3)org			(H_3BO_3)aq	(H_3BO_3)org	
50	89,8	21,8	4,1	80	103,4	20,1	5,1
	70,5	16,3	4,3		62,1	13,7	4,5
	53,6	12,9	4,2		47,0	9,2	5,1
	37,5	9,3	4,0		40,6	8,2	5,0
	30,4	7,2	4,2		31,0	6,5	4,8
	18,3	4,5	4,1		15,6	3,3	4,7
	12,5	3,1	4,0		7,8	1,8	4,3
	3,9	1,1	3,6		5,2	1,1	4,7

6. Stripping with alkaline solution Stripping of boric acid from solvent phase can be realized very effectivelly with alkaline solution. The latter may be borax solution or sodium hydroxide solutions of varying concentrations (Table 3). From this Table, it is possible that the remaining boric acid in the organic phase after stripping with water can be removed almost completely by contacting with NaOH solution.

TABLE 3 Data of stripping with alkaline solutions

31.5 g/l Borax Soln. 25°		0.5 N NaOH 50°		2.0 N NaOH 50°	
$(H_3BO_3)_{aq}^{**}$	$(H_3BO_3)_{org}^{*}$	$(H_3BO_3)_{aq}^{**}$	$(H_3BO_3)_{org}^{*}$	$(H_3BO_3)_{aq}^{**}$	$(H_3BO_3)_{org}^{*}$
39,2	1,69	1,7	0,00	6,9	0,00
47,6	2,27	19,5	0,32	15,6	0,00
62,7	3,50	41,1	1,23	38,3	0,01
78,1	4,83	63,5	3,9	84,7	1,1
159	18,9	138	14,6	155	2,8

* Concentration of boric acid remaining in organic phase.

** Boric acid transferred to aqueous phase divided by the volume of the aqueous phase.

MULTISTAGE EXTRACTION CONSIDERATIONS

As already discussed, the hot leaching liquor after clarification can be sent directly to the extraction equipment without cooling or heating. The extraction should serve two purposes, one is to recover boric acid, and the other is to remove the same solute as completely as possible from the raffinate which is further processed to produce metallic magnesium or high quality magnesium oxide as ultimate product. Therefore, a countercurrent multistage extraction must be considered.

1. The loading capacity of extracting solvent has been found to vary from 40 g/l at 20° to 48 g/l at 80°, a loaded solvent containing 40 g/l may be assumed.

2. Calculation of number of theoretical stages. If the conditions of extraction will be; (a) a temperature of 80° so that no crystals are separated in pipe line and pump before the leaching liquor enters the extractor; (b) a leaching liquor containing 60 g/l boric acid; (c) the solvent to be loaded with 40 g/l; (d) the recycled solvent entering the last stage n being almost free from the transferring solute, say 0,01 g/l; and (e) 99% of boric acid in the feed being extracted.

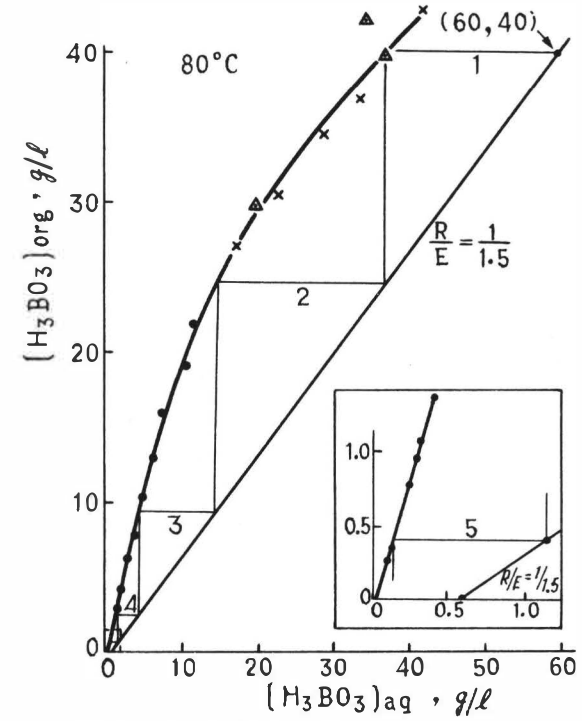

FIG. 6 McCabe-Thiele diagram for extraction

Then $$E(40 - 0.01) = R(60 - 0.01 \times 60)$$

$$E/R = \frac{60 - 0.6}{40 - 0.01} = 1{,}49 \doteq 1{,}5$$

where E and R = phase volumes of solvent and leaching liquor respectively.

Using those values given above, the number of theoretical stages n can be found by McCabe-Thiele method to be about 4,7 (see FIG. 6). When other conditions are maintained constant but $E/R = 2$, and with the solvent loaded with 30 g/l boric acid, the number of theoretical stages required can be reduced to 3,5 (not shown in FIG. 6).

STRIPPING CONSIDERATIONS

The loaded solvent is stripped first with water and then with sodium hydroxide solution in order to obtain aqueous solutions of boric acid and borax respectively. Both boric acid and borax will be recovered by cooling and crystallization as final products. It seems advisable to select the following conditions:

(a) Temperature of stripping is maintained at 80° to ensure favourable distribution, high rate of mass transfer and low tendency to emulsify.

(b) Possibly low phase ratio a/o (aqueous to organic) is used in order to obtain possibly high concentration of the solute and hence good crop of crystals in each cycle.

(c) Final stripping with alkaline liquor follows water stripping to remove almost all remaining boric acid from solvent which has to be recycled to meet the condition of extraction cycle, i.e. a residual concentration of 0,01 g/l.

In the foregoing section the loaded solvent has been assumed to contain 40 g/l boric acid, the amount of which distributed between water and alkaline solution will depend upon the operating conditions of the water stripping and subsequent crystallizing steps. When the stripping is carried out at 80° and phase ratio $o/a = 4$, the pregnant aqueous solution entering crystallizer (see FIG. 8) is assumed to be 67% saturated with boric acid at 80°, i.e. 0.67×244 (solubility at 80° as found in FIG. 4, curve 1) = 164 g/l. The concentration of the partly depleted aqueous solution to be recycled to the water stripping equipment and consequently, crystal crop, will be found from the final operating temperature of the crystallizer. If this temperature is 30°, from FIG. 4, curve I, the solubility is found to be 64 g/l which is the concentration of recycled liquor, and the crop will be approximately 164 - 64 = 100 gram per liter of aqueous solution. And the partly stripped solvent still contains x_n g/l:

$$a\,(164 - 64) = o\,(40 - x_n)$$

Since $o/a = 4$, $x_n = 15$ g/l

This amount of boric acid will be converted to borax in alkaline stripping solution and recovered in crystallizer II. The distribution of boron value between boric acid and borax can be calculated as (40 - 15)/40 = 62,5% and (15/40) = 37,5% respectively. The McCabe-Thiele diagram for water stripping is illustrated in FIG. 7. Number of theoretical stage is found to be about 2,7.

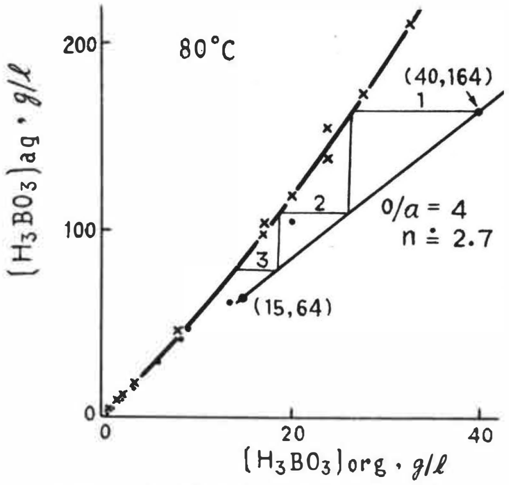

FIG. 7 McCabe-Thiele diagram for water stripping

MIXER-SETTLER PERFORMANCE

Extraction and stripping can be carried out either in column or mixer-settler. A preliminary test in a pulsed perforated plate column of 100 mm diameter was not very encouraging because of high value of HETS. This may be attributed to insufficient time of contact between the two phases in the column, but final conclusion should only be drawn after further experimentation. However, mixer-settlers were then used, i.e. a six-stage one for extraction and a three-stage one for water stripping which was followed by two stages of alkaline stripping. After steady state had been attained, clear samples were taken from respective settlers for analysis. The experimental results have been tabulated as follows:

TABLE 4

Aq. feed:	$MgCl_2$ 288 g/l,	$CaCl_2$ 75 g/l,	H_3BO_3 10.8 g/l.
Solvent:	2-ethylhexanol:	Kerosene = 1:1,	H_3BO_3 0.22 g/l.

Concentrations in settler of the numbered stage, expressed as g/l of boric acid

	1		2		3		4		5		6	
	org	aq	org	aq	org	aq	org	aq	org	aq	org	aq
Extraction	9,1	6,3	4,2	2,0	2,0	0,8	1,1	0,41	0,62	0,20	0,45	0,12
H_2O stripping	13	23	7,6	17	5,1	8,0						
Alk. stripping	0,3	31	0,01	3								

The mixer-settler available is made of Plexiglass which cannot be used above 50° C. Therefore, the experiments were carried out at 45° C.

The dimensions of mixer and settler of a single stage are 6 x 6 x 9 and 6 x 18 x 9 (all in cms) respectively. Phase ratios of organic to aqueous in extraction and in water stripping were 1,5 and 4. The residence time in mixer was about 2,6 min.

As estimated from McCabe-Thiele diagrams at the changing conditions of extraction and water stripping, it has been found that the overall stage efficiency is about 70%.

THE PROPOSED FLOW SHEET

For the recovery of both boron and magnesium values from ascharite a flow scheme is proposed as shown in FIG. 8.

Powdered ascharite is decomposed at 100-105° in a pipe reactor made of reinforced plastics by hydrochloric acid, the amount of which is sufficient to neutralize 85% of MgO and CaO in the ore. At the feed end, solid to liquid ratio should be properly adjusted with recycled hot concentrated $MgCl_2$ solution and hydrochloric acid so that for each ton of ore 3.7 to 4 m^3 liquid mixture are used. Due to reasonable short reaction time (30 to 40 minutes) required to attain a high degree of decomposition of ascharite, the pipe reactor can be designed without excessive length, the performance of which will be reported elsewhere.

After reaction, the mixture is sent to a thickener and the insoluble residue is removed in a continuous filter. Both the thickener and the filter should be operated at a temperature somewhat above 80°.

From the clarified leaching liquor boric acid is extracted by 50% 2-ethylhexanol in kerosene. The loaded solvent is stripped of the boric acid first with water and then with sodium hydroxide solution. The extraction and stripping are both carried out at 80°. The pregnant stripping solutions of boric acid and borax are cooled in separate crystallizers to produce the final products of boric acid and borax respectively.

The raffinate, after being freed from iron and aluminium by adding MgO, still contains a certain amount of $CaCl_2$ which can be removed by the addition of an equivalent.

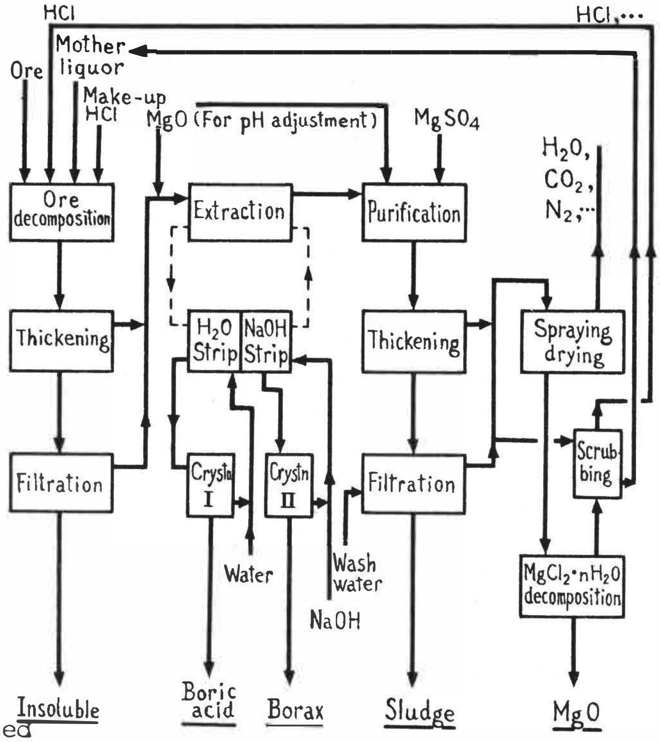

FIG. 8 Proposed flowsheet

quantity of $MgSO_4$ and subsequent thickening and filtration. From ore decomposition step to purification there will be no heater or cooler necessary to deal with corrosive acidic chloride solutions, and fixed charge and operating cost can be cut down to minimum.

From thermochemical calculation and heat balance of the proposed flow scheme, it can be shown that the only heat energy required is almost confined to the drying of $MgCl_2$ solution to $MgCl_2.nH_2O$ (n = 1-2) and hydrolytic thermal decomposition of the latter compound to MgO and HCl. The hot waste gas from the drier is used to evaporate water in the raffinate (see the right part of FIG. 8) and that from decomposition furnace containing HCl is used to concentrate the recycled $MgCl_2$ solution. This $MgCl_2$ solution and recovered hydrochloric acid of moderate concentration are maintained at a temperature as near as possible to the ore decomposition temperature (100-105°) and recycled to the feed end of pipe reactor. In consequence, little or no additional heat is necessary to be supplied to initiate the reaction.

As a gross result of the process, ascharite (B_2O_3-2MgO-H_2O) is split into H_3BO_3 and MgO by recycling use of HCl. There will be much less solid and liquid wastes (about 20% instead of over 100% residue of the weight of the ore treated in the present alkaline process) and problem of their disposal will abate.

ACKNOWLEDGEMENT

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"EQUILIBRIUM DISTRIBUTION BEHAVIOR OF ZIRCONYL-HAFNYL THIOCYANATES BETWEEN METHYL ISOBUTYL KETONE AND AQUEOUS PHASES."

Donald O. Voit

Teledyne Wah Chang Albany
P.O. Box 460
Albany, Oregon USA 97321

"ABSTRACT"

The solvent extraction behavior of zirconium and hafnium was studied for the aqueous thiocyanate-MIBK system. The results of the study led to the development of a model describing much of the behavior. The model,

$$ZrO^{+2}_{aq} + 2\ SCN^{-}_{aq} \overset{2\ \mathrm{MIBK\ free}}{\longleftrightarrow} [ZrO(SCN)_2 \cdot 2\ MIBK]_{org}$$

assumes that the extracted species is a doubly solvated with MIBK, dithiocyanate of zirconium. Subtle differences between the behavior of hafnium and zirconium can be observed by examining the influence of system variables on $\alpha_{Hf/Zr}$, the separation factor for the two elements.

INTRODUCTION

The most significant difference between the properties of zirconium and hafnium is their different neutron capture crossections. It is this difference that led to the development of the commercial process for the production of hafnium free zirconium. Were it not for the need to have hafnium free zirconium in the fuel rod assemblies in nuclear reactors, the solvent extraction process for separating zirconium and hafnium would probably never have been developed.

Current free world production of hafnium free zirconium is 10,000,000 lb/yr. The rate is small in comparison with many other metals that are produced using solvent extraction processes. The production rate is intermediate between tungsten at 100,000,000 lb/yr and tantalum at 5,000,000 lb/yr.

The process used to separate zirconium and hafnium was developed in the late 1940's. The process is based on the partitioning of zirconium and hafnium between aqueous thiocyanate solution and MIBK solvent. The literature gives detailed explanations of the process, however, there has never been a complete understanding of the mechanisms of the extraction or an understanding of the influence of the effects of the various parameters on the equilibria.

Systems with complex equilibria, such as the Zr-thiocyanate system, are typically studied by examining the system within the range of variables that are likely to be encountered in the process. The data is frequently presented as a table of results for the various conditions studied. (3,4,6) The utility of such tables is limited however, since one rarely encounters a stream in a process that duplicates the conditions of the test. Stage-to-stage calculations using these tables are almost impossible.

The equilibria for the Zr-thiocyanate system is complicated by several aspects. First, the stoichiometry of the extracted species was unknown. Literature references contain mention of species having SCN/Zr ratios of 1 to 6. (7,8,9) Second, the organic phase contains thiocyanate as HSCN, zirconium thiocyanate and hafnium thiocyanate. There is no method that can distinguish the amount of thiocyanate in each species present. Third, the aqueous chemistry of zirconium is dominated by hydrolysis and polymerization. (1,2) The very nature of the aqueous zirconium species is a question. We have no method for distinguishing between the various hydrolysis products possible. Fourth, concentrations of interest are high and activities are unknown for the species present. Acidities are such that conventional pH measurements are meaningless. Fifth, the solvent effects are unknown. (10,11,12)

The method used to study a complex system when little is understood of the mechanisms involved is to select a central, compositional point and examine the behavior around this point along the axes of interest. Such is basically the approach that was used in the work presented here. The variables considered significant to the equilibria were free acidity, HSCN, NH_4SCN, ZrO_2 and HfO_2 concentrations and temperature. The outcome of the project was that a model was developed that could be used to explain much of the system's behavior.

The model developed can be written

$$ZrO^{+2}_{aq} + 2\ SCN^{-}_{aq} \xrightleftharpoons{2\ MIBK} [ZrO(SCN)_2 \cdot 2\ MIBK]_{org}$$

It was noted that the solvent phase contains both free and complexed MIBK. Only the free MIBK was capable of entering into the extraction reaction.

Since hafnium and zirconium behave qualitatively identical, all references to zirconium will apply to hafnium as well. Where the difference between zirconium and hafnium are significant, hafnium will be referred to directly. Although much of the behavior is described by the above reaction, there is still a systematic variability in the behavior which requires further study. The model fails to describe the behavior at low acidities and low concentrations. It is suspected that these conditions are causing significant hydrolysis which is not taken into account by the model.

THE EXPERIMENTS

The procedure used to obtain the equilibrium data was basically a standard separatory funnel contact of the desired solutions at the desired temperatures. Solutions of $ZrOCl_2$ containing 2% Hf/Zr, $HfOCl_2$, HCl, NH_4OH, and NH_4SCN were mixed with water to give the desired concentrations of each parameter of interest. Mixtures of HSCN in MIBK were mixed with MIBK to give the desired initial thiocyanate levels in the solvent. Additionally the system was studied by contacting metal loaded solvent with water.

The range of variables studied was 0.5 to 1.5 initial aqueous metal molarity, 0.5 to 3.0 initial solvent thiocyanate molarity, -0.4 to +0.4 initial 'free' acid, 1.9 to 2.9 initial aqueous NH_4SCN/ZrO_2 molar ratio, 2-70% initial aqueous Hf/Zr+Hf and -10 to 55°C equilibrium contact temperature. Free acidity is defined as any titratable acidity present beyond twice the metal molarity.

The results from each experiment were analyzed for total acidity, total thiocyanate, total MO_2, specific gravity, and final phase volumes. The MO_2 samples were spectrographically or x-ray analyzed for % HfO_2. The results were used to calculate $K_{D,Hf}$, $K_{D,Zr}$ and $\alpha_{Hf/Zr}$. Material balances were performed on the ZrO_2, HfO_2 and SCN.

The system was examined for any kinetic limitations that might affect the attainment of equilibrium. No significant difference was observed between samples contacted for 15 seconds and for samples contacted for several minutes. Consequently the system was assumed to reach equilibrium rapidly if thoroughly mixed. The procedure adopted was a 60 second hand agitation for all contacts.

RESULTS AND INTERPRETATION OF RESULTS

The simplest method for examining behavior of complex systems is to plot $K_{D,Zr}$ versus the varied initial conditions. Such presentations are useful in developing a qualitative understanding of the system behavior. Such an approach shows that the extraction is favored by lowering the free acid, organic HSCN, decreasing the Hf/Zr+Hf, raising the ZrO_2 and lowering the temperature.

Such an approach fails when multiple input variables changes are made. With multiple variables changes there is no convenient coordinate system to represent the input variables. Studying the combined effect of simultaneous changes of more than two variables greatly expands the number of experiments being conducted. For this reason if for no other it is advantageous to develop a model that describes the system.

The first stage in the evolution of an extraction model was noting that the parameter $K_{D,Zr}/SCN^2_{aq}$ had some consistency to it. By assigning a 2:1 stoichiometry to the extracted zirconium species it became possible to distinguish the thiocyanate of HSCN from the thiocyanate of $ZrO(SCN)_2$ in the organic phase.

A plot of $K_{D,Zr}/SCN^2_{aq}$ versus $HSCN_{org}$, seen in Figure I, on semilogarithmic coordinates showed remarkable linearity. Since such behavior is not typical of equilibria dependence on concentration, an alternative explanation was sought. The concept of 'free' and 'complexed' MIBK was used to explain the behavior. The 'free' MIBK concentration was calculated using the equation

$$MIBK_{free}\ \text{g.mole/l} = \frac{1000 - 266\ HSCN - 400\ ZrO(SCN)_2}{125} \qquad (1)$$

The molar volume for HSCN, 266 ml/g.mole, was estimated by assuming that the solvated HSCN species is $HSCN \cdot 2$ MIBK. (5) The molar volume for $ZrO(SCN)_2$, 400 ml/g.mole, was estimated from the assumption that $ZrO(SCN)_2 \cdot 2$ MIBK was the solvated metal species in the organic phase. The molar volume for pure MIBK is 125 ml/g.mole. Since the majority of the MIBK is solvated with the HSCN, the actual molar volume of the metal species has little influence on the $MIBK_{free}$ calculation.

In Figure II a plot of $K_{D,Zr}/SCN^2$ versus MIBK free on log-log coordinates is shown. The slope is clearly 2; indicating the bimolecularity of the MIBK in solvating the extracted metal species.

At this point we can write

$$ZrO^{+2}_{aq} + 2\ SCN^{-}_{aq} \quad 2\ MIBK \quad ZrO(SCN)_2 \cdot 2\ MIBK_{org}$$

to express the chemical reaction that leads to the extracted zirconium equilibria. Mathematically the expression

$$K_{e,Zr} = \frac{Zr_{org}}{Zr_{aq}\ SCN^2_{aq}\ MIBK^2_f} \qquad (2)$$

would describe the interaction of the various reacting species.

The parameter $K_{e,Zr}$ can be plotted against reciprocal temperature on semilogarithmic coordinates as in Figure III. Although the data is quite scattered, an approximate free energy of formation for the reaction of -3.6 kcal/g.mole can be obtained from the slope of the curve.

The system unfortunately contains additional complexities that have significant effects on the system. Figure II shows a systematic family of parallel curves that suggest that there is an additional parameter playing a role in the equilibria. Figure IV is a plot of $K_{e,Zr}$ versus NH_4^+ concentration. While the NH_4^+ appears to describe much of the behavior quite well, it seriously fails to describe the behavior when the ammonium levels are low and when the system is ammonia free, as in Figure V. These regions where the model fails are probably resulting from our failure to include hydrolysis effects in the model. A prerequisite for including these hydrolysis effects is a method for measuring hydrogen ion concentrations at values greater than 0.1 molar.

In spite of the failure of the model to predict all behavior in the system, there is considerable behavior that is explained. The model permits a method for comparison between zirconium and hafnium that is useful for observing the subtle differences in their behavior. The separation factor for hafnium and zirconium, $\alpha_{Hf/Zr}$, is not a constant, and in fact varies with all the parameters in the system.

Figure VI is a plot of $K_{D,Hf}$ versus $K_{D,Zr}$. Clearly the assumption of constant $\alpha_{Hf/Zr}$ describes the system behavior quite well. However Figure

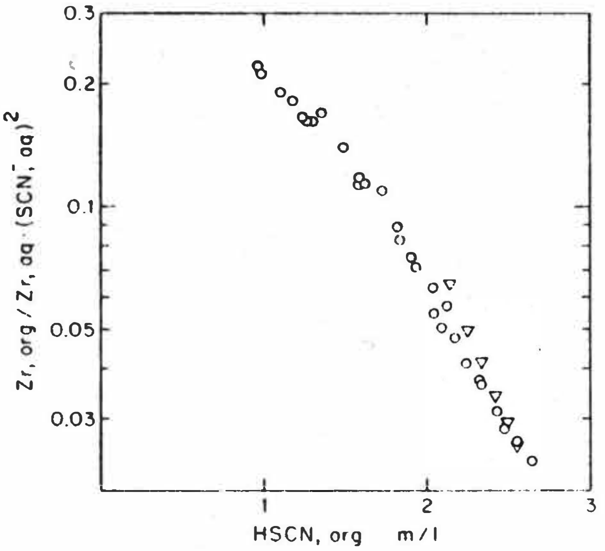

FIG. I. Variation of the parameter Zr, org / Zr, aq $(SCN^-_{aq})^2$ with the organic HSCN concentration.

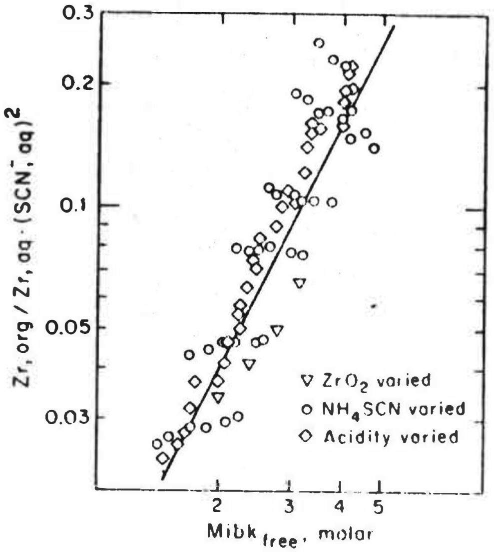

FIG. II. Variation of the parameter Zr, org / Zr, aq · $(SCN^-_{aq})^2$ with the free methyl isobutyl ketone concentration.

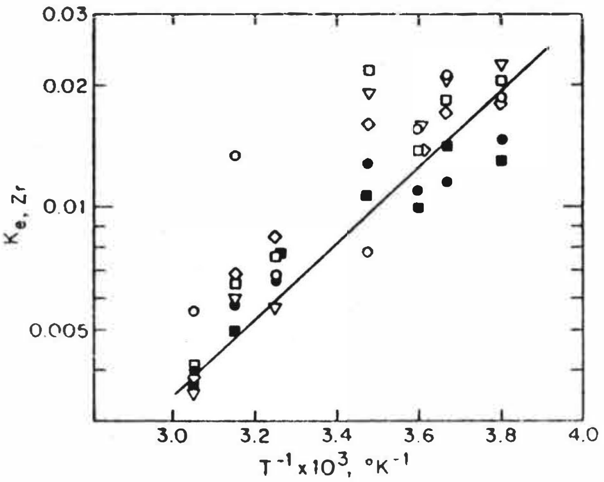

FIG. III. Effect of temperature on the zirconium equilibrium constant for various initial conditions.

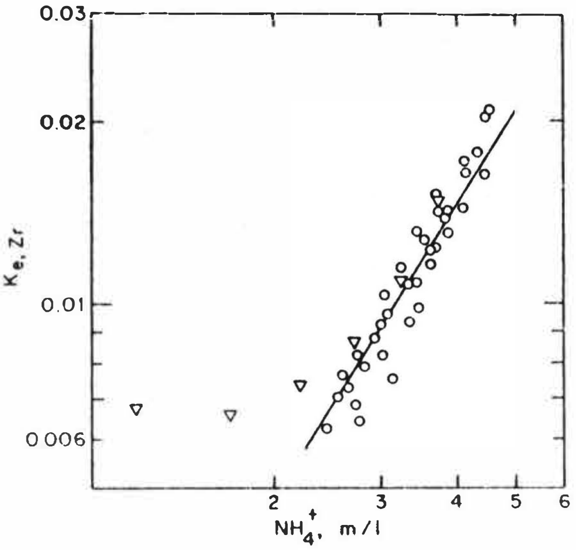

FIG. IV. Variation of the zirconium equilibrium constant with the ammonium concentration in the aqueous phase.

VII shows that $\alpha_{Hf/Zr}$ has very significant variability depending on the chemical nature of system. If $K_{e,Zr}$ is varied by reducing the system acidity, $\alpha_{Hf/Zr}$ is reduced. If $K_{e,Zr}$ is varied by changing the thiocyanate concentration the effect on $\alpha_{Hf/Zr}$ is much less. Such behavior suggests a competition between hydrolysis and thiocyanate complex formation.

The effect of temperature on $\alpha_{Hf/Zr}$ can be seen in Figure VIII. A plot of $\alpha_{Hf/Zr}$ versus reciprocal temperature on semilogarithmic coordinates shows essentially linear behavior. Thus another difference between hafnium and zirconium lies in a roughly 1 Kcal/mole larger free energy of formation for the hafnium extraction reaction.

The different solvent extraction behavior of hafnium and zirconium probably results from the different formation constants of their thiocyanate, hydrolysis and solvated complexes. There is probably no difference between the distribution coefficients of the distributing species. When conditions favor hydrolysis, the separation factor decreases. Thus the formation constant for the zirconium species is greater than that of the hafnium while the formation constant of the thiocyanate complex is greater than that of the zirconium. The separation factor is maximized when conditions minimize hydrolysis effects; low temperatures, high acidities, and high concentrations. Polymerization is not significant at the conditions examined for if it were, there would be a variation in $\alpha_{Hf/Zr}$ with Hf/Hf+Zr that was not seen.

Acknowledgements: The careful attention to detail by technicians Ed Dirrett, Fred Jung and Tim McQueary to this project is gratefully acknowledged.

CONCLUSIONS

The equilibrium distribution behavior of zirconium thiocyanates between aqueous and MIBK phases can be described by a single equation that assumes that zirconyl ions combine with thiocyanate ions and free MIBK to form the extracted complex containing Zr, SCN and MIBK with 1:2:2 molar ratios. The model ignores hydrolysis effects, which introduce considerable error when the system conditions favor hydrolysis.

The differences between zirconium and hafnium become most apparent when the separation factor, $\alpha_{Hf/Zr}$ is examined as a function of process variables. The separation factor deteriorates when conditions favor hydrolysis. Thus $\alpha_{Hf/Zr}$ is maximized at high acidities, low metal concentrations and low temperatures.

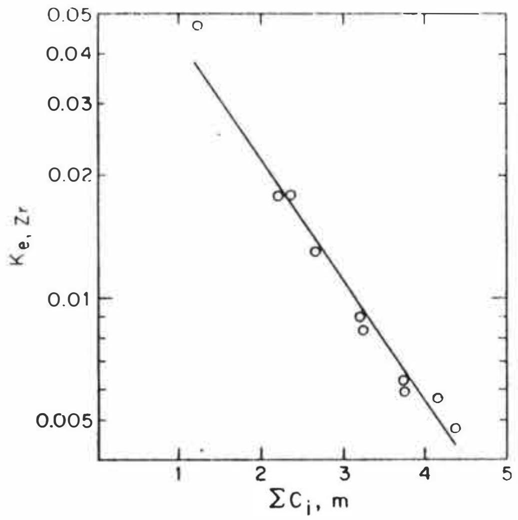

FIG. V. Effect of total ion concentration on the zirconium equilibrium constant for zirconyl-hafnyl thiocyanates in an HSCN-H_2O-methyl isobutyl ketone system.

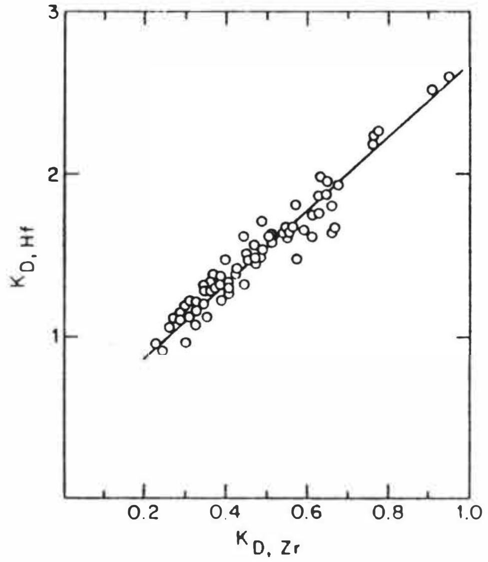

FIG. VI. Relationship between the distributions of zirconium and hafnium thiocyanates between aqueous and methyl isobutyl ketone.

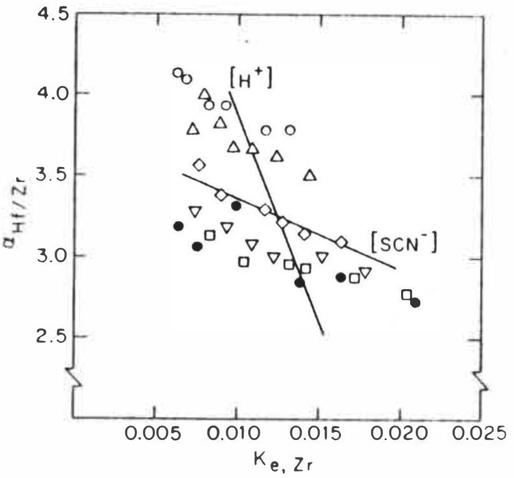

FIG. VII. Variation of the hafnium-zirconium selectivity with the zirconium equilibrium constant for varied acidity and thiocyanate levels.

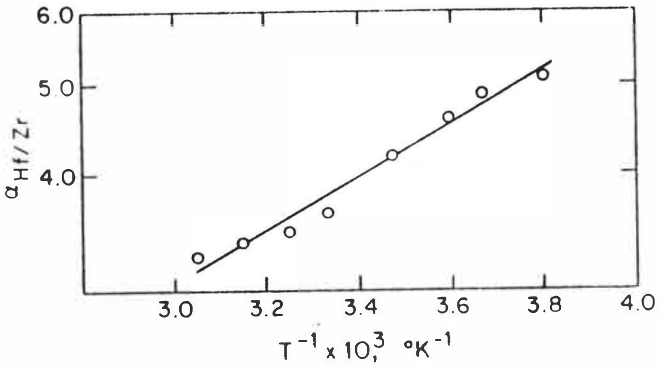

FIG. VIII. Effect of temperature on the selectivity of hafnium and zirconium thiocyanate between aqueous and methyl isobutyl ketone.

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THE EXTRACTION OF URANYL NITRATE FROM AQUEOUS NITRATE SOLUTIONS BY OPEN CELL POLYURETHANE FOAM SPONGE (OCPUFS)

H. D. Gesser and B. M. Gupta
Chemistry Department
University of Manitoba
Winnipeg, Canada R3T 2N2

ABSTRACT

The extraction of uranyl nitrate into open cell polyurethane foam sponge (OCPUFS) from aqueous solution, in the presence of salting agents, has been examined. The extraction efficiency was observed to depend on the concentration of uranyl and nitrate ions. The charge of the cations was also found to influence the distribution ratio. The effect of the change in temperature and pH was also studied. The results are interpreted in terms of OCPUFS acting as a viscous organic ether of moderate dielectric constant.

INTRODUCTION

Recent work from this laboratory on the solvent extraction of gallium and iron as the acid chloride complex into open cell polyurethane foam sponge (OCPUFS)(1,2,3) has indicated that the OCPUFS can act as a viscous organic ether of moderate dielectric constant. It was of interest to extend the study to other ether extractable complexes much as uranyl nitrate which was shown to be absorbed by OCPUFS (4). The extraction of uranyl nitrate by diethyl ether has been studied extensively and the distribution characteristics have been reported in detail (5). Thus a close comparison of OCPUFS with diethyl ether could be made.

EXPERIMENTAL

Cylindrical plugs (4.0 cm in diameter and 4.7 cm in length - average dry weight 2.00 ± 0.17 g) were cut from sheets of polyurethane foam obtained from Union Carbide - Type A. Each plug prior to use was squeezed in 2 M HCl in a batch extractor for one hour, washed with distilled water until free of HCl and squeezed dry. The foam plug was then rinsed with acetone squeezed and air-dried overnight before use.

The uranium in solution was determined by the thiocyanate method (6,7) except that a 10% (W/V) solution of hydroxylamine hydrochloride was used instead of stannous chloride in order to suppress the interference from iron (III) by its reduction to iron (II).

The cleaned foam plug was equilibrated with test solution by automatically squeezing the plug in solution 7.5 times/min with a 3 cm compression stroke.

The amount of uranium absorbed by the foam was determined from the difference between the initial and final concentration of U in solution.

RESULTS & DISCUSSION

A) Rate of Extraction:

The rate of reaching equilibrium between foam and solution was established by sampling the solution as a function of time during the squeezing process. This is shown in FIG. 1 for the extraction of 150 ml of 500 ppm U in 11 M NH_4NO_3 solution at 25°C. Extraction equilibrium was achieved in 150 min. which was much longer than the 30 min. required for gallium (2) or iron (3).

The recovery of the uranium from the loaded foam into 150 ml of water is also shown in FIG. 1 (filled circles) and indicates a faster rate than the extraction process, probably due to hydrolysis of the UO_2^{+2} ion. The extraction and recovery leads to a mass balance of about 98%. At higher uranium concentration, the time required to reach equilibrium was extended to as much as 3 hours.

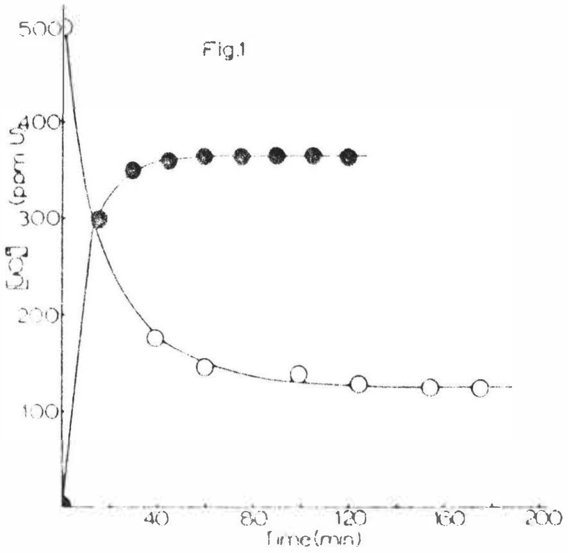


FIG. 1

(Open circles) The absorption of $UO_2(NO_3)_2$ from 150 ml of 11 M NH_4NO_3 500 ppm U by a 2 g OCPUFS at 25°C as a function of time. (Filled circles) The recovery of the absorbed $UO_2(NO_3)_2$ into 150 ml of H_2O at 25°C.

B) Effect of Uranyl Concentration:

The effect of equilibrium uranyl concentration in the aqueous phase on the distribution coefficient, D,

$$(D = \Sigma[U]_{org}/\Sigma[U]_{aq})$$

is shown in FIG. 2, where the effect of temperature is also illustrated.

The decrease in the distribution coefficient of uranyl nitrate with increase in the equilibrium uranyl concentration in solution could not be explained by considering ionization or dimer formation of the extracted complex in the foam.

Experiments on the diffusion of uranyl nitrate and ammonium nitrate through thin polyurethane membrane films indicates that ammonium nitrate also dissolves to some extent in polyurethane. Thus a relation is derived, taking into account the extraction of uranyl nitrate as well as ammonium nitrate and their subsequent ionization in the foam.

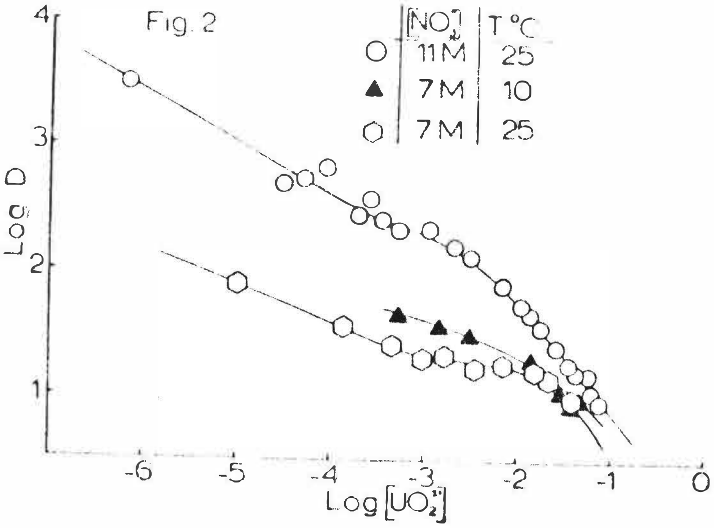


FIG. 2

Log D (distribution coefficient) against $\log[UO_2^{-2}]$ (aqueous uranyl concentration at equilibrium) at various temperatures and nitrate concentrations. (NH_4NO_3)

The hydrolysis of the uranyl ion under the conditions of the experiments (i.e. pH < 3 and high nitrate concentrations) is insignificant (8). Thus the possible uranium species present in the aqueous phase are UO_2^{++}, $UO_2NO_3^+$ and $UO_2(NO_3)_2$(neglecting associated H_2O).

In the aqueous phase

$$UO_2^{++} + NO_3^- \overset{K_1}{\rightleftharpoons} UO_2NO_3^+ \tag{1}$$

where $$[UO_2NO_3^+] = K_1[UO_2^{++}][NO_3^-] \tag{1a}$$

and $$UO_2NO_3^+ + NO_3^- \overset{K_2}{\rightleftharpoons} UO_2(NO_3)_2 \tag{2}$$

where $$[UO_2(NO_3)_2] = K_1K_2[UO_2^{++}][NO_3^-]^2 \tag{2a}$$

the extraction equilibrium of uranyl nitrate is represented by

$$UO_2(NO_3)_2 \overset{K_D}{\rightleftharpoons} (UO_2(NO_3)_2)_f \tag{3}$$

(The subscript f represents the species in foam whereas the species in the aqueous phase are written with no subscript.)

and $$K_D = \frac{[UO_2(NO_3)_2]_f}{[UO_2(NO_3)_2]} \tag{3a}$$

Assuming dissociation of the extracted complex in the foam, the following equations can be written

$$(UO_2^{++})_f + (NO_3^-)_f \overset{F_1}{\rightleftharpoons} (UO_2NO_3^+)_f \tag{4}$$

where $$[UO_2NO_3^+]_f = F_1[UO_2^{++}]_f[NO_3^-]_f \tag{4a}$$

and $$(UO_2NO_3^+)_f + (NO_3^-)_f \overset{F_2}{\rightleftharpoons} (UO_2(NO_3)_2)_f \tag{5}$$

where $$[UO_2(NO_3)_2]_f = F_1F_2[UO_2^{++}]_f[NO_3^-]_f \tag{5a}$$

The distribution ratio, D, may be defined as

$$D = \frac{\text{Total uranium concentration in organic phase}}{\text{Total uranium concentration in aqueous phase}}$$

$$D = \frac{\Sigma[U]_f}{\Sigma[U]_{aq}} = \frac{[UO_2(NO_3)_2]_f + [UO_2NO_3^+]_f + [UO_2^{++}]_f}{[UO_2(NO_3)_2] + [UO_2NO_3^+] + [UO_2^{++}]} \tag{6}$$

From equations (1a), (2a) and (4) to (6)

$$D = \frac{[UO_2(NO_3)_2]_f + \dfrac{[UO_2(NO_3)_2]_f}{F_2[NO_3^-]_f} + \dfrac{[UO_2(NO_3)_2]_2}{F_1F_2[NO_3^-]_f^2}}{K_1K_2[UO_2^{++}][NO_3^-]^2 + K_1\ [UO_2^{++}][NO_3^-] + [UO_2^{++}]} \tag{7}$$

$$D = \frac{[UO_2(NO_3)_2]_f \left(1 + \dfrac{1}{F_2[NO_3^-]_f} + \dfrac{1}{F_1F_2[NO_3^-]_f^2}\right)}{[UO_2^{++}]\left(K_1K_2[NO_3^-]^2 + K_1[NO_3^-] + 1\right)} \tag{8}$$

From equations (2a), (3a) and (8)

$$D = \frac{K_1K_2K_D[UO_2^{++}][NO_3^-]^2 \left(1 + \dfrac{1}{F_2[NO_3^-]_f} + \dfrac{1}{F_1F_2[NO_3^-]^2_f}\right)}{[UO_2^{++}]\left(K_1K_2[NO_3^-]^2 + K\ [NO_3^-] + 1\right)} \tag{9}$$

Substituting $K_1K_2K_D[NO_3^-]^2 + K_1[NO_3^-] + 1 = Y$

$$DY = K_1K_2K_D[NO_3^-]^2 \left(1 + \frac{1}{F_2[NO_3^-]_f} + \frac{1}{F_1F_2[NO_3^-]^2_f}\right) \tag{10}$$

Assuming extraction of ammonium nitrate by the foam and its subsequent ionization, we may write the equilibria in the foam as:

$$(NH_4^{++}) + (NO_3^-) \overset{K_A}{\rightleftharpoons} (NH_4NO_3)_f \tag{11}$$

$$(NH_4NO_3)_f \overset{K_{dA}}{\rightleftharpoons} (NH_4^+)_f + (NO_3^-)_f \tag{12}$$

The electroneutrality in the foam is represented as:

$$[NO_3^-]_f = [NH_4^+]_f + [UO_2NO_3^+]_f + 2[UO_2^{++}]_f \tag{13}$$

Assuming incomplete dissociation (9) of the extracted complex, the relative concentrations of the species in the foam can be written as:

$$[UO_2(NO_3)_2]_f \gg [UO_2NO_3^+]_f \gg [UO_2^{++}]_f$$

Thus, $[UO_2^{++}]_f$ may be neglected in the electroneutrality equation (13).

i.e. $$[NO_3^-]_f \simeq [NH_4^+]_f + [UO_2NO_3^+]_f \tag{14}$$

From equations (11) and (12)

$$[NH_4^+]_f = \frac{K_{dA}\ [NH_4NO_3]_f}{[NO_3^-]_f} = \frac{K_{dA}K_A\ [NH_4^+][NO_3^-]}{[NO_3^-]_f} \tag{15}$$

From equations (2a), (3a), (5a), (14) and (15), we may write:

$$[NO_3^-]_f = \frac{K_{dA}K_A\ [NH_4^+][NO_3^-]}{[NO_3^-]_f} + \frac{[UO_2(NO_3)_2]_f}{F_2[NO_3^-]_f}$$

i.e. $$[NO_3^-]_f^2 = K_{dA}K_A[NH_4^+][NO_3^-] + \frac{K_DK_1K_2[UO_2^{++}][NO_3^-]^2}{F_2} \tag{16}$$

Substituting the value of $[NO_3^-]_f$ into equation (10), we get:

$$DY = K_1K_2K_D[NO_3^-]^2 + \frac{K_1K_2K_D[NO_3^-]^2(F_2)^{\frac{1}{2}}}{F_2\left(K_{dA}K_AF_2[NH_4^+][NO_3^-] + K_DK_1K_2[UO_2^{++}][NO_3^-]^2\right)^{\frac{1}{2}}}$$

$$+ \frac{K_1K_2K_D[NO_3^-]^2\ F_2}{F_1F_2\left(K_{dA}K_A[NH_4^+][NO_3^-] + K_DK_1K_2[UO_2^{++}][NO_3^-]^2\right)}$$

$$DY = K_1K_2K_D[NO_3^-]^2 + \frac{K_1K_2K_D[NO_3^-]^{3/2}}{\left(K_{dA}K_AF_2^{\,2}[NH_4^+] + K_DK_1K_2F_2[UO_2^{++}][NO_3^-]\right)^{\frac{1}{2}}}$$

$$+ \frac{K_1K_2K_D[NO_3^-]}{K_{dA}K_AF_1F_2[NH_4^+] + K_DK_1K_2F_1[UO_2^{++}][NO_3^-]} \tag{17}$$

Log DY = Log D + Log Y = Log (A + B + C)

$$\log DY = \mathrm{Log}\left\{\underbrace{K_1K_2K_D[NO_3^-]^2}_{(A)} + \underbrace{\frac{K_1K_2K_D[NO_3^-]^{3/2}}{\left(K_{dA}K_AF_2^{\,2}[NH_4^+] + F_2K_DK_1K_2[UO_2^{++}][NO_3^-]\right)^{\frac{1}{2}}}}_{(B)} + \underbrace{\frac{K_1K_2K_D[NO_3^-]}{K_{dA}K_AF_1F_2[NH_4^+] + K_DK_1K_2F_1[UO_2^{++}][NO_3^-]}}_{(C)}\right\} \qquad (18)$$

Presumably $F_1 > F_2$

At a constant ammonium nitrate concentration, the slope of the curves in the different regions of uranium concentrations may be explained as follows:

At very low concentration of uranium, the second terms in the denominators of the B and C parts of equation 18 may be neglected, since

$$K_{dA}K_AF_2^{\,2}[NH_4^+] \gg F_2K_DK_1K_2[UO_2^{++}][NO_3^-]$$

and
$$K_{dA}K_AF_1F_2[NH_4^+] \gg K_DK_1K_2F_1[UO_2^{++}][NO_3^-]$$

Therfore $$\frac{d(\log D)}{d\left(\log[UO_2^{++}]\right)} = 0$$

At higher concentrations of uranium, the second terms in the denominators of the B and C part become important, but since $F_1 > F_2$, the C part on the whole is negligible compared to the B part. Thus the slope of the curve of log D vs log $[UO_2^{++}]$ in that region is

$$\frac{d\left(\log D\right)}{d\left(\log[UO_2^{++}]\right)} = -\frac{1}{2}$$

At very high concentrations, the foam is saturated with uranium i.e.

$$\log D = \log \Sigma[U]_f - \log \Sigma[U]_{aq}$$

(constant)

$$\frac{d\left(\log D\right)}{d\left(\log\ [UO_2^{++}]\right)} = -1$$

Extraction at very low concentrations of uranium has not been examined. The initial part of the curve obtained at 11 M ammonium nitrate (25°C) shows a slope of about -0.42, a value close to that expected theoretically (-0.50). As the equilibrium uranium concentration increases, the slope of the curve is observed to increase (-0.85) approaching -1.0 as the saturation point is reached. The curves obtained at lower ammonium nitrate concentrations (7 M) follow the same general shape, though the values of the slopes do not agree well with expected values.

C) Effect of Nitrate Concentration:

The effect of increasing nitrate concentration on the extraction of uranyl nitrate into foam was examined in the presence of different cations e.g. NH_4^+, Ca^{2+} and Al^{3+} in order to make a comparison between the foam and diethyl ether (5) as extractants for uranyl nitrate.

The results are shown in FIG. 3 where comparison is made with diethyl ether extraction. The OCPUFS is from 10 to 100 times more effective as an extractant than diethyl ether a fact consistent with previous studies (1) (2) (3).

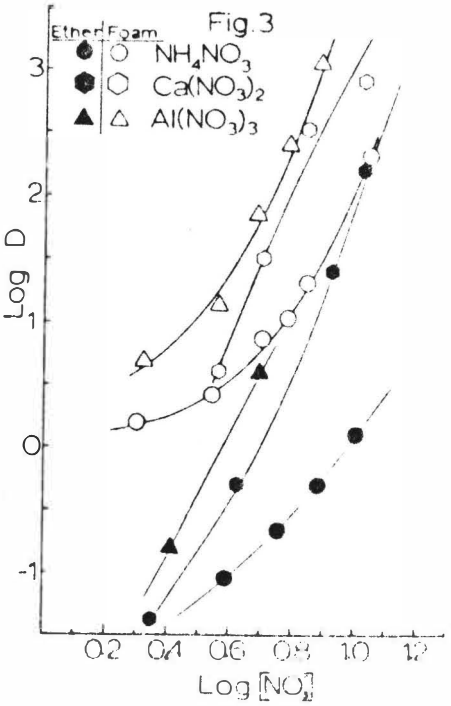
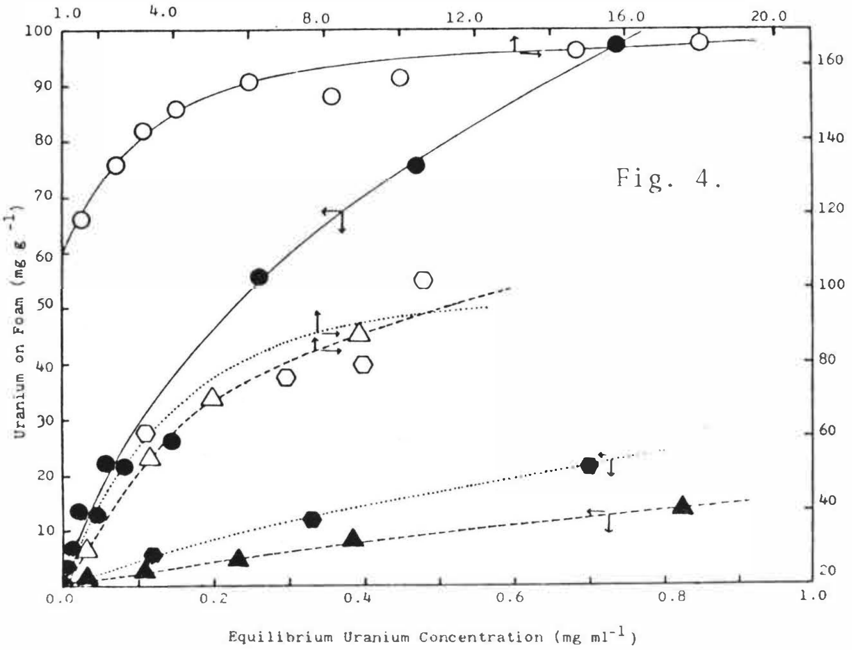


FIG. 3

A comparison between diethyl ether and OCPUFS for the variation of log D as a function of log $[NO_3^-]$ for various salting agents. Initial [U] = 500 ppm in 150 ml solution. Temp. 25°C
OCPUFS 2 g

FIG. 4

Amount of Uranium loaded on foam (mg g^{-1}) as a Function of Equilibrium Uranium Concentration (mg g^{-1}) in Aqueous Phase under Different Conditions of Temperature and $[NH_4NO_3]$.



Circles:
11 M $[NH_4NO_3]$, 25°C

Triangles:
7 M $[NH_4NO_3]$, 25°C

Hexagons:
7 M $[NH_4NO_3]$, 10°C

Filled Symbols: Left ordinate and lower abscissa

Open Symbols: Right ordinate and upper abscissa

D) Capacity of the foam:

The data in FIG. 2 were recalculated and are plotted in FIG. 4 showing the amount of uranium in the foam in equilibrium with the uranium in solution. At 11 M NH_4NO_3 and 25°C the capacity of the foam is over 160 mg U/g foam when the aqueous concentration is about 8 mg U/ml of solution. Higher capacity could be achieved at lower temperatures.

E) Effect of Temperature:

The effect of temperature (0°C to 46°C) on the Distribution Coefficient, D is shown in FIG. 5.

Assuming D to represent an equilibrium function then

$$\log D = \frac{-\Delta H}{2.303RT} + \frac{\Delta S}{2.303R}$$

and one obtains $\Delta H = -4.1 \pm 0.5$ kcal/mole and $\Delta S = -7.8 \pm 1.7$ cal/°K mole. Comparable values for the extractions of uranium by various solvents vary from -3 to -8 kcal/mole for ΔH and -7 to -16 cal/°K mole for ΔS (76-79). Thus OCPUFS shows thermodynamic extraction parameters similar to organic liquids.

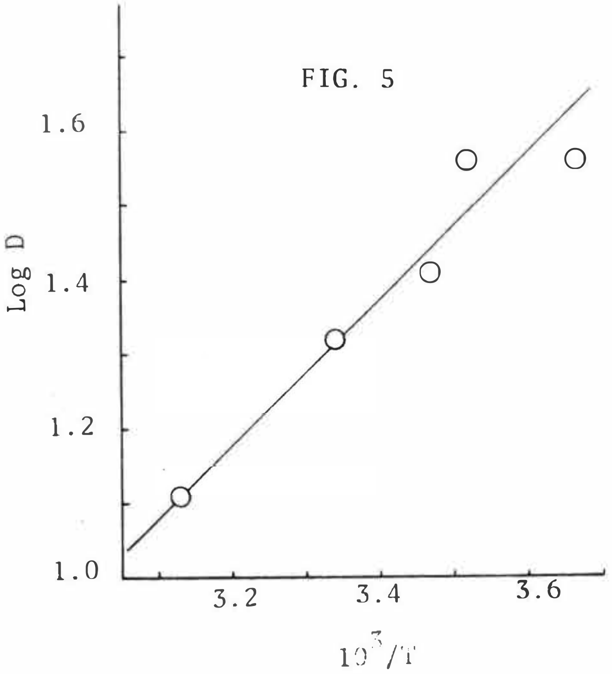


FIG. 5

Variation of log D as a function of 1/T for the extraction of $UO_2(NO_3)_2$

Initial Conditions [U] = 500 ppm

$[NH_4NO_3]$ = 7 M

Volume of solution = 150ml

Weight of Foam = 2 g

F) Effect of pH:

The pH of the test solution was adjusted by the addition of NH_4OH. A plot of log D as a function of pH is shown in FIG. 6. The sharp decrease in extraction at pH > 3.2 is probably due to the hydrolysis of the uranyl ion (8) into non-extractable species.

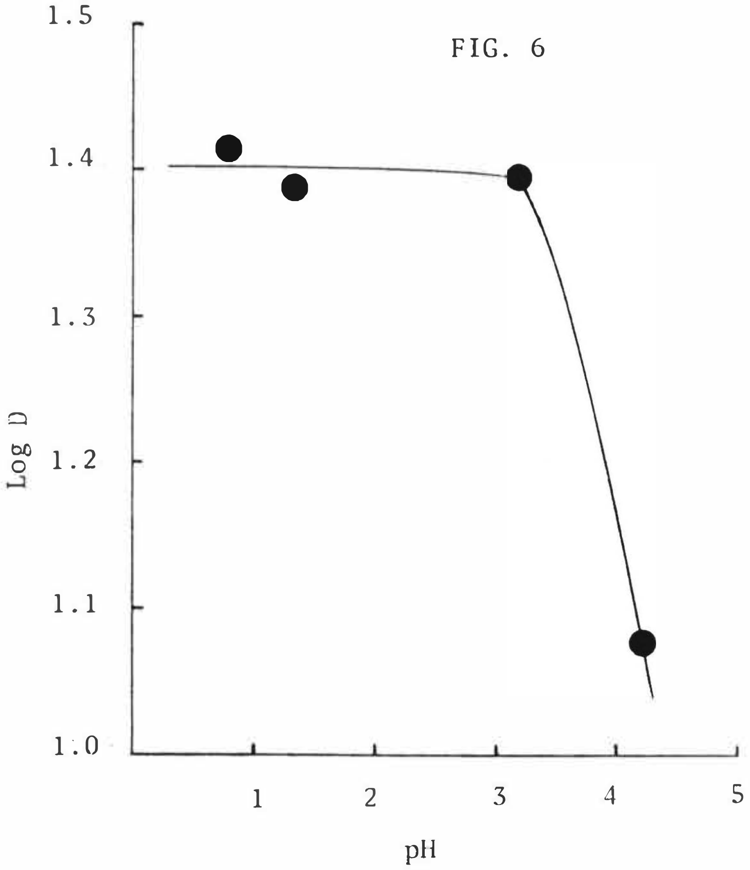


FIG. 6

Variation of Log of Distribution Coefficient as a Function of pH at Room Temperature.

Initial Conditions:
[U] = 500 ppm

$[NH_4NO_3]$ = 11 M

Volume of Solution = 150 ml

Weight of Foam ≈ 2 g

CONCLUSIONS:

The extraction of uranyl nitrate by OCPUFS has been shown to be similar to and more effecient than diethyl ether. The foam can also be used in a column (1) and can be repeatedly reused. It has no volatility and does not contaminate the effluent. Work is continuing on the development of the extraction characteristics for low levels of uranium as well as effluent clean-up.

ACKNOWLEDGMENT:

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PRODUCTION OF KCl FROM BRINES USING PRECIPITATION AND SOLVENT EXTRACTION

E.Barnea, J.E.Gai, G.Harel and J.Metcalfe

I.M.I. Institute for Research & Development
P.O.B. 313,
HAIFA, ISRAEL

Production of KCl from bitterns is generally carried out using fractional crystallization. Alternative routes involving selective precipitation and solvent extraction have been investigated previously. However the solvent extraction routes suggested are unlikely to be viable because either they require consumption of stoichiometric quantities of chemicals(1) or else the cycle requires an energy input and produces an impure KCl product(2). An isothermal solvent extraction cycle has been investigated which should overcome these problems.

1. $NaClO_4 + K^+ \ \underline{(brine)} \longrightarrow KClO_4 + Na^+ \ (brine)$
2. $KClO_4 \ (sl) + \overline{R^+Cl^-} \longrightarrow KCl + \overline{R^+ClO_4^-}$
3. $NaCl + FeCl_3 \ (\beta) + \overline{R^+ClO_4^-} \longrightarrow NaClO_4 + \overline{R^+FeCl_4^-}$
4. $\overline{R^+FeCl_4^-} \xrightarrow{H_2O} FeCl_3 \ (\alpha) + \overline{R^+Cl^-}$
5. $FeCl_3 \ (\alpha) \xrightarrow{NaCl(s)} FeCl_3 \ (\beta)$

where (sl) and (s) represent a slurry and a solid respectively, (α) and (β) represent solutions of $FeCl_3$ in water and in a solution saturated with NaCl respectively, R^+ is an anion exchanger and a line above a component represents a non-aqueous phase. Theoretical analysis of the ion-exchange cycle (reactions 2-5) using reversible thermodynamics indicates that part of the free energy of solution of NaCl can be utilized in the cycle and the concentrations of the products which can be obtained from the cycle, based on experimental results, confirm this conclusion(3).

Solvents composed of the same ion exchanger but with different modifiers gave different concentrations of the product solutions because the selectivities for the anions Cl^-, ClO_4^- and $FeCl_4^-$ change. The changes observed can be explained on the basis of hydrogen-bonding and electro-static effects.

Conditions for implementing the cycle in an industrial application must be based on a techno-economic analysis of the cycle in order to optimise (a) number of operating stages, (b) concentration of the products and (c) purity of the products. Such an analysis has not been carried out on the process, but potential problems have been identified by assigning operating parameters similar to those expected for a commercial operation.

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PRODUCTION OF ALUMINA BY LEACHING SOLVENT EXTRACTION METHOD

Cheng Hsiung Lin and Cherng Sheng Yu

Department of Materials Science,
National Tsing Hua University,
Hsinchu,
Taiwan, China.

Alumina can be produced from high silica, aluminum-containing minerals by leaching solvent extraction method. The minerals are first leached with the hydrochloric acid to obtain a leaching solution and then the leaching solution is purified by removing the ferric ion from the solution. A tributyl phosphate solution diluted with 10 volume % of kerosene was used in this experiment as a solvent to remove the ferric ion by solvent extraction.

Since the distribution coefficient of ferric ion in the system of tributyl phosphate solution and water depends on the concentration of ferric chloride, aluminum chloride, and hydrogen chloride of the aqueous phase, in order to find the distribution coefficient of the ferric ion in this system, a series of simulated leaching solution containing aluminum chloride, ferric chloride, and hydrogen chloride was made in such way that the simulated solutions were approximately equal to the real leaching solution of aluminum-containing minerals. The ferric chloride in the simulated solution was then extracted with the tributyl phosphate solution and then the concentration of ferric ion and aluminum ion in the simulated solution were analysed after the equilibrium was reached.

It is showed from this experiment that the distribution coefficient of ferric ion is proportional to the initial concentration of the aluminum ion in the aqueous solution. When the initial concentration of ferric ion is 3 g/l and the initial concentration of hydrogen ion is 3 N in the simulated leaching solution, the distribution coefficient increases linearly from 500 to 1200 when the concentration of aluminum increases from 12 g/l to 45 g/l. When the initial concentration of ferric ion is changed to 10 g/l, the distribution coefficient increases linearly with the concentration of aluminum ion initially from 700 to 2500 and then levels off at the same range of the aluminum concentration. The distribution coefficient of the ferric ion increases linearly with the acidity of the leaching solution from 1500 to 3200 when the hydrogen ion increases from 1 N to 2.5 N and the concentration of ferric ion and aluminum ion are kept in a constant value of 13.8 g/l and 36 g/l respectively. This experiment also shows that the distribution coefficient increases from 700 to 3000 when the concentration of ferric ion increases from 3 g/l to 14 g/l and the distribution coefficient decreases from 3000 to 2000 when the concentration of the ferric ion continues to increase from 14 g/l to 25 g/l.

The reason that the distribution coefficient increases with the concentration of the ferric ion, aluminum ion and hydrogen ion is that the increase of those ions represents the increase of the chloride ion in the aqueous phase. The increase of chloride ion favors the formation of $FeCl_3 \cdot (TBP)_n$ and $HFeCl_4 \cdot (TBP)_n$ complex, which are the form to be extracted to the organic phase. The reason that the distribution coefficient decreases with the concentration of the ferric ion at high ferric ion concentration because the organic phase gradually becomes saturated with ferric chloride.

INVESTIGATION INTO THE KINETICS OF HYDROCHLORIC ACID EXTRACTION BY CERTAIN TERTIARY AMINES

Tarasov V.V., Nikolaeva T.D.,
Kruchinina N.E.
Mendeleev Institute of Chemical
Technology,
Moscow, USSR

Investigation into the extraction reaction mechanisms under arbitrary hydrodynamic conditions is 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:

$$r = k_1\{[\overline{R_3N}]\cdot[HCl]_{aq} - k_2\cdot[R_3NHCl]\}/\{[R_3N] + k_3\}\sqrt{t}$$

where $K_1 = \sqrt{D_{HCl}/\pi} = 3.14\cdot10^{-5}\,m\cdot s^{-1/2}$; 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*	TLA*
k_2, $kmol\cdot m^{-3}$	$1.61\cdot10^{-2}$	$11.26\cdot10^{-2}$ $2.38\cdot10^{-2}$	$16.9\cdot10^{-2}$ $3.03\cdot10^{-3}$
k_3, $kmol\cdot m^{-3}$	$3.74\cdot10^{-2}$	$23.98\cdot10^{-2}$ $5.05\cdot10^{-2}$	$37.64\cdot10^{-2}$ $6.76\cdot10^{-2}$

*NOTE: the higher values of k_2 and k_3 correspond to $[HCl]_{aq} \leq 10^{-3}M$.

The equation shows that all reactions are diffusion-controlled because $r \to \infty$ at $t \to 0$. Thus the diffusion kinetics may be described by equations identical to chemical kinetics equations that suggested Danesi. The STCM gives the possibility to identify these cases as the values of k_1 and k_2/k_3 may be calculated a priori.

The HCl extraction by TDA and TLA at the $[HCl]_{aq} \leq 10^{-3}M$ was complicated by formation of thin interfacial highly viscous films which sharply decrease the extraction rate (see table). The film formation leads not only to the occurrence additional diffusion resistance but also changes the equilibrium constants of the interfacial reactions.

Organic Processes
Session 8

Co-chairmen : J. Durandet (Institut Français du Pétrole, Rueil-Malmaison, France)
U. Onken (University of Dortmund, Germany)

8A

80-227 Liquid-liquid equilibrium of acetonitrile-alcohol-hydrocarbon systems.
I. Kikic, P. Alessi and M.O. Visalberghi, Instituto di Chimica Applicata e Industriale, Università di Trieste, Trieste, Italy.

80-191 Correlation of equilibrium data for liquid-liquid multicomponent systems of type : aromatics-paraffines-selected solvent.
Z. Maksimović, A. Tolić and M. Sovilj, Boris Kidric Institute of Nuclear Sciences, Beograd and Institute of Petrochemistry, Gas, Naphta and Chemical Engineering, Novi Sad, Yugoslavia.

80-62 Aromatic solubility in aqueous sulphuric acid.
A.N. Strachan, J.P. Field and K.A. Fleming, Loughborough University of Technology, Loughborough, Leicestershire, U.K.

80-63 A new method for the purification of citric acid by liquid-liquid extraction.
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80-65 Separation of ortho-phenyl phenol from ortho-cyclohexyl phenol by LL-extraction with a sodium hydroxide solution.
G.P. Clement and A.J.F. Simons, DMS Central Laboratory, Geleen, The Netherlands.

80-64 Developments in dissociation extraction.
M.W.T. Pratt, M.M. Anwar and M.Y. Shaheen, University of Bradford, Bradford, U.K.

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80-232 Production of the ammonium salt of 3,5-dinitro-1,2,4-triazole (ADNT) by solvent extraction.
Kien-Yin Lee, D.G. Ott and M.M. Stinecipher, Los Alamos Scientific Laboratory, Los Alamos, U.S.A.

LIQUID-LIQUID EQUILIBRIUM OF ACETONITRILE-ALCOHOL-HYDROCARBON SYSTEMS.

I.Kikic, P.Alessi, M.O.Visalberghi

Istituto di Chimica Applicata e
Industriale, Università di Trieste

Trieste Italy

Liquid-liquid equilibrium data at 25°C for acetonitrile-alcohol-n.paraffin systems are reported. The paraffins used were n.hexane, n.heptane and n.octane. The alcohols were n.propanol and n.butanol. The data were correlated with NRTL and UNIQUAC equations. The parameters, obtained by simultaneously fitting the data for all the systems studied were compared with those reported in the literature.

INTRODUCTION

The correlation of equilibrium data of fluid phases is a continually developing subject, especially as regards the improvements in the characterization of liquid mixtures. Since the description and calculation of thermodynamic properties of liquids is still now a difficult task, the study of liquid-liquid equilibrium for the description of the liquid state has become very important. Phase instability is, in fact, a characteristic feature of liquid solutions, and this can allow the nature of the interactions between the different components to be understood. Therefore, experimental determinations of liquid-liquid equilibrium data in ternary systems were carried out. The components chosen are representative of three classes of organic compounds and show different energies of interaction:

- "dispersional" interaction forces: these are typical of non-polar compounds (hydrocarbons);
- "polar" interaction forces: these dipole-dipole interactions are typical of components with high dipole momentum (e.g. nitriles);
- "specific" interaction forces: hydrogen-bonding compounds are

typical examples (alcohols).

To vary the importance of the different interaction forces, the alcohols and the paraffins were changed. The equilibrium data at 25°C were determined for the following systems: acetonitrile-n.propanol-n.hexane (A), acetonitrile-n.propanol-n.heptane (B), acetonitrile-n.propanol-n.octane (C), acetonitrile-n.butanol-n.hexane (D), acetonitrile-n.butanol-n.heptane (E), acetonitrile-n.butanol-n.octane (F).

EXPERIMENTAL

Liquid-liquid equilibrium data were obtained with an apparatus consisting of five cells of the Renon type (1). The experimental procedure was that proposed in (1). The two-phase compositions and the mutual solubilities of the binary mixtures were determined by gas-liquid chromatography. A C. Erba, mod. A.C.T., chromatograph fitted with a thermal conductivity detector was used. The stainless steel column (2 m lenght, 4 mm I.D.) was packed with 60-80 mesh Chromosorb W (sylanized) coated with 25 wt% PEG 1500 (column temperature 55°C). The hydrocarbons and acetonitrile employed were Fluka products (99% purity); the alcohols (Fluka products) were distilled and dried. No detectable impurities in the components could be revealed by the GLC analyses.

RESULTS AND DISCUSSION

Table 1-6 report the concentrations of the two liquid phases in equilibrium at 25°C for the ternary systems acetonitrile-alcohol-paraffin. In the diagrams of Fig. 1 the distribu-

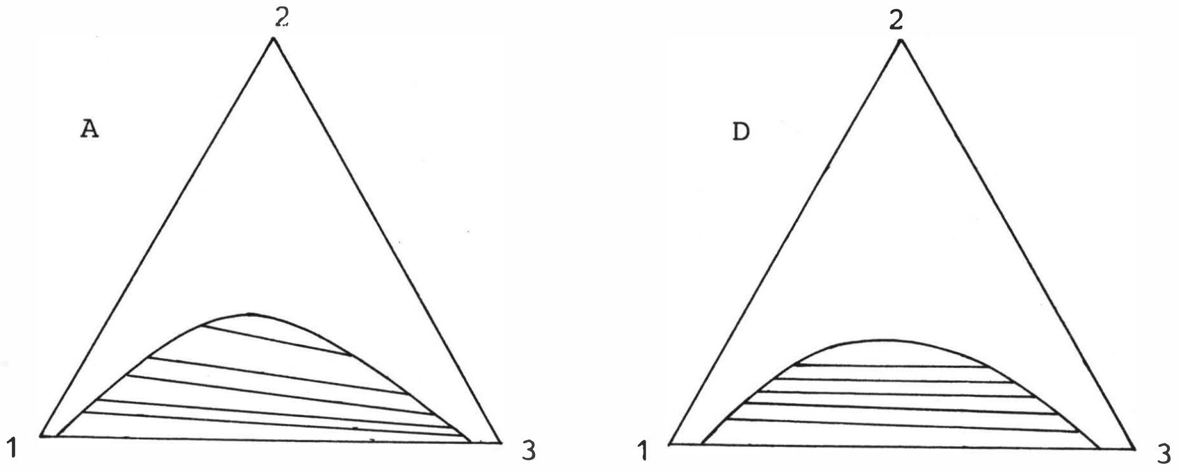

FIG. 1 - Distribution isotherms for acetonitrile (1) - n.propanol (2) - n.hexane (3) and acetonitrile (1) - n.butanol (2) - - n.hexane (3) systems (respectively A and D).

TABLE 1

Acetonitrile (1) - n.Propanol (2) - n.Hexane (3)

Phase I		Phase II	
x_1	x_3	x_1	x_3
0.5089	0.2269	0.2543	0.5459
0.6563	0.1385	0.1460	0.7508
0.7266	0.1091	0.1071	0.8308
0.8188	0.0861	0.0965	0.8764
0.8743	0.0685	0.0901	0.8964
0.9459	0.0541	0.0870	0.9130

TABLE 2

Acetonitrile (1) - n.Propanol (2) - n.Heptane (3)

Phase I		Phase II	
x_1	x_3	x_1	x_3
0.5938	0.1531	0.1529	0.6943
0.6230	0.1361	0.1307	0.7359
0.7203	0.0920	0.0960	0.8282
0.8047	0.0677	0.0795	0.8746
0.8967	0.0476	0.0727	0.9137
0.9620	0.0380	0.0631	0.9369

TABLE 3

Acetonitrile (1) - n.Propanol (2) - n.Octane (3)

Phase I		Phase II	
x_1	x_3	x_1	x_3
0.6091	0.1217	0.0657	0.8264
0.6674	0.0871	0.0517	0.8759
0.7096	0.0704	0.0481	0.8916
0.7590	0.0594	0.0480	0.9060
0.8609	0.0315	0.0370	0.9496
0.9754	0.0246	0.0369	0.9631

TABLE 4

Acetonitrile (1) - n.Butanol (2) - n.Hexane (3)

Phase I		Phase II	
x_1	x_3	x_1	x_3
0.6519	0.1465	0.2105	0.6030
0.6876	0.1320	0.1811	0.6632
0.7387	0.1147	0.1448	0.7404
0.7769	0.1048	0.1181	0.8086
0.8339	0.0841	0.0958	0.8717
0.9459	0.0541	0.0870	0.9130

TABLE 5

Acetonitrile (1) - n.Butanol (2) - n.Heptane (3)

Phase I		Phase II	
x_1	x_3	x_1	x_3
0.5970	0.1718	0.2304	0.5687
0.6998	0.1164	0.1389	0.7207
0.7837	0.0831	0.0903	0.8352
0.8290	0.0741	0.0854	0.8585
0.8615	0.0601	0.0779	0.8908
0.9620	0.0380	0.0631	0.9369

TABLE 6

Acetonitrile (1) - n.Butanol (2) - n.Octane (3)

Phase I		Phase II	
x_1	x_3	x_1	x_3
0.6063	0.1588	0.1964	0.5962
0.6346	0.1111	0.1231	0.7266
0.7674	0.0826	0.0952	0.8016
0.8582	0.0486	0.0475	0.9217
0.9101	0.0356	0.0366	0.9473
0.9754	0.0246	0.0369	0.9631

tion isotherms for the systems A and D are reported as an example. All the other systems appear similar in that they all consist of one partially miscible pair and two miscible pairs. The experimental data were correlated by the NRTL (2) and the UNIQUAC equations (3). NRTL and UNIQUAC parameters were determined with the aid of the computer program reported in (4). For more details on these equations the reader is referred to (2,3). Table 7 reports the values of the NRTL and UNIQUAC parameters obtained for the binary systems. The agreement between experimental and calculated equilibrium mole fractions is satisfactory: the mean deviation (expressed in calculated - experimental mean square root) is 0.005, the maximum deviation is 0.008 (Table 8). The NRTL parameters obtained in this work for the acetonitrile-n.heptane pair were compared with those reported in the literature. The agreement with the data reported in (5) (A_{ij} = 651.5, A_{ji} = 580.8, α = 0.2) is quite good. The UNIQUAC parameters obtained for the same system are practically identical with those reported in (6) (A_{ij} = 35.16, A_{ji} = 567.4), in which the data for the system acetonitrile-n.heptane-benzene are correlated. A further comparison can be made on the basis of the values obtained by correlating vapour-liquid equilibrium data (7). The numerical values of the parameters (Table 9) are different from those reported herein. This can be ascribed to the different equilibrium temperatures and types of equilibrium used. The comparison based on the values of the activity coefficients at infinite dilution obtained for paraffins in acetonitrile by liquid-liquid chromatographic determination (8) shows very good agreement between the data obtained experimentally and those calculated by means of the here reported parameters (Table 10). Table 11 reports, for comparison, the values of the plait points calculated through the NRTL and UNIQUAC equations and those determined by means a method proposed by Treybal (9) i.e., with the aid of Hand's correlation (10). The plait points calculated by NRTL and UNIQUAC are in very good agreement; they agree sufficiently well with those based on Hand's correlation, except for the system D and F. The plait point values for the systems investigated vary in a regular way: the mole fraction of acetonitrile in the plait point decreases linearly with increasing number of C atoms in the paraffin and decreases in passing from n.butanol to n.propanol. This means that the alcohol has an effect on the miscibility gap (e.g., it is wider in the case of n.propanol than in that of n.butanol), as is confirmed by the two-branches isotherms found for the systems acetonitrile-methanol-paraffins. This suggests that the presence of alcohols with higher molecular weight (increased lenght of the hydrocarbon chain) results in a reduction of the miscibility gap, because the alcohol gradually becomes the component which best solubilizes both the acetonitrile and the n.hexane.

TABLE 7

NRTL and UNIQUAC parameters

Binary pair	UNIQUAC parameters (K)		NRTL parameters (K)		
	A(ij)	A(ji)	A(ij)	A(ji)	ALPHA
Acetonitrile-n.propanol	-112.04	-166.70	331.81	-747.04	0.2
Acetonitrile-n.butanol	-822.67	- 46.98	-639.91	-623.86	0.2
Acetonitrile-n.hexane	48.20	515.19	659.10	428.74	0.2
Acetonitrile-n.heptane	35.16	567.41	762.88	436.64	0.2
Acetonitrile-n.octane	23.68	680.54	791.58	573.04	0.2
n.Propanol-n.hexane	260.36	-188.46	2002.90	-640.79	0.2
n.Propanol-n.heptane	- 10.44	8.21	1048.00	-590.40	0.2
n.Propanol-n.octane	- 89.01	162.33	324.02	-187.73	0.2
n.Butanol-n.hexane	203.86	-815.11	2184.20	-1474.00	0.2
n.Butanol-n.heptane	- 33.21	-636.86	241.34	-1107.40	0.2
n.Butanol-n.octane	-108.84	-571.28	- 22.44	-986.21	0.2

TABLE 8

Deviation between calculated and experimental concentrations (in mole fraction) expressed as root mean square.

	RMS (calc-exp) x 10^2	
Systems	UNIQUAC	NRTL
A	0.5241	0.5289
B	0.3184	0.2983
C	0.4782	0.4252
D	0.5953	0.5318
E	0.4369	0.4992
F	0.4835	0.4903

TABLE 9

UNIQUAC parameters obtained from vapor-liquid equilibrium data (7).

	T	A(ij)	A(ji)
n.Propanol-n.hexane	45°	-44.46	338.80
n.Propanol-n.heptane	75°	-90.69	405.63
n.Butanol-n.hexane	25°	111.32	41.20
n.Butanol-n.heptane	50°	-112.73	378.42

TABLE 10

Comparison between experimental (8) and calculated activity coefficients at infinite dilution of paraffins in acetonitrile at 25°C

	$\ln \gamma^{\infty}_{exp}$	$\ln \gamma^{\infty}_{NRTL}$	$\ln \gamma^{\infty}_{UNIQUAC}$
n.Hexane	3.24	3.29	2.96
n.Heptane	3.52	3.65	3.58
n.Octane	3.96	3.96	3.93

TABLE 11

Experimental and calculated plait points (1 = acetonitrile; 2 = alcohol).

Systems	Hand (9)		NRTL		UNIQUAC	
	x_1	x_2	x_1	x_2	x_1	x_2
A	0.3619	0.2652	0.3659	0.2711	0.3647	0.2619
B	0.3433	0.3204	0.3445	0.2839	0.3396	0.2886
C	0.2479	0.3398	0.2538	0.3223	0.2492	0.3390
D	0.4654	0.2443	0.4234	0.2579	0.4312	0.2439
E	0.4267	0.2571	0.4107	0.2541	0.4013	0.2635
F	0.3398	0.2699	0.3943	0.2679	0.3832	0.2761

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CORRELATION OF EQUILIBRIUM DATA FOR LIQUID-LIQUID MULTICOMPONENT SYSTEMS OF TYPE: AROMATICS-PARAFFINES-SELECTED SOLVENT

Z.Maksimović, A.Tolić[*], M.Sovilj[*]
Boris Kidrič Institute of Nuclear Sciences, P.O.Box 522, Beograd
[*]Institute of Petrochemistry, Gas, Naphtha and Chemical Engineering, Novi Sad, Yugoslavia

ABSTRACT

On the basis of our experimental results on characterization of phase equilibrium for five multicomponent liquid-liquid systems of type: aromatics-paraffines-selected solvent, in which tetraethyleneglycol, n-methylpyrolidone, sulpholane, dimethylsulphoxide and trimethylphosphate have been used as solvents, at elevated temperatures and increased pressure, equilibrium data have been correlated. All five systems were treated as pseudothreecomponent ones and correlations of Hand, Othmer-Tobias and Rod were used.

INTRODUCTION

In order to remove aromatic from aliphatic hydrocarbon mixtures obtained by modification of primary naphtha products, the liquid-liquid extraction, as an effective treatment, has been used. Several papers(1-7) have been published in this field treating different solvents for separation of aromatics from aliphatics for various feed solutions. In order to consider quantitatively the aromatic extraction, it is important to determine the equilibrium values for the investigated systems. An original apparatus has been made for these measurements. Phase characterization of five multicomponent systems has been performed: aromatics-paraffines and selected solvent. All five systems were treated as pseudothreecomponent ones and correlations of Hand, Othmer-Tobias and Rod were used. Application of these correlations decreases a number of experiments for determination of equilibrium data and enables their prediction.

EXPERIMENTAL AND CALCULATING PROCEDURE

The starting components of the investigated system were paraffines and aromatics obtained from pyrolitic gasolene (Oil Refinery Pančevo). Paraffines were mixtures consisted of 28.76% of n-paraffine; 70.14% of i-paraffine and 1.10% of benzene while aromatics, also mixtures contained 73.68% of benzene and 26.32% of toluene, all in mass percentage. Tetraethyleneglycol, n-methylpyrolidone, sulpholane, dimethylsulphoxide and trimethylphosphate in pure grade were used as solvents.

Experimental determinations of the equilibrium data were carried out on an apparatus described in earlier papers(8,9) and shown in Figure 1.

Data for binodal curves were determined by using the turbidity method(10) which was based on the following procedure: two-phase mixtures with different but constant mass ratio of two components and changeable mass fraction of the third one were heated to be transparent and then cooled to be turbid. A cathetometer was used for all measurements and observations. The results are presented in diagrams: turbidity temperature - the mass fraction of the third component; for single ratio of two components the corresponding curve was obtained. From these diagrams, the points of binodal curves at the selected temperatures were determined by interpolation.

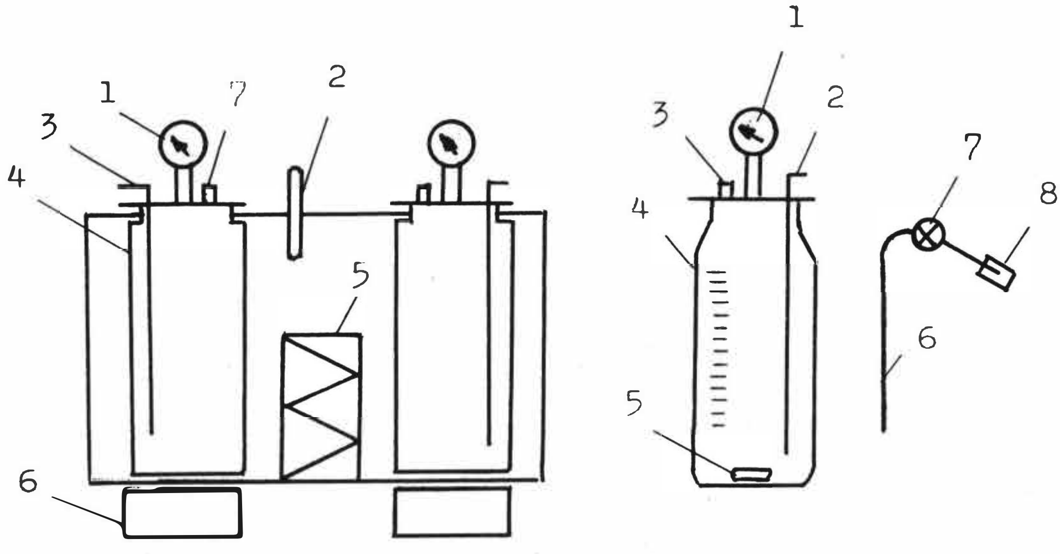
The tie lines were determined by a two-phase equilibrium procedure at constant temperature. By the applied procedure the known two-phase mixture was equilibrated at the selected temperature and both the volumes of raffinate (light phase) and the extract (heavy phase) as well as the aromatic content in raffinate phase were measured. Aromatic content in the extract phase was calculated from the mass balance. All measurements were performed by the gas-chromatographic method.

Plait-point was determined by the method of Brancroft(11).

Since the experimental determination of the equilibrium data for multicomponent systems is a very complex procedure, it is more usual and simple to treat these systems as pseudothreecomponent ones. Reduction of the multicomponent systems to the pseudothreecomponent ones can be made on the basis of some additive characteristics of the systems such as: formation of groups based on their chemical similarities(12). In this paper all the components were classified according to their chemical similarities as aromatics (the first), paraffines (the second) and selected solvent (the third component). The equilibrium data of the pseudothreecomponent systems were correlated by the selected empirical correlations, this enables interpolation and extrapolation of the equilibrium data and decreases the necessity for experimental determinations.

The used apparatus as well as the applied procedures enabled both the maintaining of the investigated temperatures within the range of 0.5°C and good precision of the obtained results so that the error does not exceed ± 3%.

The experimental data for all investigated systems, at all selected temperatures, were correlated by the correlations of Hand(13) (Eq. 1), Othmer-Tobias(14) (Eq. 2) and Rod(15) (Eq. 3):



a) b)

FIG. 1.

a) Thermostat with glass test tube and magnetic stirrer

1. Burdon`s pressure gauges
2. thermometer of the temperature control
3. thermocouples
4. gradued glass test tube
5. heater of the thermostat
6. magnetic stirrer
7. openings for taking samples, stoppered with teflon-cork

b) Test tube with pressure gauge and a tube with tap for taking out of samples

1. Burdon`s pressure gauge
2. thermocouple
3. opening for taking samples, stoppered with teflon-cork
4. graduated glass test tube
5. magnet in stick-form
6. steel tube with sharp end for taking of the samples
7. tap for let-out of the sample
8. sample vial (previously evacuated)

$$\frac{y_1}{y_3} = p \cdot \left(\frac{x_1}{x_2}\right)^q \qquad (1)$$

$$\frac{1-y_3}{y_3} = k \left(\frac{1-x_2}{x_2}\right)^r \qquad (2)$$

$$\ln m_i = \sum_{m=0}^{M} a_{im} \cdot x_1^m \quad i = 1,2,3 \qquad (3)$$

where : x_1, x_2 - are respectively weigth the fractions of aromatics and paraffins in the raffinate phase.
y_1, y_3 - are respectively weigth the fractions of aromatics and solvent in the extract phase.
m_i - is the distribution coefficient of the i-component.
p, q, k, r, a_{im} - are the experimental constants.

On the basis of these equations the equilibrium data, at the elevated temperatures, were completed using the interpolation and extrapolation procedure. For making calculations, FORTRAN program for all selected correlations (Eqs. 1-3) has been set for a Varian Digital Computer. Original Rod's program has been used for his correlation.

RESULTS AND DISCUSSION

The results of phase characterization of all investigated systems under selected conditions were presented in our earlier papers (8,9,16,17), while the summary of the obtained distribution coefficients (D_M) and the separation factors (α) are given in Table 1. It has been shown, on the basis of the experimentally determined equilibrium data for all investigated multicomponent systems, that increase of temperature decreases the heterogeneous region limited by the binodal curve, what is illustrated by Fig. 2. It can be concluded comparing the values of the distribution coefficients (D_M) and the separation factors (α), from Table 1, for the investigated solvents used for the extraction of aromatics from the mixture of the same starting composition, that the most suitable solvent is sulpholane. It has the greatest capacity as well as the greatest selectivity for aromatics.

The equilibrium data, experimentally obtained, for all investigated multicomponent systems were correlated by the correlations of Hand, Othmer-Tobias and Rod. Agreement of the calculated with the experimental results was compared by using of the criterion given by the following expression :

$$\delta = \sqrt{\frac{\sum_{i=1}^{N} (x_{j,i}^{exp} - x_{j,i}^{cal})^2 + (y_{j,i}^{exp} - y_{j,i}^{cal})^2}{N}} \qquad (4)$$

j=1,2,3

TABLE 1. Distribution coefficients (D_M) and separation factors (α) for the investigated systems.

Starting mixture content	System: aromatics-paraffines-tetraethyleneglycol							
	t = 100°C		t = 115°C		t = 130°C		t = 145°C	
	D_M	α	D_M	α	D_M	α	D_M	α
I	0.298	4.50	0.235	2.76	0.242	2.24	0.343	2.50
II	0.317	4.46	0.252	2.90	0.271	2.40	0.312	2.20
III	0.296	4.18	0.305	3.40	0.307	2.66	0.274	1.84
IV	0.344	3.63	0.307	2.66	0.355	2.44	0.378	2.00
V	0.295	2.67	0.310	2.27	0.326	1.91	0.350	1.57
VI	0.301	2.70	0.293	1.75	0.323	1.54	0.453	1.78
VII	0.340	2.08	0.352	1.65	0.385	1.32	0.539	1.29

	System: aromatics-paraffines-sulpholane					
	t = 100°C		t = 115°C		t = 130°C	
	D_M	α	D_M	α	D_M	α
I	1.56	54.2	1.52	24.5	1.55	33.8
II	1.72	40.6	1.73	29.9	1.72	37.7
III	1.72	34.2	1.69	25.0	1.67	31.8
IV	1.78	28.1	1.72	18.0	1.68	17.9
V	1.66	22.3	1.74	15.0	1.63	13.7
VI	1.64	16.3	1.68	11.3	1.65	9.04
VII	1.44	10.6	1.47	6.80	1.41	3.79

	System: aromatics-paraffines-dimethylsulphoxide							
	t = 90°C		t = 105°C		t = 120°C		t = 135°C	
	D_M	α	D_M	α	D_M	α	D_M	α
I	0.113	4.83	1.19	3.10	0.154	2.75	0.257	2.02
II	0.423	7.47	0.422	5.27	0.463	3.61	0.486	3.09
III	0.448	6.64	0.477	4.43	0.500	3.62	0.532	2.75
IV	0.444	3.62	0.455	3.33	0.506	2.65	0.907	3.17
V	0.443	3.01	0.449	2.38	0.550	2.19	0.842	-
VI	0.442	2.43	0.541	2.26	0.794	1.58	-	-
VII	0.481	1.76	0.590	1.50	0.842	1.00	-	-

	System: aromatics-paraffines-n-methylpyrolidone							
	t = 50°C		t = 55°C		t = 60°C		t = 75°C	
	D_M	α	D_M	α	D_M	α	D_M	α
I	0.361	9.65	0.414	34.3	0.266	289	0.406	10.4
II	0.329	8.88	0.310	31.8	0.242	221	0.412	9.11
III	0.392	7.20	0.341	13.5	0.283	141	0.385	7.38
IV	0.463	6.51	0.460	13.2	0.545	81.0	0.476	4.74
V	0.622	4.48	0.548	9.01	0.546	65.5	0.380	4.00
VI	0.654	3.73	0.672	6.03	0.711	24.3	0.493	2.48
VII	0.643	3.27	0.684	4.83	0.943	14.2	-	-

TABLE 1. (continued)

	System : aromatics-paraffins-trimethylphosphate					
	t = 50 °C		t = 60 °C		t = 70 °C	
	$\underline{D}_M$	α	$\underline{D}_M$	α	$\underline{D}_M$	α
I	1.73	15.00	2.20	13.77	1.20	8.82
II	2.09	12.60	2.10	8.81	1.44	8.17
III	1.95	9.55	2.02	7.40	1.68	7.06
IV	1.74	5.41	1.65	4.18	1.56	3.89
V	1.42	3.78	1.53	3.26	1.51	2.63
VI	1.29	2.68	1.46	2.75	-	-

Notes to Table 1 :

1. Starting mixture content for determination of the tie lines :

	X_B	X_C
I	5.00	45.00
II	6.67	43.33
III	8.33	41.67
IV	16.67	33.33
V	20.00	30.00
VI	25.00	25.00
VII	30.00	20.00

where : X_C - is the weigth percentage of aromatics in starting mixture.
X_B - is the weigth percentage of paraffins in starting mixture.
X_A - is the weigth percentage of the solvent in starting mixture.
$X_A = 100 - (X_C + X_B)$.

2. $\underline{D}_M$ - is the distribution coefficient for aromatics.

3. α - is the aromatic separation factor relatively to paraffin

$$\alpha = \frac{X_{C1}\ (100 - X_{C2})}{X_{C2}\ (100 - X_{C1})}$$

where :

X_{C1}, XC_2 - are the weigth percentage of aromatics respectively in solvent free extract and in solvent free raffinate.

TABLE 2. Results of comparison of the experimental with the calculated equilibrium data of the system: aromatics-paraffines-selected solvent at selected temperatures.

Temperature °C	Number of points N	Hand's correlation δ	Othmer-Tobias' correlation δ	Rod's correlation δ
	System: aromatics-paraffines-tetraethyleneglycol			
100	14	0.244	0.048	0.021
115	14	0.267	0.064	0.010
130	14	0.263	0.081	0.051
145	14	0.252	0.076	0.033
	System: aromatics-paraffines-sulpholane			
100	14	0.075	0.018	0.002
115	14	0.103	0.021	0.003
130	14	0.132	0.032	0.003
	System: aromatics-paraffines-dimethylsulphoxide			
90	14	0.221	0.039	0.052
105	14	0.230	0.052	0.036
120	14	0.222	0.056	0.008
135	10	0.255	0.044	0.006
	System: aromatics-paraffines-n-methylpyrolidone			
50	14	0.213	0.062	0.008
55	14	0.073	0.031	0.005
60	14	0.175	0.050	0.006
75	10	0.222	0.138	0.022
	System: aromatics-paraffines-trimethylphosphate			
50	12	0.073	0.022	0.002
60	12	0.094	0.033	0.006
70	10	0.162	0.033	0.002

where:

- is the root mean square deviation,
1 - is the index for the aromatic component,
2 - index for the paraffine component,
3 - index for the solvent component,
N - is the number of the experimental points,
$x^{exp}_{j,i}, x^{cal}_{j,i}$ - are the experimental i.e. the calculated values for the mass fractions of the components in raffinate at single points,
$y^{exp}_{j,i}, y^{cal}_{j,i}$ - are the experimental i.e. the calculated values for the mass fractions of the components in extract at single points.

The results of comparison of the calculated with the experimental equilibrium data for all investigated systems are given in Table 2.

The minimum δ values, Table 2, for all three correlations were obtained using sulpholane. It indicates that the best agreement of the used correlations with the experimental results has been achieved by this solvent.

The best correlation of the equilibrium data for all systems at selected temperature can be obtained using Rod`s correlation. Since the minimum $\delta$ values for all investigated systems in Table 2 were obtained using this correlation, greater deviations in agreement of the calculated with the experimental results were obtained using Othmer-Tobias` and Hand`s correlation.

Agreement of the equilibrium data obtained experimentally with the calculated data obtained by Rod`s correlation is shown graphically for all treated systems at selected temperatures in Figure 2.

The used correlations as well as the set computer programs for them were the attractive tools for construction of the tie lines, that is, for determination of the equilibrium pairs for the investigated systems. In addition the Rod correlation can be also used for prediction of the equilibrium data if the constants are previously determined for a given system and conditions, within the scope of the correlation validity(15).

CONCLUSION

The results of correlation of the equilibrium data for the investigated multicomponent extraction systems: aromatics-paraffines-selected solvent are presented. Tetraethyleneglycol, dimethylsulphoxide sulpholane, n-methylpyrolidone and trimethylphosphate have been used as solvents. The Hand, Othmer-Tobias and Rod correlations have been used.

Comparing the equilibrium data obtained experimentally, for all investigated systems, with the calculated data, it has been found that the best agreement has been achieved using the Rod correlation. The best agreement for all three correlations has been obtained using sulpholane as a solvent.

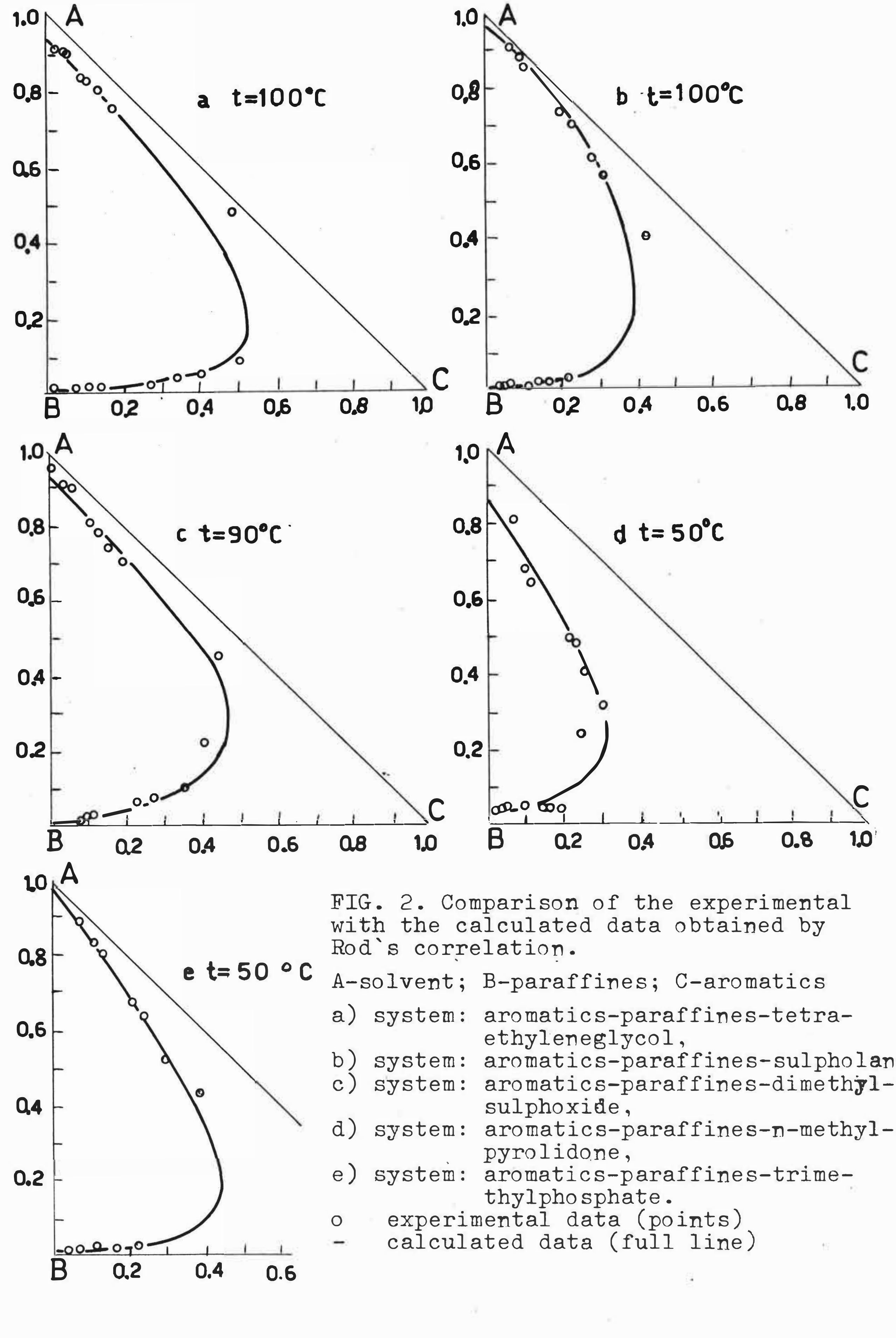


FIG. 2. Comparison of the experimental with the calculated data obtained by Rod`s correlation.

A-solvent; B-paraffines; C-aromatics

a) system: aromatics-paraffines-tetraethyleneglycol,
b) system: aromatics-paraffines-sulpholane,
c) system: aromatics-paraffines-dimethylsulphoxide,
d) system: aromatics-paraffines-n-methylpyrolidone,
e) system: aromatics-paraffines-trimethylphosphate.
o experimental data (points)
\- calculated data (full line)

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AROMATIC SOLUBILITY IN AQUEOUS SULPHURIC ACID

A.N.Strachan, J.P.Field and K.A.Fleming

Department of Chemistry,
Loughborough University of Technology

Loughborough, Leicestershire, LE11 3TU
England.

ABSTRACT New data on the solubilities of o- and m-nitrotoluene and hexafluoro-m-xylene in H_2O-H_2SO_4 mixtures are presented and compared with previous and similar data for other aromatics. In all cases, as the H_2SO_4 content is raised, an initial salting out is followed by a steady and significant increase in solubility such that aromatics are over 100 times more soluble in 100% H_2SO_4 than in water. The increase in solubility is accompanied by a decrease in the heat of the solution and, in the case of nitrobenzene and o-nitrotoluene, by the appearance of a new peak in the U.V. spectrum. These features to the solubility behaviour of aromatics in aqueous sulphuric acid are discussed, and are considered to be best explained by complex formation between the aromatic ring and undissociated H_2SO_4, possibly involving charge transfer.

INTRODUCTION

Hydrocarbon mixtures are often contacted with aqueous sulphuric acid in both oil refining and other industrial processes. The solubility behaviour of different hydrocarbons in this medium is therefore of considerable importance. In addition the solubility of aromatics and nitroaromatics is of special interest in two phase aromatic nitration, which has many features in common with solvent extraction (1). The nitration proceeds via extraction of the aromatic substrate from the organic phase into the aqueous phase where reaction occurs. The nitro-products are then extracted back from the aqueous phase into the organic phase. The rate of nitration, whether kinetically or mass transfer controlled, is directly proportional to the solubility of the aromatic in the acid phase (2), and the recovery of the nitroproducts is likewise dependent on their solubilities in the spent acid. Further knowledge and understanding of the factors which determine the solubilities of aromatics in aqueous sulphuric acid is therefore desirable. This paper seeks to make a contribution to this end.

When toluene is nitrated a mixture of all three mononitrotoluenes is formed. This is often nitrated further without separation. While there is information in the literature on the solubility in aqueous sulphuric acid of p-nitrotoluene (3), no comparable data is available on the ortho or meta isomers. The ortho isomer comprises the major part (∿60%) of the mononitrotoluene mixture and the meta isomer a very minor part (∿4%) (4). An investigatation of the solubility behaviour of o-nitrotoluene has therefore been undertaken and limited data also obtained on the solubility of m-nitrotoluene.

The solubilities of several nitroaromatics are known over a wide range of sulphuric acid concentrations (3). However in the case of aromatics without a nitro group, the onset of sulphonation usually prevents solubilities being determined at the higher acid strengths. An exception is hexafluoro-m-xylene and fresh data on the solubility of this compound is combined with previously published data (5,6) to enable the solubility behaviour of nitroaromatics to be compared with that of an aromatic without a nitro group.

EXPERIMENTAL

Materials Aqueous sulphuric acid was prepared by the addition of analytical reagent grade concentrated acid (98 wt %) to distilled water. Compositions were determined by density measurements. The hexane was spectroscopic grade, the nitrobenzene analytical grade and the o- and m-nitrotoluene both laboratory reagent grade. The hexafluoro-m-xylene was Fluorochem Limited 97-100%. It was redistilled and a middle cut used in the experiments.

Solubility Determinations Solubilities were determined by stirring an excess of the aromatic vigorously with 100 cm^3 of aqueous acid of known composition for 30 minutes in a flask placed in a water bath controlled to ±0.1°C. The stirrer was then removed. After allowing the two phases to separate over several hours, a known sample of the acid phase was removed, extracted with hexane and its absorbance measured at a particular wavelength. Known solutions of the aromatic in hexane were used to determine the extinction coefficient at this wavelength. With both nitrotoluenes absorbances were measured at 350 nm and the extinction coefficients found to be 245 and 119.5 dm^3 mol^{-1} cm^{-1} for the ortho and meta isomers respectively. In the case of hexafluoro-m-xylene, absorbances were measured at 265 nm, at which wavelength the extinction coefficient was found to be 246 dm^3 mol^{-1} cm^{-1}.

Usually experiments were carried out in duplicate and two samples taken from the acid phase in each experiment. Thus normally four values for the solubility were obtained and the agreement between these was almost always within 2 or 3%. An average was taken in each case and this is the value shown in the Tables.

U.V.Spectra The absorbance measurements in the solubility determinations were made with a Pye Unicam SP 30 Spectrophotometer. This instrument was also used in the investigation of the U.V. spectra of solutions of nitrobenzene and o-nitrotoluene in aqueous sulphuric acid.

RESULTS

The solubility of o-nitrotoluene (ONT) as a function of aqueous sulphuric acid composition and temperature is shown in Table 1 and the solubility of m-nitrotoluene (MNT) at one acid composition and several temperatures in Table 2. The solubilities of hexafluoro-m-xylene (HFMX) from 100% H_2O to 100% H_2SO_4 are listed in Table 3.

Preliminary investigation of the U.V. spectra of solutions of nitrobenzene and o-nitrotoluene in aqueous sulphuric acid showed that a new peak appeared in each case as the H_2SO_4 content was increased.

Table 1 The solubility of o-nitrotoluene as a function of H_2SO_4-H_2O composition and temperature

H_2SO_4/mol %	21.6	29.8	35.9	43.1	44.2
Temp./^oC	ONT solubility/mol dm^{-3}				
25	1.21×10^{-2}	2.31×10^{-2}	4.35×10^{-2}	10.2×10^{-2}	13.2×10^{-2}
50	1.55×10^{-2}	2.82×10^{-2}	-	11.1×10^{-2}	-
80	2.02×10^{-2}	3.59×10^{-2}	5.94×10^{-2}	12.6×10^{-2}	16.4×10^{-2}
Heat of solution/kcal mol^{-1}	2.01	1.75	1.14	0.80	0.73

Table 2 The solubility of m-nitrotoluene in 43.1 mol % H_2SO_4 as a function of temperature

Temp./^oC	MNT solubility/mol dm^{-3}
25	9.03×10^{-2}
35	9.45×10^{-2}
45	9.97×10^{-2}
55	10.5×10^{-2}
65	11.0×10^{-2}
75	11.4×10^{-2}

Heat of solution
= 0.93 kcal mol^{-1}

Table 3 The solubility of hexafluoro-m-xylene as a function of H_2SO_4-H_2O composition

H_2SO_4/mol %	HFMX solubility/mol dm^{-3}		Source
	20^0C	25^0C	
0	-	1.91×10^{-4}	this work
20	-	1.18×10^{-4}	this work
30	5.3×10^{-4}	5.9×10^{-4}	reference 6
50	-	14.7×10^{-4}	this work
60	51.4×10^{-4}	-	reference 5
80	168×10^{-4}	-	reference 5
83.5	176×10^{-4}	145×10^{-4}	reference 6
100	393×10^{-4}	-	reference 5

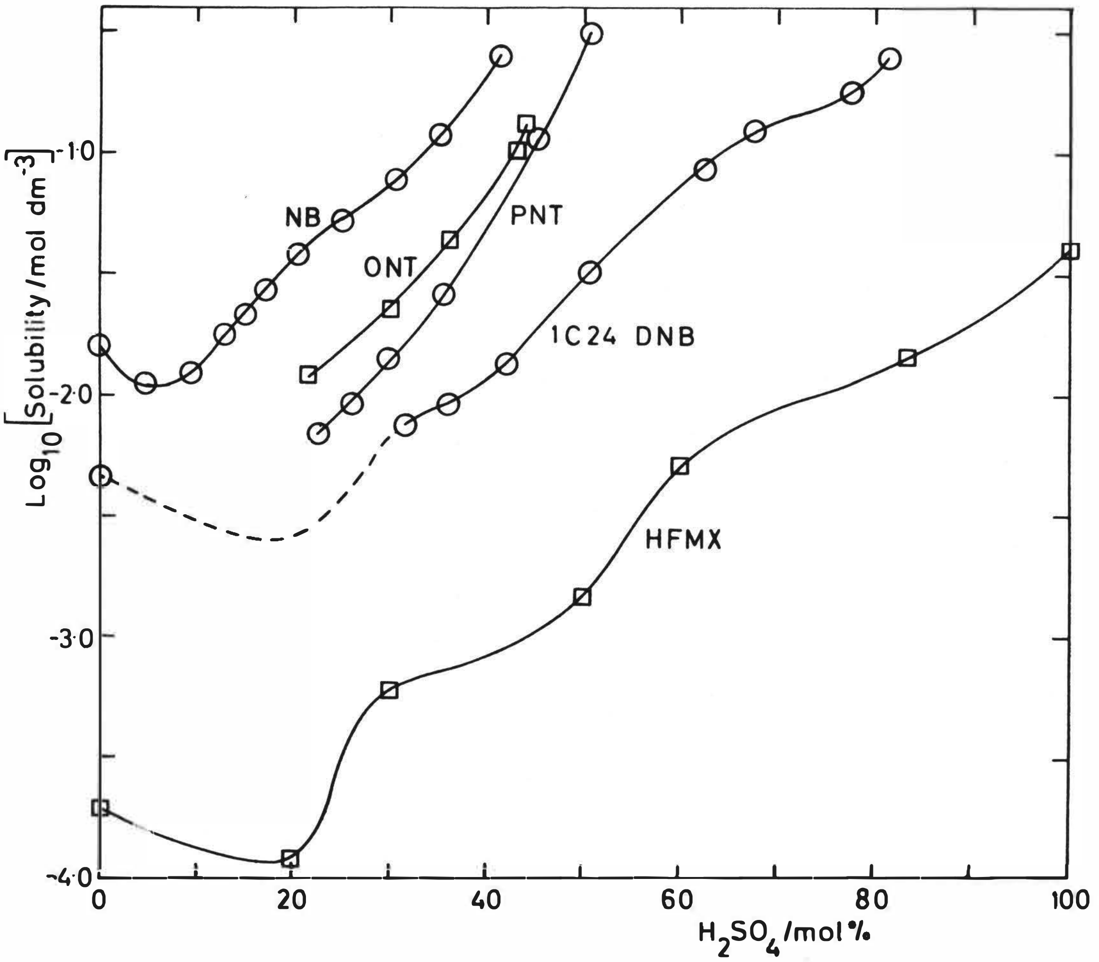


FIGURE Log$_{10}$ solubility versus mol % H_2SO_4 for 5 aromatics

DISCUSSION

The Figure shows log$_{10}$ solubility plotted against mol % H_2SO_4 for five different aromatics. With ONT the solubilities are those at 25°C from Table 1. For HFMX the solubility at 25°C at a given acid strength (Table 3) has been used except where it has not been determined, in which case the solubility at 20°C has been employed. With the remaining three aromatics the solubibities are all 25°C values. The data for nitrobenzene (NB) are those of Hammett and Chapman (7) and the solubilities of p-nitrotoluene (PNT) and 1-chloro-2,4-dinitrobenzene (1C24DNB) are those determined by Grabovskaya and Vinnik (3).

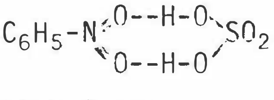
It is clear from the Figure that while the curves for the five aromatics are by no means parallel, they do all follow a common pattern. At first there is a decrease in solubility when small amounts of sulphuric acid are added to water. However this trend is soon reversed and the solubility starts to increase again and does so quite dramatically as the mol % H_2SO_4 is increased. The HFMX data and extrapolation of the other curves indicates that aromatics are over 100 times more soluble in pure H_2SO_4 than in pure water. This means that any like nitrobenzene with solubilities greater than $10^{-2}M$ in water are likely to be completely miscible with 100% H_2SO_4.

The initial decrease in solubility is undoubtedly a salting out effect due in the main to the sulphate ions. Salt effects on the solubilities of non-electrolytes in water are correlated by the Setschenow equation (8) viz $\log_{10} (S^0/S) = K C_s$, where S^0 is the solubility in water and S the solubility in a solution containing C_s mol dm^{-3} of electrolyte. Positive values of the Setschenow constant K means S is less than S_0 and salting out occurs. Negative values of K mean S is greater than S^0 and salting in occurs.

For non-electrolytes of low solubility K is equal to the salt-non-electrolyte interaction parameter k_s (9). With benzene the values of k_s are 0.548, 0.198 and 0.048 dm^3 mol^{-1} for Na_2SO_4, NaCl and HCl respectively (9). Since the contributions of the ions to the k_s values are generally additive (9), k_s for H_2SO_4 would be expected to be 0.548 + 2x0.048-2x0.198=0.248. This being positive, benzene should be salted out in dilute H_2SO_4, which is what is observed (10). Similar behaviour is to be expected and clearly occurs with other aromatics, although with those which are polar, the larger the dipole moment, the smaller is k_s likely to be, and hence the smaller the degree of the initial salting out (9).

Various suggestions have been made to account for the further and dominant trend of the steady and significant increase in solubility between 20 and 100 mol % H_2SO_4. The increase is accompanied by a decrease in the heat of solution. This is demonstrated in the data for ONT shown in Table 1. Similar behaviour is observed with NB (11) and HFMX (6). In the latter case the heat of solution decreases from 3.8 kcal mol^{-1} in 30 mol % H_2SO_4 to become negative in 83.5 mol % H_2SO_4 (6). The increasing solubility and decreasing heat of solution cannot be explained by protonation (7) nor by changes in the internal pressure of the medium (12). The most likely explanation is complex formation between the aromatic and one of the species present in the aqueous acid.

Some workers (13) have suggested that with nitroaromatics it is protons which are complexing, one per nitro group. This seems unconvincing since it is hard to conceive complex formation with protons being any different from protonation. The more probable complexing agent is undissociated H_2SO_4. While this is present in negligible amounts in dilute sulphuric acid, it becomes appreciable and increases in amount as the acid becomes more concentrated (10). There is evidence (14) that NB forms a 1:1 compound with H_2SO_4. The suggestion has been made (12, 15) that hydrogen bonding is involved and that the compound or complex has the structure



If this were the case one might expect a shift in frequency but no great change in intensity of the NO_2 band between a solution of the nitroaromatic in water and a solution in concentrated H_2SO_4 (16). Preliminary examination of the U.V.spectra of such solutions with NB and ONT shows that in both cases, instead of a shift in frequency, an entirely new peak is observed. The intensity of the peak increases with mol % H_2SO_4, which suggests strongly that it arises from the complex formed. Since the solubility behaviour of HFMX, which is without a nitro group, is similar to that of the nitroaromatics, it seems likely that complex formation occurs between undissociated H_2SO_4 and the aromatic ring rather than through hydrogen bonding with the nitro group and possibly involves charge transfer.

Nitrotoluenes Compared The Figure shows that the solubility of ONT and its variation with mol % H_2SO_4 is very similar to that of PNT, and comparison of Tables 1 and 2 shows that at 43.1 mol % H_2SO_4 the solubilities and heats of solution of ONT and MNT are very close. By interpolation of the data of Grabovskaya and Vinnik (3) the solubility of PNT in 43.1 mol % H_2SO_4 at 25°C is estimated to be $8.0\text{x}10^{-2}$ mol dm^{-3} which compares with $9.03\text{x}10^{-2}$ mol dm^{-3} for MNT (Table 2) and $10.2\text{x}10^{-2}$ mol dm^{-3} for ONT (Table 1). Not unexpectedly then, the solubilities and their variations with mol% H_2SO_4 and temperature of the three nitro toluenes in aqueous sulphuric acid appear to be very similar.

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A NEW METHOD FOR THE PURIFICATION OF CITRIC ACID BY LIQUID-LIQUID EXTRACTION

Ronald Wennersten
Dept. of Chemical Engineering

S-220 07 Lund, SWEDEN

ABSTRACT

Citric acid is commonly made by fermentation. The recovery of the acid from the aqueous fermentation solution is a complex process which gives calcium sulphate as a nonsaleable residue.

In this work the possibility of using solvent extraction for the recovery of citric acid from water solutions has been studied.

INTRODUCTION

Citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid), $C_6H_8O_7$ is the most widely used organic acid in the food and pharmaceutical industries. It is also used to sequester ions, neutralise bases and as a buffer. Esters of citric acid are used commercially as plasticisers in the preparation of polymer compositions, protective coatings and adhesives.

Citric acid is produced by many yeasts, moulds and bacteria. With the development of fermentation technology, most citric acid is now produced by this technique. The acid is recovered from the aqueous fermentation solution by first separating the microorganisms and then precipitating the citrate ion as the insoluble calcium salt. Citric acid is then obtained by adding sulphuric acid. Technically the recovery of the product is a highly complex process. The calcium sulphate is an unsaleable residue. The main objective of this work (1) has been to study whether solvent extraction can be used as an alternative to precipitation for the recovery of citric acid from aqueous fermentation solutions.

SOLVENT SELECTION

The choice of a solvent affects the design of the whole process in a significant way, both in the extraction section and, especially, in the solvent recovery cycle. A solvent for industrial purposes where the product value is rather low must have a low price and high availability. For use in the food industry, the requirement of low toxicity is also important. Citric acid, having one hydroxy- and three carboxyl groups, is very soluble in water. To be able to extract citric acid from a water solution, the interaction energies between the solvent molecules and citric acid must be in the range of the hydrogen bonds which exist between water molecules and citric acid. There are three main classes of solvent which could be of interest in this special case; carbon-bonded oxygen-donor solvents, high molecular weight amines and phosphorus-bonded oxygen-donor solvents.

CARBON-BONDED OXYGEN-DONOR SOLVENTS

When extracting with these solvents the oxygen acts as a Lewis base which can solvate an organic acid. Solvents of this type are ethers, alcohols, ketones, aldehydes and esters. Extraction of citric acid with solvents of this class has been frequently described in the literature (2-5). As can be seen from table 1, the distribution coefficients for citric acid (with 0.16 wt% feed conc.) are rather low.

Solvent	Distribution coefficient
n-Butanol	0.29
Ethyl acetate	0.1
Ethyl ether	0.1
Methyl-iso-butyl ketone	0.1
Methylethyl ketone	0.33
Cyclohexanone	0.21

TABLE 1
Distribution coefficients for citric acid (3)

With such low distribution coefficients a large number of contacting stages and a high V/L ratio are needed to extract the main part of the citric acid. Moreover, these solvents are relatively soluble in water and often they form azeotropes with water. The solvent recovery cycle will therefore by costly and this yields poor process economy.

HIGH MOLECULAR WEIGHT, ALIPHATIC AMINES

Smith and Page (6) have reported on acid-binding properties of long-chain aliphatic amines. The acid binding properties of these bases depend on the fact that their salts with acids are almost insoluble in water, but readily soluble in many organic solvents. They suggested also that these amines could be used for the recovery of valuable organic acids from biological material of fermentation liquors. In our case however, shake tests using fermentation solutions showed that these solvents gave very stable emulsions which did not separate at all. Because of this and the unknown toxicity no further tests were made with these solvents.

PHOSPHORUS-BONDED OXYGEN-DONOR SOLVENTS

These reagents contain the phosphoryl group which is a stronger Lewis base than the carbon-bonded oxygen group. Furthermore solvents belonging to this class co-extract less water and are less soluble in water than the first class. The basicity of the phosphoryl oxygen increases in the order: Trialkyl phosphate ($(RO)_3P=O$), dialkylalkyl phosphonate ($(RO)_2RP=O$), alkyldialkyl phosphinate ((RO)$R_2P=O$), trialkyl phosphine oxide ($R_3P=O$). Wardell and King (7) found that for the extraction of acetic acid from a 0.5 wt-% water solution, the basicity increased with the number of butoxy groups ($-OCH_2CH_2CH_2CH_3$) according to table 2.

Compound	Number of butoxy groups	K_D
Tributyl phosphate	3	2.3
Dibutylbutyl phosphonate	2	2.7
Butyldibutyl phosphinate	1	-
Tributyl phosphine oxide	0	4.4*

TABLE 2
Effect of number of butoxy groups on the distribution of acetic acid

*37.3 wt-% in Chevron Solvent 25. No diluent used for other solvents

Tributyl phosphate is readily mixed with non-polar diluents such as kerosene, but to obtain higher concentrations of the phosphine oxides more polar solvents are needed. The separation of relatively volatile organic acids from these solvents can be easily achieved by means of distillation. This method can not however be applied to citric acid because of its high boiling point and tendency to decompose. Stripping using a base dissolved in water would require a recovery process for the acid which is similar to that now used and nothing would be won. The possibility of using these solvents however, lies in the fact that the distribution coefficient is very dependent on temperature. This means that extraction can be carried out at one temperature and stripping at another temperature. The important parameter then turns out to be not so much K_D but the temperature dependence of K_D. As can be seen from table 3, this temperature dependence of K_D for trioctyl phosphine oxide (TOPO) is about the same as for n-tributyl phosphate (TBP).

To obtain higher solubilities of TOPO, a more polar solvent must be added which would result in higher solvent losses. TOPO is also very expensive compared with TBP. Among the phosphoryl reagents TBP has become the most widely used in industry. The availability and price make TBP the most promising solvent for this special application.

EXPERIMENTAL WORK

The high viscosity of TBP and the fact that its density is close to unity makes it necessary to use some kind of diluent with low viscosity and density. The choice of diluent affects the distribution coefficient, as can be seen in table 3. The highest values of K_D were obtained using ethers and ketones. As mentioned earlier the important parameter is the variation of K_D with temperature and this variation is more pronounced using hydrocarbons as diluents. The TBP concentration should be as high as possible, taking the phase separation properties into consideration. Two types of kerosenes have been used; namely Shellsol A and Shellsol H having aromatic contents of 99% and 16% respectively. K_D is somewhat higher using Shellsol H, probably because the interaction between the diluent and TBP is less. Figure 1 shows equilibrium curves for the system citric acid-water-75 vol-% TBP in Shellsol A at 4 different temperatures.

Solvent	Conc. of citric acid in water solution, M	Temperature °C	K_d
0.4 M TOPO in 50 vol-% n-heptane + 50 vol-% n-octanol	0.21	20.6	0.01
50 vol-% n-heptane + 50 vol-% n-octanol	0.21	20.6	0.001
0.2 M TOPO in Shellsol H	0.072	21.0	0.28
	0.072	40.0	0.12
50 vol-% TBP + 50 vol-% di-iso-propylether	0.026	17.5	0.68
	0.026	60.0	0.27
	0.26	17.5	0.56
	0.26	60.0	0.23
50 vol-% TBP + 50 vol-% MIBK	0.026	17.5	0.61
	0.026	60.0	0.20
	0.26	17.5	0.50
	0.26	60.0	0.20
50 vol-% TBP + 50 vol-% Shellsol H	0.026	17.5	0.43
	0.026	60.0	0.10
	0.26	17.5	0.33
	0.26	60.0	0.10
50 vol-% TBP + 50 vol-% Shellsol H	0.21	20.6	0.32
25 vol-% TBP + 75 vol-% Shellsol H	0.21	20.6	0.06
50 vol-% TBP + 50 vol-% Shellsol A	0.026	17.5	0.36
	0.026	60.0	0.09
	0.26	17.5	0.31
	0.26	60.0	0.09
50 vol-% tri-iso-octyl amine + 50 vol-% Shellsol H	0.486	25.0	6.5
50 vol-% tri-iso-octyl amine + 50 vol-% Shellsol H	0.486	80.0	0.33

TABLE 3

Distribution coefficients for the extraction of citric acid from a water solution to an organic solvent

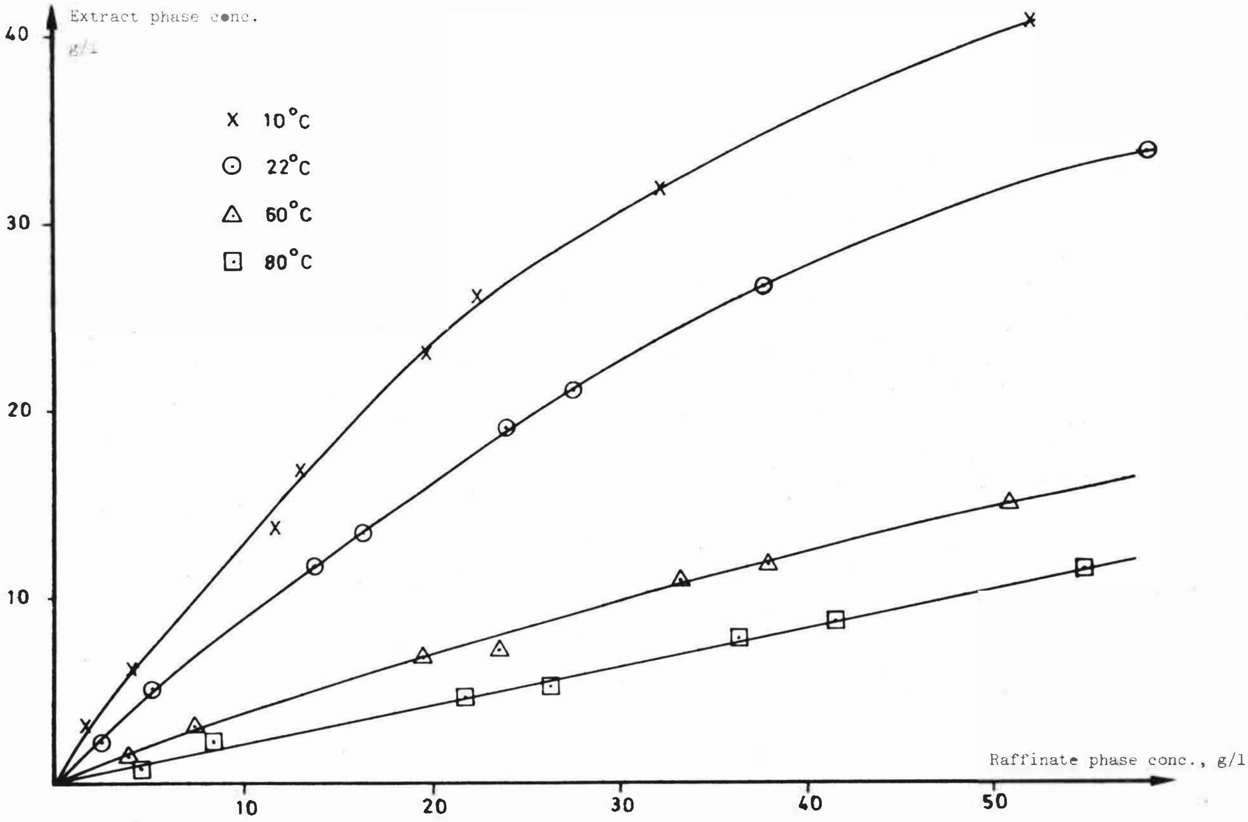

FIG. 1

Equilibrium curves for the extraction system
Water - Citric acid - 25 vol-% TBP in Shellsol A

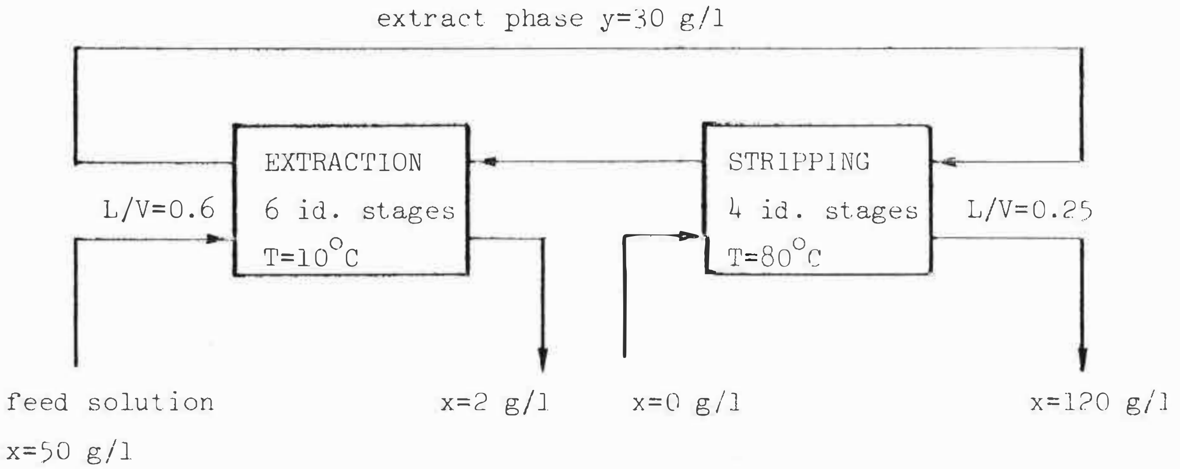

FIG. 2
Results from calculations using the McCabe Thiele method

The results of calculations for one case using the McCabe Thiele method and fixed concentrations in the feed raffinate and recirculated solvent are shown in figure 2. Experiments for determining equilibrium data were made using an AKUFVE-equipment (8).

Experimental runs in small laboratory mixer-settlers gave results in good agreement with calculations. The intention was then to carry out similar runs using a feed solution obtained by fermentation of a residual solution from an industrial process. In addition to citric acid (50 g/l), this solution contained proteins, fats, vitamins, salts etc. These components may change the distribution of citric acid and, as it turned out, greatly affected the phase separation properties. The surfactants stabilize the emulsion obtained in the mixer in such a way that the settlers flooded in spite of very low throughputs. Substances such as lecithin can increase the coalescence rate, but this can hardly be done on an industrial scale.

Tests were also carried out in a pulsed column (height 3 m, diameter 50 mm). The water phase was kept continuous, but when the phase ratio V/L exceeded 1.4 phase inversion occurred and the column flooded. It was not possible to run the column with the water dispersed. When the phase ratio was higher than 1.4 the concentration of citric acid in the raffinate phase could not be reduced below 15 g/l (the temperature was kept at 20°C and the concentration of citric acid in the feed was 37 g/l).

With this feed, the only way to carry out mixing and phase separation successfully was to use some kind of centrifugal equipment. Runs were therefore performed in a 3 stage mixer-settler battery using small Alfa Laval centrifuges as settlers. Some results from these runs are given in table 4. The solvent in this case was 70 vol-% TBP dissolved in Shellsol H.

Phase ratio V/L	Concentration in leaving raffinate, g/l
0.63	18.3
1.18	12.7

TABLE 4
Results from runs in mixer-settlers with centrifuges as settlers
(Temperature: 22°C, Feed conc.: 37 g/l)

Lowering the temperature would make it possible to use centrigual extractors type Alfa Laval ABE 216 to carry out the extraction. The process economy is however uncertain and the present work is therefore concentrated on improving the coalescence in order to be able to use ordinary settlers for the phase separation.

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SEPARATION OF ORTHO-PHENYL PHENOL FROM ORTHO-CYCLOHEXYL PHENOL BY LL-EXTRACTION WITH A SODIUM HYDROXIDE SOLUTION

G.P. Clement and A.J.F. Simons

DSM Central Laboratory

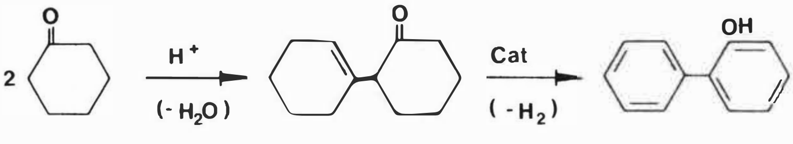
Geleen, The Netherlands

ABSTRACT

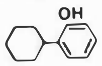
A physico-chemical model has been developed which describes the equilibrium distribution of OPP and CHP between toluene and an aqeuous sodiumhydroxide solution.
The ionisation constants and distribution constants have been calculated from results of phase equilibria measurements. The model has been applied for calculating separation efficiencies in multi-stage separation, - the calculated results have been compared with experimental data gained in mixer-settlers.

INTRODUCTION

Ortho-phenyl phenol (OPP) is a white crystalline product whose applications include use as a desinfectant and preservative for citrus fruits and as a dye carrier for improving the dyeability of textile fibres (1). These applications require a purity of over 95 %. OPP can be prepared e.g. by dehydrogenating 2-cyclohexenyl-cyclohexanone obtained from cyclohexanone:



In addition to OPP ($C_{12}H_{10}O$, M_{AH} = 0.170 kg mol^{-1}), this reaction yields ortho-cyclohexyl phenol CHP ($C_{12}H_{16}O$, M_{BH} = 0.176 kg mol^{-1});



, and a number of non-phenolic products (by-products and unconverted cyclohexenyl-cyclohexanone). The reaction product, solid at room temperature, has the following approximate composition:

OPP	60-90 wt.%
CHP	1-16 wt.%
non-phenolics	5-28 wt.%

It is from this mixture that OPP is to be recovered. Because the difference in boiling point between OPP and CHP is only small, distillation cannot be used for recovery, and therefore liquid-liquid extraction was studied as a possible separation method.

Good separation of OPP and CHP can be obtained by washing a solution of the reaction product in toluene with a 2-5 % solution of sodium hydroxide at room temperature. A large proportion of the OPP originally present is found to be dissolved in the alkaline phase, but only a small proportion of the CHP is so dissolved. OPP is separated not only from CHP, but also, from the non-phenolic products: if the alkali contains 5 % wt. NaOH, the non-phenolics remain in the organic phase.

In practice this extraction process can be performed in several stages. The alkaline phase is further processed by acidifying it with sulphuric acid, liberating the OPP to be taken up in fresh toluene from which the final product OPP is obtained by distillation. The organic phase (toluene phase) is further treated by distilling off the toluene; the OPP, CHP and non-phenolic products remaining in the residue can for the greater part be recycled to the dehydrogenating reactor.

Our investigation is limited to the extractive separation of OPP and CHP by means of NaOH as washing agent.

The separation between OPP and the non-phenolics, although very important, is here not touched upon. Where in the following we speak of toluene, what is meant is toluene plus non-phenolics.

EXPERIMENTS

The design of an industrial-scale extraction unit, or the determination of its operation requires knowledge of equilibrium data on the distribution of OPP and CHP, in this case between toluene and NaOH. To obtain data for the concentration range to be anticipated in counter-current apparatus, equilibrium experiments were performed using a known number of ideal stages. An additional advantage of this kind of experiment is that it provides an impression of the values the concentration and the physical phase properties may have along column height. The experimental results are given in Tables 1 and 3.

Two types of counter-current extraction tests were performed: 1. Experiment A: a batchwise simulation in a number of funnels, as described by Treybal (2). 2. Experiment B to E:, continuous tests in the Horbury Technical Services mixer-settler apparatus, a cascade of mixer-settlers (4). The two types of experiments gave the same kind of information: equilibrium data for the individual stages, and extraction results for the cascade of stages. The remaining experiments referred to in table 1 originate from segregation-time experiments.

Because the equilibria can be affected even by traces of foreign components (e.g. certain by-products of the OPP preparation) technical solutions were used instead of synthetic mixtures. Most experiments were performed at ambient temperature (23 °C). Several separate experiments done at 50 and 80 °C did not reveal any influence of temperature on the equilibrium. During the experiments it was found also that the (distributive) equilibrium state is reached very quickly.

TABLE 1

Experimental equilibrium results (single-stage)

expt. number	temp.	supply data				output data				experimental		calculated	
		NaOH conc.	$\frac{OPP + CHP}{OPP + CHP + toluene}$	$\frac{NaOH}{OPP}$	$\frac{CHP}{OPP}$	C_{OPPtw}	C_{CHPtw}	C_{OPPs}	C_{CHPs}	R	S	R	S
	°C	wt-%	kg/kg	kg/kg	kg/kg	mol/kg	mol/kg	mol/kg	mol/kg	-	-	-	-
A1	23	2.34	0.468	0.113	0.109	0.552	0.0120	1.58	0.30	0.501	4.87	0.497	5.76
A2	23	2.34	0.456	0.128	0.165	0.534	0.0132	1.34	0.43	0.546	6.44	0.544	5.37
A3	23	2.34	0.402	0.197	0.416	0.468	0.0552	0.57	0.68	0.739	3.40	0.704	3.95
A4	23	2.34	0.244	0.776	1.524	0.156	0.132	0.05	0.47	0.927	1.74	0.920	1.83
B1	23	2.34	-	-	-	< 0.0012	< 0.0012	< 0.001	0.005	-	-		
B2	23	2.34	-	-	-	< 0.0012	< 0.0012	< 0.001	0.011	-	-		
B3	23	2.34	-	-	-	< 0.0012	0.004	< 0.001	0.027	-	-		
B4	23	2.34	0.0671	15.3	3.25	0.0084	0.0216	0.006	0.072	0.939	1.23	0.998	1.02
B5	23	2.34	0.378	0.555	0.300	0.230	0.0494	0.088	0.220	0.966	1.36	0.969	1.32
C1	23	2.34	-	-	-	< 0.0012	0.0096	< 0.001	0.042	-	-		
C2	23	2.34	-	-	-	< 0.0012	0.0420	< 0.001	0.135	-	-		
C3	23	2.34	0.139	~ 31.7	~ 34.9	0.0036	0.0888	0.004	0.323	~ 0.84	~ 1.4		
C4	23	2.34	0.273	1.31	2.45	0.096	0.142	0.030	0.557	0.948	1.61	0.949	1.53
C5	23	2.34	0.453	0.243	0.412	0.436	0.0636	0.464	0.753	0.830	2.73	0.812	2.89
D1	23	2.34	-	-	-	< 0.0012	0.011	< 0.001	0.046	-	-		
D2	23	2.34	-	-	-	< 0.0012	0.035	< 0.001	0.120	-	-		
D3	23	2.34	0.113	49.3	30.9	0.0024	0.0552	0.003	0.225	~ 0.87	~ 1.3		
D4	23	2.34	0.246	2.08	2.43	0.048	0.101	0.130	0.400	~ 0.74	~ 1.1		
D5	23	2.34	0.450	0.343	0.419	0.348	0.0756	0.228	0.595	0.922	1.86	0.917	1.85
E1	23	2.34	0.357	0.151	0.197	0.538	0.0192	0.787	0.367	0.641	5.33	0.597	4.97
E2	23	2.34	0.471	0.0891	0.130	0.581	0.0096	1.751	0.353	0.410	7.60	0.399	6.64
E3	23	2.34	0.497	0.0789	0.0721	0.590	0.0108	2.000	0.309	0.370	5.69	0.365	6.87
E4	23	2.34	0.477	0.0856	0.110	0.588	0.0072	1.836	0.310	0.399	8.68	0.387	6.73
E5	23	2.34	0.467	0.0899	0.110	0.565	0.0072	1.798	0.301	0.397	8.32	0.400	6.63
F	23	7.00	0.543	0.0720	0.153	1.23	0.034	2.42	0.426	0.274	5.32	0.300	5.11
G	57	11.0	0.602	0.186	0.0665	1.635	0.0398	1.72	0.210	0.70	2.64	0.746	2.51
H	57	11.0	0.602	0.213	0.0665	1.82	0.056	1.01	0.188	0.855	2.05	0.825	2.04
I	57	6.97	0.602	0.160	0.0665	1.34	0.023	1.84	0.222	0.68	3.79	0.659	3.01
J	57	7.00	0.602	0.213	0.0665	1.23	0.028	1.26	0.216	0.80	2.78	0.829	2.02
K	56	5.01	0.595	0.239	0.0568	0.80	0.017	1.44	0.244	0.78	2.58	0.892	1.66
L	56	6.00	0.595	0.231	0.0568	0.96	0.023	1.28	0.233	0.777	3.32	0.875	1.75
M	56	4.94	0.595	0.238	0.0568	0.89	0.023	0.99	0.227	0.856	2.14	0.891	1.67
N	56	6.00	0.595	0.335	0.0568	0.82	0.034	0.39	0.148	0.902	1.58	0.968	1.19
O	23	2.00	0.602	0.238	0.0665	0.40	0.011	0.92	0.210	0.869	2.26	0.910	2.03
P	23	1.97	0.602	0.286	0.0665	0.36	0.011	0.45	0.153	0.943	2.03	0.955	1.54
Q1	23	5.00	0.762	0.104	0.0445	1.059	0.0114	3.55	0.244	0.445	4.01	0.464	4.11
Q2	23	5.00	0.633	0.196	0.0713	0.976	0.0284	1.41	0.307	0.789	2.37	0.790	2.27
R1	23	5.00	0.811	0.140	0.100	0.976	0.0284	3.34	0.605	0.552	3.33	0.608	3.29
R2	23	5.00	0.557	0.397	0.183	0.624	0.0795	0.235	0.307	0.958	1.38	0.970	1.19

THEORY OF THE PHYSICO-CHEMICAL EQUILIBRIUM MODEL

If the toluene-dissolved product is brought into contact with water, hardly any OPP and CHP will dissolve. However, if NaOH is added to the water, the absorption capacity for these two products increases enormously, due to the formation of the respective phenolates. The phenols OPP and CHP behave as weak acids (pK_a has an order of magnitude of 11), so that in contact with an alkaline solution ionisation occurs, according to the equations

$AH + OH^- \rightleftharpoons A^- + H_2O$

$BH + OH^- \rightleftharpoons B^- + H_2O$

where AH and BH represent the acids OPP and CHP. It has now been found that upon dissolution in NaOH, there is a preference for OPP to CHP, and it is on this fact that the desired separation of the two products is based. This preference can be explained by a difference between the ionisation constants and the distribution constants of the two species. A separation caused by a difference in ionisation constants is called 'dissociation extraction'; in the system under discussion, however, the difference in distribtion constants also plays a major role.

If the separation is based on unequal ionisation constants, the choice of the ratio of NaOH to OPP is very important. With an excess of alkali (> 1 mole equivalent alkali relative to the OPP and CHP available) both ionisation equilibria are completely on the right, which means that the alkali attacks practically all the OPP and CHP. The extraction efficiency of OPP is then virtually 100 %, but so is that of CHP. Hence, there is zero separation. With a deficiency of alkali, on the other hand, OPP-CHP separation proceeds succesfully, in the way described, but the extraction efficiency of OPP is low (not more than 1 mole OPP plus CHP can dissolve per 1 mole NaOH). The optimum choice appears to be a slight deficit of NaOH relative to OPP.

Anwar, Hanson and Prattt (3) deal with the theory of dissociation extraction for the case of separation of two weak bases by washing with a strong acid. In the same way it is possible to derive equilibrium relations for the case of two weak acids in contact with a strong base. In the model of Anwar c.s. C_{H^+} and C_{OH^-} are both neglected with respect to the other concentrations, in the model to be developed hereafter, C_{OH^-} will not be neglected.

Basic relations

The net ionisation reactions in the aqueous phase are:

$AH + OH^- \rightleftharpoons A^- + H_2O$

$BH + OH^- \rightleftharpoons B^- + H_2O$

with equilibrium constants:

$$K_{AH} = \frac{C_{A^-}}{C_{AHw} \cdot C_{OH^-}} \tag{1}$$

$$K_{BH} = \frac{C_{B^-}}{C_{BHw} \cdot C_{OH^-}} \tag{2}$$

(K_{AH} and K_{BH} are the reciprocals of the dissociation constants for the conjugate bases). The relation for electro-neutrality in the aqueous phase is:

$$C_{Na^+} = C_{OH^-} + C_{A^-} + C_{B^-} \tag{3}$$

where C_{H^+} is neglected (with pH ≈ 13, C_{H^+} is in the order of 10^{-13}).
The mass-balances for the aqueous phase are:

$$C_{AHtw} = C_{A^-} + C_{AHw} \quad (4)$$

$$C_{BHtw} = C_{B^-} + C_{BHw} \quad (5)$$

The distribution equilibria of the undissociated acids are defined by:

$$D_{AH} = C_{AHs}/C_{AHw} \quad (6)$$

$$D_{BH} = C_{BHs}/C_{BHw} \quad (7)$$

where D_{AH} and D_{BH} are the distribution constants of OPP and CHP, respectively

Derivation of equilibrium relations

Inserting C_{A^-} and C_{B^-} from equations 1 and 2 in Eq. 3 results in

$$C_{OH^-} = C_{Na^+}/(1 + \varphi_{AH} C_{AHs} + \varphi_{BH} C_{BHs}) \quad (8)$$

where φ_{AH} and φ_{BH} are combined equilibrium constants:

$$\varphi_{AH} = K_{AH}/D_{AH} \quad (9)$$

$$\varphi_{BH} = K_{BH}/D_{BH} \quad (10)$$

From Eqs. 4 and 6 it follows that:

$$C_{AHtw} = \varphi_{AH} \cdot C_{AHs}\, C_{OH^-} + C_{AHw} = \varphi_{AH}\, C_{AHs}\, C_{OH^-} + C_{AHs}/D_{AH} \quad (11)$$

Inserting Eq. 8 into Eq. 11 gives:

$$C_{AHtw} = \varphi_{AH}\, C_{AHs}\, C_{Na^+}/(1 + \varphi_{AH}\, C_{AHs} + \varphi_{BH}\, C_{BHs}) + C_{AHs}/D_{AH} \quad (12)$$

It can be derived that the concentration of Na^+ can be related to the concentration, m, of Na^+ by the following equation:

$$C_{Na^+} = m_{Na^+}\ (1 - M_{AH}\, C_{AHtw} - M_{BH}\, C_{BHtw}) \quad (13)$$

where M_{AH} and M_{BH} are the molecular masses of OPP and CHP.

Note that m_{Na^+} is related to the sodiumhydroxide content L (in % wt. of the fresh alkaline solution) by: $m_{Na^+} = 10\ L/40$. In a given extraction cascade L and m_{Na^+} have constant values throughout the cascade.
Inserting Eq. 13 in Eq. 12 gives:

$$C_{AHtw} = \varphi_{AH} C_{AHs}\, m_{Na^+}\ (1 - M_{AH}\, C_{AHtw} - M_{BH}\, C_{BHtw})/ \quad (15)$$

$$(1 + \varphi_{AH}\, C_{AHs} + \varphi_{BH}\, C_{BHs}) + C_{AHs}/D_{AH}$$

In order to find a relation between the OPP concentration in the aqueous phase and the phenol concentration in the toluene phase (C_{AHs} and C_{BHs}) we must eliminate C_{BHtw} from Eq. 15. From Eq. 11 and an anologous relation for C_{BHtw} we find, after elimination of C_{OH^-}:

$$C_{BHtw} = C_{BHs}/D_{BH} + (C_{AHtw} - C_{AHs}/D_{AH})\ \varphi_{BH} \cdot C_{BHs}\ /(\varphi_{AH} \cdot C_{AHs}) \qquad (16)$$

Equations 15 and 16, in combination with 9 and 10, give after some rearrangements, the final relation for the equilibrium between C_{AHtw} (OPP) and the concentrations in the toluene phase C_{AHs} (OPP) and C_{BHs} (CHP):

$$C_{AHtw} = \frac{C_{AHs}}{y_2\ D_{AH}} \left[y_1 + K_{AH}\ m_{Na^+} \left\{ 1 - M_{BH}\ \frac{C_{BHs}}{D_{BH}} \left(1 - \frac{K_{BH}}{K_{AH}}\right) \right\} \right] \qquad (17)$$

In a simular way we can derive:

$$C_{BHtw} = \frac{C_{BHs}}{y_2\ D_{BH}} \left[y_1 + K_{BH}\ m_{Na^+} \left\{ 1 - M_{AH}\ \frac{C_{AHs}}{D_{AH}} \left(1 - \frac{K_{AH}}{K_{BH}}\right) \right\} \right] \qquad (18)$$

where:

$$y_1 = 1 + K_{AH}\ C_{AHs}/D_{AH} + K_{BH}\ C_{BHs}/D_{BH} \qquad (19)$$

$$y_2 = 1 + (1 + M_{AH}\ m_{Na^+})\ K_{AH}\ C_{AHs}/D_{AH} + (1 + M_{BH}\ m_{Na^+}) \cdot K_{BH}\ C_{BHs}/D_{BH}$$

$$= y_1 + M_{AH}\ m_{Na^+}\ K_{AH}\ C_{AHs}/D_{AH} + M_{BH}\ m_{Na^+}\ K_{BH}\ C_{BHs}/D_{BH} \qquad (20)$$

If the four parameters, K_{AH}, K_{BH}, D_{AH} and D_{BH} are known, C_{AHtw} and C_{BHtw} can be calculated with Eqs. 17 and 18 from the composition in the toluene phase. It is interesting to note that, if $M_{BH} \cdot C_{BHs} \ll D_{BH}/(1 - K_{BH}/K_{AH})$ the term in braces of Eq. 17 can be put equal to unity. Now $M_{AH} \cdot C_{BHs}$ represents the mass fraction of BH in the organic phase, a quantity that is always ≤ 1. This means that if $D_{BH} \gg 1 - K_{BH}/K_{AH}$, the term in Eq. 17 can be put equal to unity. The same is the case for Eq. 18, if $D_{AH} \gg 1 - K_{AH}/K_{BH}$. It appears that, for the system under discussion, both conditions are satisfied. The equilibrium relations now become:

$$C_{AHtw} = \frac{C_{AHs}}{y_2\ D_{AH}} (y_1 + K_{AH}\ m_{Na^+}) \qquad (21)$$

$$C_{BHtw} = \frac{C_{BHs}}{y_2\ D_{BH}} (y_1 + K_{BH}\ m_{Na^+}) \qquad (22)$$

DERIVATION OF THE PARAMETERS K_{OPP}, K_{CHP}, D_{OPP} AND D_{CHP}

If the parameters are known, it is possible to calculate the OPP and CHP concentrations in the water phase for each of the equilibrium experiments in Table 1, using Equations 17 and 18. These concentrations should be in agreement with the values measured and the values of the parameters could have been determined by an iterative procedure. For calculating the parameters in this particular case we have used the separation quantities R and S as criteria, instead of C_{OPPtw} and C_{CHPtw}, R being the recovery factor of OPP and S the enrichment factor, for a mixing stage or a multi-stage arrangement. These quantities are defined as:

$$R = \frac{\text{OPP mass in outflowing alkaline phase}}{\text{OPP mass supplied}} \qquad (23)$$

$$S = \frac{\text{(OPP mass/CHP mass) in outflowing alkaline phase}}{\text{(OPP mass/CHP mass) supplied}} \qquad (24)$$

R is a measure of the extraction efficiency, S a measure of the purity (In practice, the prediction of R and S is of more importance than the prediction of C_{OPPtw} and C_{CHPtw}). Use was made, further, of the potentiometrically determined ratio of the ionisation constants, $K_{OPP}/K_{CHP} = 2$, a value that had been determined before. The parameters arrived at in this way are shown in table 2.

TABLE 2

NaOH content of fresh hydroxide soln. (L) % wt.	D_{OPP} -	D_{CHP} -	K_{OPP} kg/mol	K_{CHP} kg/mol	Standard of R %	deviation of S %
2.34	30	173	300	150	2	15
5	50	181	450	225	5	9
11	95	333	665	333	5	4

Range of validity: 23 and 57 °C; single-stage supply ratios: 0.05-2.5 kg CHP/kg OPP, 0.24-0.80 kg (OPP + CHP)/kg organics, 0.07-1.3 kg NaOH/kg OPP (= 0.3 - 5.5 mol/mol).

It should be noted here that the concentrations mentioned are not molarity values (moles/litre), but represent the number of moles per kg of solution.

That the D- and K-values are functions of the NaOH concentration was to be expected, because equilibria in the aqueous phase are dependent on ionic strength. Other influencing factors may well be the presence of non-phenolics in the organic phase, and the fact that these non-phenolics become more readily soluble according as the NaOH content increases.

Calculated values of R and S, based on the above model parameters, are given in Table 1.

From a comparison with literature (5-8) data on the acid dissociation contant K_a (K_a is related to K by $K_a = K \cdot K_w$, where K_w is the autoprotolysis constant of water), it followed that there is no agreement between the several values. Indeed, we did not intend to investigate K_a values: our object was to determine the model parameters K, which are not equal to K_a. Furthermore we are concerned with technical liquors, not with ideal ones.

COUNTER-CURRENT EXTRACTION IN SEVERAL STAGES

A calculatory programma like the one the basic flow diagram of which is given in Fig. 1 can be used to explore the separation possibilities provided by a counter-current extraction system working with a cascade of stages, for given feeds of organics and hydroxide solution. In this stage-to-stage calculation use is made of the parameters obtained in the way outlined above.

Experimental results of counter-current extraction experiments using 4 and 5 stages have been compiled in Table 3. This table also gives a comparison of the values of R and S, the separation quantities, as calculated by means of the abovementioned programma and as found in experiments. They appear to be in reasonable agreement.

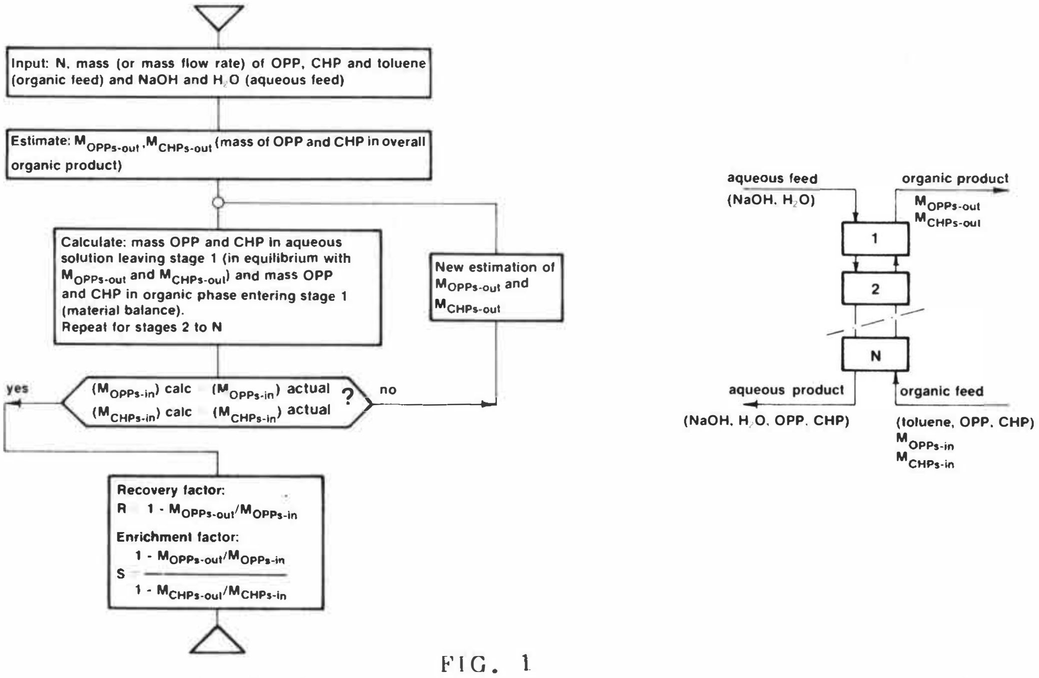


FIG. 1

Flow diagram for calculation of R and S in counter-current extraction with N mixing stages

TABLE 3

Results of counter-current extraction in N stages

expt. number	N	overall-feed data					experimental results		calculated results	
	-	NaOH conc. wt.-%	$\frac{CHP}{OPP}$ kg/kg	$\frac{OPP+CHP}{OCT\ *)}$ kg/kg	$\frac{NaOH}{OPP}$ kmol/kmol	$\frac{NaOH}{OPP}$ kg/kg	R kg/kg	S $\frac{kg/kg}{kg/kg}$	R kg/kg	S $\frac{kg/kg}{kg/kg}$
A	4	2.34	0.176	0.330	0.939	0.221	0.979	10.1	0.977	9.71
B	5	2.34	0.176	0.359	2.44	0.573	0.999	1.01	1.00	1.00
C	5	2.34	0.175	0.364	1.25	0.293	1.00	1.10	1.00	1.11
D	5	2.34	0.175	0.364	1.58	0.372	1.00	1.07	1.00	1.003
E	5	2.34	0.175	0.364	0.621	0.146	0.653	13.35	0.658	10.36

*) OCT = OPP + CHP + toluene

When the OPP and CHP concentrations in the aqueous phase and in the organic phase for experiment A, in which a small stoichiometric deficiency of NaOH was applied, are plotted versus the stage number (concentrations are given in Table 1) it appears that the OPP concentration in the water phase sharply increases, from the entry of the hydroxide solution, in the first two stages, and rises more slowly in the last two. The CHP concentration, also as observed from the entry of the alkaline solution, rises in the first stage, and decreases again in the following stages, which means that the direction of transfer is reversed, and that the CHP concentration passes through a maximum. This reversal in mass transfer is connected with the fact that the equilibrium concentration for CHP in the aqueous phase depends not only on the concentration of CHP in the organic phase but also, and strongly, on the OPP concentration (see Eq. 18); when the latter rises from stage to stage the related CHP equilibrium concentration shifts so drastically that the driving force transferring CHP from the organic phase to the aqueous phase, is reversed.

The effect of the NaOH/OPP supply ratio is shown in Fig. 2, where for a given feed composition the calculated R and S values are related to supply ratios for several ideal stages.

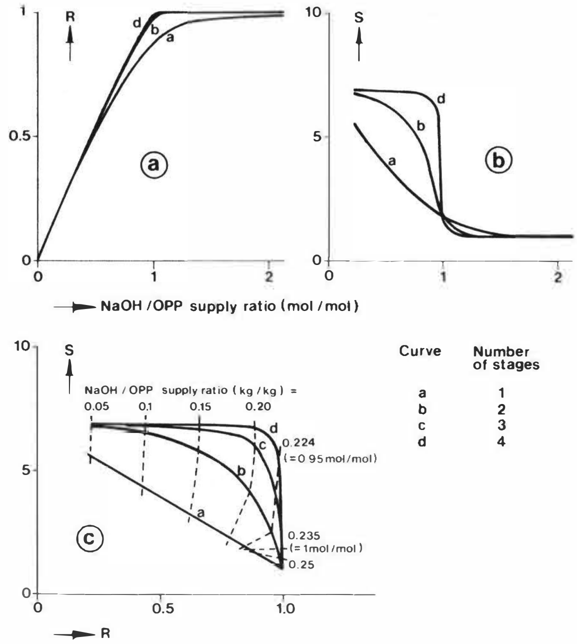


FIG. 2 a, b, c

Effect of NaOH/OPP supply ratio on R and S for counter-current extraction of OPP and CHP with 5 % wt. NaOH solution (calculated).
Feed ratios: CHP/OPP = 0.1 kg/kg; (OPP + CHP)/(OPP + CHP + toluene) = 0.6 kg/kg.

It follows that

(1) If the NaOH/OPP supply ratio is greater than 1 mol/mol, R and S approach to unity, in other words, all the OPP and CHP present dissolves in the alkaline phase.

(2) When the supply ratio decreases, S increases, but R becomes smaller. From the point where NaOH/OPP becomes smaller than 1 mol/mol, S rises sharply. It can be demonstrated that the value of S can never be higher than that of the combined equilibrium constant $K_{OPP}\ D_{CHP}/K_{CHP}\ D_{OPP}$, which is 11.2 at 2 % wt. NaOH, 7.25 at 5 % wt. and 7 at 7 % wt. In practice these values are never reached.

(3) As shown by Fig. 2c the optimum NaOH/OPP supply ratio is 0.85-0.95 mol/mol, which means that a small stoichiometric deficiency of NaOH with respect to OPP is required. The exact ratio to be used depends on the specific demands made on S and R.

It should be noted that the NaOH/OPP supply ratio varies strongly from one stage to another. In experiment A, where the overall ratio is 0.94 mol/mol (= 0.221 kg/kg), the individual ratios are 0.48, 0.54, 0.84 and 3.3 mol/mol. This can be explained from the fact that on its way through the cascade, the initial quantity of NaOH encounters a decreasing quantity of OPP.

FINAL DISCUSSION

The equilibrium model described above enables calculation of the quality of a separation between OPP and CHP in a counter-current extraction of OPP, CHP and non-phenolics dissolved in toluene by means of a sodium hydroxide solution, for a number of stages and for known feeds.

The agreement between model and experiments is reasonable (table 3). Further application of the result is a simple matter. In the case of multi-stage batchwise extraction, the model allows of constructing a number of figures, essentially similar to Fig. 2, from which direct information can be obtained on the quantities to be supplied in order to obtain OPP of required purity, with a feed of given composition. The results of experimental checking on pilot-plant scale were in very good agreement with the results obtained with the model.

For column extraction it would suffice to carry out only very few experiments on pilot-plant scale, and the model could be used to arrive at an optimum design, given the feed composition, the end-product purity requirements and the efficiency requirements. The model can be used also to determine, for an existing column, the optimum settings in dependence on varying feed composition or separation requirements.

NOMENCLATURE

C	Concentration (number of moles of material in 1 kg of solution), mol kg^{-1}
D	Distribution constant of undissociated species
K	Equilibrium constant (reciprocal of the base dissociation constant), kg mol^{-1}
K_a	Acid dissociation constant, mol kg^{-1}
L	NaOH content in fresh alkaline solution, % wt.
m	Concentration (per kg toluene or kg H_2O + NaOH), mol kg^{-1}
M	Molecular mass, kg mol^{-1} (In Fig. 1: mass, kg or mass flow rate, kg s^{-1})
N	Number of (ideal) mixing stages, -
R	Recovery factor of OPP, - (Eq. 23)
S	Enrichment factor (in kg - units), - (Eq. 24)
φ	= K/D, kg mol^{-1}

Subscripts

AH, BH	Refers to the acids OPP and CHP
A^-, B^-	Refers to dissociated OPP and CHP (in the aqueous phase)
CHP	Ortho-cyclohexyl phenol
OPP	Ortho-phenyl phenol
s	Refers to organic phase
tw	Refers to dissociated plus undissociated species (in aqueous phase)
w	Refers to aqueous phase (only used for undissociated species)

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DEVELOPMENTS IN DISSOCIATION EXTRACTION

M.M.Anwar*, M.W.T.Pratt** and M.Y.Shaheen†

*Dept. of Chemical Engineering, Teesside Polytechnic, Middlesbrough, England.
**Chemical Engineering Dept. University of Bradford, England.
†P.C.S.I.R. Laboratories, Lahore, Pakistan.

ABSTRACT

The separation of mixtures of m- and p-cresols by dissociation extraction is described. Separation factors were measured for various experimental conditions with the weakly basic monoethanolamine as reagent in the aqueous phase. Then, caustic soda was used as reagent to achieve separation of the isomers. It was found possible to reverse the reaction in the aqueous phase and recover m-cresol from caustic soda solution simply by contact with the organic solvent octan-1-ol, which has a high affinity for cresols. The caustic soda reagent results in higher separation factors and aqueous phase loadings. Results are given for distribution equilibria and multistage modelling of the separation process.

INTRODUCTION

Dissociation extraction is a technique for the separation of mixtures of organic acids or bases which depends upon differences in the dissociation constants of the components of the mixture. It can be applied to closely related or isomeric compounds, the separation of which may be difficult by the more common methods of distillation, solvent extraction or fractional crystallisation.

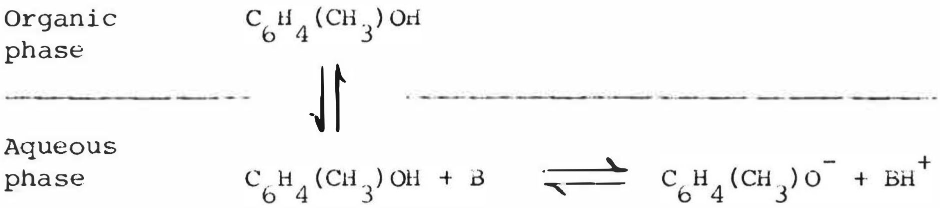
To illustrate the principle of dissociation extraction, consider, as an example, a mixture of the weak organic acids: m- and p-cresol. These have normal boiling points differing by only a fraction of a degree and have closely similar solubilities in many solvents. The difference in molecular arrangement of the two isomers does result, however, in an appreciable difference in their strengths as acids, shown by their relative dissociation constants: 9.8×10^{-11} for m-cresol and 6.7×10^{-11} for p-cresol. This difference may be exploited as the basis of practicable separation by dissociation extraction. Thus, if the mixture is partially neutralised by strong base, for example, aqueous caustic soda, there will be competition between the two organic acids for reaction with the base. The stronger organic acid, having the larger dissociation constant (m-cresol), will react preferentially with the base to form in the aqueous solution an ionised cresylate salt, insoluble in organic solvents. The weaker acid (p-cresol), will remain predominantly in its undissociated form, soluble in organic solvents. If the partial neutralisation is followed by a conventional extraction with an organic solvent, the weaker acid will be concentrated in the solvent, and the stronger, as its dissociated salt, in the aqueous phase. If this process of dissociation extraction is applied in a multi-stage system with counter-current flow of organic solvent and aqueous caustic soda, the feed mixture of cresols may be separated into its component isomers of high purity. In the 'classical' process of dissociation extraction, m-cresol would be regenerated from its salt in the aqueous phase by treatment with a strong mineral acid. Clearly, a mixture of organic bases may be separated similarly by treatment with a stoichiometric deficiency of aqueous strong acid.

Although the basic principle of dissociation extraction has been known at least since the work of Warnes (1) in 1924, the theory of the technique has been adequately developed only during the last decade. Its first practical applications were merely in laboratory separations of particular mixtures. It was later applied on a commercial basis using multi-stage contactors, first achieved by Twigg (2) in 1949. Application of dissociation extraction has been chiefly considered for the separation of organic acids and bases occurring in coal tar, particularly of m- and p-cresols (3,4,5), xylenols (6) and the 2.6-lutidine, 3- and 4-picoline system (7,8). It has been applied commercially for the separation of dichlorophenols, penicillin acids and for benzoic acid derivatives.

In early work on dissociation extraction at the University of Bradford, the theory of the process was developed for those systems, such as the 3- and 4-picoline mixtures, in which the organic compounds to be separated have a reasonably high affinity for the aqueous phase, so that the reaction in that phase with the mineral acid or base goes to completion (9,10).

Although dissociation extraction processes have been applied commercially, their application on a wide scale has been hampered by the continuous consumption of strong alkali and strong acid. This operating cost has limited the application of the 'classical' dissociation extraction process, described above, to the separation of compounds of high intrinsic value in comparison with the mineral acid and alkali used in their recovery. This high operating cost is always involved in separation processes where there is a strong interaction between the component to be separated and the reagent used to achieve the separation (e.g. the strong reaction between mineral acids or alkalis and organic bases or acids, or between a metal ion and a strong complexing agent). This is due to the difficulty in breaking down the product formed in order to free the purified component and regenerate the extractant reagent. Ideally, there will be only a weak interaction between the extractant and the component to be separated, sufficiently strong to achieve the separation, but weak enough to be broken down without the expenditure of a large amount of chemical or thermal energy. The basis of the modified process of dissociation extraction developed later (11) is the use, in place of strong mineral acids or alkalis, of only weakly acidic or basic reagents so that the reaction product between them and the organic components may be broken down simply by contact with a solvent having a strong affinity for the separated component. The reagent is thereby regenerated and can be recycled. This avoids the continuous consumption of materials and the significant reduction in operating costs which results should make dissociation extraction a cheaper and therefore more versatile process.

The modified process has been applied to the separation of m- and p-cresol using a weak base as reagent. If the cresols, either alone or dissolved in an organic solvent which has only a moderate affinity for cresols, are contacted with an aqueous solution of a weak base, B, the proportion of base being less than stoichiometric, the competition between the cresols for reaction with the base enables a normal separation by dissociation extraction to be achieved. The reaction, which does not proceed to completion in the aqueous phase due to the weakly basic nature of the reagent, can be summarised as follows:



The more acidic m-cresol reacts preferentially forming a dissociated salt soluble in the aqueous phase and the less acidic p-cresol remains predominantly in its undissociated form, soluble in the organic phase. In this way the isomers are partially separated and a high degree of separation may be achieved in a multi-stage process. The aqueous phase containing the dissociated cresylate salt is subsequently contacted with an organic solvent having strong affinity for cresols. The reaction is reversed and the basic reagent is regenerated and can be recycled. The cresol is recovered from the organic solvent by distillation.

The weak base used first was sodium phosphate, Na_3PO_4 (11). Although experimental results confirmed the viability of the process, the low separation factor and aqueous phase loadings of cresols necessitated liquid-liquid contactors with many stages and capable of handling large flow volumes. The result of these process complications was that the overall economics of the process were less advantageous than initially expected (12). The weakly acidic or basic reagent used in the modified dissociation extraction process need not necessarily be an inorganic compound. Weak organic acids or bases can be considered, provided that they are preferentially soluble in the aqueous phase, and these may have practical advantages. Further work (13) established that the organic base monoethanolamine could be used successfully to separate mixtures of 2-3 and 2-6 dichlorophenols, a process which also is of commercial interest.

Knowledge of the efficiency of the modified process has been extended by the study, reported first in this paper, of the use of the weak organic base monoethanolamine $C_2H_4(NH_2)OH$, (MEA), as reagent for the separation of the m- and p-cresol isomers. The effects are shown of various parameters, such as isomer ratio and organic and aqueous phase loadings, on the separation factor, which varies between 1.3 and 1.4, indicating that this separation could successfully be achieved by a multi-stage process. With this system, and with weak reagents in general, the reaction in the aqueous phase is incomplete, resulting in relatively low aqueous phase loadings and higher equipment and processing costs.

In the latter part of the paper is described a novel approach to dissociation extraction which combines the advantages of both the classical and modified processes. This involves the use of a strong aqueous reagent, such as caustic soda, for the separation of the cresol isomers so that higher aqueous phase loadings and separation factors are obtained. Even although a strongly basic reagent has been used, it has been found possible to reverse the reaction by contact with an organic solvent with a very high affinity for the undissociated organic component, so that the advantage of separation without continuous consumption of chemicals is maintained. The new principle has been established that the extent of reaction in the aqueous phase between the acidic or basic organic compounds to be separated and the strong base or acid reagent varies considerably with the nature of the organic solvent and this can be exploited as the basis of a separation. The technique is here applied to the separation of mixtures of m- and p-cresol with caustic soda as the strong reagent in the aqueous phase. After separation of the isomers, m-cresol is efficiently back-extracted from the aqueous phase by contact with octan-1-ol. Distribution data are presented for the cresols with caustic soda reagent for a variety of organic solvents. The effect is given of isomer ratio on the separation factor, which is generally in the range 1.4 to 1.5. The validity of the separation process was confirmed using a multi-stage laboratory mixer-settler, both for separation of the cresol isomers and the back-extraction of m-cresol.

EXPERIMENTAL

Distribution equilibria were determined for m- and p-cresols distributed between (a) toluene and aqueous MEA and (b) toluene and other organic solvents and aqueous caustic soda.

(a) For the MEA system, a 20 ml sample of a mixture of known concentrations of m- and p-cresol, dissolved in toluene, was shaken vigorously for 5 mins. with 20 ml of aqueous MEA and held in a thermostat at 25°C ± 1°C for 20 mins. These conditions were shown to be fully adequate for equilibrium distribution to be obtained. After equilibration, the two phases were separated and the isomer ratio of cresols in each phase found by GLC analysis. The concentrations of cresol isomers in each phase could then be calculated by mass balance, since the total amount of each isomer in the system was known. In the GLC column, 1.5 m x 3 mm, Chromosorb G AW DMCS of 80-100 mesh size was used as support and 8% w/w of Matexil added as stationary phase. A high resolution of m- and p-cresol within 20-26 mins. retention time was achieved at a column temperature of 195°C. The GLC was calibrated with standard solutions of m- and p-cresols in toluene and reproducibility of analytical results was ± 0.1%. Samples of both organic and aqueous MEA phase could be analysed for cresols by direct injection into the GLC column.

(b) For the sodium hydroxide system, distribution equilibria at 25°C were first determined for the individual cresol isomers with several different organic solvents. Samples (20 ml) of each phase were equilibrated as before and separated. A known weight of o-cresol was added to the organic phase as an internal standard before GLC analysis for the concentration of m- or p-cresol. Aqueous phase concentration was calculated by difference from the known total amount of cresol. Separation factors for mixtures of m- and p-cresols, distributed between toluene and aqueous caustic soda, were then determined after equilibration and phase separation. Samples of organic and aqueous phases were analysed by GLC without addition of interal standard to give isomer ratios and concentrations as before, except that aqueous phase samples were neutralised with dilute hydrochloric acid and made homogeneous by addition of methanol before injection.

For multi-stage tests, a laboratory mixer-settler with up to 10 stages was used, similar to that developed for earlier work (14) but modified to prevent losses of organic phase by evaporation and with impellers of new design. To model the separation of the cresol isomers, counter-current streams of toluene and aqueous caustic soda were fed at room temperature to the end stages by calibrated metering pumps and an equimolar mixture of m- and p-cresols in toluene was introduced at an intermediate stage. The wanted iso-[illegible]s in the product streams were decided, together with the flow rat[illegible]trations of the organic and aqueous phases. From this, the feed flow rate of cresols was determined. A stage-to-stage calculation, based on the measured distribution equilibria at 25°C, was then computed by a trial and error method to find the reflux ratios necessary to give the desired products in the number of stages used. The calculated reflux streams were fed to the end stages and adequate time allowed for equilibrium to be reached. Samples from both phases of every stage were then taken for analysis so that the actual cresols concentrations could be compared with the theoretically predicted values. To model similarly the recovery of m-cresol, 5 mixer-settler stages were used with counter-current flows without reflux of octan-1-ol and aqueous caustic soda containing from 108 to 125 g/l of m-cresol.

RESULTS AND DISCUSSION

A) Separation of m- and p-cresol by aqueous MEA

In Table 1 is shown the equilibrium distribution of an equimolar mixture of m- and p-cresols between 20 ml toluene and 20 ml aqueous MEA of from 2% to 10% w/w concentration. The total weight of cresols added to the system and equilibrium weight in each phase of both isomers are listed, together with the separation factor for the isomers, defined as the expression:

$$[\text{p-cresol}]_o \cdot [\text{m-cresol}]_a \; / \; [\text{m-cresol}]_o \cdot [\text{p-cresol}]_a$$

where terms in square brackets denote concentrations and subscripts o and a denote organic solvent and aqueous phases respectively.

There were indications from GLC analysis that at MEA concentrations above 10% the MEA-cresol salt is slightly soluble in the organic phase so higher MEA strengths were not used. Separation factors varied only between 1.27 and 1.38 and tended to increase with total cresol loading, but were insensitive to MEA concentration. The total cresols concentration in the aqueous phase (dissociated plus undissociated) increases with cresols loading in the system, but reaches an almost constant level for a given MEA concentration: 24, 31, 38, 45 and 52 g/l respectively for MEA strengths of 2, 4, 6, 8 and 10%. The limiting cresols concentration in the aqueous phase therefore increases linearly with MEA concentration, but is not directly proportional to it.

The effect of cresol isomer ratio on the distribution is shown in Fig. 1. The same phase volumes were used with 4% MEA in the aqueous phase and approximately 3g total cresols (150 g/l) initially present in the aqueous phase. Separation factor increases from 1.31 to 1.42 as the ratio m-cresol/p-cresol in the system decreases from 9 to 0.1. The variation in separation factor was virtually the same with other MEA strengths in the range 2% to 10%. In all cases, the total cresols loading in the aqueous phase was not significantly affected by change in isomer ratio.

These results show that the separation of m- and p-cresols by dissociation extraction with the weak base MEA as reagent is practicable, although the separation factor of 1.3 to 1.4 implies that the number of equilibrium stages necessary to achieve a high degree of separation will not be small. Also, the aqueous phase loading of cresols is limited, as it is when the other weakly basic reagent, Na_3PO_4, is used. After separation, recovery of m-cresol from aqueous MEA may be achieved by contact with an organic solvent having a high affinity for cresols, as described previously (13) and in a later section of this paper.

B) Separation of m- and p-cresol by aqueous caustic soda

The distribution of the separate cresol isomers between aqueous 1N caustic soda and the organic solvents carbon tetrachloride and octan-1-ol is shown in Fig. 2, in which the aqueous phase concentration of cresols includes both dissociated and undissociated forms. If cresol is progressively added to the carbon tetrachloride-caustic soda system, little cresol is present in the organic solvent, which has low affinity for cresols, until after there is 1 mole/l of cresol present in the aqueous phase. For the solvent octan-1-ol, which has high affinity for cresols, there is, in contrast, a substantial concentration of cresol in the organic phase long before the stoichiometric equivalent of the caustic soda has been added and the cresols concentration in the aqueous phase never reaches 1 molar (108 g/l), the maxima achieved being 74 g/l and 64 g/l for m- and p-cresol respectively. This demonstrates the relative incompletion of reaction in the aqueous phase when this organic solvent is present. The behaviour of the solvent toluene is close to that of carbon tetrachloride. Hexane was found to be a very poor solvent for cresols and a third phase was formed at high loadings of m-cresol, although this did not occur with p-cresol. For the solvents carbon tetrachloride and toluene, an aqueous phase cresol concentration greater than 1 mole/mole caustic soda is eventually achieved, but this does not necessarily imply complete reaction of the caustic soda, as part of the cresol content may be undissociated. It was shown that at least 270 g/l of m-cresol (> 2 molar) will dissolve in 1N caustic soda without formation of a second phase; thus, although cresols are sparingly soluble in water, they will readily dissolve in sodium cresylate salt solution. Clearly the degree of reaction between cresols and caustic soda in the aqueous phase is strongly influenced by the nature of the organic solvent, even for this strongly basic reagent, and this variation may be used as the basis of a separation process. For all the organic solvents it is the m-cresol isomer which has greater solubility in the aqueous phase than p-cresol, reflecting its greater acidity (dissociation constant) and consequent affinity for reaction with caustic soda. However, the difference between the distribution of the two separate isomers is small, although their dissociation constants differ appreciably. It cannot be established from the separate distributions of the two isomers whether a separation by dissociation extraction is possible or not, because competition between the isomers to react can only be exploited when both are present. Results in this situation are presented in Table 2 for the equilibrium distribution of mixtures of m- and p-cresols between toluene and aqueous caustic soda at $25^{O}C$. The volume of each phase was 10 ml and the total weight of cresols in the system was 3g. The Table shows isomer ratio of the total cresols, the normality of caustic soda in the aqueous phase, the equilibrium content of each isomer in each phase and the separation factor. Separation factors are rather greater for caustic soda than for MEA reagent and increase from 1.4 to 1.5 as the total cresols isomer ratio m-cresol/p-cresol decreases from 9 to 0.1. Separation factors are not much affected by caustic soda normality. The total cresols concentration in the aqueous phase remains approximately constant for a particular normality of caustic soda, 0.65 molar for 0.5N, 1.1 molar for 1N, and 2.0 molar for 2N. The total cresols loading in the aqueous phase is thus slightly greater than the stoichiometric equivalent of the caustic soda and is greater than for the weakly basic reagent MEA. The separation of the cresol isomers for 0.5N caustic soda as reagent is illustrated in Fig. 3.

The separation of mixtures of m- and p-cresols dissolved in toluene by multi-stage contact with aqueous caustic soda was modelled using a laboratory mixer-settler with up to 10 stages and 100% stage efficiency. Artificial reflux streams were provided at both ends of the contactor and the feed stream was introduced at an intermediate stage. The results showed that a considerable degree of separation could be obtained and the experimental results agreed well with theoretical predictions made on the basis of simplifying assumptions by a graphical method, described earlier (10), analogous to the McCabe-Thiele method. Space does not permit full presentation of these

TABLE 1

Distribution of an equi-molar mixture of m- and p-cresols between 20 ml toluene and 20 ml aqueous MEA

MEA Aqueous Concentration	Total Cresols g	Equilibrium Cresols Content (g)				Separation Factor
		Organic Phase		Aqueous Phase		
		p-cresol	m-cresol	p-cresol	m-cresol	
2%	1.00	0.278	0.241	0.222	0.259	1.33
	2.00	0.788	0.734	0.212	0.267	1.35
	3.00	1.292	1.228	0.208	0.272	1.37
4%	1.00	0.218	0.184	0.283	0.317	1.32
	2.00	0.725	0.660	0.275	0.339	1.35
	3.00	1.230	1.151	0.271	0.349	1.37
6%	1.00	0.165	0.136	0.336	0.364	1.31
	2.00	0.658	0.587	0.342	0.413	1.35
	3.00	1.165	1.075	0.335	0.425	1.37
8%	1.00	0.169	0.142	0.331	0.359	1.29
	2.00	0.605	0.536	0.396	0.464	1.32
	3.00	1.099	0.993	0.402	0.498	1.37
10%	1.00	0.028	0.022	0.472	0.478	1.27
	3.00	1.046	0.954	0.454	0.546	1.32
	5.00	2.047	1.913	0.453	0.587	1.38

TABLE 2

Distribution of m- and p-cresol mixture (3g) between 10 ml toluene and 10 ml aqueous NaOH

NaOH Normality (N)	Isomer Ratio		Equilibrium Distribution (%)				Separation Factor
	p- %	m- %	Organic Phase		Aqueous Phase		
			p-cresol	m-cresol	p-cresol	m-cresol	
0.50	10	90	10.58	89.42	7.63	92.37	1.43
	30	70	31.71	68.29	24.17	75.83	1.45
	50	50	51.94	48.06	42.35	57.65	1.47
	70	30	71.72	28.28	63.07	36.93	1.48
	90	10	90.72	9.28	86.56	13.44	1.52
1.00	10	90	11.19	88.81	8.10	91.90	1.43
	30	70	32.96	67.04	25.36	74.64	1.44
	50	50	53.71	46.29	44.28	55.72	1.46
	70	30	72.81	27.19	64.56	35.44	1.47
	90	10	91.31	8.69	87.52	12.48	1.49
2.00	10	90	12.34	87.66	9.12	90.88	1.40
	30	70	35.72	64.28	28.00	72.00	1.42
	50	50	56.72	43.28	47.56	52.44	1.44
	70	30	75.60	24.40	67.91	32.09	1.46
	90	10	92.11	7.89	88.81	11.19	1.47

results which are given elsewhere (15) but, for example, it was shown that an equimolar feed of cresols (0.12 moles/h) was separated in 10 stages into product streams at each end of 80/20 isomer ratio, using 1N caustic soda (0.5 l/h) as the reagent. Reflux streams of the same isomer ratios were fed at approximately 0.5 moles/h. After multi-stage separation of the isomers, m-cresol must be recovered from an aqueous phase containing its salt. The back extraction of m-cresol from aqueous caustic soda by octan-1-ol is affected by the pH of the aqueous phase, which is still alkaline even when the m-cresol concentration is more than twice the stoichiometric equivalent of caustic soda. The lower the pH, the greater was the amount of cresol extracted by octan-1-ol from an equal volume of 1N caustic soda. As pH of an aqueous mixture of 1N caustic soda and m-cresol decreased from 13.28 to 11.18 (i.e. 5.5 g/l to 221 g/l m-cresol) the extraction of m-cresol increased from zero to 65.4%. At the equivalence point of m-cresol (108 g/l) the pH is 12.3 and the extraction is 31.4%. There is a lower limit on the proportion of m-cresol per mole of sodium hydroxide (about 25 g/l m-cresol) below which extraction is difficult because the aqueous phase is too alkaline. However, in practical separation processes, the concentration of m-cresol in the aqueous phase fed to the m-cresol recovery section would be at least equal to that of the caustic soda, assuming that the solvent used during the isomer separation would have only a moderate affinity for cresols. The recovery of m-cresol from aqueous caustic soda was modelled by counter-current contact with octan-1-ol in a 5 stage mixer-settler. For example, when the feed 1N caustic soda aqueous phase contained 108.1 g/l of m-cresol and the flow rates of octan-1-ol and aqueous phases were were respectively 520 ml/h and 100 ml/h, the exit aqueous phase contained only 25.8 g/l m-cresol and so the extraction was 76%. The decreasing pH of the aqueous phase as m-cresol is extracted will, as noted earlier, make complete extraction impossible, but this is not essential for a practical process as the aqueous phase may be recycled containing some m-cresol.

The flow diagram, Fig. 4, is suggested as the basis for a practical industrial separation process. The feed mixture of m- and p-cresols in toluene is fed to the dissociation extraction multi-stage contactor, where the counter-current flow of toluene and aqueous caustic soda leads to separation of the cresol isomers. Part of the distilled organic product, rich in p-cresol, is used in an aqueous reflux. The aqueous phase from the primary contactor, enriched in m-cresol, is fed to the secondary separation (solvent extraction) stage, where m-cresol is extracted with octan-1-ol and distilled. Some of the m-cresol product is used as reflux in the toluene stream to the dissociation extraction stage, to which the aqueous caustic soda is recycled.

The types of dissociation process described here could well be capable of application to the industrial separation of other mixtures of acidic or basic organic isomers or closely related compounds difficult to achieve by more common methods.

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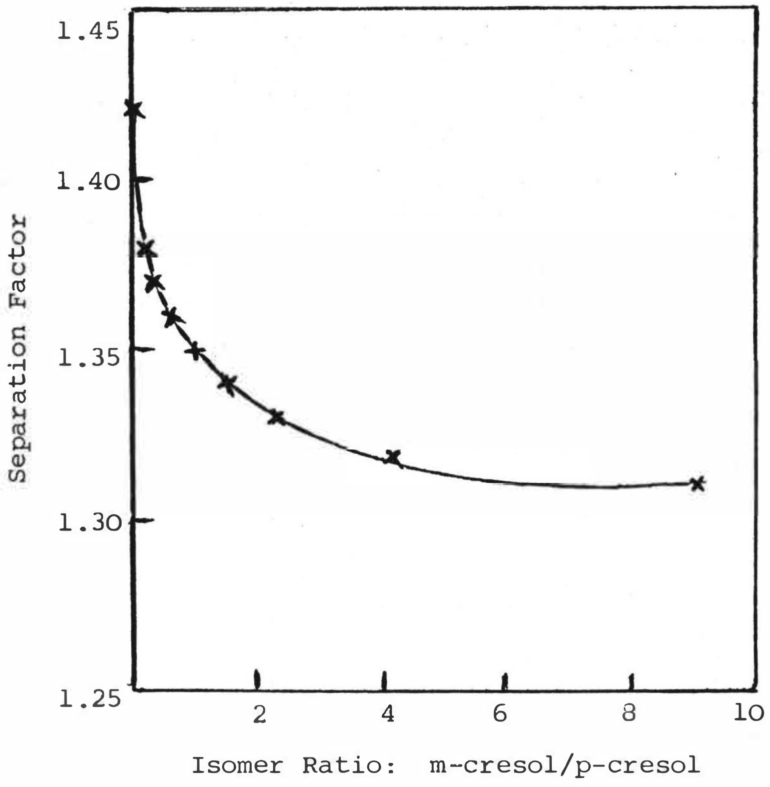


FIG. 1

Variation in Separation Factor with Isomer Ratio:

Toluene/4% MEA System.

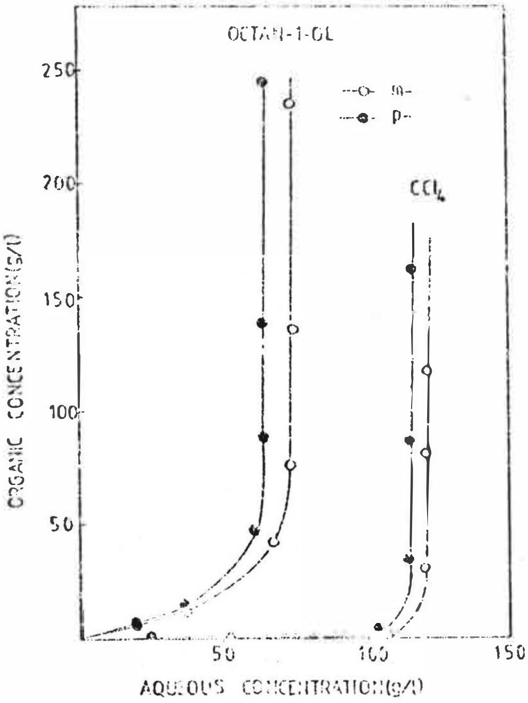


FIG. 2

Distribution of cresols between 1N NaOH and organic solvents.

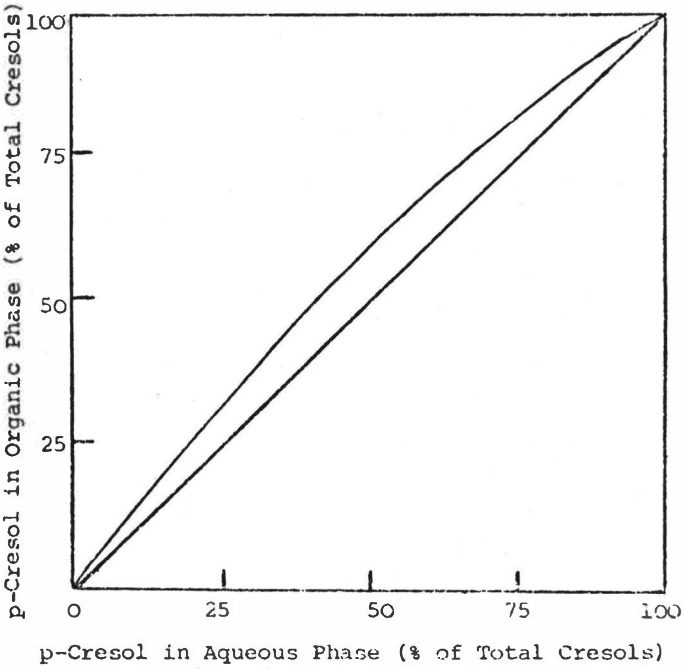
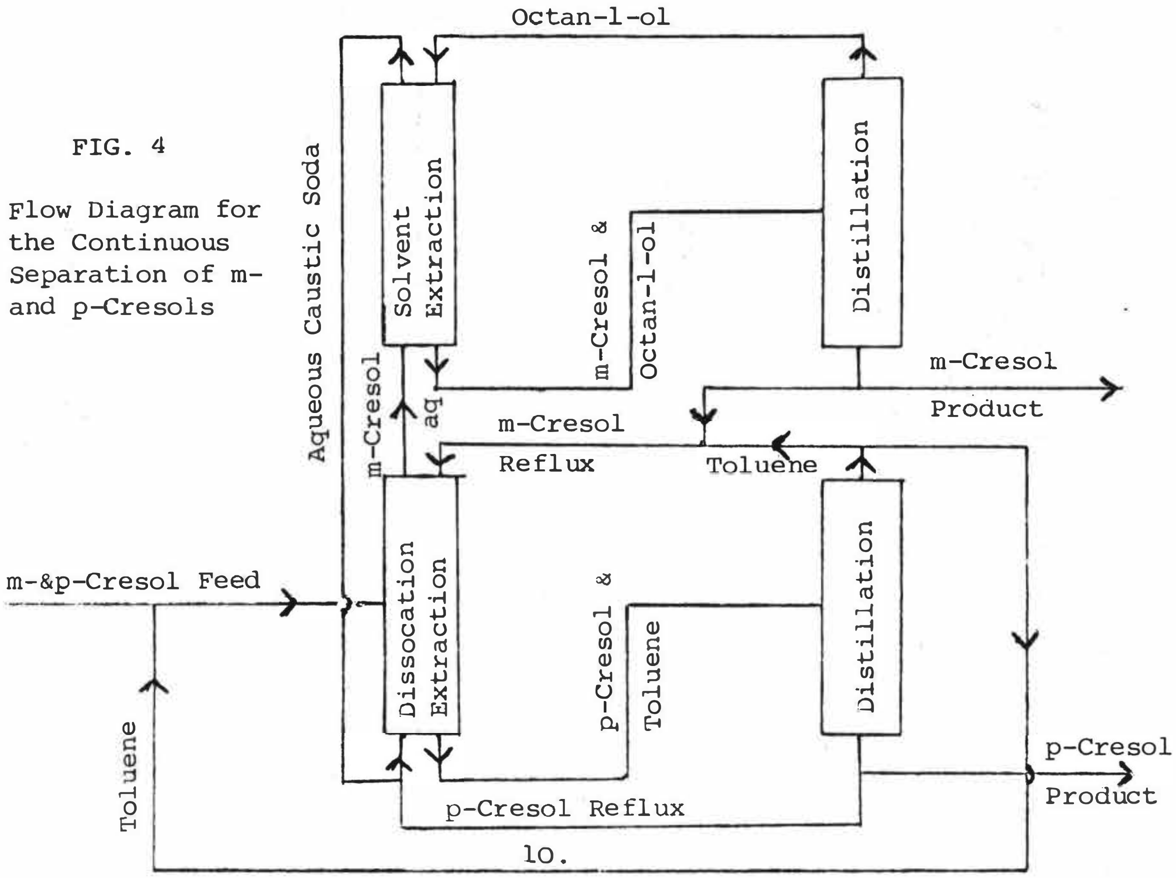


FIG. 3

Equilibrium Isomer Distribution for cresol mixtures.

FIG. 4

Flow Diagram for the Continuous Separation of m- and p-Cresols



PRODUCTION OF THE AMMONIUM SALT OF 3,5-DINITRO-1,2,4-TRIAZOLE (ADNT) BY SOLVENT EXTRACTION

KIEN-YIN LEE, DONALD G. OTT, MARY M. STINECIPHER,

LOS ALAMOS SCIENTIFIC LABORATORY

Los Alamos, NM, 87545, USA

We have developed a process that involves using a liquid anion exchanger for the extraction of an organic acid from its aqueous acidic reaction mixture and the recovery of the organic acid as its ammonium salt by amination in the organic phase with anhydrous ammonia. The organic acid is 3,5-dinitro-1,2,4-triazole (DNT), and the liquid anion exchanger is a water-insoluble, high-molecular-weight, long-chain tertiary amine (Alamine 304). The extraction of DNT is based on the reaction of the free-base form of the amine with acid to form the water-insoluble DNT-amine salt, and the formation of ADNT is achieved by regeneration of the amine to its free-base form with a basic stripping agent in a suitable diluent. Both the extraction and amination cycles of the process are very efficient and safe, and the amine extractant can be recycled.

The process described can be applied to the production of any ammonium salt with properties similar to those of ADNT. Any types of amines that behave as liquid anion exchanger in an appropriate organic diluent can be used for the production process, but different extraction efficiency and production rates for ADNT will be observed.

In selecting a solvent for best extraction power, the following criteria were taken into consideration for our particular system: 1) the solvent should give a good and rapid phase separation between the organic and aqueous phase; 2) it should have a high solubility for ammonia and 3) it should have no solubility for ADNT. Among the many solvents tested, including dichloromethane and dichloroethane, toluene was found to fulfill the requirements.

The extraction efficiency (per cent extraction) for DNT by the amine in the organic solvent is proportional to the amount of the extractant used. With a higher amine/DNT mole ratio, a higher per cent extraction is observed. Contrary to the results obtained for extraction efficiency, the per cent recovery of DNT as ADNT is independent of extraction **efficiency**.

The ammonium salt of 3,5-dinitro-1,2,4-triazole (ADNT) is an explosive with several interesting properties. It is quite soluble in water (28 g/100 ml), has a calculated P_{CJ} of 262 kbars at its crystal density of 1.632 g/cm^3, melts with loss of ammonia at 170°C, has ERL Type 12/12B drop-weight impact sensitivities of 59/80 cm, and has a critical temperature of 222°C in 0.8-mm-thick slab geometry.

Environment

Session 9

Co-chairmen : N.M. Rice (University of Leeds, U.K.)
L. Delvaux (University of Liège, Belgium)

9A

80-69	Solvent extraction using impregnation in a porous medium. C. Roux-Guerraz, D. Defives and J. Durandet, Institut Français du Petrole, Rueil-Malmaison, France.
80-32	Coalescence practice in the petroleum industry. M. Perrut, M. Angles and M. Guttierrez, Ecole Supérieure des Industries Chimiques, Nancy and Centre de Recherches Elf-Aquitaine, Saint Symphorien d'Ozon, France.
80-68	Extraction of organic polluante from an effluent stream in the manufacture of p-nitrobenzoic acid. R. Wennersten, Lund, Sweden.
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80-70	Decomposition of butex in nitric acid systems and the implications for safety in its use as a solvent. C. Hanson and I. Waden, University of Bradford, Bradford, U.K.

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80-171	Purification of oily water by solvent extraction. K.R. Robillard, G. Thorsen and A. Grislingas, Technical University of Norway, Trondheim, Norway.
80-173	Mechanism of raffinates contamination with the organic phase in liquid-liquid extraction and methods of their purification. I.N. Kremenskaya, Solid State Physics Institute, Acad. of Sc., Moscow, U.S.S.R.

SOLVENT EXTRACTION USING IMPREGNATION IN A POROUS MEDIUM

C. ROUX-GUERRAZ - D. DEFIVES - J. DURANDET
INSTITUT FRANCAIS DU PETROLE
1 et 4, Avenue de Bois-Préau
92500 RUEIL-MALMAISON (FRANCE)

ABSTRACT

Solvent extraction using impregnation on a porous medium provides an effective method for removal or recovery of pollutants in liquids. The method allows use of low solvent ratios with good efficiencies. Analysis of breakthrough curves gives an evaluation of efficiency by means of METS following a simple model for percolation, and a prediction of cyclic operations. The use of adsorbent porous media, such as active carbon, may be combined with extraction.

Examples are given concerning absorption of aromatics from water and by another may, phenols from water.

Solvent extraction is an effective method for eliminating and recovering pollutants from liquids.

This paper describes a separation method based on solvent extraction in which the solvent impregnates a porous medium inside of which it is immobilized. This technique has been described for analytic purposes (1). Extraction is performed by a percolation technique, and the solvent is used for regeneration.

The pollutants are present at concentrations ranging from several parts per million to several percent in effluents coming from the petroleum, petrochemical and chemical industries. When the liquid to be purified is water, purification is all the more important as discharge specifications concerning the environment are more severe. Furthermore, pretreated water must often be recycled after the troublesome traces have been eliminated.

No matter what solvent extraction process is used, the most important point lies in the choice of a solvent having quite specific properties. First of all the partition coefficient of the impurity between the solvent and the liquid to be purified must be as high as possible, so that theoretically a small amount of solvent can be used. In addition the solvent must be as insoluble as possible in the liquids to be purified so as to prevent any losses of solvent and any danger of secondary pollution. Lastly both liquids must have sufficiently different specific gravities that they can be separated by gravity and not lead to the formation of stable emulsions.

For eliminating traces of impurities, it is all the more important to have a solvent with a high partition coefficient since it would no be economical to use large amounts of solvent.

Since countercurrent extraction columns are not very efficient under such conditions, when this extraction technique is used the amount of solvent must be more than the minimum calculated for a specific degree of purification.

With the technique of immobilized solvent, the solvent impregnates a bed of particles of a highly porous solid. The percolation of polluted liquid in a column filled with this impregnated solid is a highly efficient way of extracting impurities. This extraction is halted in the vicinity of the breaking point depending on the degree of purification desired. Regeneration is then performed by counter current percolation of the minimum amount of pure solvent to return the absorbant bed to a state so that an absorption identical to the first one can be performed. The amount of solvent is then defined as the quotient of the amount of solvent used to regenerate the amount of liquid processed. We will see that the amount of solvent can be very small and near the theoretical minimum amount.

The experimentally obtained curves for the breakthrough of impurities show the instantaneous reduced concentration of these impurities as a function of percolated volume or of time. These curves can be used to calculate the number of stages in the column with the help of the mathematical model developed by Mayer and Tompkins (2). This model is based on the following assumptions : the column is divided up into equal stages in the direction of liquid flow, with each stage being considered to be perfectly mixed so that the equilibrium between the stationary phase and the mobile phase is attained, and the mobile phase is then transferred in a single operation into the next stage where a new equilibrium is attained. In this way we attain the concentration of impurities at the column outlet as a function of percolated volume. The program can also simulate a cyclic operation by stopping absorption when the mean concentration of the effluent attains a predetermined threshold, and desorption by pure solvent is controlled by a diffusion mechanism of the impurities extracted by the stationary phase in pure solvent, and the partition coefficient is equal to one. The establishing of a steady state is investigated as a function of the amount of desorption solvent, i.e. the solvent rate. The solvent rejected at the beginning of absorption can be recycled or not, as can the feed rejected at the beginning of desorption.

The data to be included to represent the absorption and desorption curves are the following : the grain porosity of the absorbant (α), the porosity of the column (ε), the partition coefficient (K_D) of the impurity between the extraction solvent and the liquid to be purified, and the number of stages representing the column according to the model that has just been described.

The partition coefficients can be determined experimentally. In some cases they can be calculated. In all cases they can be deduced from the breakthrough curve by determining the stoichiometric wave front to the extent where a linear relationship exists between the impurity concentration in the liquid and in the solvent, which is often obtained at low concentration. The velocity of the stoichiometric wave front (W) and the mean velocity of the percolated liquid (U) are connected by the following equation :

$$W = \frac{U}{1 + \frac{1-\varepsilon}{\varepsilon} K_D \alpha}$$

which can be used to determine K_D.

In the simplest cases, when it is easy to find a solvent having a satisfactory partition coefficient, the porous support may be perfectly inert, i.e. it may not have any selective adsorption for the constituents in the liquid to be purified and the solvent, but the extracting power of the solvent can also be associated with the adsorbing power of the porous medium for the impurity, meaning that a larger volume of liquid can be treated with the same volume of bed.

The following examples, i.e. the elimination of aromatic hydrocarbons in solution in water and the elimination of phenols in solution in water, demonstrate the possibilities of this purification methods using immobilized solvents.

ELIMINATION OF AROMATIC HYDROCARBONS IN SOLUTION IN WATER

Pollution by aromatic hydrocarbons is very frequent. Their solubility in water is a few hundred parts per million (ppm) and ordinarily must be lowered to about 1 ppm. As examples, we have chosen pollution by benzene, ethylbenzene and styrene.

Experimental analysis is performed in the laboratoy in columns 1 cm in diameter and 40 cm high, filled with the porous support, and the support is impregnated by solvent by percolation. The liquid to be purified is percolated at a constant flow rate by means of a proportioning pump. It begins by displacing the solvent contained in the intergranular space without displacing the solvent in the pore space. Water samples are preserved as briefly as possible before analysis in hermetically closed recipients. Analysis is done by gas chromatography after pentane extraction in a stationary phase of 10 % tricyanoepoxypropane on Chromosorb at 80 °C. The detection limit is one ppm of saturated hydrocarbon in an aqueous solution.

The solvent was chosen according to the criteria described above. Aliphatic hydrocarbons effectively meet the requirements of the method. They are not very soluble in water and are miscible in all proportions with aromatics. The partition coefficient of aromatics between aliphatics and water is high. In addition the viscosity of aliphatics is fairly low so that they can be easily regenerated on account of their good diffusion. The solvents used were n-pentane and isooctane. The porous medium must immobilize a large ammount of solvent, meaning that it must have high porosity. It must not undergo any irreversible chemical transformation on contact with the liquid to be purified and with the solvent. Its mechanical strength must be sufficient to withstand being stacked up inside the column.

As porous supports we used sifted pumice stone and Chromosorb which do not have selective adsorbent properties for the constituents present and an active carbon which has preferential adsorption for aromatics.

The results obtained are given in the form of tables and breakthrough curves representing the influence of the different parameters, i.e. the influence of the solvent (FIG. 1), the porous medium (FIG. 2), the flowrate (FIG. 3) and the nature of the aromatic hydrocarbon (FIG. 4) results are summed in Table 1. In addition Table 2 represents the results of cyclic operations and FIG. 5 gives an example of a desorption curve. The following conclusions can be deduced from these results.

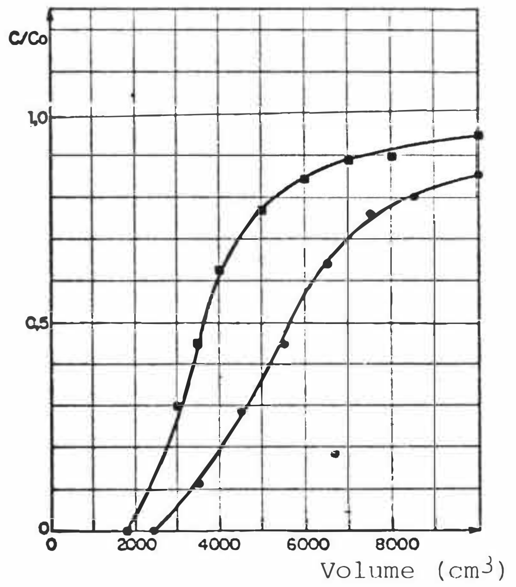

FIGURE 1 - Effect of Solvent
Co 60 ppm styrene, flowrate 600 cm^3/h, bed length 32 cm
Bed porosity ε 0.44, solid porosity α 0.45, parous medium pumice particle size 0.025 cm, solvent ● N-pentane ■ isooctane

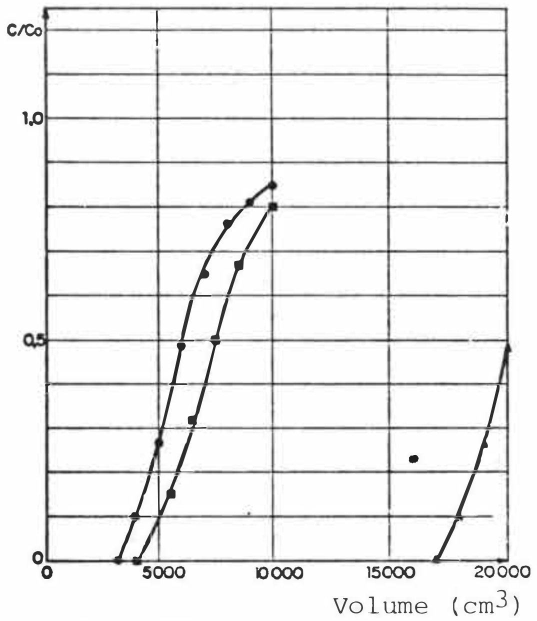

FIGURE 2 - Effect of parous media
Co 60 ppm styrene, flowrate 300 cm^3/h, bed length 32 cm, solvent n-pentane porous media ● pumice, particle size 0.025 cm, bed porosity 0.44, solid porosity 0.45 ■ chromosorb, particle size 0.03 cm, bed porosity 0.41, solid porosity 0.52 ▲ activated carbon, particle size 0.09 cm, bed porosity 0.39, solid porosity 0.54

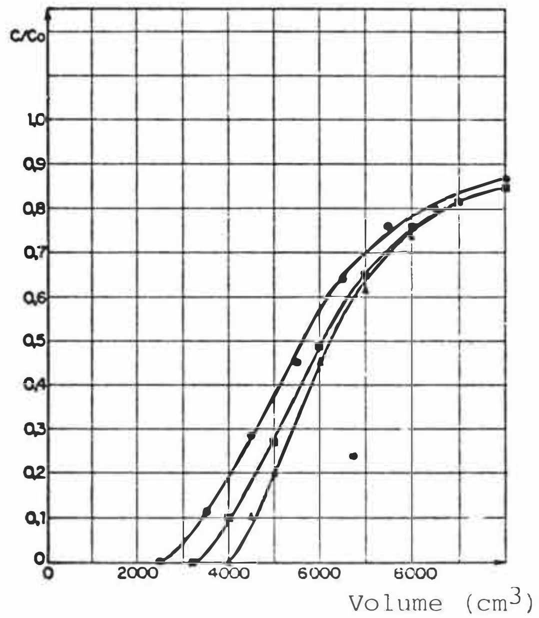

FIGURE 3 - Effect of flowrate
Co styrene 60 ppm, bed length 32 cm, solvent n-pentane porous medium pumice particle size 0.025 cm, bed porosity 0.44, solid porosity 0.45
flowrates ● 600 cm^3/h, ■ 300 cm^3/h, ▲ 120 cm^3/h

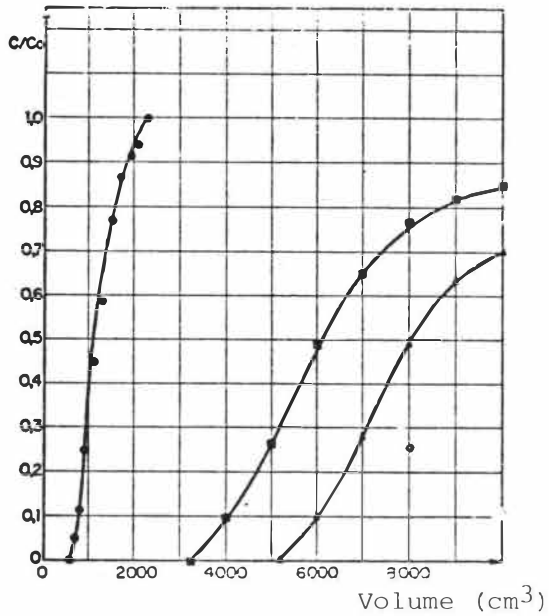

FIGURE 4 - Effect of aromatics
Bed length 32 cm, porous medium pumice, particle size 0.025 cm, bed porosity 0.44, solid porosity 0.45, solvent n-pentane aromatics ● benzene Co 60 ppm, ■ styrene Co 60 ppm, ▲ ethylbenzene Co 60 ppm

TABLE 1

AROMATIC EXTRACTION FROM WATER

Solute	Solvent	Porous medium	Particle size cm	Feed rate cm^3/h	Spatial velocity cm/s	Column height cm	Column diameter cm	Bed porosity ε	Solid porosity α	Partition coefficient (expérimental)	Partition coefficient (calculated)	HETS cm
Styrene	N-Pentane	Pumice-stone	0.025	600	0.206	32	1.0	0.44	0.45	1005	1118	7.4
Styrene	Isooctane	Pumice-stone	0.025	600	0.206	32	1.0	0.44	0.45	667	664	8.4
Styrene	N-Pentane	Chromosorb	0.030	300	0.103	32	1.0	0.41	0.52	1030	1118	3.9
Styrene	N-Pentane	Pumice-stone	0.025	300	0.103	32	1.0	0.44	0.45	1054	1118	6.2
Styrene	N-Pentane	Activated carbon	0.090	300	0.103	32	1.0	0.39	0.54	3150		3.2
Styrene	N-Pentane	Pumice-stone	0.025	120	0.041	32	1.0	0.44	0.45	1085	1118	5.7
Benzene	N-Pentane	Pumice-stone	0.025	300	0.103	32	1.0	0.44	0.45	192	194	5.2
Ethyl-benzene	N-Pentane	Pumice-stone	0.025	300	0.103	32	1.0	0.44	0.45	1427	1443	7.3
Ethyl-benzene	Isooctane	Pumice-stone	0.025	600	0.108	46	2.0	0.44	0.45	882	893	6.7
Ethyl-benzene	Isooctane	Activated carbon	0.090	400	0.086	14	1.6	0.39	0.54	2702		1.7

TABLE 2

RESULTS FROM CYCLIC OPERATION

Solute	Benzene	Ethylbenzene	Benzene	Ethylbenzene
Feed concentration ppm (weight)	60	100	60	170
Solvent	N-Pentane	Isooctane	N-Pentane	Isooctane
Porous medium	Pumice-stone	Pumice-stone	Act. carbon	Act. carbon
Particle size (cm)	0.025	0.025	0.090	0.090
Column height (cm)	32	46	100	14
Column diameter (cm)	1.0	2.0	2.4	1.6
Bed porosity (ε)	0.44	0.44	0.39	0.39
Solid porosity (α)	0.45	0.45	0.54	0.54
Breakthrough concentration (ppm)	8	10	9	12
Volume percolated at breakthrough (cm^3)	800	10,000	35,000	9,600
Effluent mean concentration (ppm)	<1	1	1	2
Volume of solvent for regeneration (cm^3)	18	30	600	35
Solvent ratio	0.025	0.003	0.017	0.0042
Equivalent number of theoretical stages	2.6	4.3	3.8	3.7

TABLE 3

PHENOLS EXTRACTION FROM WATER

Solute	m-Cresol	3-5 Dimethylphenol
Feed concentration ppm (weight)	100	100
Solvent	Toluene	Toluene
Porous medium	Activated carbon	Activated carbon
Particle size (cm)	0.09	0.09
Column height (cm)	32	32
Column diameter (cm)	1	1
Bed porosity (ε)	0.39	0.39
Solid porosity (α)	0.54	0.54
Feed rate (cm^3/h)	60	60
Volume percolated at break through (cm^3)	470	1270
Effluent mean concentration (ppm)	1	1
Volume of solvent for regeneration (cm^3)	160	180
Solvent ratio	0.34	0.14
HETS (cm)	1.1	1.8
Partition coefficient between toluene and water	8.5	39
Apparent partition coefficient	66	202

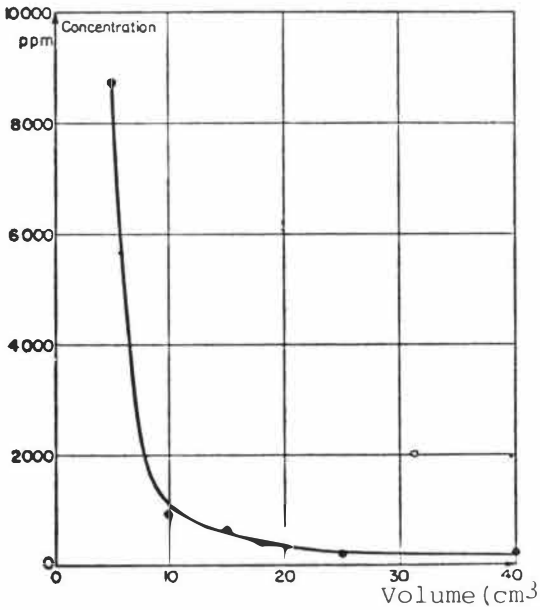

FIGURE 5 - Desorption of benzene
bed length 32 cm, porous medium pumice,
particle size 0.025 cm
bed porosity 0.44, solid porosity 0.45
solvent pentane, flowrate 30 cm^3/h

The volumes of water processed in a column impregnated with pentane are greater than with an impregnation with isooctane. This is due to the difference in the partition coefficients. Table 1 shows the partition coefficients corresponding to the different tests performed. The experimental coefficients are the result of an analysis of the breakthrough curves. The calculated coefficients for infinite dilution are based on an evaluation of the activity coefficients by considering the hydrocarbon solutions in water as regular solutions. The agreement among these results is fairly satisfactory.

The influence of the porous medium used is slight when the extraction phenomenon is the only one to occur. This is the case for pumice stone and Chromosorb. With active carbon everything occurs as if the partition coefficient were higher. This is due to the adsorbent power of the carbon for aromatics.

The flow rate of the water in the column has an influence on the shape of the breakthrough curve. In all cases the impurity appears in the effluent for a smaller volume of percolated water when the flowrate is faster. This may be linked to the transfer kinetics between the phases.

The amount of water treated depends on the nature of the dissolved aromatic hydrocarbon. Benzene is the most difficult to extract. Ethylbenzene is the easiest. This phenomenon is the direct consequence of the difference in the partition coefficients.

When several aromatics are simulataneously found in the water at similar concentrations, the one with the lowest partition coefficient is the one that appears first in the effluent. This appearance occurs for the same percolated volume as the one obtained with the same hydrocarbon alone and at the same concentration.

The results of Table 2 representing cyclic operations show that the amount of solvent that can be used is slight and corresponds to high process efficiency. The absorption-regeneration cycle was repeated many times without any detectable decline in the operation of the absorber.

ELIMINATING PHENOLS FROM AN AQUEOUS SOLUTIONS

Phenols in an aqueous solution can be separated by various methods, and in particular by extraction and adsorption. Adsorption by active carbon is an efficient process, but regeneration raises a problem that is difficult to solve. In the case of phenol, carbon can be regenerated by percolating a soda solution, but for higher phenols the amount of soda to be used is prohibitive. We will examine the possibilities of treatment by an immobilized solvent in the case of two substituted phenols, i.e. m-cresol and 3-5 dimethylphenol.

A great deal of research has been done on solvent extraction (3-4-5-6). There are a great many possible solvents that can be classified roughly in two categories. On one hand there are the solvents for which the partition coefficient is high. These are ketones, alcohols or esters. They cannot be used as immobilized solvents because of their excessive solubility in water. On the other hand there are solvents with a low partition coefficient and low solubility in water such as aliphatic hydrocarbons. Some aromatic hydrocarbons such as toluene have intermediate properties and, although their partition coefficient is fairly low, they result in a weak capacity for purifying columns. This capacity can be improved by combining them with an adsorbent porous medium.

Pumice stone does not have any adsorbent power for phenols and does not make a good support in this case.

Active carbon was chosen in association with toluene. The results obtained are shown in Table 3 and FIG. 6-7-8-9. An analysis of the breakthrough curves shows greater apparent partition coefficients than the partition coefficients measured in Table 3 between toluene and water. Furthermore, the results of cyclic tests in Table 3 indicate that this system is fairly efficient under the conditions described.

CONCLUSION

This investigation has shown the importance of the immobilized solvent technique for liquid purification processes by the separation of traces. The import parameters were analyzed, and a mathematical model can be used to interpret the breakthrough curves and to calculate the cycles.

The results obtained with aromatic hydrocarbons in water and with some phenols can be applied to the continuous purification of water polluted by such impurities by using a set of two columns, with one working by adsorption while the other is being regenerated.

This process can apparently be advantageously applied if a solvent having a high partition coefficient is known because it enables small amounts of solvents to be used. It can sometimes be improved by the simultaneous use of an adsorbent support. It can be applied even if the specific gravities of

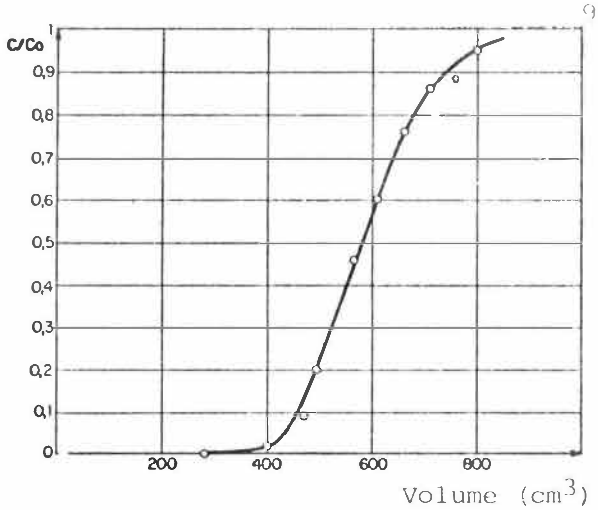

FIGURE 6 - Absorption of m-cresol
Bed length 32 cm, porous medium activated carbon, particle size 0.09 cm, bed porosity 0.39, solid porosity 0.54, solvent toluene, water flowrate 60 cm^3/h, concentration Co 100 ppm m-cresol

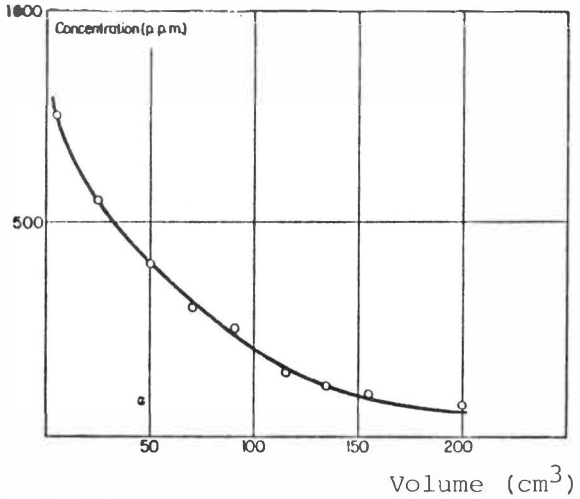

FIGURE 7 - Desorption of m-cresol
Bed length 32 cm, porous medium activated carbon, particle size 0.09 cm, bed porosity 0.39, solid porosity 0.54 toluene flowrate 30 cm^3/h

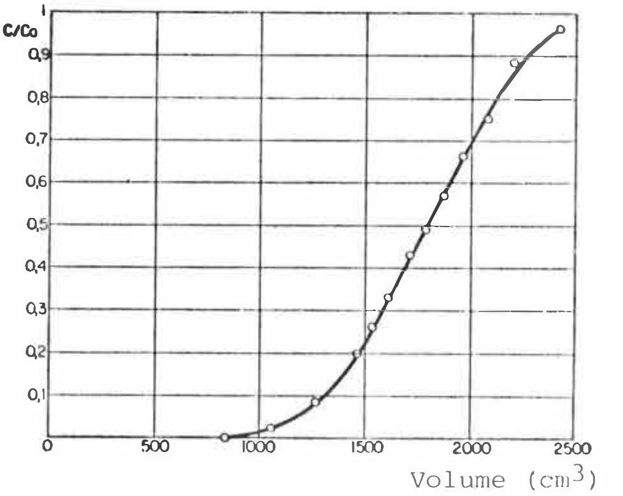

FIGURE 8 - Absorption of 3.5 dimethylphenol
Bed length 32 cm, porous medium activated carbon, particle size 0.09 cm, bed porosity 0.39, solid porosity 0.54, solvent toluene, water flowrate 60 cm^3/h, concentration Co 100 ppm

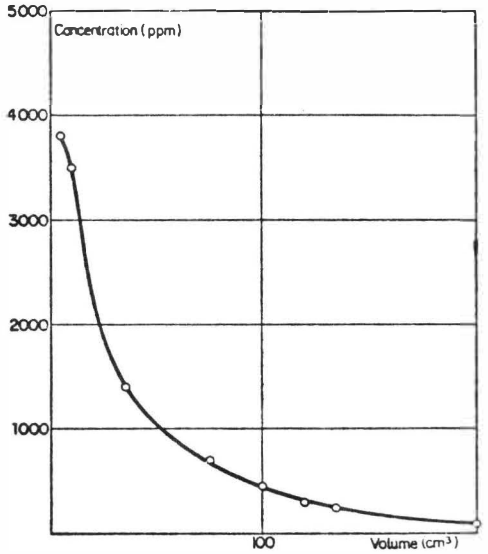

FIGURE 9 - Desorption of dimethyl 3.5 phenol
Bed length 32 cm, porous medium activated carbon, particle size 0.09 cm, bed porosity 0.39, solid porosity 0.54, toluene flowrate 30 cm^3/h

the phases present are close to one another and if the formation of emulsions is to be feared.

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COALESCENCE PRACTICE IN THE PETROLEUM INDUSTRY

PERRUT M., Ecole Nationale Superieure des
Industries Chimiques - 1 rue Grandville
54042 NANCY CEDEX - FRANCE
ANGLES M.)Centre de Recherches Elf-
GUTTIERREZ M.)Aquitaine - B.P. 22
69360 SAINT SYMPHORIEN D'OZON - FRANCE

ABSTRACT

In the petroleum refining industry, both O/W and W/O emulsions are processed; this paper deals with the experience gathered by Elf-Aquitaine in the following industrial operations:

- Desalting crude oil in electrical desalters;
- Drying gas-oil and jet-fuel on fibrous bed coalescers,
- De-oiling steam condensates on a new, coalescing material called "oleophilic resin";
- Hydrocarbon recovery in waste water settlers by a new device consisting in an oleophilic rotating drum.

From oil production to the delivery of petroleum products, the petroleum industry processes all kinds of emulsions; either W/O emulsions in the main production streams or O/W emulsions in utility streams especially in water effluents.

Breaking these emulsions is very often both a difficult and a highly important task for the refining industry. This paper deals with the industrial practice for four typical coalescence processes and describes in particular three of those for which Elf-Aquitaine has some original experience.

DESALTING CRUDE OIL

As is well known oil is very often produced with large amounts of salt water; crude oil is desalted and dewatered on the field to lower the water content to about 1% and the Na Cl content to 40-60 mg/l with techniques (depending on the water and salt content, emulsion and oil characteristics) which are described in (1). However sea transport frequently increases the salt content ("load-on-top techniques") and it is necessary to re-treat the crude oil when it reaches the refinery in order to lower the Na Cl content to 5 mg/l. In fact, it is very important for the refiner to obtain as low a salt content as possible to prevent:

- acid corrosion of atmospheric distillation equipment;
- plugging of heat exchangers and other subsequent equipment;

- deposition of salt mixtures on tubes in fuel heaters (Na lowers the fusion point of the salt mixtures containing V, Ni, Na S and leads to a thick crust on heater tubes).

So, most refineries are equipped with electrical desalters in which an a.c. electric field of high tension (- 10 to 20 kV) leads to dipole coalescence of the small droplets of water dispersed in the oil; as described by many investigators (2 - 6), the electric field accelerates droplet coalescence drastically especially for high water contents; the resulting droplets have a diameter much greater than those of entering droplets but are limited by a large droplet instability in an electric field.

FIG.1

DESALTING CRUDE OIL: Process flow chart

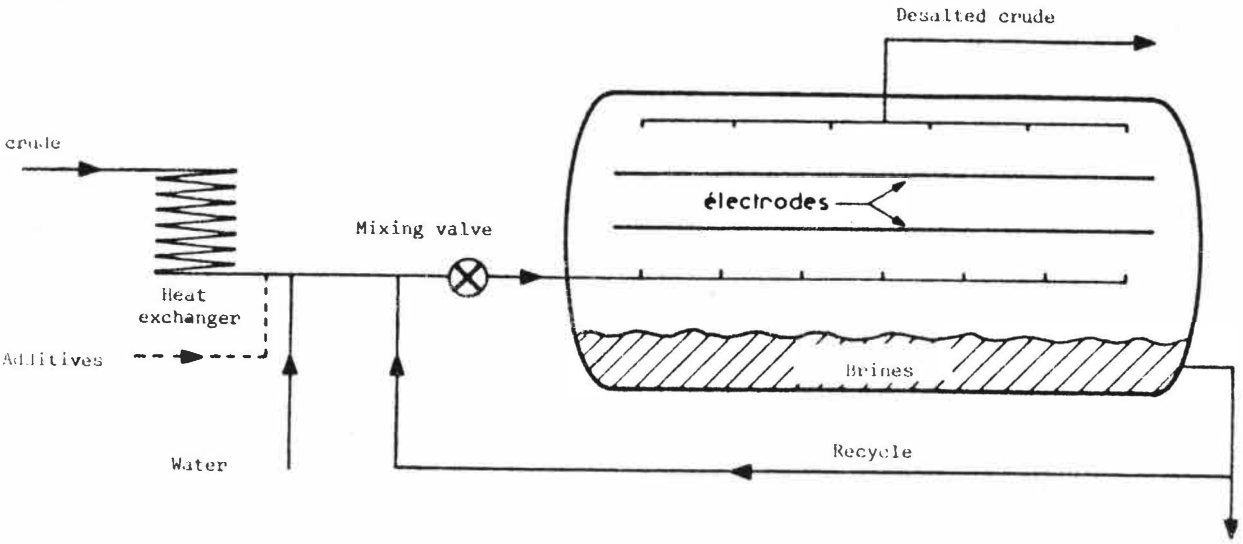


Figure 1 presents the process flow chart around a desalter; from a practical point of view, several things should be noted:

- The W/O separation consists of two operations (7)

° Dipole coalescnence between the electrodes leading to much larger water drops;

° Gravity decantation of these drops.

- In order to increase the desalter performance, it is necessary to optimise the dipole coalescence by:

° Increasing the water content of the emulsion up to 10% (depending on crude oil characteristics); this amount of water also dissolves the crystals of salt present in the crude oil (8);

° Adding additives to counteract the asphaltene activity that lowers the coalescnence efficiency.

- But it is also necessary to increase the gravity settling tate of the water drops; as it is well known settling velocity u of a small diameter (d) drop is given by Stoke's Law

$$u = \frac{g \, \Delta \rho}{18 \, \mu c} d^2$$

u being proportional to the density difference to oil viscosity ratio $\Delta\rho/\mu c$.

For crude oils, the $\Delta\rho/\mu c$ ratio and the settling rate increase sharply when temperature T is increased, so the desalter is always fed with preheated crude oil.

In practice the temperature is chosen taking account of: the flexibility of the crude oil preheat exchangers, the $\Delta\rho/\mu$value and pressure variations with T depending on the crude oil characteristics. For example, the average temperatures vary from 100°C for light crudes to 110-120°C for medium crudes (30-40°API) and 130-150°C for heavy crudes (< 30°API). It is much better to treat very heavy crudes with lighter ones when possible (8).

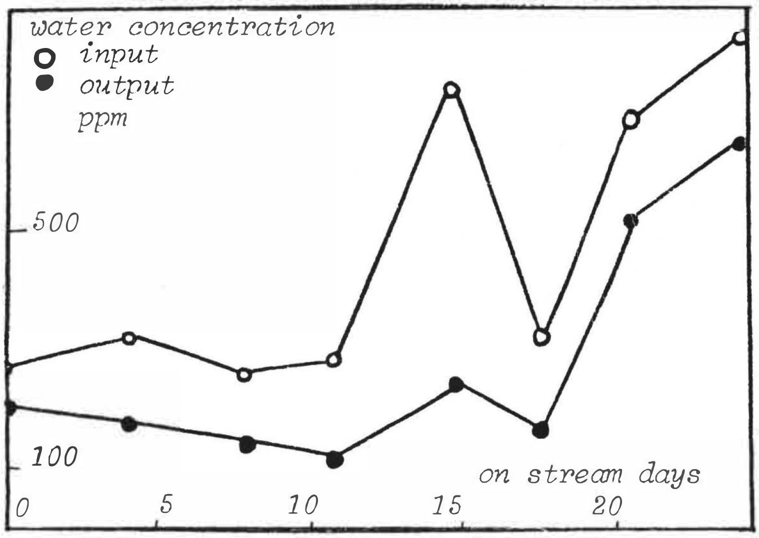
Furthermore it is very important to pay much to the oil inlet and outlet design in order to obtain a "smooth" and uniform flow without any turbulence. In many cases, bad performance of desalters is caused by damage (corrosion, plugging ...) or poor design of these parts.

DRYING GAS-OIL AND JET FUEL

The water content in commercial jet fuel must be very low to prevent it from icing when planes fly at high altitudes; although not so severe, the same applies to gas-oil that must remain clear on winter conditions. Coalescence of water droplets in straight-run products cannot lead to sufficiently low water contents - because of water solubility before complete cooling to ambient temperature - but is interesting to study further drying on salt filters or coalescence cartridges. Fibrous bed coalescence investigations have been completed both on a bench scale and on an industrial pilot plant to select the most efficient materials and process conditions (9). The main problem encountered appeared to be a drastic loss of the separation efficiency after some weeks (see Figure 2).

FIG. 2

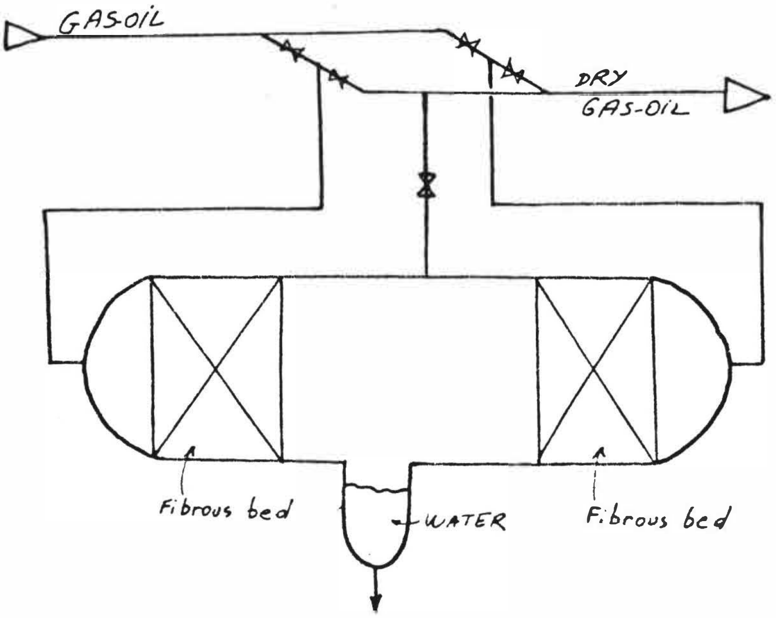
EVOLUTION OF EFFICIENCY DURING A RUN



Further investigations (10) confirmed that it was very important that the last layer of fibres swept by the coalescing emulsion should be preferentially wetted by the continuous phase while the opposite is true for the bulk of the coalescing medium. In fact, the wettability of this last layer permits the formation of large drops of coalesced dispersed phase that settle easily; on the contrary, if the last later is wetted by the dispersed-phase, a foam-like medium of continuous phase trapped in dispersed-phase film is formed in the continuous phase, leading to redispersion in fine droplets, especially at high flowrates.

An original device that can cope with the loss of efficiency with time met with gas-oil streams in is called a "regenerative coalescer" (shown on Figure 3).

FIG. 3
REGENERATIVE COALESCER DESIGN



The inlet flow sweeps the fibrous beds in which water is coalesced before settling in the empty central zone; after several days, the inlet flow is sent to only one fibrous bed and the dry product flows through the second fibrous bed; this reverse flow has been shown to "regenerate" the fibrous bed capacity for coalescing water droplets, probably by washing the parrafins adsorbed on the fibres that ruin the coalescing ability of the fibres by changing their wettability. The efficiency of a pilot scale device working on cyclic conditions (regenerating one bed for one or two days per week or per month depending on the fluid quality) remains efficient with industrial streams for a long period and full-scale operations are planned.

DE-OILING STEAM CONDENSATES

Recycling of steam condensates requires perfect de-oiling down to 1 mg/l while the oil contents commonly measured oscillate erratically between 0 and 2500 mg/l.

A new coalescing material called "oleophilic resin" leads to consistent performances in industrial coalescing units.

The oleophilic resin consists of a classical cation ion-exchange resin on which a cationic surface active agent is irreversibly fixed, giving the material a durable oleophilic surface (Figure 4) (11, 12)

FIG.4

OLEOPHILIC RESIN BEAD

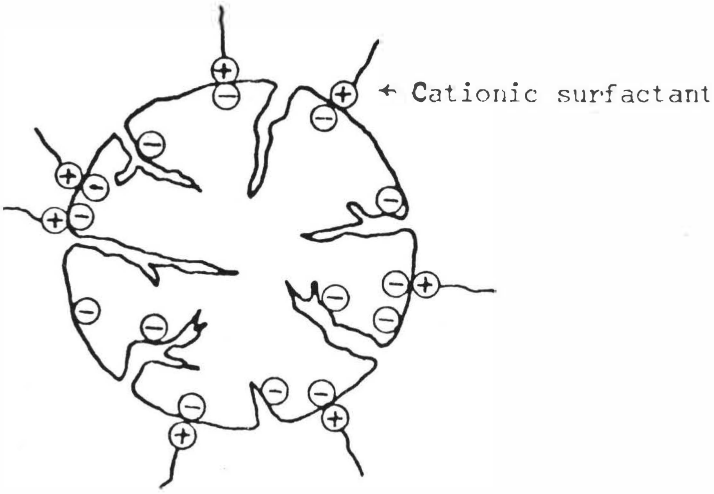
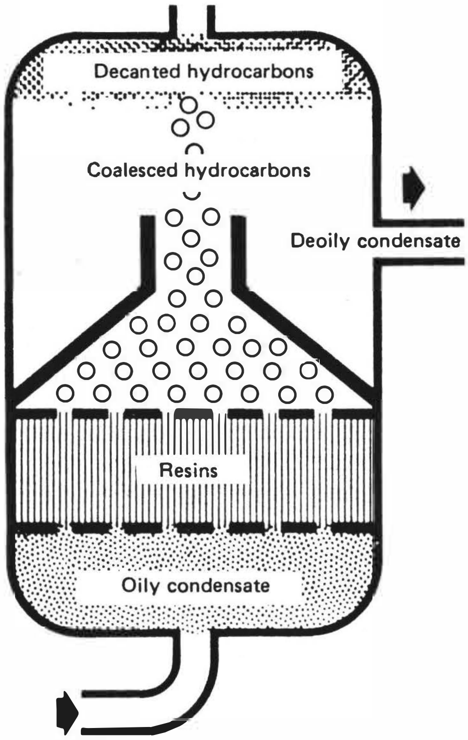


FIG.5

PROCESS FLOW CHART



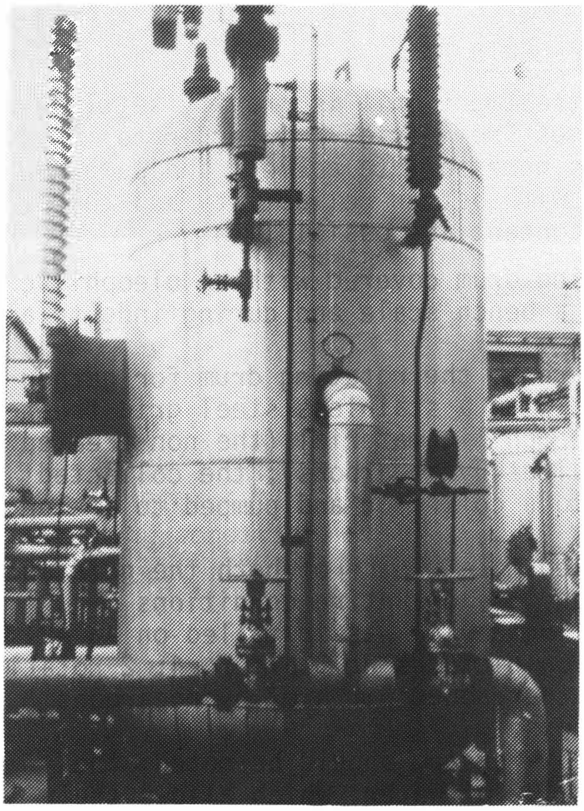
INDUSTRIEL UNITS :

PICT.1

AMBES Refinery :

Ø 1.600 m Flowrate 20 $m^3.h^{-1}$

H 3.200 m

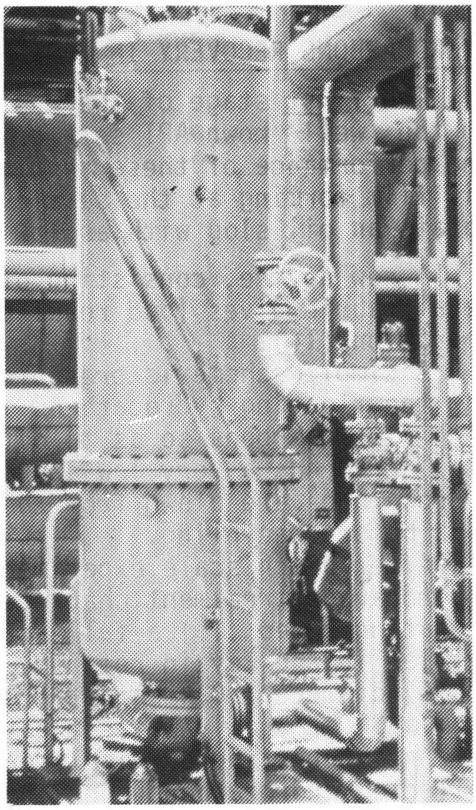


PICT.2

FEYZIN Refinery :

Ø 0.8 m Flowrate 5 $m^3.h^{-1}$

H 3.0 m



This oleophilic film can be easily regenerated when partially collapsed; but industrial experience on condensate streams proved that the film is very strongly fixed on the solid and regeneration has not been necessary even after several months of operation.

The coalescer flow chart is presented in Figure 5 and two industrial units are shown (pictures no 1 and 2). These two coalescers have very good performance and the hydrocarbon content in the water effluent - measured by infra-red spectroscopic titration - always remains lower than 1 mg/l. This satisfactory industrial experience, leading to important energy savings by recycling condensates and hydrocarbons, confirms the main advantages of this process:

- Viability of de-oiling,
- Very high flow rate: the velocity is about 0.3 cm/s in the original design; by using an oil "guide" (to drive the coalesced oil to the water/hydrocarbon interface) consisting in a knit material, the velocity is increased sharply, up to about 1 cm/s.
- Excellent thermal resistance of the resin up to 120°C;
- Long service life without "deactivation";
- Low treatment costs and easy operations (no additions of additives or no moving parts);
- Recovering good quality hydrocarbons.

However, the solid content of the input flow must be low to prevent plugging of the resin bed. For high solid content effluents, another design must be used with cyclic de-plugging of the bed by fluidization of the resin pellets with clean water; for example it is possible to treat ground water polluted by hydrocarbons.

This new coalescing medium can also be used for liquid-liquid extraction processes and water dephenolation has been investigated recently (13).

From the commercial point of view, it should be noted that this coalescence process is licensed in Europe and will be soon available in the USA and Japan.

HYDROCARBONS RECOVERY IN WASTE WATER EFFLUENTS

The first stage of the waste water treatment unit is gravity settling in the well known API settler used in most refineries. In order to improve the performance of these settlers, it is necessary to collect and pump the oil film forming at the settler surface with better reliability and to obtain an oil slop with as low a water content as possible.

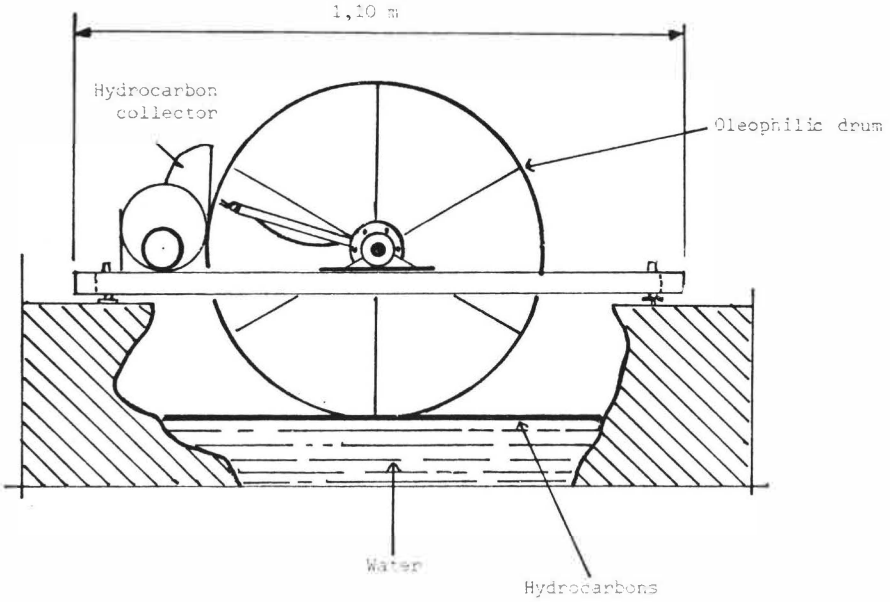
A new device, consisting of a rotating drum covered with an oleophilic metal fabric gives food results both on a bench scale and during industrial operation (14).

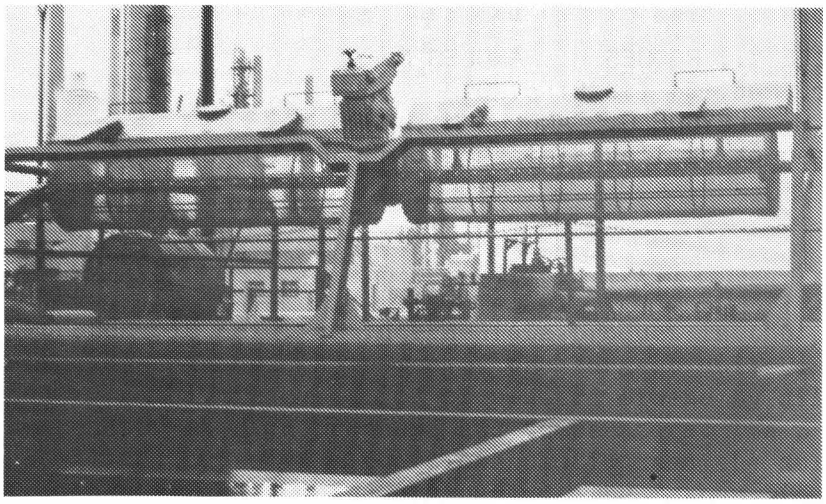
A simple scheme is presented on Figure 6: the rotating drum for gathering the floating hydrocarbons is covered with a stainless steel grid treated with fluorocarbons so as to obtain an oleophilic material (the non-treated steel grid has a very low ability to collect hydrocarbons); the collected hydrocarbons are blown from the grid into a collector and pumped to a slop tank before recycling.

After bench scale experiments that led to a choice of both the grid and fluorocarbon treatment characteristics and the operating conditions (rotating speed ...) a full scale operating device was installed on an API settler in the Feyzin refinery as shown on pictures no 3 and no 4: 2 rotating drums (diameter: 0.4m length: 1.60 m) gather about 5 m^3/h of hydrocarbons from a 300 m^3/h oily water treatment process.

An interesting original feature of this system should be noted: the collected hydrocarbons contain less than 10% of water, which allows their recycle in good condition.

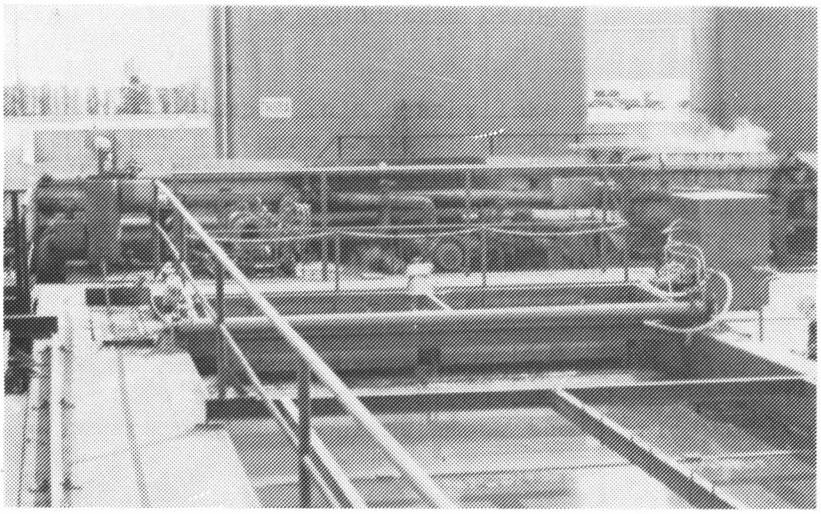
FIG.6
OLEOPHILIC DRUM SCHEME





PICT.3
FEYZIN Refinery :
Oleophilic drum on API settler (pictures n° 3 and 4)

PICT.4
Working conditions



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EXTRACTION OF ORGANIC POLLUTANTS FROM AN EFFLUENT STREAM IN THE MANUFACTURE OF P-NITROBENZOIC ACID

Ronald Wennersten

Dept. of Chemical Engineering
Lund Institute of Technology

S-220 07 Lund, SWEDEN

ABSTRACT

Solvent extraction can successfully be applied to purify the mother liquor obtained in the production of p-nitrobenzoic acid. The mother liquor, which discharged earlier in a lake, is a dilute nitric acid solution containing some organic pollutants at low concentrations. A recovery process has been designed in which a mixture of toluene and o-nitrotoluene extracts the organic pollutants while the purified nitric acid is recycled to the main process. Toluene is recovered by vacuum distillation and o-nitrotoluene is burnt together with the organic pollutants.

INTRODUCTION

p-Nitrobenzoic acid, an intermediate product in the pharmaceutic industry, is manufactured in Sweden in one of the largest units in the world. It is produced by catalytic oxidation of p-nitrotoluene by dilute nitric acid in a tube reactor at high pressure and temperature. The p-nitrobenzoic acid is crystallized out of the reaction solution and the solid product is separated off in centrifuges, dried and packed. The mother liquor from the centrifuges contains 15 weight-% nitric acid and a total of about 1 weight-% organic pollutants that are more or less toxic, p-dinitrobenzene being the most dangerous.

The polluted mother liquor has been dumped in a nearby lake after neutralization. In the disposal of this stream there are both environmental and economic factors to be considered. The industry concerned recently received a notification from the Swedish environmental authorities that this effluent must be treated before discharge. Several methods for lowering the organic content and recovery of nitric acid have been investigated. Adsorption by active carbon was thoroughly examined but the costs estimated were too high. Biological treatment of the effluent is not possible because of the toxicity of some of the pollutants. The mother liquor has also been recirculated within the process without treatment (with occasional bleed-off), but the build-up of p-nitrobenzene caused severe health problems among the people working in the factory.

This project (1) has studied the possibility of using solvent extraction to treat this effluent stream. The main objective has been to reduce the pollutants to such a level that the nitric acid can be recirculated to the reactor.

SOLVENT SELECTION

The mother liquor from the centrifuges has a temperature of 80°C and contains a large number of organic substances. Table 1 gives the identifiable pollutants. These are present at concentrations far below 1 weight-%. Some of these substances are quite polar and are able to form hydrogen bonds with water molecules.

Dinitrobenzoic acids	(2,6-, 2,4-, 3,5- and 3,4-DNBA)
Nitrobenzoic acids	(o-, m- and p-NBA)
Dinitrobenzenes	(m- and p-DNB)
Trinitrobenzene	(TNP)
Picric acid	
Nitrotoluenes	(o- and p-NT)
Dinitrotoluenes	(2,4- and 3,4-DNT)
Nitroxylene	
Unidentified substances	

TABLE 1
Organic pollutants in mother liquor

There are some important restrictions on the choice of a solvent in this special case. The solvent must have a very limited solubility in the raffinate phase not only for economic reasons but also to avoid undesirable reactions in the reactor. For the same reason the solvent should be chemically related to the organic pollutants. Shake tests in an earlier stage of the investigation indicated that toluene, which is widely used within the company, could be a suitable solvent.

The tests showed that most of the pollutants could be extracted except for some of the benzoic acids. In order to extract these, it was necessary to find a more polar solvent. Within the company, o-nitrotoluene (o-NT) is obtained as a nonsaleable byproduct. However, o-NT has a density that is very close to that of the mother liquor. The melting point is also quite high (-2.9°C) which makes it unsuitable for storage outdoors.

Mixtures of o-NT with toluene offer a possibility of obtaining a solvent with the proper physical properties. Shake tests showed that a mixture of 70 vol-% toluene with 30 vol-% o-NT gave the physical properties required. The distribution coefficients, obtained with this mixture, are shown in table 2. As can be seen the hazardous substance p-DNB is readily extracted. The acids are able to form hydrogen bonds with water and, as expected have the lowest distribution coefficients; 2,6-DNBA has significantly lower K_D than the other acids. In order to study the relative importance of different attractive forces, 2,6-DNBA was extracted separately from a water solution (0.0123 weight-%) into 6 different solvents. The results of shake tests, carried out at 19.5°C and with a phase ratio of 1.0, are given in table 3.

The acids contain the strongly electron-attracting nitro group which gives them acceptor properties. Toluene on the other hand, acts as a π-donor, which means that the π-molecular orbitals can be shared. If more electron-

Component	Conc. in raffinate phase, weight-%	Conc. in extract phase, weight-%	$D = \frac{C_{extr}}{C_{raff}}$
2,6-DNBA	0.0280	0.0002	0.01
	0.0270	0.0004	0.01
	0.0270	0.0005	0.02
	0.0250	0.0006	0.02
	0.0280	0.0008	0.03
2,4-DNBA	0.0530	0.0520	0.98
	0.1740	0.1320	0.76
	0.1690	0.2510	1.49
	0.2180	0.4030	1.85
	0.3760	0.4120	0.91
3,5-DNBA	0.0009	0.0013	1.44
	0.0060	0.0045	0.75
	0.0100	0.0064	0.64
	0.0050	0.0160	3.20
	0.0050	0.0340	6.80
3,4-DNBA	0.0020	0.0080	4.00
	0.0140	0.0400	2.86
	0.0250	0.0590	2.36
	0.0340	0.1170	3.44
	0.0480	0.1580	3.29
p-DNB	0.0003	0.0100	33.33
	0.0003	0.0210	70.00
	0.0005	0.0440	88.00
	0.0008	0.0750	93.75

TABLE 2

Distribution coefficients for organic pollutants in the mother liquor (Solvent: 70 vol-% toluene + 30 vol-% o-NT, Temp.: 20 °C)

donating methyl groups are attached to the ring as in o-xylene and mesitylene, this donor character is enhanced. As can be seen in table 3 there is no difference in extraction capability between toluene, o-xylene and mesitylene. The conclusion would be that energies from π-complexes could be neglected in this case. A possible reason for this could be the steric interference between the two nitro groups and the carboxyl group. A close ring to ring attachment between 2,6-DNBA and the solvent molecules is then more difficult to establish. This steric interference will also affect the resonance in 2,6-DNBA in such a way that the electron attracting power of the nitro group is diminished. This effect can explain why 2,6-DNBA is extracted less than the other acids when o-NT is used as a solvent. Resonance effects should make 2,6-DNBA a weaker dipole than the other acids and this will make the dipole-dipole interaction to o-NT smaller.

Extraction of 2,6-DNBA to a higher degree requires a stronger Lewis base than n-TBP where the phosphoryl oxygen can form hydrogen bonds with the carboxyl group. Consequently, as can be seen in table 3, TBP extracts 2,6-DNBA better than methyl-iso-butyl ketone since the carbonyl group is a weaker Lewis base than the phosphoryl group.

Solvents, vol-%	Conc. in raffinate phase, weight-%
70% Toluene + 30% o-NT	0.0121
70% Toluene + 30% Methyl-iso-butyl ketone	0.0118
70% Toluene + 30% n-Tributyl phosphate	0.0070
Toluene	0.0121
o-xylene	0.0121
Mesitylene	0.0122

TABLE 3
Extraction of 2,6-DNBA by different solvents

MIXER-SETTLER RUNS

Mixer-settler runs were carried out in laboratory glass units. In order to avoid further crystallization, the feed was kept at a temperature of 80°C which is that of the mother liquor leaving the centrifuges. No heat was added to the mixer-settler stages and the temperature in the stages therefore varied from 40°C in the first stage to about 25°C in the last stage. The solvent, which was kept at 20°C, consisted of 70 vol-% toluene and 30 vol% o-NT. The density of the solvent was 957 kg/m^3 (20°C) and that of the feed 1080 kg/m^3 (65°C). In 6 mixer-settler stages, countercurrent extraction was investigated with 3 different phase ratios as shown in table 4 below.

Flow of raffinate phase, L, g/min	Flow of extract phase, V, g/min	V/L
29	28	0.97
26	44	1.69
50	28	0.56

TABLE 4
Conditions for mixer-settler runs

A complete run analysis using a phase ratio of 0.56 is shown in table 5. As expected, most of the 2,6-DNBA stays in the raffinate phase. This component can however, be allowed to be bulit up to a higher concentration level without any disturbances in the reactor as can be seen. Some of the recirculated components may also be destroyed in the reactor if the concentration is raised, so that a constant level can be obtained without any bleed-off.

SOLVENT REGENERATION

Solvent regeneration includes the separation of toluene from the o-NT and the organic pollutants which are burnt. Toluene is recycled to extraction after being mixed with 30 vol-% o-NT. Three different methods for distillation have been investigated; namely continuous and batch steam distillation and vacuum distillation. The advantage of using vacuum distillation is that, by keeping a low temperature, the risk of thermal decomposition of the organic compounds is minimized. The advantage of using steam distillation is that a low temperature can be used at normal pressure but this gives a higher steam consumption than vacuum distillation. Equilibrium data was calculated with a computer program AZTROP (2) which utilizes the UNIFAC model. Optimization and calculation of the required number of ideal distillation stages was carried out with another computer program DESTLA (3). From the calculations, vacuum

Component	Raffinate phase conc., weight-%	Extract phase conc., weight-%	Feed conc., weight-%
2,6-DNBA	0.025	0.003	0.030
2,4-DNBA	0.105	0.620	0.680
o-NBA	0.010	0.025	0.030
Picric acid	-	0.170	0.100
3,5-DNBA	-	0.005	0.010
m-NBA	0.005	0.350	0.260
p-NBA	0.005	0.180	0.120
3,4-DNBA	-	0.230	0.170
o-NT	0.050	-	0.0002
p-NT	0.001	-	0.004
Nitroxylene	0.001	0.008	0.004
p-DNB	0.001	0.0505	0.0235
m-DNB + unid.*	0.0008	0.0760	0.0230
2,4-DNT	-	0.100	0.055
3,4-DNT	-	0.008	0.004
TNB	-	0.0140	0.006
Unidentified	0.0008	0.0245	0.0101

TABLE 5
Results from a mixer-settler run
(Number of stages: 6, V/L: 0.56)

*probably 2,6-DNT

distillation and continuous steam distillation turned out to be the best alternatives to carry out the separation, vacuum distillation having higher capital cost but lower operating cost. Considering the reliability of the calculations vacuum distillation must be recommended.

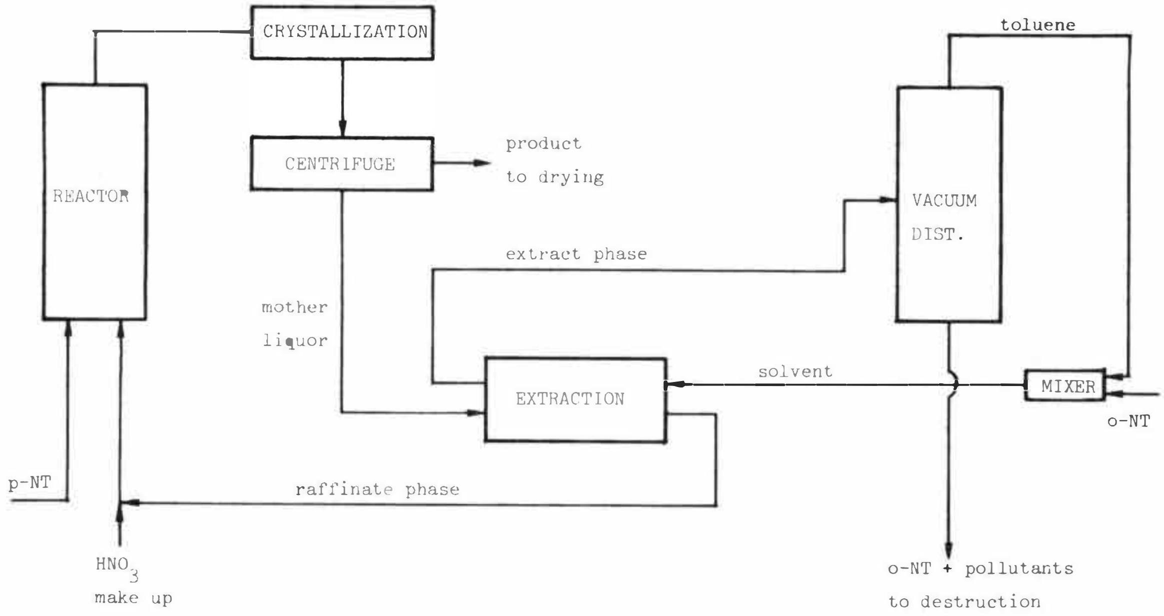

FIG. 1
Flow sheet for HNO_3 recovery from mother liquor

PROCESS DESIGN

Figure 1 shows the process flow sheet for purification of the mother liquor. From the centrifuges the mother liquor is fed to an extraction battery where the organic pollutants are extracted in counter-current mixer-settlers. The raffinate phase, mainly dilute nitric acid, is recycled to the reactor after make-up with nitric acid. The extract phase containing toluene, o-NT and organic pollutants is fed to a vacuum distillation tower. At the top, toluene is recovered and after adding fresh o-NT, is reused as solvent in the extraction. The bottom product consisting of o-NT and organic pollutants is sent to thermal destruction.

ANALYSIS

Analysis were carried out on a Waters Associates 440 HPLC using the column Bondapak C 18 (Reverse phase) and a flow of 1 ml/min.

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REMOVAL AND RECOVERY OF CARBOXYLIC ACIDS AND PHENOLS FROM DILUTE AQUEOUS STREAMS

C. Judson King

Department of Chemical Engineering
University of California

Berkeley, California 94720, U.S.A.

ABSTRACT

Conventional solvents and Lewis-base extractants are evaluated for removal of acetic and formic acids and di- and tri-hydric phenols from dilute aqueous solution. For acetic acid, amines and phosphoryl compounds give distribution ratios considerably higher than those for conventional solvents. The nature of the diluent affects distribution ratios greatly. A solvent composed of Alamine 336 and diisopropyl ketone is attractive for extraction of acetic acid. Methyl isobutyl ketone gives distribution ratios far superior to those of diisopropyl ether for di- and tri-hydric phenols. The effect of pH for these solvents agrees well with a simple ionization model. Amine extractants are less effective for phenols. Phosphoryl extractants appear to be more attractive.

INTRODUCTION

Removal of highly polar organics from dilute aqueous solution is one of the most difficult industrial separations problems. One class of such separations consists of organic-rich process-effluent waters -- such as waters from the manufacture of acetaldehyde and acetic acid, and process condensates from coking, coal conversion, and oil-shale retorting. Another class is composed of processes where a polar organic is manufactured in dilute aqueous solution -- such as production of ethylene glycol, formation of acetic acid by fermentation, and conversion of biomass to ethanol by enzymatic and/or acid-hydrolysis processes. Among the commonly encountered polar organics in such circumstances are carboxylic acids and phenols, the subjects of this paper.

If the concentration of organics is high enough to warrant recovery, biological treatment is precluded. Large and/or fluctuating organics loadings and toxic or refractory solutes can also make biological treatment difficult or impossible. Distillation is frequently used for recovery of polar organics from water; that class of distillations accounts for a substantial portion of the world's energy consumption (1). However, distillation processes often encounter low relative volatilities and azeotropes. Furthermore, acetic acid, polyhydric phenols, ethylene glycol, and a number of other polar organics are less volatile than water, with the result that water must be taken overhead in a distillation. The cost per unit quantity of solute recovered therefore increases greatly as the solute becomes more dilute in the feed. For such situations there is considerable incentive for a recovery process which removes the solute from the water, rather than *vice versa*. Solvent extraction is such a process.

GENERAL CONSIDERATIONS

The most important factor in generation of a process for extraction of polar organics from a dilute water stream is solvent selection. Since water flows are often large, it is important to choose a solvent which will give a high distribution ratio for the solute(s) in question; this is needed to keep solvent circulation rates from becoming excessive. An effective solvent for highly polar organics frequently has a substantial solubility in water itself. In such cases, the dissolved solvent must be removed somehow from the raffinate water, and the solvent properties must be well suited to whatever process is used for that purpose. Methods for removal and recovery of residual dissolved solvent include atmospheric steam stripping; inert-gas stripping, as in the Lurgi Phenosolvan process (2,3); vacuum steam stripping (4), and volatile-solvent extraction (5). Alternatively, one can seek a solvent with a combination of low enough solubility, emulsification tendency, and cost so that removal and recovery of solvent from the raffinate water are not necessary. The solvent must not be toxic or refractory itself.

For any but the lowest concentrations of soluble organics in the feed water, it will be necessary to regenerate and reuse the solvent. Regenerability -- often by distillation or stripping -- and chemical stability of the solvent under regeneration conditions thereby become important attributes so as to keep solvent consumption economically low.

An important distinction is that between high-boiling and low-boiling solvents. If the solvent has a lower boiling point than the extracted solute(s), the solvent must be taken overhead in a distillation column. Therefore higher-boiling solvents are ususally favored from the standpoint of reducing energy consumption. However, when the solvent has a higher boiling point than the extracted solute(s) and regeneration is by distillation, high-molecular-weight tars and degradation products may build up in the recirculating solvent. This may require continual purge and processing of solvent to preclude excessive solvent loss. A high-boiling solvent may lead to high reboiler temperatures in a distillation column, requiring expensive heating media and/or leading to solvent degradation. Since these factors are important to different extents in different situations, it is desirable to identify both low-boiling and high-boiling solvents which are effective for a given solute or class of solutes.

CARBOXYLIC ACIDS

The lower-molecular-weight carboxylic acids are the most difficult to extract from water. Acetic acid is a common constituent of aqueous streams from organics processing, since it is a relatively stable oxidation product. Hence we have given principal attention to acetic acid, with some comparative data also being obtained for formic acid.

The more common solvents, such as esters, ethers and ketones give values of the equilibrium concentration distribution ratio D_c for acetic acid no greater than about 1.4, at best (6)*. Alcohols give relatively high values of D_c, but are subject to esterification upon regeneration by distillation. Also, the more effective conventional solvents have substantial solubilities

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*-In references 5, 6, 9, 14 and 15, equilibrium data are reported as K_D=wt. fraction solute in organic phase/wt. fraction solute in aqueous phase.

in water. Thus there is incentive to identify novel solvents which will give higher values of D_c. Because of the inherently acidic nature of acetic acid, organic Lewis bases are a potentially attractive class of extractants. Tributyl phosphate gives D_c of 2.2 for extraction of acetic acid at high dilution (6). Phosphine oxides are stronger bases than phosphates; trioctyl phosphine oxide (TOPO) has been put forward as an extractant for acid acid by Grinstead (7) and Helsel (8). The higher-molecular-weight amines are another class of organic bases. We have explored the amines and TOPO further as extractants for acetic acid.

AMINE EXTRACTANTS

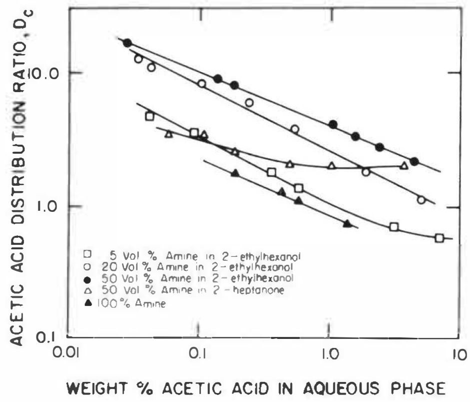
Preliminary experiments (9) showed that primary amines gave high mutual solubility with water and that secondary amines led to irreversible amide formation with acetic acid. Tertiary amines cannot form amides. Therefore we have concentrated upon tertiary amines, principally Alamine 336 (General Mills, Inc.), which was found gas-chromatographically to be a mixture of mostly tri- C_8 to C_{10} tertiary aliphatic amines (10).

The desirable molecular weight for the amine extractant reflects a compromise between excessive solubility of the acetate complex in water for low molecular weights and lower D_c for higher molecular weights. Alamine 336 was found to be a good choice in this regard. Tri-n-butyl amine as an extractant gave excessive water solubility of the complex, to such a degree that D_c was substantially reduced (6). The solubility of tributyl amine in a 1% acetic acid solution was found to be 3.1 wt. %, while that of Alamine 336 is less than 10 ppm, too low to be measured gas-chromatographically (9). Apparently significant aqueous solubilities of the acetate complex of trioctylamine from a different supplier, reported earlier (6), were probably the result of low-molecular-weight impurities in the amine.

For effective performance the tertiary amines require a diluent. Figure 1 (9) shows one important reason for this. For solvent mixtures of Alamine 336 and 2-ethylhexanol D_c reaches a maximum at an intermediate solvent composition; the value for 50% amine in the solvent is a factor of three or more larger than D_c for 5% amine or D_c for 100% amine. Exploratory tests (6,9) indicate that this behavior comes from the necessity of solvating the amine-acetate complex. The tertiary amine itself is a rather poor solvent for the complex, and a well chosen diluent thereby provides the solvating medium itself. One of the prospective diluents studied, it was found

FIG. 1

Extraction of Acetic Acid by Alamine 336 in Various Diluents (9).



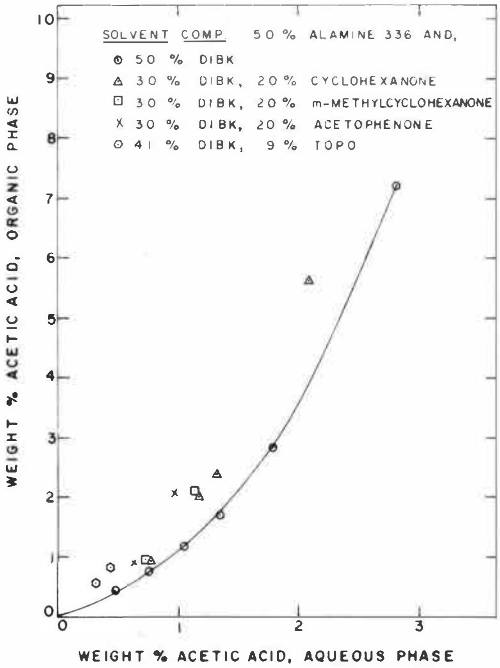
that alcohols and chloroform led to the highest values of $\underline{D}_c$ for acetic acid with Alamine 336, possibly because of hydrogen bonding between the electropositive hydrogen of the diluent and the carbonyl oxygen of the complexed acid. With the exception of such specific diluent-complex interactions, it was found that the effectiveness of diluents tended to increase with increasing polarity or solubility parameter; ketones as diluents gave higher $\underline{D}_c$ than esters, which in turn gave much higher $\underline{D}_c$ than hydrocarbons. Chloroform is undesirable as a diluent if the raffinate water is to be released to the environment. Alcohol diluents tended to esterify with acetic acid during regeneration by distillation. Ketones were selected as the next most promosing class of diluents from the standpoint of high $\underline{D}_c$ (see Figure 1), and most subsequent work was carried out using ketone diluents with Alamine 336.

For solvents composed of various mixtures of Alamine 336 and diisobutyl ketone (DIBK) it was found that roughly 1.5 moles of water were extracted per mole of acetic acid (9). If there is a strong incentive for less co-extraction of water, it may be desirable to use a less polar diluent and accept the lower value of $\underline{D}_c$.

Selection of the appropriate molecular weight of the diluent reflects a compromise among lower volatility and solubility in water for higher molecular weights and higher $\underline{D}_c$ for lower molecular weights. The volatility can be an especially important consideration if distillation is used for regeneration of the solvent, since the volatility of acetic acid is depressed in the presence of the amine because of the complexing reaction. Measurements of vapor-liquid equilibria under these conditions (11) showed that, in the presence of Alamine 336, acetic acid has relative volatilities in the range 0.77 - 2.2 with respect to methyl isoamyl ketone as diluent, and in the range 2.8 - 4.7 with respect to DIBK as diluent. The C_9 ketone, DIBK, seems therefore to be more suitable. Repeated regeneration and reuse of Alamine 336/DIBK solvents showed no evidence of thermal degradation or loss of solvent power.

FIG. 2

Extraction Equilibria for 50 Volume % Alamine 336 in DIBK and in Mixtures of DIBK and Polar Modifiers (9). Solvent density = 0.81 g/cm^3 for Alamine 336/DIBK.



As shown in Figure 1, Alamine 336 with 2-ethylhexanol and 2-heptanone diluents showed higher values of D_c at lower acetic concentrations, down to 0.1 wt. % acetic acid and less. This is probably attributable to a mass-action effect for the complexing reaction. However, for DIBK diluent it was found that D_c decreased at low acetic acid concentrations, as shown in Figure 2 (9). This may result from an insufficiently polar solvating medium for the complex at low acetic acid concentrations. Various more polar ketone modifiers were tried, mixed with Alamine 336 and the DIBK diluent. These served to increase D_c somewhat at low acetic acid concentrations, as shown in Figure 2. TOPO proved to be still more effective as a modifier at low levels of acetic acid.

TOPO AS EXTRACTANT

Values of D_c for acetic acid found for trioctyl phosphine oxide (TOPO) with several different diluents tended to be somewhat lower under equivalent circumstances than for Alamine 336, but higher than those with conventional solvents (6,9). For a feed water containing 6.6 wt. % acetic acid, measured values of D_c for 50 wt. % TOPO in the solvent mixture were 0.9, 2.3 and 1.7 for 2-ethylhexanol, 2-heptanone and Chevron Solvent 25 as diluents, respectively (9). Chevron Solvent 25 is a mixture of primarily C_8 and C_9 alkylated aromatics (Chevron Chemical Co., Richmond CA, U.S.A.). Chloroform and a 2:1 by volume mixture of n-heptane and n-hexanol as diluents with TOPO gave D_c values equivalent to or somewhat less than those for Chevron Solvent 25 diluent (6). The alcohol and chloroform diluents are therefore relatively much less effective with TOPO than with Alamine 336. We postulate that this is due to strong directional hydrogen bonding of the electropositive hydrogen atoms with the phosphoryl oxygen of TOPO, making the phosphoryl oxygen less available for complexing with acetic acid. On this basis, ketones appear to be the better diluents for use with TOPO, since they do not have the electropositive hydrogen.

Measured solubilities of water in a TOPO/2-heptanone solvent (10) are similar to those found for Alamine 336/DIBK. Gas-chromatographic measurements showed that the solubility of TOPO (30 wt. % mixture in Chevron Solvent 25) is less than 1 ppm in a 10% aqueous acetic acid solution.

FORMIC VS. ACETIC ACID

Spot measurements with amine and TOPO extractants (6) showed that D_c for extraction of formic acid from water is substantially higher than that for acetic acid from water. This is in line with the stronger acidity of formic acid.

PROCESS DESIGN AND ECONOMICS

Ricker et al (11) considered conceptual designs for extraction of acetic acid from 22.7 Mg/h of 5% aqueous solution. A cost (1978 basis) of 1.9$/m^3 of water was projected for 50% Alamine 336 in DIBK as solvent. No credit for the value of recovered acetic acid is included in this cost. For 40% TOPO in 2-heptanone as solvent, most constituents of the processing cost are similar to those for Alamine 336/DIBK, but the cost of make-up solvent will probably be much greater and could be dominant, since TOPO is approximately ten times as costly as Alamine 336, per kg. More information on degradation tendencies, loss due to emulsification and/or upsets, etc., is needed in order to assess this point. On the basis of current information, TOPO does not appear to offer advantages over the amines.

For situations where build-up of non-volatile constituents in a high-boiling solvent is a problem, it will be necessary to add facilities for purge and reprocessing of solvent, or to revert to a low-boiling solvent or other separation processes. Ricker, et al (11) estimate a cost of \$3.9/m^3 for extraction of 5% acetic acid from water using ethyl acetate.

PHENOLS

Phenol itself is relatively easy to extract from water, and has been recovered by solvent extraction from coke-oven effluent waters for many years (2,3). Alkylated phenols are easier to extract than the corresponding unalkylated phenols. Additional -OH groups make polyhydric phenols more difficult to extract. Polyhydric phenols frequently appear in aqueous streams from coal processing, where a high pH can further complicate extraction because of ionization. Polyhydric phenols in aqueous effluents have received relatively little attention until recently, one reason being the difficulty of analyzing for them gas-chromatographically. Yet polyhydric phenols are known to be important color precursors, even at very low concentrations. The trihydric phenols are also refractive biologically (12).

The history of commercial processes for phenol extraction from waters derived from coal processing is reviewed by Jauernik (2) and Wurm (3). Earlier use of benzene, tri-cresyl phosphate (TCP) and n-butyl acetate as solvents was supplanted by use of diisopropyl ether (DIPE) in the Lurgi Phenosolvan process. DIPE is chemically more stable than butyl acetate, has a higher capacity for phenols than does benzene, and is a low-boiling solvent not subject to build-up of nonvolatile impurities in the way that TCP is. More recently methyl isobutyl ketone (MIBK) has been put forward as a low-boiling solvent for phenols.

We have explored DIPE and MIBK as low-boiling solvents for polyhydric phenols, have investigated the effect of pH on $\underline{D}_c$, and have investigated the use of amines and phosphoryl compounds as high-boiling extractants for the weakly acidic phenols.

EFFECT OF pH

Phenols ionize appreciably in aqueous solution when the pH rivals or exceeds the value of pK_a for the phenol (K_a = dissociation constant). Reported values of pK_a at 298K (13) for the phenols considered here are shown in Table 1.

Figure 3 shows measured values of K_D vs. aqueous-phase pH for resorcinol, extracted from water into DIPE (14,15). The curve gives the prediction of a simple model whereby only the unionized resorcinol distributes, according to the value of $\underline{D}_c$ (1.50) observed at low pH.

$$\underline{D}_c = \frac{\underline{D}_{c,\text{low pH}}}{1 + \frac{K_a}{[H+]}} \qquad (1)$$

Since K_a is known independently, the model has only one fitted parameter. Similarly good agreement with such a model was found for extraction of phenol by DIPE, and of hydroquinone by both DIPE and MIBK (14).

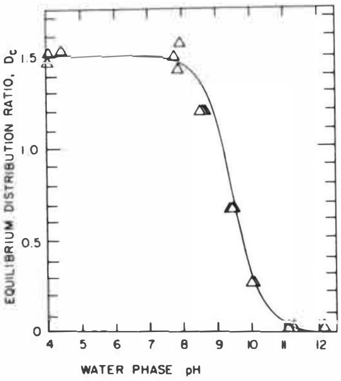
Table 1. Experimental Values of D_c at pH 3.9-5.9 for Various Phenols Extracted from Water into DIPE and DIBK. Aqueous Phase Concentration = 1400 to 3000 ppm (14,15).

		Equilibrium Concentration Distribution Ratio, D_c	
Solute	pK_a (14)	DIPE	MIBK
Monohydric			
Phenol	9.98	27	(88)*
Dihydrics			
Pyrocatechol (1,2)	9.98	3.6	15.0
Resorcinol (1,3)	9.47	1.50	14.4
Hydroquinone (1,4)	10.1	0.75	7.9
Trihydrics			
Pyrogallol (1,2,3)	9.01	-	2.9
Hydroxyquinol (1,2,4)	-	0.13	4.0
Phloro-glucinol (1,3,5)	8.44	-	3.1

*-From (16).

FIG. 3

Concentration Distribution Ratio vs. pH for Extraction of Resorcinol by Diisopropyl Ether (14.15).



EXTRACTION OF DI- AND TRI-HYDRIC PHENOLS BY DIPE AND MIBK

Table 1 shows measured values of D_c for the di- and tri-hydric phenols at values of pH adequately below pK_a for ionization to be insignificant (14, 15). Values of D_c for the dihydric phenols into DIPE are disturbingly low, and that for the trihydric phenol is much too low, for a commercial extraction process. Values of D_c for MIBK are much higher than for DIPE, making MIBK much more suitable for extraction of polyhydric phenols.

Values of D_c reported in Table 1 compare well with other values reported previously (15,16,17,18,19). Where there is scatter among reported values, that from the present work agrees well with at least one of the previously reported values.

AMINE EXTRACTANTS

Resorcinol and pyrogallol were extracted by Alamine 336 at 50 vol. % concentration in various diluents (20). Aqueous-phase concentrations were about 2000 ppm, and pH was from 6 to 8. For 2-ethylhexanol diluent, D_c was about 4.0 and 0.7 for resorcinol and pyrogallol, respectively, as compared with 3.1 and 0.60 for the two solutes into otherwise pure 2-ethylhexanol. Therefore use of the amine extractant added rather little to what could be accomplished with the diluent alone. Lower values of D_c were found for extraction of resorcinol by Alamine 336 with DIBK, kerosene and Chevron Solvent 25 diluents. Exploratory measurements with primary and secondary amines showed no advantage in D_c over the tertiary amine (21).

PHOSPHORYL EXTRACTANTS

Undiluted tricresyl phosphate (TCP) was found to give D_c of 84, 13.8 and 1.8 for extraction of phenol, resorcinol and pyrogallol, respectively (20). It is therefore superior to amine extractants as a high-boiling solvent for phenols. Measurements of K_D for phenol extraction by solvents composed of 25 vol. % TCP in various diluents (MIBK, 2-ethylhexanol and Chevron Solvent 25) showed that D_c was approximately a linear blend of D_c for undiluted TCP and D_c for pure diluent; no synergism was evident (20). Nonetheless, a diluent may be desirable to reduce viscosity and/or to reduce the reboiler temperature for regeneration by distillation. The fact that TCP has a specific gravity (1.17) greater than that of water complicates the selection of diluents in practice.

Preliminary experiments with a solvent composed of 25 wt. % TOPO in DIBK gave a strikingly high D_c of 90 for extraction of pyrogallol at an aqueous-phase pH of 3.3-3.8. We are currently investigating the extraction of phenolic solutes by TOPO further.

ACKNOWLEDGEMENTS

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RECOVERY OF ALUMINUM FROM WATER TREATMENT PLANT SLUDGES

David A. Cornwell

Department of Civil Engineering
Michigan State University

East Lansing, Michigan 48824
USA

ABSTRACT

Potable water treatment plants add alum to coagulate surface water supplies. The coagulation process produces a sludge residual which is expensive to dewater and dispose of. Recovery of the aluminum from the sludge would have the benefits of reducing in-plant chemical costs, reducing the weight of sludge requiring treatment and rendering the residual sludge easier to treat. Liquid ion exchange has been shown to recover a purified and concentrated recovered alum with the same qualities as commercial alum. The sludge is fed directly to the extraction circuit for 90% aluminum recovery. The extract is stripped in 2 countercurrent stages with sulfuric acid. Results of demonstration testing at two plant sites indicate favorable economics.

PRODUCTION OF ALUM SLUDGES

Potable water treatment plants add aluminum (in the form of aluminum sulfate, commonly called alum) to coagulate color and turbidity in surface water supplies. Alum coagulation of surface waters accounts for about 70% of all the potable water treated in the United States. Alum is generally purchased as liquid alum containing 17.1% Al_2O_3 (50% $Al_2(SO_4)_3 \cdot 14H_2O$). The reactions of alum with water lead to the formation of insoluble aluminum hydroxide species such as represented below:

$$Al_2(SO_4)_3 \cdot 14H_2O + 6HCO_3^- = 2Al(OH)_3(s) + 6CO_2 + 3SO_4^{-2} + 14H_2O. \quad (1)$$

Under equilibrium conditions the alum reacts with the bicarbonate to form aluminum hydroxide. However, water plants generally do not operate at equilibrium conditions and consequently various intermediates are formed. Figure 1 shows some of the reactions involved in the hydrolysis of Al^{3+}. In the pH range of 6-8 in which most plants coagulate, the insoluble aluminum hydroxide complex of $Al(H_2O)_3(OH)_3$ probably predominates. Each kg of alum added as a coagulant would therefore produce about 0.44 kg of sludge by weight of dry solids. Water plants typically add 15-20 mg/ℓ of alum although some add as much as 100 mg/ℓ . Any suspended solids present in the surface water will produce sludge of an equal dry weight amount.

Following coagulation, the coagulated solids are allowed to settle in a sedimentation basin and settled solids (sludge) are withdrawn from the bottom. Alum sludge leaving the basin has a suspended solids concentration of generally under one percent. Twenty to forty percent of the suspended solids are volatile, the remainder being inorganic clays and chemical residue. The aluminum hydroxide species represent 30 to 60% by weight of the suspended solids. The volume of sludge is in the range of 0.3 to 1% of the treatment plant flow.

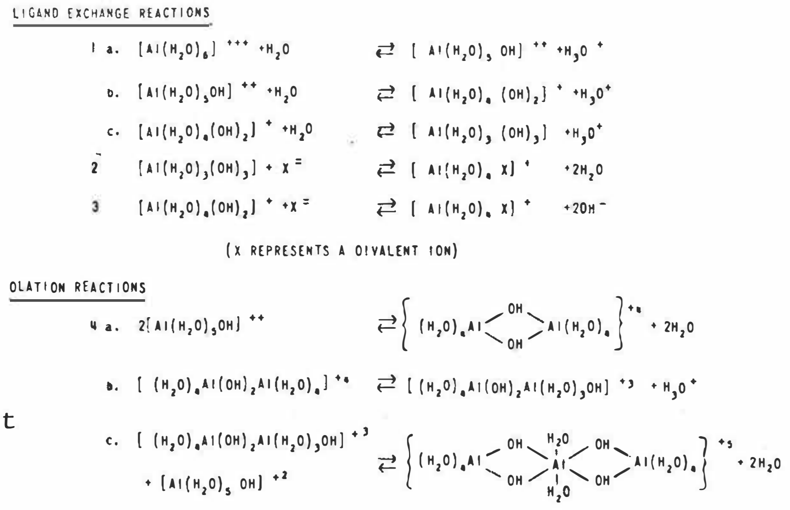

FIG. 1. Aluminum Reactions In Water

SLUDGE TREATMENT AND DISPOSAL

In the past about 97% of the sludge has been directly discharged into the watercourse. The water pollution control act ammendments of 1972 classify alum sludge as an industrial discharge and prohibit its discharge into a watercourse. The regulated elimination of direct sludge discharge has imposed both economic and technological effects on the water supply industry. Most plants have not yet complied with discharge requirements.

Most sludge treatment practices include one of the following: discharge of the waste into the sewer for codisposal with wastewater sludge; lagooning of the sludge with ultimate disposal of the residue at some future time; and mechanical dewatering with landfilling of the residue. Codisposal is often not practical, or access to a sewer may not be available. Mechanical dewatering is very expensive, especially for plants with a water treatment capacity of less than 1.9 X 10^5 m^3/day. The most viable alternative for small plants may be lagooning. Lagooning is essentially a storage method and at some future time the residual in the lagoon must be further dewatered for landfilling.

COAGULANT RECOVERY

It has been recognized since the early 1950's that recovery of the coagulant from the sludge is economically attractive. Recovery would have the benefits of: reducing the chemical requirements thereby decreasing operating costs and conserving natural resources; reducing the weight of solids to be treated since the aluminum hydroxide species would be removed; and, conditioning the sludge making it easier to dewater. Since aluminum hydroxide is amphoteric it could be dissolved by either lowering or raising the sludge pH. Raising the pH has been found to be incomplete and pH reduction is the preferred method. Previous research involved taking sludge from the sedimentation basins to which sulfuric acid is added at a concentration determined by the amount of aluminum in the sludge and the desired level of recovery. Generally, aluminum dissolution of 80% can be expected at a pH of 2.0. The dissolved aluminum, in the form of dilute alum, is separated from the residual solids by a gravity separator. The aluminum rich supernatant is recycled to the coagulant basin and the residual solids are pH adjusted and dewatered. The net aluminum recovery via this process is about 60-65%.

The acidic alum recovery process presents a potentially serious problem in that it is vulnerable to the concentration of impurities in the recovered alum. Such concentration in a recovered alum used for water treatment might cause a degradation of plant filtered water. The potential impurities include those capable of being converted to a soluble form in the acidulation process, such as iron, manganese, chromium, and other metals; a wide variety of organic materials including those associated with high color.

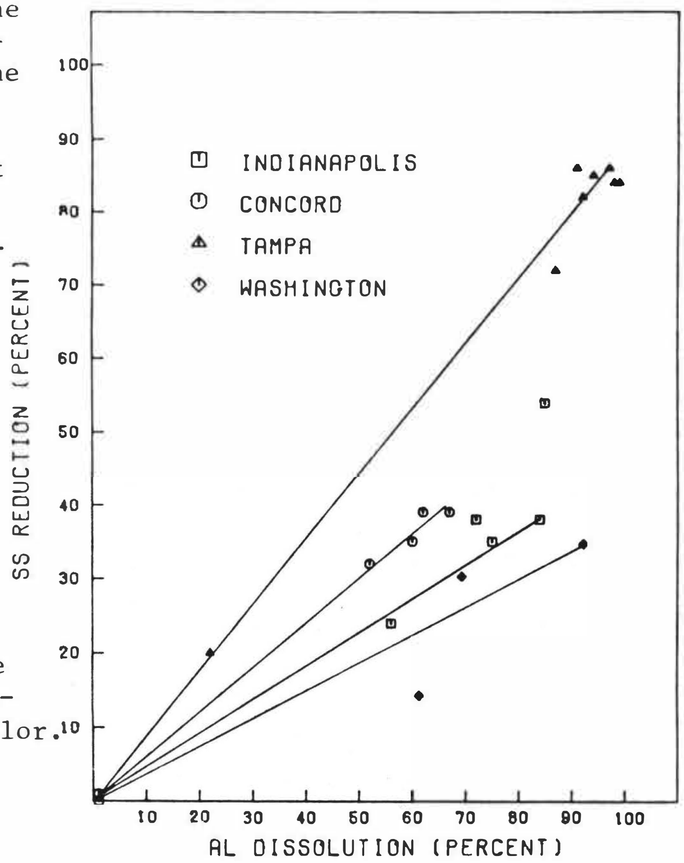

FIG. 2. Relationship Between Suspended Solids Concentration Reduction and Aluminum Dissolution

Until recently, the acidification of alum sludge was considered beneficial prior to pressure filtration at many water treatment plants in Japan Fifteen Japanese water treatment plants, five in the Tokyo area, use an acid alum recovery process ahead of pressure filtration. All of these plants were built between 1965 and 1972. Concern over the possible recycling and concentrating of heavy metals has halted this procedure at sludge treatment facilities built since 1972.

Figures 2 and 3 show the potential benefits of sludge conditioning following acidic alum recovery. Figure 2 shows the dry weight reduction resulting from aluminum dissolution. The sludge from Tampa uses a large coagulant addition for color removal and therefore has a large percentage of aluminum hydroxide species in the sludge. The other three sludges are typical of many water plant sludges, showing a 30 to 40% weight reduction. Figure 3 shows the sludge volume reduction as the aluminum was dissolved.

PREFACE TO CURRENT RESEARCH

In 1972 research was begun to develop a method to recover alum of the same characteristics as commercial liquid alum. The parameters of importance would be metal content of the alum, concentration of recovered alum and coagulant ability. The recovery process would also have to leave the residual solids in a more economically handleable form. Different processes were investigated but liquid-ion exchange appeared to be the most promising. It would be an ideal process for purifying and concentrating a metal.

The next two years were spent reviewing literature, investigating various extractants and evaluating process feasibility. In 1975 the Amercian Water Works Association Research Foundation began supporting this work.

The process development has gone through three modifications: preacidification followed by extraction in a mixer/settler; direct extraction in a mixer/settler; direct extraction in an RTL contactor. Since these modifications have involved different chemistry or flow patterns, this paper has been divided into the above three sections.

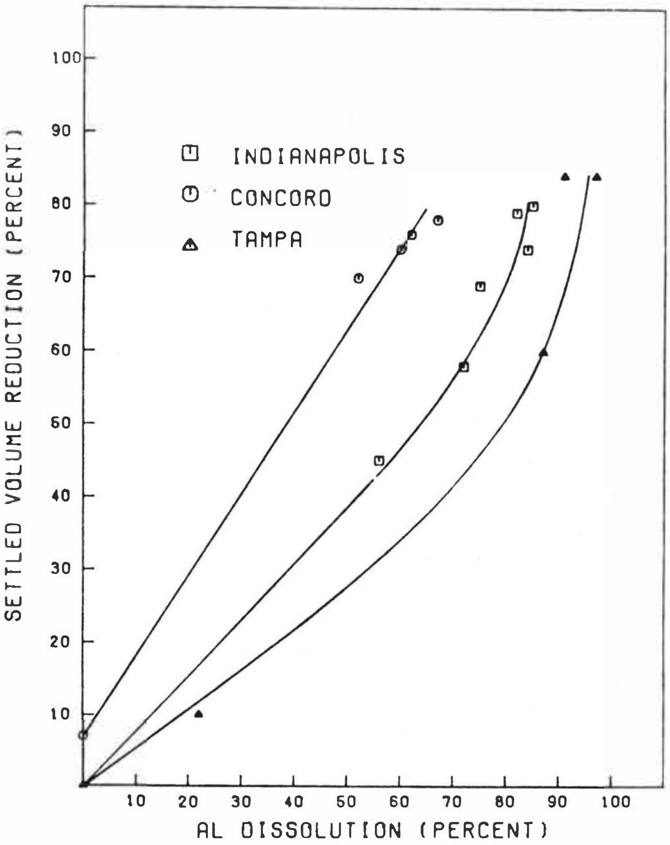

FIG. 3. Relationship Between Sludge Volume Reduction and Aluminum Dissolution

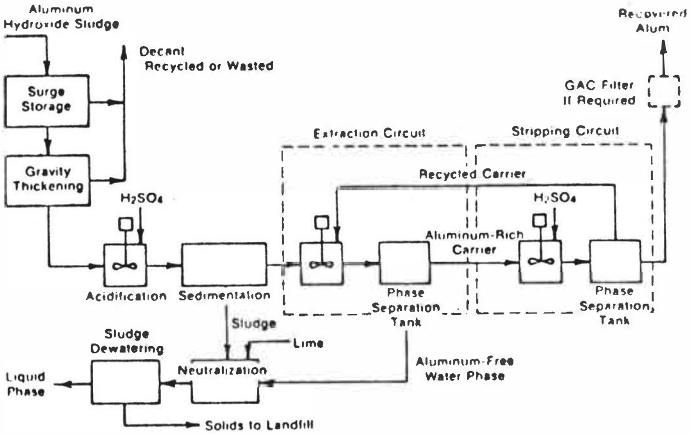

FIG. 4. Schematic Flow Diagram of Basic Process for Alum Recovery by Liquid-Ion Exchange

PREACIDIFICATION-LABORATORY STUDIES

As the process was intially conceived the sludge would be acidified to approximately pH 2 to dissolve the aluminum and potential impurities would also dissolve. The residual solids would be separated from the supernatant via sedimentation or filtration and the aqueous phase fed to the extraction circuit as shown in Figure 4. Therefore, all preliminary extraction studies were conducted at a feed pH of 2.0. Initial extractant screening tests showed that an equal mixture by weight of mono-di(2-ethylhexyl) phosphoric acid* (abbreviated MDEHPA. In this notation the mono ester has two available protons. All molecular weights are reported as the average formula weight of the two esters which is 266) had good extraction properties for aluminum at a feed pH of 2.0. The extraction equilibrium curves are shown in Figure 5. Evidence in the literature and confirmed by these studies has concluded that di(2-ethylhexyl) phosphoric acid (DEHPA) does not favorably extract aluminum at a feed pH of 2.0. Tests were also conducted on

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*Commercially available from Stauffer Chemical Company.

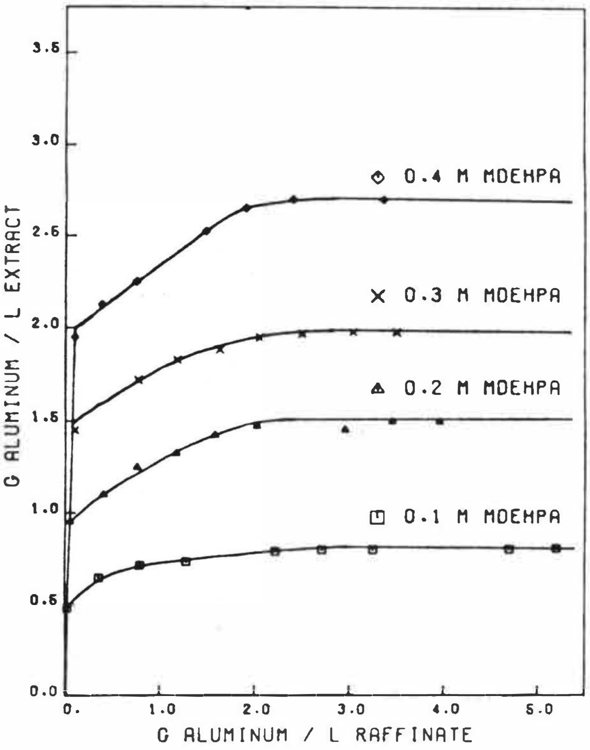

FIG. 5. Extraction Equilibrium Curves for MDEHPA

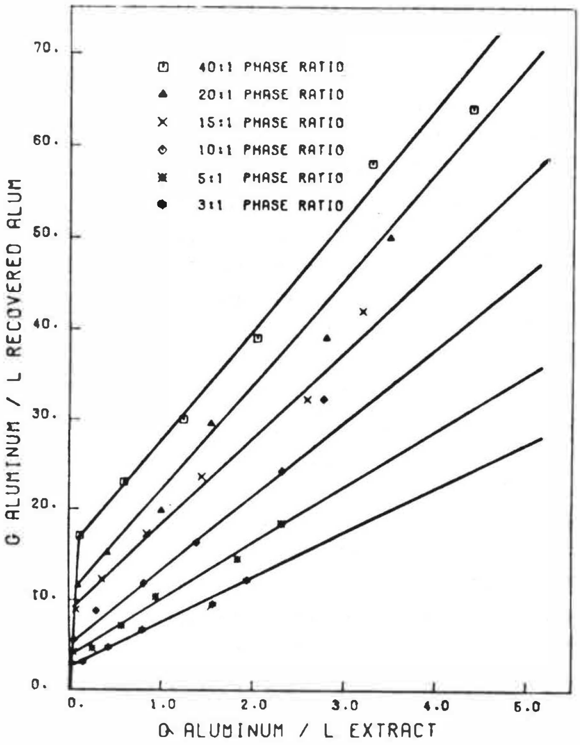

FIG. 6. Stripping Equilibrium Curves for HDEHPA-Al

various diluents, impeller tip speed, equilibration time, and varying feed pH. Separation factors comparing aluminum extraction to selected metals are shown in Table 1. Stripping studies were conducted for different acids and normalities, varying phase ratios, equilibration time and tip speed. The stripping equilibrium curves are shown in Figure 6.

TABLE 1

Selectivity of Aluminum Extraction*

Metal	Separation Factor $(E_a^o)Al^{3+}/(E_a^o)M^{n+}$
Cu(II)	90
Cd(II)	140
Mn(II)	170
Zn(II)	930
Fe(II)	75
Fe(III)	6
Cr(VI)	28

*Initial conditions were 100 mℓ of 500 mg/ℓ aluminum, 25 mg/ℓ selected metal, and 100 mℓ of 0.1M MDEHPA.

Following the first year of basic studies the process appeared feasible. An economic analysis was then conducted to determine if further work was warranted. The following conclusions were drawn: the acid for preacidification and acid requirements in stripping would require 2^+ equivalents of acid per equivalent of aluminum which was a prohibitive cost; when the raffinate stream was neutralized with lime prior to disposal a large amount of gypsum would be formed and the lime demand would be large. The costs to use HCl in preacidification or NaOH for neutralization in order to prevent gypsum formation would be prohibitive. At this point the process was not very attractive.

DIRECT EXTRACTION IN A MIXER/ SETTLER

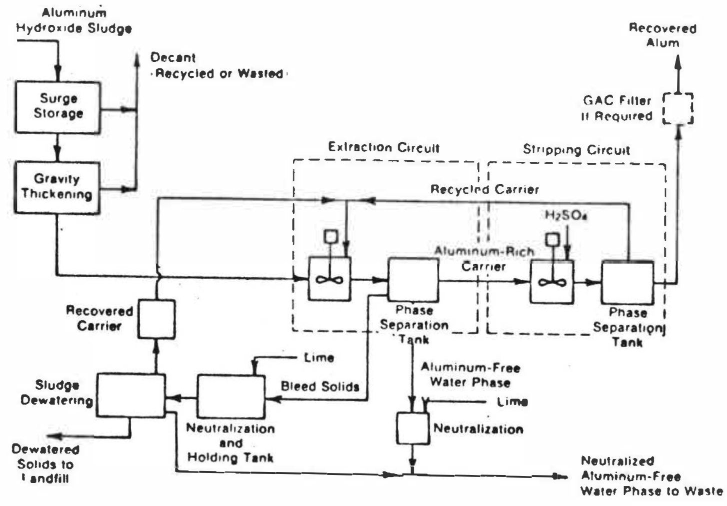

FIG. 7. Schematic Diagram of Modified Process for Alum Recovery by Liquid-Ion Exchange

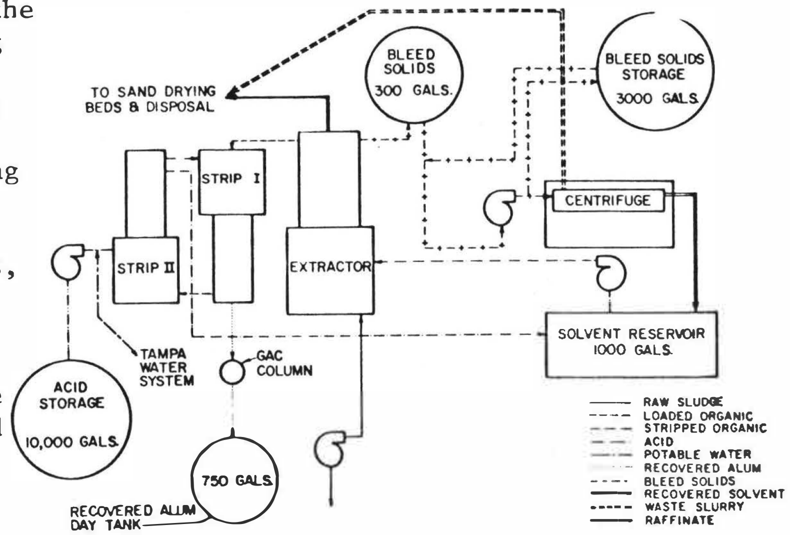

FIG. 8. Demonstration Plant Schematic for Tampa, Florida

Due to the above conclusions the second year of research was spent in process modification, as shown in Figure 7. The major change was that the sludge as received (pH 6, aluminum in the form of aluminum hydroxide) was fed directly to the extraction circuit. In this manner the acid for preacidification would be eliminated and gypsum formation would be prevented. The tradeoff would be higher solvent losses into the solids in the extraction circuit. Unfortunately, there was not sufficient time or funds to redo the extraction tests under the new feed conditions. During the second year a 5 to 15 mℓ/min bench scale plant was designed and operated. It was found that when operating aqueous continuous a stable emulsion was formed. When operating organic continuous, three phases developed in the phase separation tank: extract, raffinate and a third phase collected at the interface which was referred to as bleed solids. The bleed solids were an emulsion of solvent, water and the residual solids. The bleed solids production rate was about 20% of the feed flow rate. The bleed solids were about 50% solvent, 48% raffinate and 2% solids. Since the unextracted aluminum would be in the bleed solids as $Al(OH)_3$ only one extraction stage could be used. Two countercurrent stripping stages proved to be adequate. The bleed solids were treated in a solid bowl centrifuge for solvent recovery. Losses into the residual solids were 0.3 gal/ 1000 gal.

In the third year of research a 10-gpm demonstration plant was constructed at Tampa, Florida. The plant consisted of 1 extractor and 2 countercurrent strippers as shown in Figure 8. The feed sludge averaged 0.14% suspended solids (SS) containing 600 mg/ℓ Al^{3+}. The residual solids were 10 to

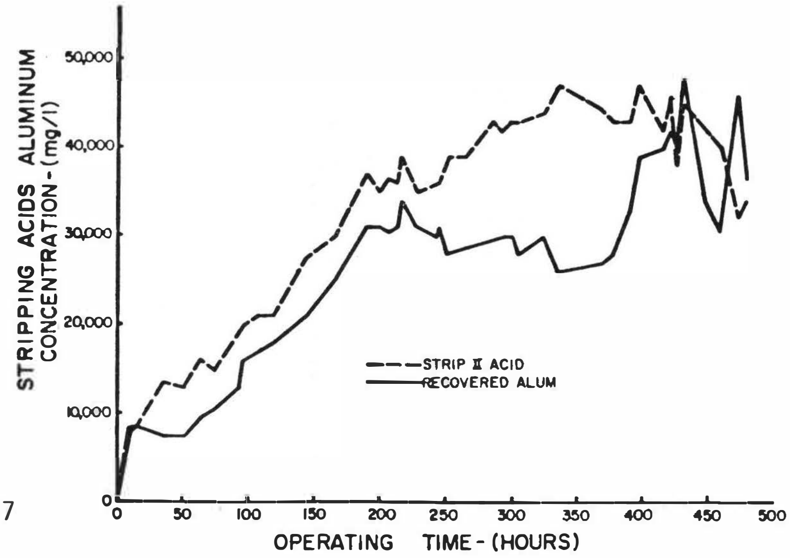

FIG. 9. Aluminum Concentration in Stripping Tanks at Tampa

40% by weight of the feed solids. The bleed solids were to be siphoned off at 2 gpm and the solvent recovered in a scroll centrifuge, simultaneously thickening the residual solids. The recovered alum was to be concentrated to 45 g/ℓ via acid flow-rate control. The extractor was designed to operate at an r of 2:1, ½ of the solvent flow provided by recycle. Extraction efficiency using 15% v/v MDEHPA and 2% v/v TBP in Kermac 627 averaged 91 ± 4%. During operation, two problems were encountered. First, the scroll centrifuge would not operate as designed and would only operate at 0.3 gpm after it was converted to a liquid/liquid separator. Solvent losses were 12 gal/1000 gal, clearly uneconomical. The extractor continually inverted to aqueous continuous even at an r of 2:1, resulting in stable emulsion formation. This was prevented by operating at a high r, however, this resulted in a large amount of aqueous entrainment which in turn made it difficult to concentrate the recovered alum. Figure 9 shows that the aluminum concentration in the second stripper was often higher than the recovered alum. This was accounted for by dilution due to aqueous entrainment in the extract of 2-4 g/ℓ . Measured and calculated aqueous entrainment was directly proportional to r. In order to verify the dilution effect the system was operated at a low r under supervised conditions during the end of the program and the alum concentration quickly rose to the desired level.

To help alleviate the solvent losses, a solids ejector centrifuge was rented for a two week period. With this centrifuge solvent losses were reduced to 2 gal/1000 gal.

Analyses of the solvent showed that the mono ester was completely gone from the solvent, and 7.5% v/v DEHPA remained. Solubility studies on the mono showed that it was lost in three recycles and that DEHPA had been extracting the aluminum. Equilibrium curves on DEHPA at a feed pH 6 (where the Al^{3+} exists as $Al(OH)_3$) showed that 10% v/v DEHPA could extract 90% of 1600 mg/ℓ Al^{3+}. At a feed pH 5.0 (where the Al^{3+} exists as an ion, such as $Al(OH)_2^+$) extraction was very poor. It was therefore indirectly found that DEHPA had a high extraction coefficient for aluminum if the aluminum was fed as $Al(OH)_3$ rather than a dissolved ion.

DIRECT EXTRACTION IN AN RTL CONTACTOR

The production of the bleed solids at such a high rate using a mixer/settler required constant operator supervision and continual centrifuge operation. The centrifuged solids contained a large amount of solvent which was uneconomical to replace and the solvent in the solids created a treatment and disposal problem. Work was therefore begun in the laboratory to minimize the production of the emulsion. A 10-cm diameter RTL contactor (formally called a Graesser raining bucket contactor) was utilized for extraction. The contactor works on the principle of gently contacting the two phases so as to maintain a defined interface. The laboratory unit operated in the laminar flow regime with a reynolds number of about 700. The extraction system was first set-up in a countercurrent flow. Extraction efficiency quickly dropped. This presumably was because the mono component of the MDEHPA was water soluble, and the di-component does not extract well at a low pH. In each successive stage of countercurrent operation, the pH would be lower and therefore efficiency would decrease. The contactor was then operated in a cocurrent flow pattern with successful extraction using a long detention time.

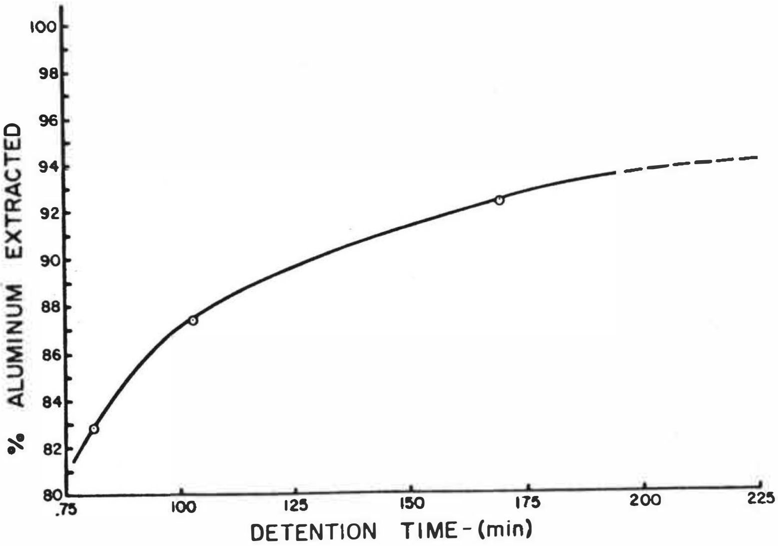

FIG. 10. Effects of Detention Time on Aluminum Extraction for RTL Contactor at Tampa.

TABLE 2

Results of 45-cm dia RTL Contactor

	mean	std dev
Al^{3+} in sludge (mg/ℓ)	1154	374
Al^{3+} in raffinate (mg/ℓ)	49	34
Feed Sludge SS (%)	0.61	.11
Raffinate SS (%)	.30	.15

The most favorable result found in the laboratory was that there was no emulsion production and that the residual solids were contained in the raffinate stream. The residual solids exhibited improved settling characteristics compared to the original sludge and quickly settled to a 6-10% SS concentration. Solvent losses were measured at 0.3 gal/1000 gal.

Due to the encouraging results, a 45-cm diameter contactor by 3-m long was installed at the Tampa pilot plant. Figure 10 shows that 90% extraction could be obtained at a detention time of 110 min using 5% v/v DEHPA to extract 1100 mg/ℓ Al^{3+}. A summary of results is shown in Table 2.

Figure 11 shows that an increase in $\underline{r}$ could increase the recovery. Only a very short period of time was available for testing but it was felt that by increasing the extractant strength that the detention time could be lowered.

The pilot contactor had a reynolds number of 4500 putting it into the turbulent region. Perhaps because of this, there was some production of emulsion. This emulsion exited the contactor with the raffinate and tended to float. The emulsion was 0.5 to 1% by volume of the raffinate and contained 20% solvent, corresponding to a loss of 1.5 gal/1000 gal if the emulsion were not treated. If this floating emulsion were collected and centrifuged, losses could be kept to under 0.5 gal/1000 gal. Purchase of a centrifuge to recover this solvent would be economically justified. The Tampa project was closed in November 1979.

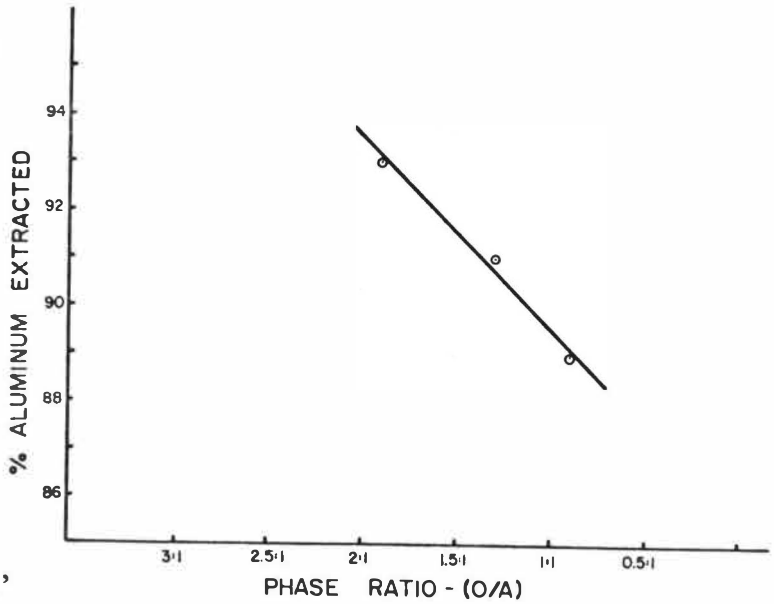

FIG. 11. Effect of Phase Ratio on Aluminum Extraction in RTL Contactor at Tampa

In February 1980 a 1 gpm pilot plant began operation in Niagara County, N. Y. This plant was built to be used with the RTL contactor for extraction. This sludge contains about 250 mg/ℓ Al^{3+} and 4% DEHPA is being used. To date, 90% recovery has been obtained at a detention time of 60 min.

RECOVERED ALUM QUALITY

Commercial alum is about 8.3% Al_2O_3. Successful concentration of the recovered alum to 8 to 8.3% Al_2O_3 has been obtained. Table 3 shows a comparison of metals in the alum recovered at Tampa compared to commercial alum. It can be seen that the metals in the recovered alum are generally lower than in commercial alum, and that a large percentage of the metal is from the feed acid used in stripping.

TABLE 3

Metal Concentration of Recovered Alum

	Metal Value, mg/ℓ		
	Recovered Alum	Acid Used in Stripping	Commercial Alum
Ba	1.0	1.0	1.0
Cd	0.4	0.4	0.7
Cr	2.3	0.1	22.0
Co	1.8	1.2	3.0
Cu	1.5	0.6	1.5
Fe	30.0	30.0	850.0
Pb	16.0	4.0	10.0
Mg	40.0	7.0	33.0
Mn	7.0	0.7	7.0
Ag	0.6	0.1	0.6

ECONOMICS

Detailed economic analyses have been conducted for various sized plants and sludge conditions based upon the results of testing at Tampa.

Figure 12 shows the operating costs of the process using the RTL contactor for extraction (not including amoritized capital). Operating costs include power, labor, chemicals, maintenance and credit for 90% alum recovery. Most plants could operate the alum recovery process under break even or better conditions. The sludge can usually be thickened in the sedimentation basin or in an external thickener to 2000 mg/ℓ Al^{3+} or greater. The key to installing a process is if the residual solids can be treated less expensively than the original sludge. The recovery process may be thought of as a "no cost" sludge conditioning step.

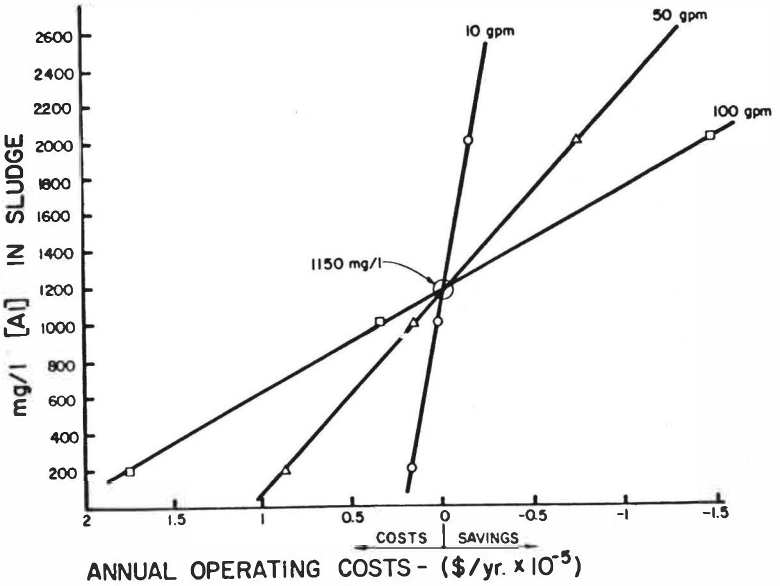

FIG. 12. Operating Costs of Alum Recovery Process for Different Sludge Flow Rates

FUTURE WORK

The Niagara County pilot plant is scheduled to run through May 1980. Several laboratory studies are ongoing to test the viability of the process on various sludges and some of these studies may lend to further pilot or full-scale installations.

Other developmental work is being conducted on recovery of alum from wastewater, pulp and paper and aluminum anodizing sludges. Studies on cadmium removal from wastewater sludges to enhance land application is also being researched. The research is expected to branch out into recovery of other metals from sludge materials.

Work is proceeding on developing an extractant which would have a higher affinity for Al^{3+} than DEHPA but not be as soluble as the mono component of MDEHPA.

For the purposes of conducting this research Michigan State University has established a research center with the primary objective of studying and developing solvent extraction techniques in waste treatment.

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DECOMPOSITION OF BUTEX IN NITRIC ACID SYSTEMS AND THE IMPLICATIONS FOR SAFETY IN ITS USE AS A SOLVENT

C. Hanson and I. Wade

Schools of Chemical Engineering,
University of Bradford,
Bradford,
West Yorkshire BD7 1DP,
UK.

ABSTRACT

Butex (ββ' dibutoxy diethyl ether) has found limited use as an extractant, particularly in nuclear fuel reprocessing. Its use in nitric acid media is complicated by unpredictable and possibly violent reaction with the acid : a "fume-off". The investigation shows the process to involve slow degradation with formation of butanol which reacts violently after reaching an adequate concentration, nitrous acid catalysing the reaction.

INTRODUCTION

During the last decade there has been increasing interest in the safety and environmental features of solvent extraction plants. Fire is an obvious hazard in most such installations and has been discussed in some detail (1,2). Similarly, attention has been called (3,4) to the possible environmental hazards from the small losses of organic reagents which may occur in aqueous raffinates and subsequently enter water courses. A third area, which has not yet received the same degree of consideration, is the possible effect of degradation by-products which can build-up in the solvent phase. These may be quite harmless but there are cases where violent reactions can take place once some critical concentration is exceeded. Consideration of the nature of degradation by-products should therefore be a feature of any safety assessment. Unfortunately, elucidation of the degradation route is often very complex, as in the case considered in this paper.

"Butex" is the commonly used name for the triether ββ'-dibutoxy-diethyl ether. This is a solvating extractant which was used in some early plants for the reprocessing of nuclear fuels. Flowsheets for some of these have been fully documented (5). It has also been reported for use in the refining of gold (6) and certain other specialist separations, e.g. polonium 210 from nitric acid solutions of irradiated bismuth (7). In all cases the Butex is contacted with aqueous solutions of nitric acid (in the gold process it is with aqua regia). It has been recognised for some time that Butex-nitric acid mixtures can exhibit explosive tendencies under certain conditions (8,9), although it has not been possible to define those conditions with certainty or to specify the precise reaction. There is not always any immediate reaction apparent and an induction period is commonly observed. Brown fumes of nitrogen dioxide are then evolved and the temperature rises rapidly. As might be expected, such a reaction does not commonly occur under the acidity conditions used on an operating plant but, nevertheless, it has been known to happen. Such plant occurrencies have been termed "fume-offs" from the brown fumes of nitric oxide which arise. The fact that these can occur without warning is a matter of concern for plant operators (5) and has led to previous work on the phenomenon. The present study arose from a specific incident on a plant using *Butex*, which prompted a desire for a better understanding of the process and the possible means by which the onset of a fume-off could be detected.

Previous work on the decomposition of *Butex* in nitric acid solutions (8, 9) suggests that the pure ether is comparatively stable, no reaction being found with even concentrated nitric acid at temperatures up to 68°C or with acid up to 6M in strength even at the boiling point. Acids above 6M react slowly at high temperatures. However, impure *Butex* is reported as being much more reactive, reacting readily with concentrated nitric acid at room temperature and with acid strengths down to about 4M at elevated temperatures. As already indicated, a period of induction is commonly observed. Chemical changes do take place during this period, the main organic product apparently being butanol. After the violent reaction or "fume-off", the main components detected have been monobutyl cellosolve, monobutyl carbitol and oxalic acid, with only a trace of butanol. The introduction of nitrogen dioxide into an otherwise unreactive mixture of *Butex* and nitric acid has been shown to result in a violent reaction, suggesting that oxides of nitrogen are necessary for reaction.

Schulz and Richardson (7) have reported that the addition of sulphamic acid is an effective way of preventing nitrite catalysed nitric acid attack on *Butex*. The nature of the decomposition products has also been considered by Howells et al (5), who have shown aliphatic acids such as butyric and oxalic to be formed as well as a mixture of gases including NO, NO_2, CO, CO_2 and H_2.

It seems clear that the violent reaction taking place in a fume-off does not involve the *Butex* itself, certainly until after the initiation, but the products of a slow prior decomposition of the *Butex*. Butanol appears to be the principal product at this stage. After reaching a critical concentration, the by-product or products react vigorously and exothermically with evolution of large volumes of CO_2 and NO_2. It seems likely that the two steps involve (i) fission and hydrolysis, followed by (ii) oxidation.

EXPERIMENTAL

Materials

A supply of *Butex* was kindly provided by British Nuclear Fuels Limited. This had received pre-treatment by the normal industrial method. It was used directly in the preliminary experiments but for all others was first dried with anhydrous sodium sulphate and then treated with lead peroxide, as recommended by Susano (8), to remove any peroxides. It was then stored in the dark. Other chemicals were of normal Analar grade.

Preliminary Experiments

A number of preliminary tests were conducted to help define the conditions under which a "fume-off" occurs. Samples of *Butex* were treated with various concentrations of aqueous nitric acid (equal volumes) both at ambient and elevated temperatures. The effects of agitation and interfacial area were also studied, the latter by using samples of identical volume in beakers of different diameter. Finally, samples of different total volume (same phase ratio) were treated in beakers of identical size to see the influence of scale.

Study of Aqueous Phase Conditions

Work was carried out to ascertain the influence of nitric acid concentration on the length of induction period and also to monitor the changes in nitric, nitrous and total acid contents of the aqueous phase during such periods. The latter was aimed both at providing a better understanding of the process and possibly a means of obtaining warning of a latent "fume-off" which could be used in industry. Equal volumes of the purified Butex and aqueous nitric acid were mixed and then allowed to stand at ambient temperature, samples of the aqueous phase being removed at fixed time intervals for analysis. Full details of the analytical techniques are available elsewhere (10).

Previous workers have spoken (7,8) of nitrites or nitrogen oxides catalysing nitric acid attack on Butex and similar materials. Tests were therefore carried out with addition of sodium nitrite, ferrous sulphate and urea.

Study of Organic Phase Conditions

The influences of various possible Butex purification methods were checked. In addition to the anhydrous sodium sulphate/lead dioxide treatment described above, comparative tests were made by (i) washing the Butex with ferrous sulphate solution acidified with sulphuric acid as used by Murdoch and Pratt (11) [basically the method recommended by Vogel (12) for removal of ether peroxides], (ii) treating with activated alumina as recommended by several workers (13-15), and (iii) washing with water. An untreated sample was used as control. Equal volumes of the Butex samples and concentrated nitric acid were placed in beakers in the laboratory and the time period noted up to appearance of a fume-off. After each of the treatments described, a sample of the Butex was analysed by G.L.C. In view of the known presence of acidic impurities in commercial Butex, the tests were also carried out on a sample after washing with 5% Na_2CO_3 solution. Finally, distillation was used as a purification method.

The second part of the investigation involved subjecting samples of the organic phase removed at regular intervals during the induction period (as in the study of changes in the aqueous phase composition) to G.L.C. analysis. This was found more useful than infra-red analysis, a conclusion also reached by Gaunt et al (16). The equipment used comprised a Pye series 104 chromatograph with flame ionisation detector. Stock columns were not found to be satisfactory. After extensive tests, a 5ft glass column was used with Chromasorb W DMCS as support and Carbowax 1500 as liquid phase (10% initial loading). Analysis was carried out at 131°C. It was found possible to separate 20 components present in the samples. Further details are available elsewhere (10).

Study of Stability of By-Products

The preliminary work showed pure Butex to be relatively stable to even concentrated nitric acid and it is clear that the Butex itself cannot be directly responsible for the violent process of a "fume-off". The latter must involve one or more of the products of a slow decomposition of the Butex. These products are known to include butanol, possibly other alcohols in small amounts, 2-butoxy-ethanol, butyl digol and oxalic acid, amongst others. Tests were carried out on each of the above compounds, involving prolonged contact with nitric acid and regular analysis of samples of the organic phase by G.L.C. to compare with the chromatogrammes obtaines in similar tests on Butex.

RESULTS AND DISCUSSION

Preliminary Experiments

No violent reaction was observed between Butex and aqueous nitric acid of up to 5N strength even at temperatures up to boiling, although some attack apparently took place as evinced by colour changes.

When concentrated nitric acid (s.g. 1.42) was used, a violent "fume-off" was observed in virtually all cases when semi-adiabatic conditions were employed (i.e. standing in the laboratory) but only after a period of induction, the length of which varied from some 50 minutes to over 21 hours, depending on the conditions. The precise length of the induction period was difficult to measure accurately because of the long duration of the experiments but certain trends were clear:

(i) If the two phases are initially mixed and then allowed to separate and stand in contact, the induction period is much shorter (by a factor of 2 or more) than when the phases are just contacted but without intermixing.

(ii) Increase in the interfacial area between the phases (but with the same volumes) results in an almost proportional decrease in the length of the induction period.

(iii) Under conditions of continuous mixing, no violent "fume-off" took place, although there was a gradual reduction in the volume of the aqueous phase.

(iv) Using beakers of identical size, doubling the quantity of the reagents more-or-less halved the duration of the induction period.

(v) Under isothermal conditions (samples held in thermostatted water bath at 40°C), no "fume-off" was observed after 43 hours, although colour changes had taken place.

(vi) If the phases were equilibrated but then removed from contact, no "fume-off" took place, although colour changes were observed.

(vii) Significantly differing induction periods were found under identical conditions when using two different samples of commercial Butex obtained from different sources.

The first three of these observations are consistent with the initial step being transfer of nitric acid from the aqueous to the organic phase. During this stage, the yellow colour of the organic phase becomes deeper. The acid phase becomes green and bubbles of gas (presumably nitrogen oxides) are formed on the acid side of the interface. Towards the end of the induction period, the temperature rises. The organic phase then turns brown in colour and fumes of NO_2 are evolved. The vigour of the reaction depends on the temperature rise at the end of the induction period. If the heat released is removed, as in the isothermal reaction, the decomposition remains controlled and no "fume-off" occurs. On the other hand, when the volume of the reactants was increased without a corresponding increase in surface area for heat dissipation (case (iv)), the vigorous reaction is enhanced. All observations point to the vigorous reaction involving one or more of the decomposition products of Butex rather than the ether itself.

Changes in Aqueous Phase Conditions

Tests were conducted with 3, 5, 10, 12 and 13.6 N nitric acid and purified Butex at laboratory temperature over periods of up to nine days. No "fume-offs" occurred. However, colour changes were observed and analysis of both phases showed a steady loss of nitric acid from the system, the rate of loss increasing exponentially with increase in initial nitric acid concentration. The total nitric acid loss was always found greater (by 20-25%) than the total acid loss (calculated as equivalents).

Concentrated nitric acid had to be used to investigate composition changes up to an actual "fume-off". No significant change in acid concentration was observed until the onset of the "fume-off". No nitrous acid was detected until immediately prior to a "fume-off", when the temperature had started to rise. Analysis of the aqueous phase thus did not provide any warning of the onset of a "fume-off".

When a sample of Butex was pre-saturated with an aqueous solution of sodium nitrite and concentrated nitric acid then added, a reaction rapidly ensued, confirming the previous finding that nitrites catalyse the process. Similarly, when a small amount of ferrous sulphate was dissolved in concentrated nitric acid and this was then added to Butex, a "fume-off" occurred almost immediately and the temperature rose to above 60°C within two minutes. This again confirms the dramatic effect of nitrous acid or nitrogen oxides. When a saturated solution of urea in concentrated nitric acid was employed, no "fume-off" was observed over an 11 day period, although some slow reaction did take place with evolution of a gas. In the corresponding control experiment, a "fume-off" took place after 3½ hours.

These observations suggest the following:

(i) Nitric acid attacks some organic component in the system, thereby liberating NO and NO_2, the proportion of the latter increasing relatively with increase in acid concentration.

(ii) The NO is either lost to atmosphere or dissolves in the organic phase (it is not appreciably aqueous soluble). The NO_2 dissolves in both phases and causes the characteristic colours which are observed.

(iii) The reaction is both autocatalytic and exothermic so that it gathers momentum rapidly once it reaches an appreciable rate, giving the familiar violent "fume-off".

(iv) There is clearly a complex relationship between the nitric acid, nitrous acid and nitrogen oxides which are distributed between the two phases.

Changes in Organic Phase Conditions

While Susano (8) failed to detect peroxides before or after a "fume-off", peroxides of ethers are notoriously dangerous and so must be considered a possible cause of the violent reaction between Butex and nitric acid, especially as it is known that peroxides do form in Butex during storage (11). The results of the various treatments for peroxide removal are summarised in Table I in terms of the period required for a "fume-off". In view of the length of time involved, it was not always possible to obtain the precise duration of the induction period but only the observation points before and after the event. An improvement is seen with each form of treatment. However, the improvement cannot be entirely correlated with peroxide removal.

TABLE I - Results of fume-off tests after various peroxide removing treatments

Treatment	Fume-off time (min.)
filtered only	$65 < t < 80$
anhyd. Na_2SO_4 + PbO_2	$t = 310$
activated alumina	$t = 430$
water washed	$555 < t < 1455$
acidified $FeSO_4$ solution	$660 < t < 2880$

The fact that the induction period is greatly lengthened by washing with either water or an aqueous solution appears significant. It could be that this saturates the Butex with water and so dilutes the nitric acid which is taken up. However, G.L.C. analysis of the water washings showed that most of the butyl digol, butyric acid and butanol present had transferred to the aqueous phase.

Washing with aqueous ferrous sulphate, sodium carbonate and water alone led to comparative induction times to "fume-off" of 228, 560 and 360 mins., respectively. Chromatogrammes showed butyric acid, butyl digol, 2-butoxy ethanol, propanol and butanol to have been removed by the sodium carbonate. It was concluded that one or more of these impurities are responsible for the "fume-off" phenomenon and that, as stated by Dukes (17), any peroxides present are not the primary cause.

A trial distillation for purification of Butex was carried out at atmospheric pressure. The product gave a "fume-off" in only 15 minutes. It was apparent that Butex decomposes on heating above 120°C (distillation range at atmospheric pressure 248-258°C). Purification must be carried out by distillation at low pressure.

In the test carried out with continuous mixing of the two phases, no "fume-off" took place, although colour changes showed a reaction to have taken place. Analysis after nine days showed significant increases in the concentrations of butyl digol, 2-butoxy ethanol, and butyric, propionic and acetic acids. Another compound appeared which is believed to be a nitro-compound of butyl digol.

Chromatogrammes carried out on samples taken during semi-adiabatic non-agitated runs showed increases in all the above components. Ethanol, propanol and butanol were also formed but some transferred to the aqueous phase. The carboxylic acids distributed between the two phases. So far as could be ascertained, the main reaction between Butex and nitric acid takes place in the aqueous phase.

The concentrations of most known impurities did not change appreciably during the period of induction. However, the concentrations of propanol and 2-butoxy ethanol were observed to fall immediately prior to a "fume-off". This suggests that butanol alone is not responsible for initiation of the "fume-off" but that propanol could be a key component.

Specific By-Products

The study was restricted to certain known impurities and by-products.

2-butoxy ethanol proved less reactive than Butex itself and did not give a "fume-off" under any conditions. It appeared to undergo slow nitration. The behaviour of butyl digol proved similar, although it was somewhat more reactive and appreciable colour changes were observed which may be involved with those observed with impure Butex. 2-butyl-ethanol plus butyric, propionic and acetic acids were all formed.

In contrast, butanol reacted quickly. After a preliminary colour change, brown fumes were evolved and a violent reaction ensued, causing the liquids to boil. Once this was over, two liquid phases remained, which continued to react slowly. Analysis showed the formation of at least ten different compounds, including propanol, ethanol and acetic, propionic and butyric acids. In contrast, when the butanol was pre-saturated with urea, no reaction took place.

It is clear from this that, of the three primary decomposition products of Butex, i.e. butyl digol, 2-butoxy-ethanol and butanol, it is the presence of the latter which is required for a violent reaction. It is also clear that nitrous acid is necessary for a "fume-off". The fact that lower alcohols and acids are formed from butanol suggests a chain reaction, the first step of which is: $C_4H_9OH + 2HNO_3 \rightarrow C_3H_7COOH + 2HNO_2 + H_2O$

If the nitrous acid formed is removed by urea, no further reaction takes place. Otherwise the following take place under the action of both nitric and nitrous acids:

$$\begin{aligned} C_3H_7COOH &\rightarrow C_3H_7OH + CO_2 \\ C_3H_7OH &\rightarrow C_2H_5COOH + H_2O \\ C_2H_5COOH &\rightarrow C_2H_5OH + CO_2 \\ C_2H_5OH &\rightarrow CH_3COOH + H_2O \end{aligned}$$

Nitrous acid or nitrogen oxides are formed at each step.

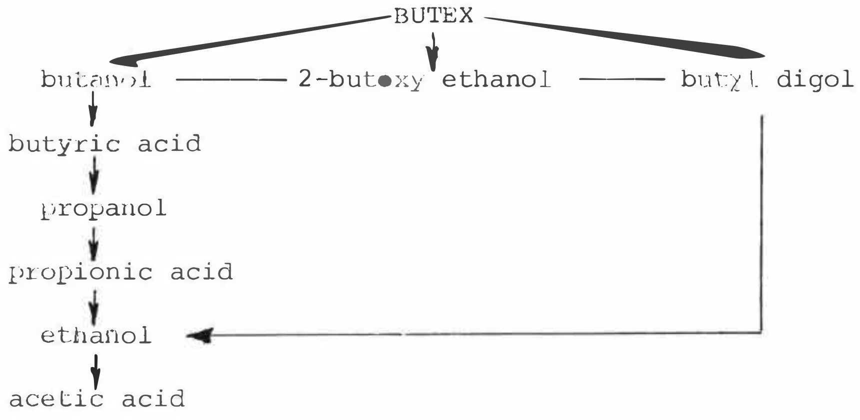
Propanol and ethanol, as expected, reacted in a similar manner to butanol.

While it has been reported (18) that the action of nitric acid on oxalic acid is autocatalytic and exhibits an induction period, we did not find any evidence of reaction after several days. Hence this is unlikely to be involved in a primary manner in a Butex "fume-off".

CONCLUSIONS

Butex is progressively decomposed by aqueous nitric acid. At low acid concentrations the reaction is primarily nitration but at high concentrations it is oxidation. Many simultaneous reactions occur but the most violent of these, and the key process in a "fume-off", involves butanol and nitrous acid, both formed as products of an initial slow decomposition. The violent nature of the reaction is accentuated in heterogeneous systems where the concentrations of butanol and nitrous acid can build-up in the separate phases during the induction period. The reaction is exothermic and autocatalytic, the rate therefore increasing rapidly unless the heat can be dissipated.

The following reaction sequence is proposed, based on the observations which have been made:



While this study has been restricted to Butex, it illustrates how slow degradation of a solvent can sometimes give products which could be deleterious to safety.

ACKNOWLEDGEMENTS

The authors would like to acknowledge financial support from the Health and Safety Executive (UK) and assistance from British Nuclear Fuels Limited with discussions and provision of Butex samples.

Note: A more detailed description of the project is available elsewhere (10).

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PURIFICATION OF OILY WATER BY SOLVENT EXTRACTION

K.R. ROBILLIARD, G.THORSEN, A.GRISLINGÅS

CHEMICAL ENGINEERING LABORATORY
TECHNICAL UNIVERSITY OF NORWAY

TRONDHEIM, NORWAY

As a result of the Intergovernmental Maritime Consultative Organization (IMCO), Conference of Marine Pollution of 1973, very stringent restrictions have been placed on the oil content of ballast and washing waters discharged from oil tankers and other vessels on the high seas (1).

Some of the processes devised to meet these requirements include the "load on top" (LOT) method, as well as the use of oil-water separators, of various brands. The former requires that the dirty (oily) water be fed to a storage or slop tank and the mixture allowed to settle and separate; thus the relatively clean water from the lower zones may be discharged and new oil cargo loaded on top, as required. This method is, however, specially unreliable since it is difficult to maintain settling conditions on board a rolling ship. The latter employs apparatuses which ingest the oil-water mixture and discharge the separated components (2,3). Such equipment contains many internal components, in order to provide a high contact surface area, and is generally quite expensive. Moreover, it does not always meet the IMCO requirements (4).

The work undertaken in this laboratory investigates the use of solvent extraction (SX), in a mixer-settler apparatus, in order to remove oil (dispersed) from polluted water.

Water is contaminated with up to 1 000 ppm of crude oil (from the North Sea and other fields) dispersion. This phase is contacted, in the mixer-settler with an organic solvent (mainly paraffinic). In the mixer, the aqueous phase is dispersed, and each phase has a residence time of one minute (or less). The process was operated at flowrates of up to 0.1 $cm^3 cm^{-2} s^{-1}$; the organic phase being recycled, while the aqueous phase made one pass through the apparatus. The discharged aqueous phase was analysed for organic content.

These results were compared with the settling rates of similar oil-water dispersions (for performance of LOT c.f. SX). Very long times (100 hours or more) were required for the lower regions of a tanker's hold filled with dispersion to reach acceptable levels for discharge (generally 100 ppm) (5). On the other hand, SX treatment (laboratory scale) of only water gave immediate outputs, consistently below 100 ppm, irrespective of the aqueous feed oil content. It should be noted, however, that this performance was dependent on the oil content of the organic phase. The use of coalescence screens packed with hydrophobic and hydrophilic fibrous material, greatly assisted phase separation in the settler.

The use of Ekofisk Crude Oil as the organic solvent phase to extract its own dispersion from an aqueous phase was quite successful. The implications of this aspect are potentially high.

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MECHANISM OF RAFFINATE CONTAMINATION BY THE ORGANIC PHASE IN LIQUID-LIQUID EXTRACTION AND METHODS OF PURIFICATION.

I.N. Kremenskaya

Institute of Solid State Physics
USSR Academy of Sciences

142432 Chernogolovka
Moscow District, USSR.

In the course of solvent extraction processes, aqueous phases (e.g. raffinates and stripping liquors) can become contaminated by the organic phase.

The contamination process can be either an equilibrium (dissolution of the extractant and diluent) or a non-equilibrium process owing to the formation of micro emulsions, microsuspensions and colloidal solutions.
Such heterogeneous process are often responsible for a sharp drop in the distribution coefficients of an extracted metal while decreasing its concentration.

A comparison between different techniques for purification of the aqueous phase leads to the conclusion that sorption method are advantageous.

Polymeric sorbents based on polystyrene and divinylbenzene are considered to be most useful. This macroporous sorbent possesses high mechanical strength, enhanced chemical stability to water and organic solvents and does not swell or dissolve in them.

A series of examples have been given concerning the purification of the salts of alkali metals, Al, Co, Ni etc. using different extractants including sorption purification of raffinates with polymeric sorbents. The pure salts obtained were characterized by the content of organic impurities. The content of the latter did not exceed 10^{-5} to 10^{-6} %.

The sorbents proposed as well as polymeric macroporous materials of other types can be used successfully not only for purification of the product but also to absorb traces of extractants and diluents from waste liquors from liquid-liquid extraction processes. The last fact is of considerable environmental importance.

Copper Extraction
Session 10

Co-chairmen : J.A.J. Tumilty (Acorga Ltd., Wilmslow, U.K.)
A.P. Van Peteghem (University of Gent, Belgium)

10A

80-217	Four years of copper solvent extraction and electro-winning at Twin Buttes. H.R. Moyer, Anamax Mining Company, Sahuarita, Arizona, U.S.A.
80-228	Solvent extraction facilities at Kennecott's ray mines division. T.I. Probert, K.J. Richards, C.K. Vance and N.J. Nebeker, Kennecott Copper Corp., Salt Lake City, Utah, U.S.A.
80-224	The orifin of the selectivity of oxine and oxime type reagents for copper (II) over iron (III). C.A. Fleming, B.R. Green and K.G. Ashurst, National Institute for Metallurgy, Randburg, South Africa.
80-73	Investigation of the catalytic mechanism in the extraction of copper with mixtures of the pure active hydroxyoxime isomers of LIX64N. L. Hummelstedt, E. Paatero, T. Nyberg and L. Rosenback. Abo Akademi, Abo, Finland.
80-76	Copper precipitation from loaded Kelex 100 by reaction with hydrogen. G.P. Demopoulos and P.A. Distin, McGill University, Montreal, Canada.
80-77	Studies on the solvent extraction of copper (I) from sulfate and chloride media. D.M. Muir, M.D. Benari and J.S. Preston, Murdoch University, Murdoch, Australia.

10B

80-60	Solvent extraction and direct hydrothermal precipitation of cuprous oxide from loaded carboxylic acid. Lung Tsuen-Ni and Chen Cheng-Kaung, Industrial Technology Research Institute, Hsin-chu, Taiwan, China.
80-72	The behaviour of Syn-2-Hydroxy-5-Nonylbenzophenone oxime in the extraction of copper with LIX65N and LIX64N. E. Paatero and L. Hummelstedt, Abo Akademi, Abo, Finland.
80-74	Colloidal silica in the solvent extraction of copper with oximes. J. Menacho Llana, Centro de Investigación Minera y Metalúrca, Santiago, Chile.
80-75	The influence of the structure of oxime derivatives of 2-Hydroxy-5-Alkyl-benzaldehyde on copper extraction from acid diluted sulphate solutions. D. Stepaniak-Biniakiewicz and J. Szymanowski, Politechnika Poznanska, Poznan, Poland.
80-80	Copper extraction studies using purified LIX34. G. Sandström and L. Hummelstedt, Abo Akademi, Abo, Finland.
80-189	Extraction of copper from sulphate aqueous solution by oxime type extractants. Z. Maksimović, A. Ruvarac, A. Kostić-Pulek and J.A.J. Tumilty, Boris Kidric Institute, Vinca, Yugoslavia and Acorga Ltd., U.K.

FOUR YEARS OF COPPER SOLVENT EXTRACTION AND ELECTROWINNING AT TWIN BUTTES

H. R. Moyer
Metallurgical Manager

Anamax Mining Company
Sahuarita, Arizona, U.S.A.

ABSTRACT Commissioned in June-August, 1975, the Twin Buttes Oxide Plant treats about 9,800 dry short tons per day of ore at 1.28 percent copper, through crushing, grinding, agitated leaching with sulfuric acid, and countercurrent decantation washing. The resulting solution, bearing 3 grams copper per liter at pH 1.9, is clarified in reservoirs, steam heated when appropriate, and treated in two solvent extraction trains at 3,100 gals. per minute each. Each train utilizes self-pumping mixer-settlers, four extracting and two stripping, and Henkel Corporation's LIX-64N extractant. About 98 tons per day of high-quality copper cathode is electrowon from the strip liquor. Raffinate at 0.09 grams copper per liter is returned to countercurrent washing, where 2 percent of the copper solublized in the plant is lost. Overall recovery of copper is about 78 percent, the remainder being insoluble native and sulfide copper.

INTRODUCTION

Twin Buttes, about twenty-five miles south of Tucson, Arizona, was one of several copper claims of the Banner Mining Company in that area. In the early sixties, work toward further definition of the orebodies and process amenability testing the ores was undertaken by The Anaconda Company in agreement with Banner. In 1964 Anaconda exercised its option under the agreement to lease, finance, and operate those properties. The Twin Buttes orebody was known to have, in addition to a very heavy overburden, an oxidized capping with high limestone content. The oxidized copper minerals could not be made to float very well. They are soluble in sulfuric acid, but the acid consumption was economically burdensome, and vat or dump leaching tests gave poor results as penetration of the rock by solution was frustrated by gypsum formation. Agitated leaching with recovery by cementation was considered, but other hydrometallurgical processes were also investigated.

In 1965 the excavation of the open-pit Twin Buttes Mine began, followed by construction of a mill for the sulfide ore. In 1969 the first sulfide ore from the pit was mined and milled. In the interim, much of the oxidized ore was mined, and stockpiled for lack of an acceptable process. The new copper extractant LIX-64 was investigated with respect to recovery from agitated leach solutions. With electrowinning, this appeared an attractive replacement for cementation, but acid cost still burdened the process. Ranchers Exploration and Development Corporation installed the first such commercial process at their Bluebird Mine, also in Arizona, but with a less problematic ore and a dump leach. Through 1970, Anaconda continued to work on other processes, leaning heavily toward an ammonia leach.

At the beginning of 1971, impending controls on sulfur dioxide emissions from smelters presaged an increase in sulfuric acid supply, and reduction in price, at least in the immediate area. The agitated acid leach, solvent extraction, electrowinning work was quickly resurrected, with a complete pilot plant. By June 1973 AMAX, Incorporated had acquired the Banner properties and joined with former lessee Anaconda in a 50-50 partnership owning and operating those properties, and the Anamax partnership had signed a contract with a joint venture of Davy Powergas and Arthur G. McKee to build the Twin Buttes Oxide Plant. Commissioning of the plant began in June 1965, with the first cathode produced in August.

CRUSHING AND GRINDING

These operations will be only briefly addressed, being somewhat aside from the principal subject.

Most of the stockpiled oxide ore was crushed previously in the mine's gyratory crusher to minus 10-inch size, but some uncrushed ore is handled with slight difficulty. The plant feed is first crushed to minus 6-inch size by a 48 x 60 inch jaw, with previously undersized material bypassed through a stationary grizzly. The following stage is a 7 foot standard cone crusher producing minus 1-inch rock, with previously undersized material bypassing through a vibrating grizzly. Finally, the material is sized to about 72 percent minus 1/2 inch size by two 8 x 20 ft. vibrating screens operating in closed circuit with two 7-foot shorthead cone crushers. Crushed ore is then stockpiled for feed to grinding mills. The crushing plant normally operates only 16 hours per day.

Wet grinding is accomplished in two trains, each consisting of a 12 x 18 foot rod mill using 4-inch rods and a 12 x 30 foot ball mill using 2-inch balls. Grinding is strictly open circuit to avoid the pulp dilution required by any particle size classification process. Ground ore, at about 84 percent minus 65 Tyler mesh size and 56 weight percent solids in pulp, is pumped to the leach. These sizing and density requirements are dictated more by solids suspension characteristics of the agitated leach than by leaching kinetics. The plant was designed to handle 10,000 dry short tons of ore per day. Progress toward that goal has been slow, nearing 9,800 per day in 1978 and finally surpassing 10,100 per day in the first quarter of 1980.

LEACHING AND COUNTERCURRENT DECANTATION WASHING

The conditions prevalent in these operations, and fundamental changes in this area of the flowsheet since plant startup, have significantly impacted solvent extraction performance.

The original flowsheet for these operations is given as Figure 1. The ground ore pulp flowed through five agitated tanks in series, each 30 feet in diameter by 31 feet high with a 9-foot diameter turbine and a retention time of about one hour. Flow between tanks is by gravity, each being at a slightly lower elevation than the preceeding tank. Concentrated sulfuric acid was added in the first two tanks, with provision for more acid in later tanks as it was thought necessary to maintain the entire leach at about

Figure 1

Leaching and Countercurrent Decantation Washing, with Neutralization Leach

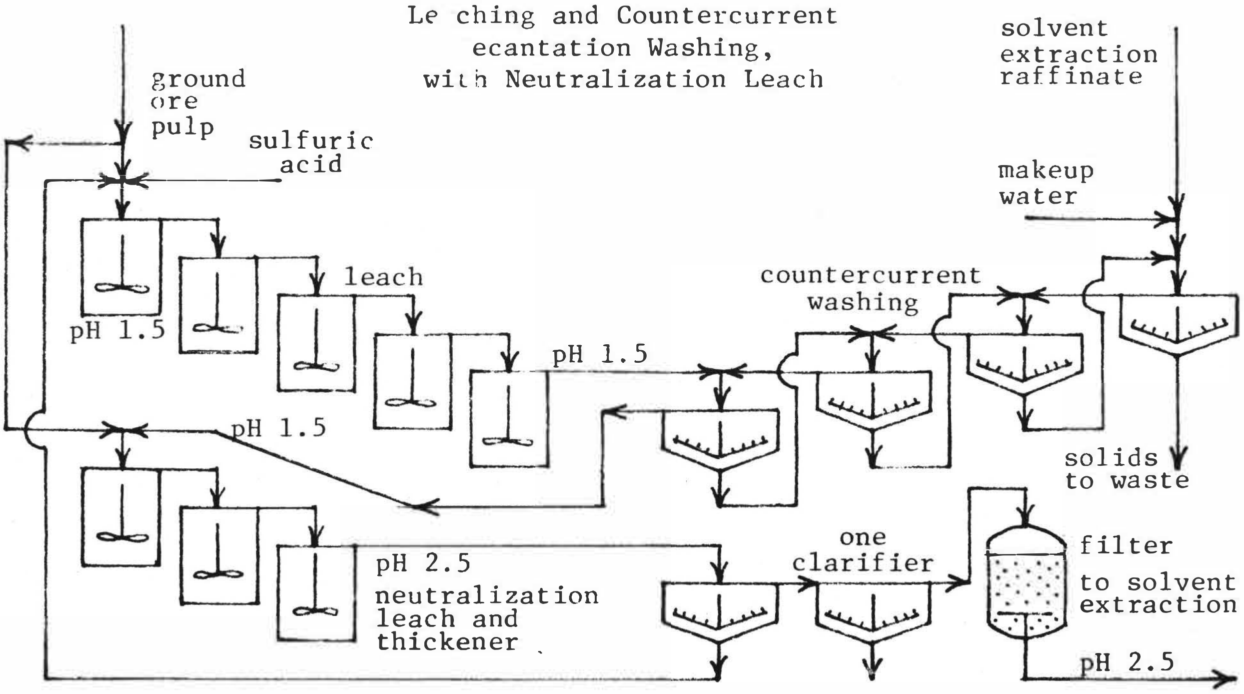
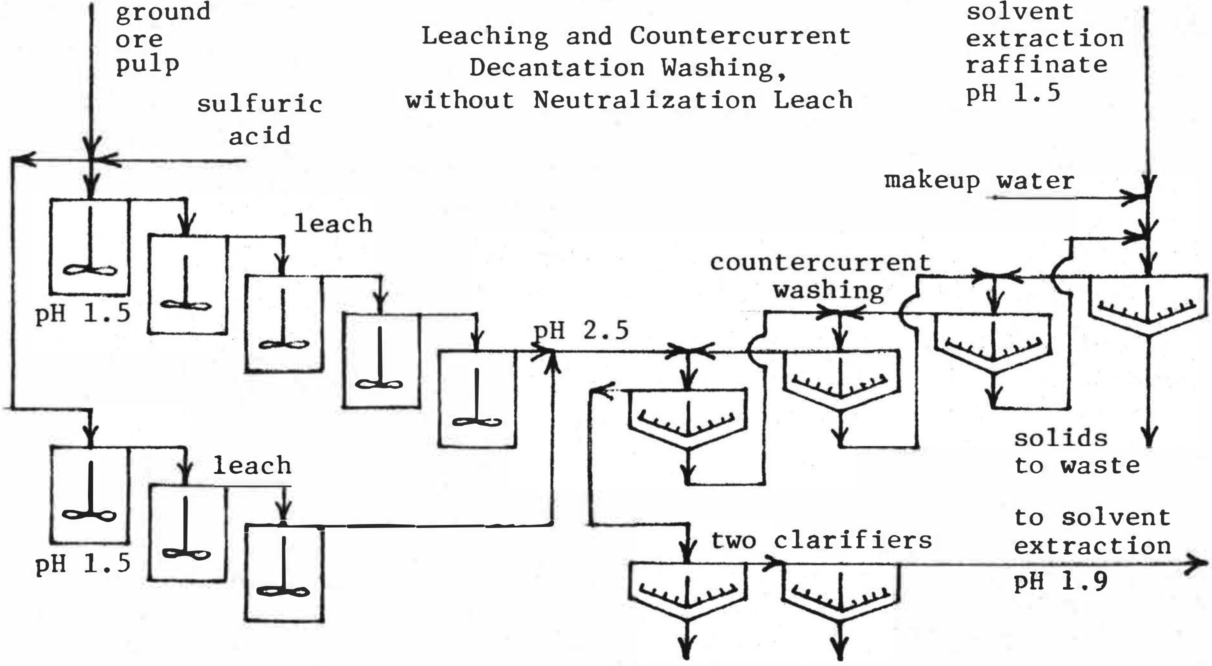


Figure 2

Leaching and Countercurrent Decantation Washing, without Neutralization Leach



pH 1.5 to maintain effective copper dissolution. The leach discharge is pumped to the first of our 400-foot diameter thickeners in series, for countercurrent decantation washing of the solute copper values from the leached solids by solvent extraction raffinate introduced at the fourth thickener. Washed solids are pumped to waste from the fourth thickener.

The copper bearing overflow solution from the first thickener, at near pH 1.5, was thought too acidic for efficient solvent extraction. It was therefore pumped to a neutralization leach consisting of three tanks, essentially identical to the first five, in which a small amount of freshly ground ore was added to consume free acid to about pH 2.5. The neutralization leach discharge was pumped to another 400-ft. thickener for solid-liquid separation. The copper bearing overflow solution at near pH 2.5 went on to clarification and solvent extraction. The underflow solids, assumed to be ineffectively leached at this pH, were pumped to the primary leach.

This neutralization leach scheme led to severe problems with gypsum formation, as hard scale in the leach tanks and interconnecting launders, and as fine suspended particulates in downstream solutions throughout clarification and solvent extraction. The high solution flow and low ore flow required into the neutralization leach also resulted in suspension problems, the leach agitators being insufficient to prevent settling out in the tanks.

Figure 2 gives the flowsheet adopted in mid-1976. The neutralization leach was abandoned, and those tanks were utilized to increase primary leach retention time. The ground ore pulp is now divided to two leach trains, of five tanks and three tanks, in portions resulting in approximately equal retention times. Sulfuric acid is added only in the first tank of each train, to about pH 1.5 in those two tanks. The pH is allowed to drift upward as the leach reaction progresses through succeeding tanks, to about pH 2.2-2.5 in the leach discharge. With the additional leach retention time, overall copper dissolution has not suffered at the higher pH. It is not clearly understood why this flowsheet, as opposed to the original, does not produce solutions supersaturated with gypsum. Nevertheless, gypsum formation is no longer a problem. The solvent extraction raffinate used for countercurrent washing is at pH 1.5. This, combined with the pH 2.2-2.5 leach discharge, results in a pH 1.9 overflow solution from the first thickener, ultimately the solvent extraction feed.

Currently the ore contains about 1.28 percent total copper of which about 80 percent is dissolved, the remainder being native and sulfide copper minerals. Of the copper dissolved, about two percent is lost with waste solids.

CLARIFICATION

In addition to the four countercurrent washing thickeners and the neutralization leach thickener, a sixth 400-foot reservoir was provided as part of the original plant design to receive and clarify the overflow solution from the neutralization leach thickener. The clarified solution then passes through a small steam injection reservoir, used only in winter months to satisfy minimum solvent extraction temperature requirements to be discussed later. Further clarification was intended to be accomplished in six 12-foot diameter high-rate downflow sand filters, operating at about 10.5

gallons per minute per square foot with a bed of nominally 36 mesh garnet. The gypsum problems associated with the neutralization leach resulted in a clarifier reservoir overflow, and filter feed, containing 100 to 500 parts per million suspended solids. The filter medium became cemented with gypsum to the extent that each filter contained one monolith.

With the abandonment of the neutralization leach, the thickener provided for that leach discharge became another clarifier reservoir. With two such reservoirs in series, and the solution no longer supersaturated with gypsum, the final overflow contains only 20 to 30 parts per million particulates and is sent to solvent extraction without filtration. Testing has shown that the filters could treat this solution without cementation of the medium, but that the remaining particulates are so fine that less than half would be removed.

SOLVENT EXTRACTION

The solvent extraction plant was designed to treat 7,120 gallons per minute aqueous feed at 2.65 grams copper per liter and pH 2.5. This solution was to be maintained at a minimum temperature of 20°C, by prior steam injection when required. The strip solution was to be at 25 grams copper and 130 grams free sulfuric acid per liter. The strip liquor (strong electrolyte) was to be at 50 grams copper and 91 grams free sulfuric acid per liter. The solvent was to be a 14 volume percent solution of LIX-64N extractant in a kerosene-type diluent, at a solvent/aqueous flow ratio of 1/1 in extraction. Four extraction and two stripping stages were provided, in two parallel trains, or a total of twelve mixer-settlers. Pilot work had indicated that this staging, with these conditions, would result in a raffinate at 0.08 gram copper per liter and a gross copper transfer of about 110 tons per day, requiring about 730 gallons per minute of strip solution flow. Allowing for control of electrolyte iron content, by bleeding lean electrolyte to the leach and replacing with water and acid, the net production was to be 100 tons copper per day.

The mixers are self-pumping, of the classic Davy Powergas design. The mixer tanks are 15 feet square by 11 feet high inside, with no baffles except for the baffling inherent in the square shape. The agitators are radial turbines, 9 feet in diameter, with 8 curved blades having top and bottom edges fully shielded by integral disks. Small straight blades are arrayed radially on the outsides of the top and bottom shield disks. The turbine is positioned about midway up the height of the tank. Aqueous and solvent are supplied separately to the eye of the turbine, by concentric draft tubes from the bottom of the tank. The dispersion exits the lid of the tank through a hole around the turbine shaft, a design which prevents any air entrainment from the dispersion-air interface. Dispersion is then channeled across the top of the tank, under a second, outer lid, to the settler. Turbines were originally equipped with variable speed drives. With experience, the speeds were fixed at 33 revolutions per minute in extraction and 37 in stripping. Power draws are 32.5 and 40 horsepower, respectively.

The settlers are 45 feet wide. The lengths of their active settling areas, not including inflow distributor boxes and outflow weir boxes, are 139 feet for third and fourth extraction settlers and 111 feet for all others. Pilot work indicated slower dispersion disengagement in those stages. At design flow rates, the dispersion disengagement rates would be

1.14 gallons per minute per square foot in third and fourth extraction settlers and 1.43 in all others. The settlers have "picket fences" at both ends, near the inflow distributors and the solvent weirs. The settlers are individually covered.

The mixer tanks, turbines, shafts, lids, settler tanks, weirs, "picket fences", covers, and all process piping, are of type 316L stainless steel. Drain piping, however, is fiberglass reinforced plastic.

Soon after startup, it became obvious that significant changes in operating parameters would be required. Solvent became heavily entrained in raffinate if the fourth extraction mixer were operated with an aqueous continuous dispersion, yet the solvent/aqueous flow ratio had to be increased to a minimum of 1.2/1 to reliably maintain solvent phase continuity. All extraction settlers, regardless of dispersion phase continuity, gave entrainment problems if the design total dispersion flow rate was far exceeded. The plant has therefore been run since early 1976 with a 6,200 gallon per minute aqueous feed (3,100 per train), and a solvent/aqueous flow ratio of 1.2/1 to 1.4/1 in extraction. There is no problem maintaining the desired aqueous continuous dispersions in the first extraction mixers at these ratios. At the lower aqueous feed rates, feed copper content rose to about 3 grams per liter. At the higher solvent/aqueous ratios, LIX-64N content of solvent was lowered to 12.5 volume percent.

The change in feed pH from 2.5 to 1.9, which later resulted from abandonment of the neutralization leach described previously, did not have significant effect on solvent extraction. Raffinate at 0.09 grams copper per liter and pH 1.5 is typical.

McCabe-Thiele diagrams for recent extraction and stripping profiles are given in Figures 3 and 4, respectively. The critical compositions for those particular profiles were as follows:

Table 1, Compositions for Extraction
and Stripping Profiles in Figures 3 and 4

Stream	gpl Copper
Aqueous feed	3.03
Stripped solvent	0.26
Raffinate	0.13
Loaded solvent	2.04
Strip solution	23.46
Strip liquor	45.77

The solvent/aqueous flow ratio in extraction was 1.63/1 in this case, and was atypically high to compensate for a LIX-64N content which had been inadvertently allowed to fall to 11.75 volume percent. The raffinate copper content was slightly above normal for the same reason, but the flexibility of the system is demonstrated. The strip solution contained 140 grams free sulfuric acid per liter. The dashed lines on Figures 3 and 4 are mixer efficiencies (percent approach to equilibrium). These are 80 to 85 percent in extraction and 87 percent in stripping.

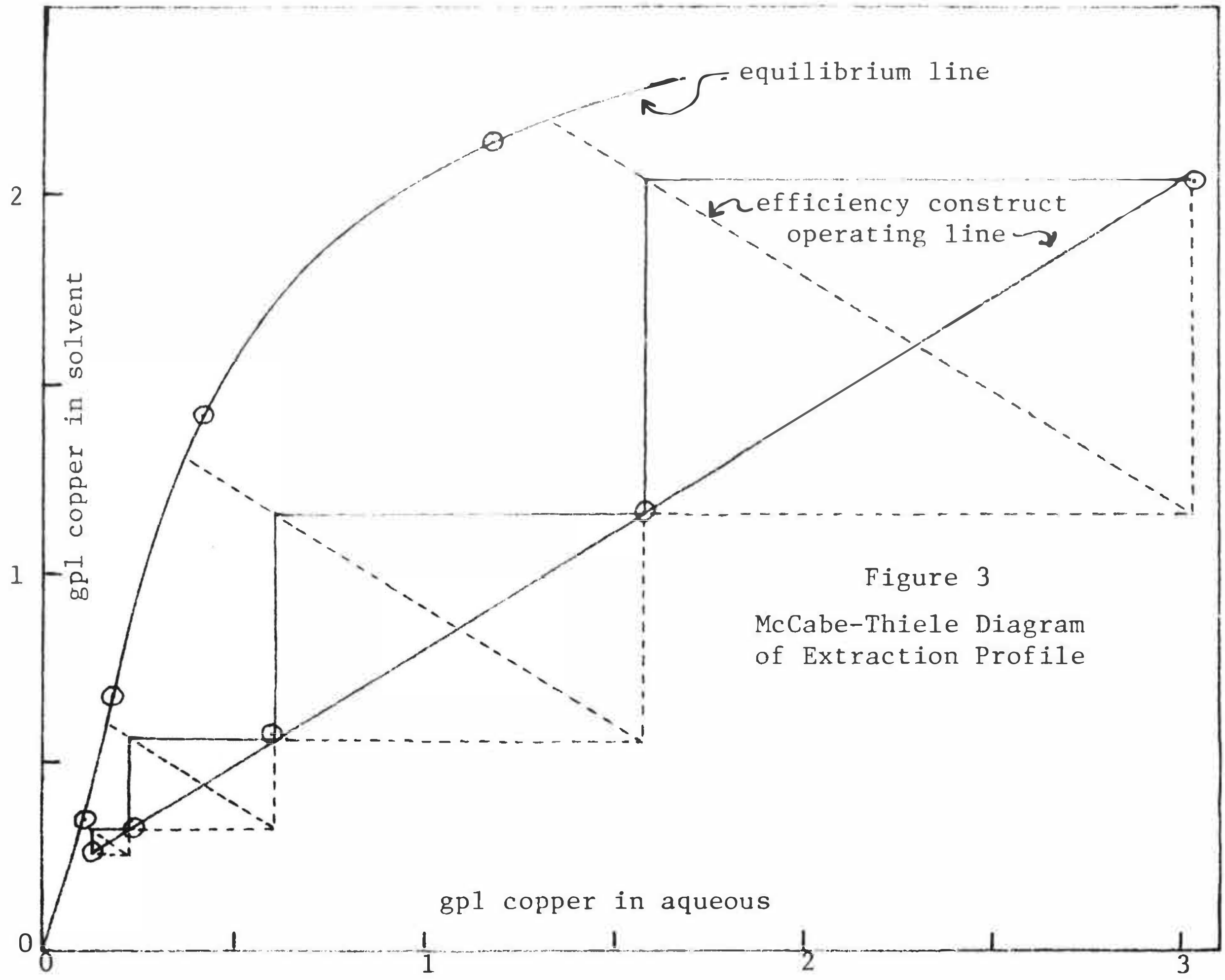


Figure 3

McCabe-Thiele Diagram of Extraction Profile

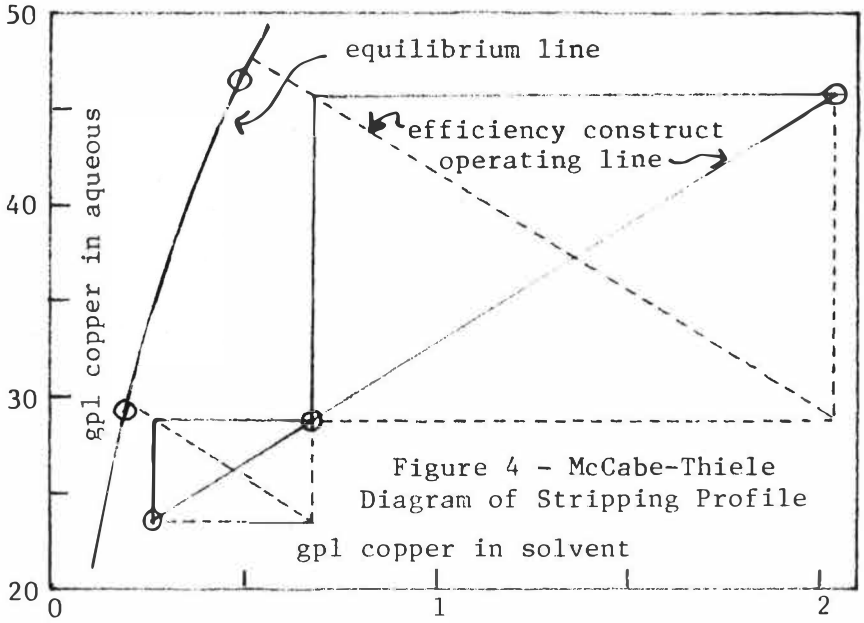


Figure 4 - McCabe-Thiele Diagram of Stripping Profile

The previously stated 20°C minimum design temperature for solvent extraction feed has proven insufficient to allow full design flow rates, in all but a very few instances when the settlers were extraordinarily free of particulate-stabilized emulsions ("crud"). The effective settling areas are normally limited by crud accumulation, to the extent that the first extraction mixers must be maintained at 23-24°C to allow full flow. The heat loss from the plant is such that the feed temperature must be still higher, by about 1°C, to maintain the first extraction temperatures. In the coldest winter weather, the solution overflowing the final clarifier reservoir can be at 12°C, and the steam requirement for heating it can be in the neighborhood of 50,000 pounds per hour. For the warmest half of the year, no steam is required.

Failure to maintain adequate temperature can result in entrainment of aqueous in loaded solvent at upwards of 0.1 volume percent. Under best conditions, this entrainment is 100-200 volume parts per million. Under any conditions, it is much worse if the first extraction mixers are run with solvent-continuous phase. Entrainment of solvent in raffinate is about 30 parts per million, and less sensitive to temperature. Entrainment of stripping solution in stripped solvent is normally less than 100 parts per million, but a very strange temperature relationship is observed in this case. The second stripping mixers are run with aqueous-continuous phases in the summer and solvent-continuous phases in the winter to minimize this entrainment, and at very high solvent/aqueous ratios in the latter instance. Aqueous recycles are provided on all stripping stages to allow a wide range of solvent/aqueous ratios.

The suspended solids in solvent extraction feed, as well as the particulate content of crud which forms in the extraction settlers, consist of silica, clay, gypsum, and unidentified iron salts. The particulate content of crud which forms in the stripping settlers, on the other hand, is almost pure silica in a semi-colloidal form. It is concluded that these solids found in the stripping settlers originate from solute silica in the solvent extraction feed solution entrained in loaded solvent, which precipitates upon mixing with the highly acidic stripping solution. In addition to forming crud in the settlers, these solids become wetted with solvent and entrained in the strip liquor. When allowed to enter the electrowinning circuit, the solids release solvent, which was a serious impediment to the production of quality cathode copper. Upon release of solvent, the solids still did not settle out of suspension completely, but returned to solvent extraction in the stripping solution. A high recirculating load of silica thus accumulated, carrying more solvent to the tankhouse with each cycle. Strip liquor often contained 150 parts per million each, silica and solvent. The packed fibre type coalescers originally provided to remove entrained solvent from strip liquor would not work, as they were rapidly plugged with silica. The final remedy was a filter similar to a sand filter, using a garnet medium. This was installed on the strip liquor stream in 1978, and reduced the total of suspended particulates and solvent reaching the tankhouse to about 8 parts per million. However, the strip liquor fed to this filter now contains only about 25 parts per million solids and solvent, due to the reduction of the recirculating load.

In the first year of operation, the rate of formation of crud in settlers far exceeded the ability to remove it. The plant was, in fact, totally incapacitated twice for more than a week at a time. When the neutralization leach was abandoned and suspended solids in solvent extraction feed reduced to 20-30 parts per million as discussed previously, the cleanout of crud became a more manageable task. At the same time, a second solvent surge tank was installed, isolating the two trains of solvent extraction so that upset conditions in one would not affect the other. Each settler is now cleaned out once or twice a year as needed, one at a time, involving complete shutdown of a single train for 6-8 hours. The settler must be drained and washed out, as some of the crud is too heavy to "flood" over the solvent weir and divert, and in fact accumulates in mounds on the settler floor. Crud and "dirty" solvent drained from the settler during such a cleanout is accumulated in a special reservoir, for later recovery of solvent. This is accomplished in a continuous "cream separator" type centrifuge, which can produce clean solvent at 10 gallons per minute. The centrifuge bowl automatically splits, on a timed cycle, to discharge accumulated solids. This centrifuge was not provided as part of the original plant design, but is now regarded as an absolute necessity.

ELECTROWINNING

Solvent extraction strip liquor (strong electrolyte) is filtered as discussed above and flows through two surge reservoirs on its way to the tankhouse at about 730 gallons per minute. At the tankhouse, it flows through four recirculation tanks in series and then to a strip solution makeup tank for return to solvent extraction. Lean electrolyte, from the third recirculation tank, is pumped to the leach in sufficient quantity to remove iron transferred to the circuit by solvent extraction. In the strip solution makeup tank, sufficient water and concentrated sulfuric acid are added to replace this loss.

Electrolyte is pumped from each of the four recirculating tanks to a separate group of electrolytic cells, in parallel, at about 60 gallons per minute per cell, and then returns to the same tank. The first and second tanks feed 36 cells each, and the third and fourth 72 each. The starting sheets are produced in the second recirculation system, allowing any remaining suspended particulates or solvent a final opportunity to settle out in a cathode production cell before reaching the critical starter sheets.

Three rectifiers are provided, each supplying 72 cells in series with a capability of 25,000 amperes. The first rectifier therefore serves the first two recirculating systems including the starter sheet production.

Starter sheets are grown on titanium cathodes, from which they are manually stripped on a 24-hour cycle. They measure 35.5 inches wide by 45 inches long, and 0.021 inches thick. The first rectifier is normally run at 20,000 amperes. The starter sheets, and the cathodes in that circuit, are therefore deposited at a current density of 17.7 amps per square foot. After stripping, they are straightened and equipped with hanger loops by a single semi-automatic machine.

The currents in the second and third rectifier circuits vary widely with production rate. At an average rate of 98 tons cathode copper per day, these circuits are at 15,000 amperes each, or a current density of 13.3 amperes per square foot. Cathodes are harvested on a 7-1/3 day cycle, and weigh about 142 pounds. Current efficiency is 86 percent, and power consumption about 0.95 kilowatt-hours per pound of copper.

Each cell contains 51 cathodes and 52 anodes, spaced at two inches, center to center, cathode to anode. The anodes are a lead alloy. Three vertical polyvinyl chloride bars are attached to each face of each anode to positively prevent cathode contact. These protrude about 0.25 inches from the anode surface.

The electrolyte is maintained at a minimum of 35°C by steam injection in the first two recirculation tanks. However, electrolytic action adds more heat to the extent that an evaporative water cooling system, with heat exchangers to the electrolyte, is employed in summer to maintain third and fourth recirculation temperatures at less than 50°C.

As discussed earlier with respect to solvent extraction, the strong electrolyte contains about 50 grams copper and 91 grams free sulfuric acid per liter, and is depleted in the tankhouse to about 25 grams copper per liter. Iron content of the electrolyte is maintained at less than 3 grams per liter. Cobalt and chloride are added to maintain about 60 and 30 parts per million, respectively.

The electrolyte cooling system for third and fourth recirculation systems was not provided for in the original plant design. Before its installation in early 1976, high temperatures caused severe problems with corrosion of cathode hanger loops, allowing cathodes to fall into cells. The next problem encountered was the high corrosion rate of the original lead alloy anodes, due to inappropriately high antimony content of 11-12 percent. This, and the small button-type plastic spacers originally used on the anode surfaces, resulted in high lead content in cathode copper. A change in the anode alloy and adoption of the vertical bar anode spacers described earlier have essentially eliminated that problem. By far the greatest problem encountered was the solvent influx from solvent extraction. This caused cathode copper to be soft and porous, and also resulted in a low yield of useable starter sheets resulting from spotty deposition on the titanium. The filtration of electrolyte has finally eliminated these problems entirely.

Current production cathodes are hard, bright, high quality copper containing less than 3 parts per million lead and 7 parts per million sulfur.

SOLVENT EXTRACTION FACILITIES AT KENNECOTT'S RAY MINES DIVISION

T. I. Probert, K. J. Richards
Process Technology
Salt Lake City, Utah, USA
N. J. Nebeker, C. K. Vance
Hayden, Arizona, USA
Kennecott Minerals Company

ABSTRACT

Early in 1980, solvent extraction facilities were commissioned at Kennecott's Ray Mines Division in Arizona, U.S.A. The SX step was incorporated into the 11-year-old silicate ore leach plant to improve electrowinning current efficiency, reduce costs, and increase cathode purity. SX plant start-up culminated a 2-year study of bench and pilot testing. Solvent systems and their effect on copper extraction, selectivity, and entrainment were studied in the laboratory. Stage efficiency, sludge generation, and cathode purity were emphasized at the pilot scale. This paper discusses the project development, plant design and the highlights of the first half year's operations.

INTRODUCTION

The ore body of Kennecott's Ray Mines Division in Arizona contains commercially minable amounts of copper silicates, primarily chrysocolla. Recovery of copper from this silicate rock was begun in 1969 with the commissioning of a new plant to treat 9000 tonnes per day of ore. The process involved crushing of the ore to a nominal size of less than 1.3 cm. After the fines were removed by rake classifiers, the ore was charged to large vats for leaching with sulfuric acid. Copper was partly recovered from the leach liquors by direct electrowinning. After the copper content had been lowered from about 20 g/l to 5 g/l, electrowinning was no longer economical and the remaining copper was recovered by precipitation with iron.

In 1976, the silicate ore production was increased to 13,000 tonnes per day. The process was modified to accommodate the increased throughput. Improved classification allowed better separation of fines from the vat leach feed. Complete removal of the slimes fraction from the ore improved both the solution distribution and drainage in the vats. This fine fraction is now ball milled to a minus 0.3 mm product and pachuca leached. The additional copper from pachuca leaching has been recovered by iron cementation. Total leach solution flow increased to 23,000 l/min.

Predictably the problem area in the plant design has been in copper recovery. The solutions from vat leaching contain high concentrations of iron as well as copper. In direct electrowinning of these solutions, a substantial amount of electrical energy is lost in the repeated oxidation and reduction of iron ions in solution. Overall electrowinning current efficiencies have been consistently below 50%. The high ferric ion concentrations cause corrosion problems that can only be controlled by reducing the temperature of the electrolyte. This in turn causes poor quality copper deposits. The high iron content of all leach solutions also affects the iron cementation process. Ferric ions consume some of the iron that could be used to precipitate copper thus adding to the recovery costs.

Overall, the inability to purify and concentrate the leach solutions has made the recovery process inefficient and costly. Additionally, the copper products have not been marketable directly and their reprocessing through our smelters and electrorefineries has added further to the production costs and increased our in-process inventories.

There were no solid or liquid ion exchange reagents available to purify and concentrate the leach solutions when the original silicate production plant was designed. When it was expanded in the mid-70's, solvent extraction (SX) based on the solvent LIX64N had been commercialized; however, this system could not treat our leach solution directly because of their high acid concentration. Neutralization might have allowed the use of LIX64N, but this approach was rejected because of the projected process costs and because of problems of gypsum based sludge formation that had occurred in industrial leach-SX operations. (1,2)

Despite the fact that there were no industrial SX systems available at the time, the potential economic benefits were so large that the Kennecott Research Center initiated a major technical effort to assure the early identification and application of an effective solvent extraction process for our Ray silicate leaching operation. The thrust of that ultimately successful program was first to seek out and evaluate all experimental, uncommercialized reagents. When one was found that met our needs, we had to support its commercialization to assure its availability and to develop a process that could be integrated into the existing leach-direct electrowinning operation.

PROCESS DEVELOPMENT

Solvent/Electrolyte Selection Batch shakeout tests were used to develop distribution isotherms for all available and experimental copper extractants. Kelex 100, LIX64N, SME-529, LIX70 and the Acorga P-5000 series were evaluated. Kelex 100 back-extracted acid from stripping and showed a Cu/Fe selectivity ratio of only 20/1. LIX64N and SME-529 could not extract well enough from the low pH feed. LIX70 extracted very well but required a 300 g/l H_2SO_4 stripping solution. This would have caused unacceptable problems in tankhouse misting and lead anode corrosion. The Acorga P-5100 extractant was found to have the necessary properties to justify development of a commercial process.

A diluent had to be selected to complete the solvent system and proceed with the process development. Several years earlier Kennecott had tested Escaid 200 and found it to have rapid phase disengagement compared to other, more aromatic diluents. Escaid 200 was selected to allow testing of settlers smaller than those based on the conventional combined flow design of 80 $l/min/m^2$.

The stripping electrolyte composition affects the electrowinning operation, the stripping stages and the extractant degradation. In general, lower copper contents improve stripping while higher copper improves the cathode quality. An electrolyte composition of 40 g/l Cu and 170 g/l H_2SO_4

was chosen as a compromise. Higher acid would reduce the copper content of the stripped organic but could lead to copper solubility problems, increased anode corrosion and a higher rate of extractant degradation.

Laboratory circuit testing was the final evaluation approach. Although several solvent systems were tested, efforts concentrated on Acorga and Escaid. Results with the other solvent systems confirmed the original shakeout tests. These extractants required too many countercurrent contact stages and could not achieve the desired copper extraction. Bench scale circuit testing, in conjunction with electrowinning, confirmed that the Acorga/Escaid system had excellent pH functionality, rapid kinetics and phase disengagement, and good Cu/Fe selectivity. It also had a low sensitivity to temperature with respect to phase disengagement and copper extraction.

PROCESS DEFINITION

Development studies showed that with Acorga, only two extraction and two stripping stages (FIG 1 and 2) could achieve 90% copper extraction if the stage efficiencies were in excess of 90%. Laboratory mixer-settlers were capable of stage efficiencies near 90%. To attain ninety plus efficiency, a laboratory circuit with three mix tanks in series was constructed. Kennecott tests in 1975 had confirmed that series mixing could increase stage efficiency; other researchers had also reached this conclusion (3,4). The laboratory circuit tests confirmed that the series mix design increased stage efficiency at least four percentage points over a single mixer for the Acorga/Escaid system. Although two mix tanks in series accounted for over 70% of the increased efficiency, the concept of three mixers was adopted as a conservative reflection of questions of scalability and future solvent supply.

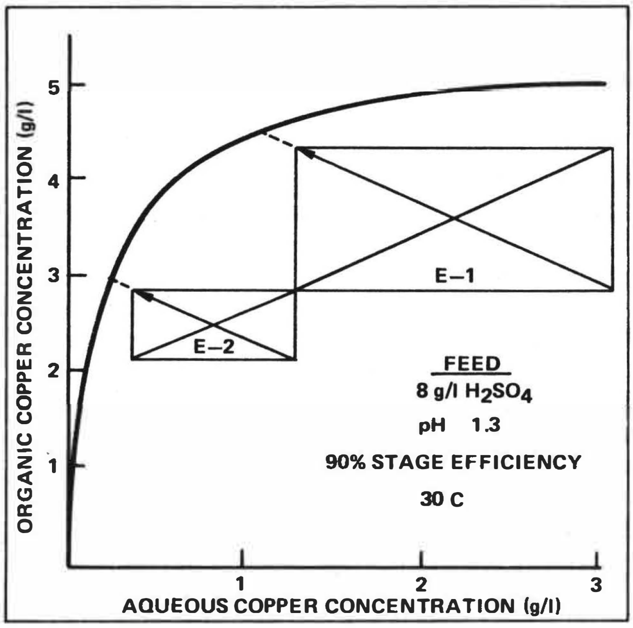


FIG 1

EXTRACTION ISOTHERM

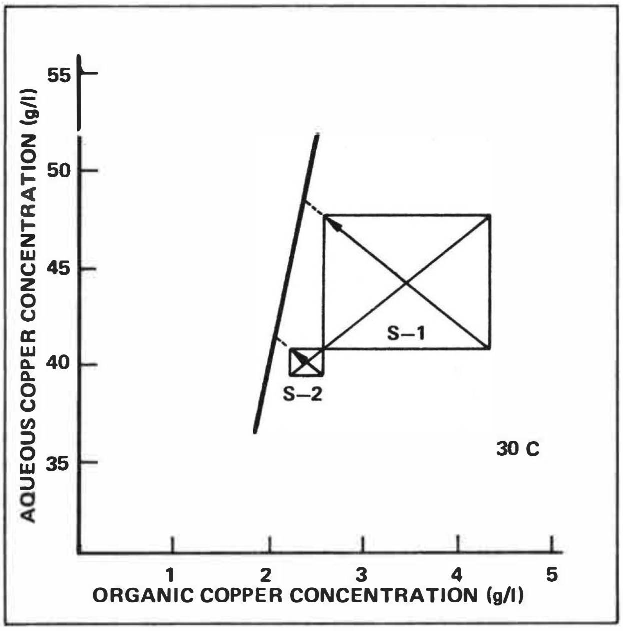


FIG 2

STRIPPING ISOTHERM

At this time, other contactors such as columns and in-line pipe mixer-settlers were considered. However, these alternatives were bypassed because of the risks in the areas of scale-up, sludge buildup and extractant degradation. Additionally, the time available for piloting was limited and the use of the more conventional mixer-settler appeared economically justified.

The selection of O/A ratios was based on McCabe Thiele analysis and previous pilot test work in a LIX64N/Escaid system on another project. The pilot work, conducted with series mix tanks, had shown that extraction O/A ratios in excess of 1.5 could lead to high solvent entrainment (Table 1).

TABLE 1
EFFECT OF EXTRACTION ORGANIC/AQUEOUS RATIO ON SOLVENT ENTRAINMENT

O/A	Solvent Entrainment (ppm)	Continuous Phase
0.50	310	Aqueous
0.75	28	Solvent
1.00	23	Solvent
1.25	20	Solvent
1.50	64	Solvent
2.00	360	Solvent

Comparable work on the strip stages showed that entrainment and stage efficiency were relatively independent of strip O/A ratio between 1 and 7. Based on the Acorga isotherms and our prior pilot work, we selected an extraction O/A range of 1.0 to 1.5 and a strip O/A of 2 to 3.

The laboratory circuit tests confirmed that these O/A ratios provided adequate performance in the areas of copper extraction and phase stability.

PILOT TESTING

The laboratory tests screened solvent systems and pinpointed the key variables of feed acid level and stage efficiency. However, the questions of scale-up, operability, sludge generation, solvent consumption and cathode quality could not be answered in the laboratory. Pilot tests using actual blended feed were conducted during four months in 1977 at Ray Mines Division.

The pilot plant available at the time included four conventional mixer-settlers, loaded solvent and rich electrolyte surge tanks and a commercial size electrowinning cell. Feed to the pilot unit was 75 l/min at about 3 g/l Cu, 5 to 10 g/l H_2SO_4 and 50 to 1000 ppm suspended solids. Extraction and strip mixing retention times were 2 min and 2.8 min, respectively in single mix tanks of conventional pump-mix design. The settlers operated at 114 $l/min/m^2$ for extraction stages and 102 $l/min/m^2$ for strip stages. Electrowinning current densities were between 200 and 250 A/m^2.

Chemical results of the pilot plant were comparable to those in the laboratory. Stage efficiencies of 90% could be attained at impeller tip speeds of 5 to 6 m/sec when the acid concentration of the feed was less than 8 g/l H_2SO_4. Acorga concentrations of 10 v/o and 85% maximum loading provided 90% copper extraction. Long-term Cu/Fe selectivity was 200/1.

The pilot plant was instrumental in uncovering problems associated with suspended solids. Sludge generation rates were approximately 400 l sludge per million liter feed; this included periods when there were 1000 ppm suspended solids in the feed. When the solids in the feed approached 1000 ppm, SX operation became very difficult. Instability of phase continuity, low copper extraction and Cu/Fe transfer ratios as low as 15/1 were the primary problems. Solids, carried as sludge from extraction into the strip stages, were partially leached of their iron content in the high acid electrolyte.

Phase disengagement and entrainments were not a problem under ordinary operating conditions. There was little dispersion downstream of the picket fence. Raffinate entrainments were generally less than 20 ppm while electrolyte entrainments were 20 to 30 ppm. Phase disengagement was rapid enough to have allowed testing of higher throughputs, but the pilot plant design did not have this flexibility.

Cathode quality was comparable to Kennecott electrorefined copper. There was no special care taken during starter sheet preparation, electrode alignment or other system work.

PLANT DESIGN

The key elements in the design of the commercial SX facilities were limited space availability, the requirement for high stage efficiencies and the need for efficient sludge removal and treatment. The limited space at the plant site influenced the equipment layout, the staging, settler sizing and number of trains. The requirement for high stage efficiency dictated a conservative approach toward mixer design. Other important considerations in the design were the materials of construction and the modification of the existing electrowinning tankhouse.

The contactor type, staging and settler size were based on the successful pilot results and the configuration of two extraction and two stripping mixer-settler stages was adopted for the commercial plant.

The pilot settler size had been conservative but was adopted, 114 $l/min/m^2$ for extraction and 102 $l/min/m^2$ for stripping. Although we felt smaller settlers would handle the primary phase disengagement, the effect of reduced retention time on entrainment was not clearly understood. Total settler depth and organic depth were left the same as in the pilot plant, 0.7 m and 0.2 m, respectively. The settler width was set so the superficial organic velocity would not exceed 6 cm/sec under the design conditions. The organic velocity constraint was based on Kennecott pilot tests and similar pilot work by Anglo-American in Zambia (5).

Settlers were designed end-to-end with a common wall between the weir end of one settler and the feed end of the next (FIG 3). Mixers are located at the side of the settler and dispersion makes a right turn through an angled picket fence.

The number of trains, or parallel lines, was based on both space and sludge considerations. Two trains were chosen, each to treat 11,350 l/min of feed. A single train would have been too vulnerable had sludge removal and sludge runaways been as troublesome as they had been in the pilot plant. More than two trains were desirable from the standpoint of plant flexibility but would have increased capital costs unnecessarily and would have exceeded the available space for the plant.

Mixers Several factors affected the mixer design. Because Acorga was a new extractant, long-term performance and mixing characteristics were uncertain. Additionally, Kennecott had no previous commercial SX experience to assure us how stage efficiency would scale-up. Two design features were incorporated to minimize risk. The three series mixer concept was adopted with a total extraction retention time of two minutes to ensure high stage

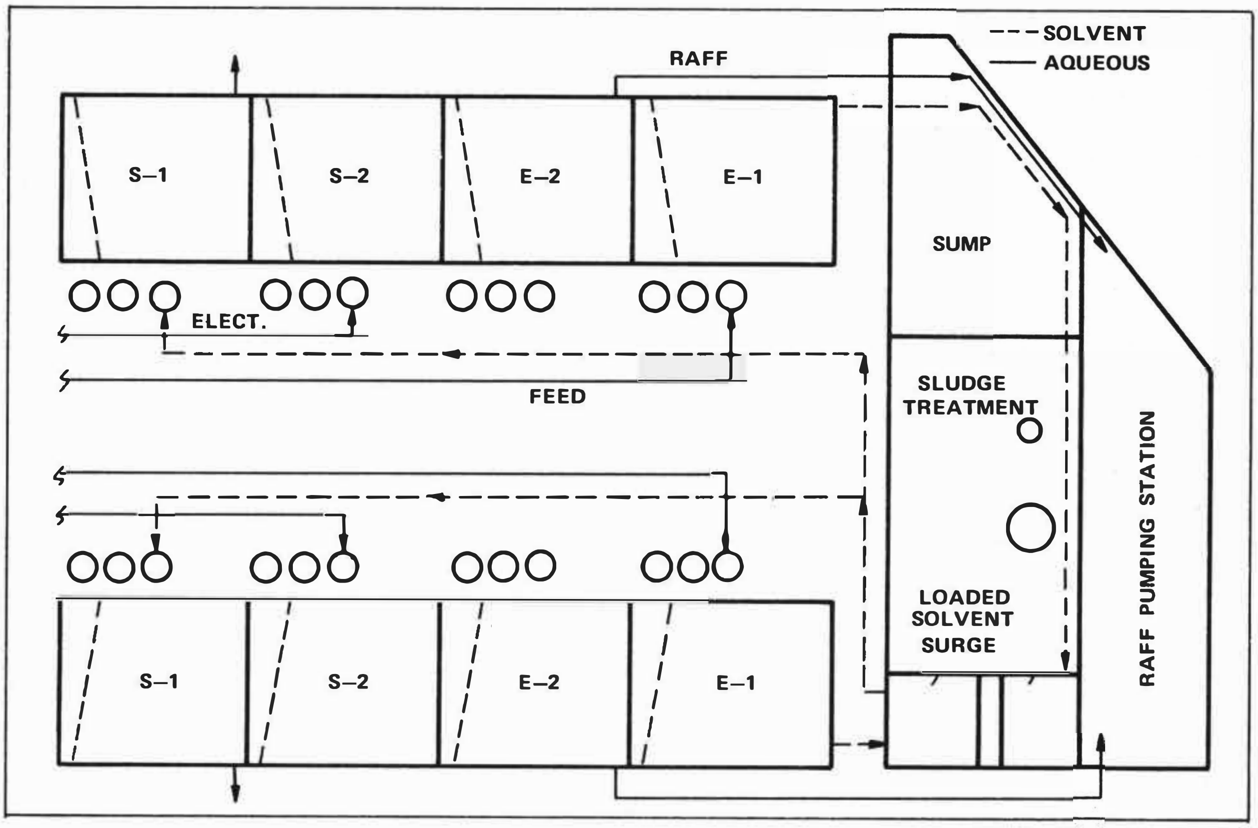


FIG 3

SX PLANT LAYOUT

efficiency in the commercial plant. The mix tanks are circular with liquid height about 80% of the diameter. The mixing and interstage pumping functions were separated so that flow and droplet size distribution could be controlled independently. Axial flow pumps, set in draft tubes in the first mix tank, provide the interstage pumping of individual phases. There are five such axial pumps in each train, ten in the entire plant. Separate mixing impellers in each mix tank create the dispersion for mass transfer.

Materials The SX plant is constructed of stainless steel and concrete. The mix tanks are 316L SS. The settler picket fence, weirs, and weir boxes are stainless also. Loaded solvent surge tanks, one for each train, are concrete lined with stainless as is the rich electrolyte surge tank. Sludge treatment tankage is stainless while the feed and raffinate tanks are concrete. Almost all piping is stainless. The plant floors are paved with concrete. Additionally, the settlers have roofs constructed of reinforced concrete T-beams suspended fully across the width. The roofs keep out dust generated in the nearby crushing and grinding operations and minimize wind-created wave action on the settlers which might otherwise increase entrainment and cause sludge movement. The roof section directly over the weirs was left off to promote visibility and to allow sludge removal by vacuuming.

Tankhouse Modifications The existing tankhouse was modified during the construction phase with minimal loss of production. The flow arrangement was converted from the cascade system to a simple distribution of rich electrolyte to each of four sections. Heat exchangers were added to preheat the rich electrolyte using the heat generated in the electrowinning cells. New cathode wash tanks were installed. The use of Dowfax demisting foam was eliminated because it is incompatible with the SX organics. Polyolefin carpet backing replaced the Dowfax for mist control. The existing starter sheet preparation, commercial electrowinning cells and power supplies were retained. Starter sheets are grown on titanium blanks using electrorefining rather than the more common method of electrowinning with the rich electolyte generated in SX. Electrorefining was retained because of a ready supply of copper anodes, low operating cost and excellent starter sheet quality.

The new SX facilities were designed and engineered by Jacobs Engineering Company of Pasadena, California. Laboratory studies, two Kennecott SX pilot operations and Jacob's prior experience in uranium SX were the background for design. A comparison of pilot and commercial plant design features is presented in Table 2.

TABLE 2
COMPARISON OF PILOT AND COMMERCIAL DESIGN PARAMETERS

	Pilot	Commercial
Feed Flow Rate, l/min/train	76	11,350
Feed Copper, g/l	3	3
Feed Acid, g/l	5	10
Extraction O/A	1.2	1.5
Strip O/A	3.0	3.0
Extraction Retention, min	2.0	2.0
Strip Retention, min	2.5	2.5
Settler Dimensions, m *	0.76W x 2.13L	16.5W x 19L
Settler Liquid Height, m	0.7	0.7
Mix Tanks, m	0.7W x 0.7L x0.7H	3.2 dia x 2.6H
Extractant Concentration, V/O	10	12
Electrolyte Acid, g/l	170	170
Electrolyte Copper, g/l	40	40

* Length includes weirs and behind fence

INITIAL PLANT OPERATION

A challenging aspect of the start-up of the new solvent extraction facility was that the process had to be functionally integrated into the ongoing leach-direct electrowinning operation with a minimum loss in production. The present flow sheet is presented in FIG 4. This required, for example, the removal of all direct electrowinning solutions from the tankhouse to avoid contamination of the new, pure electrolyte. Despite the many attendant complications, the start-up proceeded normally for a plant of this type and was completed in five weeks.

Hydraulics The first problem to develop during start-up was that the interstage axial flow pumps achieved neither the flow nor head requirements. This problem was unexpected since a prototype unit had been tested successfully in the manufacturer's test facilities. Increased rpm coupled with impeller modifications solved the problem and caused a delay of only two weeks. These units have worked well since start-up providing the rated 11,350 l/min flow capacity per train.

A problem with the systems "freeboard" was also encountered. The liquid level in the first mix tank operated close to overflowing. This was caused by an overflow baffle between the second and third mix tanks which was operating as a "freefall" weir rather than an overflow baffle. These baffles were lowered until they operated in a flooded mode which solved the

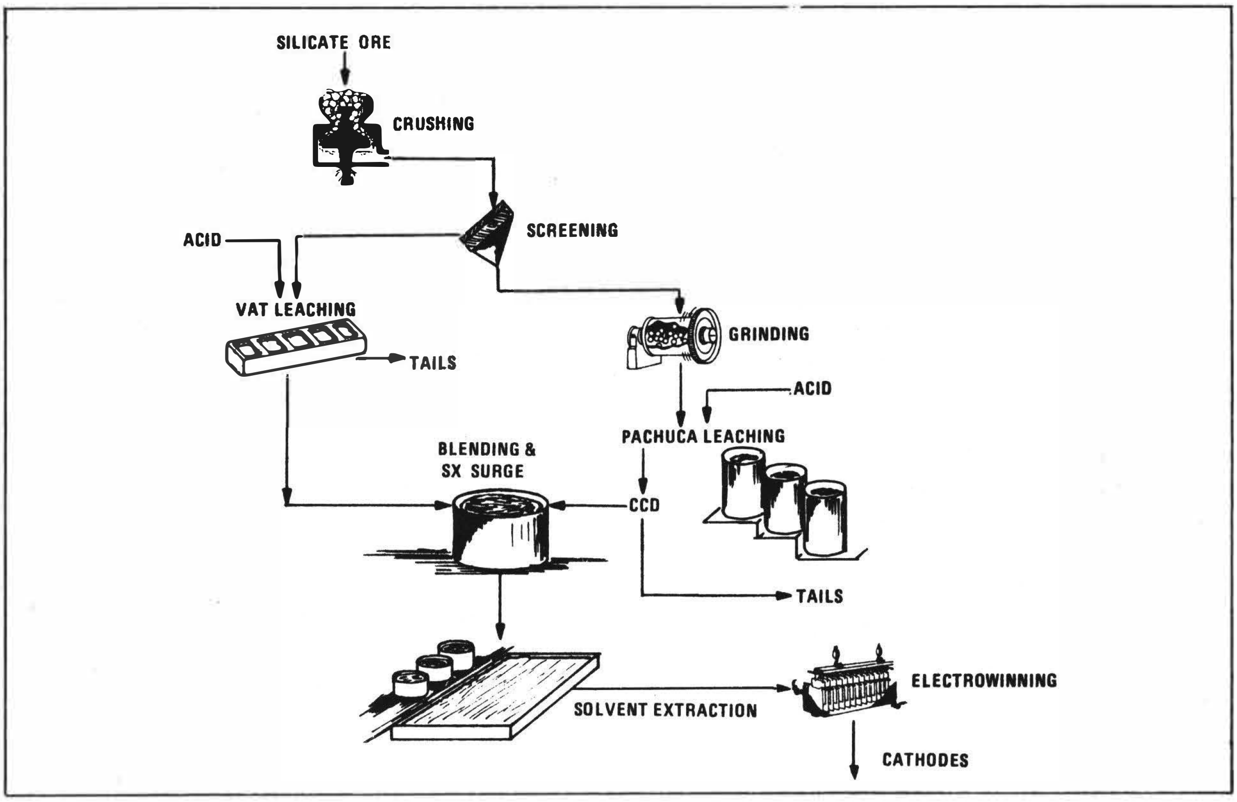


FIG 4
SILICATE PLANT FLOWSHEET

steady state freeboard problem. At about the same time as the baffle problem, one of the mixing impellers fell off the shaft. The lack of agitation caused excessive dispersed phase holdup, thus increasing the effective density in the tank with the failed impeller. This in turn raised the liquid level of the previous mix tank to the point of overflowing. While the plant was down for the baffle modification, overflow ducts were added between each mixer on every stage. These ducts are empty most of the time. However, during start-up or in the event of a mixing impeller or motor failure, dispersion flows through the duct rather than overflowing the mixer tank. The result is that the plant is now less susceptible to upset caused by mixer motor failure. Any of the mixing impellers or motors can fail without interrupting production or causing a mixer to overflow. Mixer motor maintenance or rpm changes are accomplished without shutdown.

Sludge Control Despite the rather high (approximately 50 ppm) level of suspended solids in the feed, sludge generation has been much less than expected; sludge accumulation in the extraction settlers is minimal. When it does form, the sludge is vacuumed from the first stripping stage and treated in a DeLaval centrifuge to recover the organic. Organic recovery from sludge exceeds 99%, and downtime due to sludge has been negligible. Sludge vacuuming and centrifuging work better than expected.

Stage Efficiencies Metallurgical profiles show that the two extraction stages, E-1 and E-2, operate in excess of 90% of the theoretical stage efficiency. The first strip stage, S-1, is equally effective. However, the second strip stage, S-2, efficiency varies from 50 to 90%. These results are almost identical to those in the laboratory. Perhaps the erratic nature and low efficiency of the second strip stage is related to the low driving force. The second strip stage has very little work to do because most of the available copper has been stripped off in S-1. In fact, because of the

90 to 95% stage efficiencies achieved in the commercial plant, it may have been possible to have eliminated the second strip stage.

Iron Extraction The chemical Cu/Fe selectivity ratio has varied from 100 to 400. Here, the selectivity is defined as the ratio of Cu to Fe stripped from the loaded solvent into the electrolyte. The Cu/Fe ratio does not include iron transferred physically by aqueous entrainment or in solids. Iron extraction is affected primarily by the copper loading of the solvent and the acid concentration of the feed. Above 80% of maximum loading, the iron extraction falls off rapidly. Also, as feed acid level increases, the iron extraction is depressed and the Cu/Fe selectivity ratio increases. Pilot and laboratory Cu/Fe selectivity ratios averaged 200 and the commercial plant is expected to operate at about the same level.

Solvent Entrainment Entrainments have met expectations. Raffinate and electrolyte entrainments average less than 30 ppm. Baffles to reduce entrainment to levels below 10 ppm were considered during the design phase but were rejected because of the unknown effect they might have on the sludge. However, far less sludge accumulates in the commercial extraction stages than did the pilot plant. Therefore, in retrospect, baffles may have been profitably installed. Overall solvent consumption is not yet known. Extractant degradation and diluent evaporation will certainly contribute to total solvent costs but are not yet quantified.

Electrowinning Solvent extraction has more than doubled the electrowinning current efficiency. Cathode production has increased by eliminating the production of copper precipitates. Copper cathode purity and quality have improved while the energy consumption has decreased. Previously, cathodes required fire refining and copper precipitates were smelted, cast into anodes and then electrorefined. SX has improved the product, lowered the operating costs and reduced the pipeline to market.

In the tankhouse, the initial current efficiency was lower than expected. The new lead anodes are equipped with plastic strips to help prevent the copper starter sheets from touching the anodes in the electrowinning cells. Delivery of these anode spacer strips was delayed and the plant was initially operated without them, resulting in excessive short circuiting. After installation of the spacers, the current efficiency and copper production increased to target levels.

Our approach to normal acid misting in the tankhouse was to cover the cells with polyolefin carpet backing. This carpet backing is much like a plastic burlap. While the material was on the cells, the mist suppression was acceptable, but these covers discouraged short clearing and other aspects of system work. During cell charging and pulling, the covers had to be rolled back and misting required that the current be cut off during these periods. This reduced copper production. Consequently, small plastic spheres are replacing the carpet backing. The search continues for an effective demisting foam compatible with the solvent system.

SUMMARY

A few summary comments are in order concerning the role of the laboratory and pilot tests in the design of this commercial facility. Laboratory studies, both shaker and circuit, formed the basis for selecting the solvent system. Laboratory circuit operation elucidated effects of key variables such as feed composition, O/A, series mixing, temperature and extractant concentration. Stage efficiency scaled up accurately from laboratory to commercial plant. The advantages of laboratory testing are the ability to rapidly screen many variables and set the conditions for the larger, more costly pilot testing.

Pilot studies demonstrated sustained operation under field conditions, provided data on the effects of solids and sludge and gave more reliable data on solvent consumption than did the laboratory units. Solvent entrainment scaled up accurately from pilot to commercial plant. Pilot tests were required to determine the quality of cathodes to be expected in the plant. However, nothing short of the commercial operation demonstrates final cathode quality.

The Ray Mines Division SX plant represents a step forward in the treating of low pH solutions. Additionally, the Ray Mines SX process demonstrates that it is technically and economically feasible to process solutions containing an average of 50 ppm solids while maintaining stable phase continuity and high stage efficiencies.

ACKNOWLEDGEMENTS

Grateful acknowledgement to the management of Kennecott Minerals Company is made for permission to publish this paper. Many people were involved in the inception, development and commissioning of this plant and their contributions are acknowledged.

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THE ORIGIN OF THE SELECTIVITY OF OXINES AND OXIMES FOR COPPER(II) OVER IRON(III)

C.A. Fleming, B.R. Green, and K.G. Ashurst

National Institute for Metallurgy

South Africa

ABSTRACT

Data are presented that substantiate the selectivity of KELEX 100 and LIX 65N for cupric ions over ferric ions. For KELEX 100 it is shown that this selectivity is lost when either the water-soluble precursor of KELEX 100, 8-hydroxyquinoline, is added to the reagent mixture, or when the inert organic diluent is removed from the organic phase.

For oxime reagents, it is shown that LIX 65N and its water-soluble precursor, salicylaldoxime, are selective for copper over iron, but that this selectivity is substantially reduced in the absence of a supporting inert diluent. On the basis of these results and thermodynamic data, theories are advanced on the origin of the selectivity for copper over iron of KELEX 100 and LIX 65N.

INTRODUCTION

A most important property of any successful copper reagent is that it should be able to extract copper selectively from weakly acidic solutions containing ferric ions. The reagents LIX 65N [*1*] and KELEX 100 [*2*] both achieve this selectivity, and the origin of their selectivity for copper over iron has aroused considerable interest, particularly in regard to the development of new reagents.

The stability of the ferric complex of 8-hydroxyquinoline in aqueous solutions ($\log\beta_3 = 36.9$) [1] is about 14 log units greater than that of the copper complex of 8-hydroxyquinoline ($\log\beta_2 = 23.0$) [1]. KELEX 100 is a 7-alkenyl substituted derivative of 8-hydroxyquinoline, and should show a similar relative affinity for iron and copper. It was therefore generally believed [2-4] that the selectivity of KELEX 100 for copper(II) over iron-(III) was due to kinetic effects, and results presented recently confirmed these predictions [5].

Such a comparison has not been possible for LIX 65N, since no thermodynamic data have been reported for the ferric complex of salicylaldoxime

1 LIX 65N is a registered product of General Mills Inc., Tucson, Arizona, U.S.A.

2 KELEX 100 is a registered product of Ashland Chemicals, Columbus, Ohio, U.S.A.

(SALO). Evidence in favour of a kinetic effect in the selectivity of LIX 65N for copper over iron was presented recently [5] but these results were subsequently found to be in error. On the other hand, Price and Tumilty [6] proposed that the selectivity of LIX 65N for copper is thermodynamic in origin and that it might be attributed to the ability of copper ions to form neutral, planar complexes stabilized by the formation of four annelated chelate rings. The same considerations would not apply to octahedral ferric complexes that do not have hydrogen-bonded macrocyclic structures. Furthermore, the same arguments cannot be applied to KELEX 100, since intramolecular hydrogen bonding is not possible with ligands of the oxine type.

Ritcey and Lucas [2] interpreted the results of their experiments as suggesting that LIX 65N has a thermodynamic selectivity for copper over iron but the selectivity of KELEX 100 is of kinetic origin.

In this paper, data for equilibrium loading during solvent extraction and thermodynamic data are presented to substantiate these arguments. In addition, the results of experiments carried out in this investigation on resins impregnated with these reagents shed new light on the origin of copper selectivity.

EXPERIMENTS

1. REAGENTS

A.R.-grade salicylaldoxime and 8-hydroxyquinoline were used without further purification. LIX 65N and KELEX 100 were separated from their inactive isomers and impurities by preparation of the copper complexes followed by acidolysis. The method is described elsewhere [7].

2. DILUENTS

Commercial-grade chloroform was used in the tests on equilibrium loading, and commercial-grade perchloroethylene was used in the studies on impregnated resins. In the experiments on stability constants, the solvent medium consisted of various mixtures of distilled water and dioxane of Merck extrapure grade.

3. EQUILIBRIUM LOADING TESTS

The organic phase consisted of 0.01M active reagent in chloroform, the aqueous phase of Cu^{2+} (4.39 g/l) and Fe^{3+} (4.48 g/l) in nitrate medium at a pH value of 2.00. No adjustment of pH was made during the course of the extraction process, and the final pH value was generally between 1.0 and 1.2.

In a series of separating funnels, 10 ml of the organic solution was vigorously agitated with 10 ml of aqueous solution. Samples were withdrawn over a period of 3 weeks, and the aqueous phase was analysed for Cu^{2+} and Fe^{3+} by atomic-absorption spectrophotometry. Only 0.02 ml of aqueous phase (appropriately diluted) was used for each analysis, so that, at equilibrium, the overall decrease in the aqueous volume was minimal.

4. TESTS ON IMPREGNATED RESINS

In the preparation of a conventional impregnated resin, a solution of reagent and methylenechloride was slowly concentrated in the presence of a resin matrix on a rotary evaporator. The impregnated resin thus formed was dried further under vacuum for 16 hours. A portion of the impregnated resin was modified by diluent added drop by drop. Stirring of the impregnated resin ensured even distribution of the diluent over the resin. Details of the impregnated resins used are summarized in Table 1.

TABLE 1

Formulation of Impregnated Resins

Resin	Matrix (g)		Reagent (g)			Diluent (g)
No.	XAD-2	XE-305	LIX 65N	LIX 63	KELEX 100	Perchloro-ethylene
1	5.00		2.00	0.08		
2	5.00				2.00	
3		4.20	1.50	0.06		7.00
4		2.60			1.33	4.06
5	4.20		1.50	0.06		7.00

Portions of resin, each of 1 gm, were contacted and agitated for various periods of time with 50 ml of synthetic pregnant solution. The loaded resins were then washed with water and eluted completely with sulphuric acid (120 g/l). The copper and iron in the eluate were determined by atomic-absorption spectroscopy, and separation factors were calculated from the ratio

$$\alpha_{Cu^{2+}/Fe^{3+}} = \frac{\overline{[Cu^{2+}]}[Fe^{3+}]}{[Cu^{2+}]\overline{[Fe^{3+}]}} , \qquad (1)$$

where bars denote species on the resin.

The following pregnant solutions were tested.

(i) Sulphate medium: Cu^{2+} (1 g/l) Fe^{3+} (3 g/l), and Mg^{2+} (10 g/l) as sulphates. The solution was saturated with calcium sulphate and adjusted to a pH value of 2 with sulphuric acid.

(ii) Nitrate medium: Cu^{2+} (1 g/l), and Fe^{3+} (1 g/l) as nitrates. The pH value was adjusted to 2 with nitric acid.

5. TESTS ON STABILITY CONSTANTS

The complexes formed between LIX 65N and Fe(III) and Cu(II) were investigated by use of the model compound, salicylaldoxime, because it is available in a pure crystalline state, and because it is fairly soluble in an aqueous solution. However, owing to the fact that the neutral complexes $Fe(SALO)_3$ and $Cu(SALO)_2$ are virtually insoluble in water, the reactions were investigated in various mixtures of water and dioxane, and the values for water obtained by extrapolation.

Stability constants were determined from the absorption of the complexes formed in the visible region of the ultraviolet-visible spectrum. The ratio of SALO to metal ion was varied over as wide a range as experimentally possible, and changes in the spectrum (wavelength and absorption) noted. The stoichiometry of the complex formed was then established by Job's method, in which the maximum absorption is plotted as a function of the ratio of metal to SALO. The greatest absorption is obtained at the ratio of metal to SALO of the complex in solution. Since the stoichiometry of the complex, its extinction coefficient, and the acid-dissociation constant for SALO are known, it is possible for the stability constant of the complex to be calculated.

In the iron-SALO study, acid concentrations were confined to the range 0.1 to 0.3 M to prevent the formation of hydrolysed Fe(III) species (which absorb strongly in the ultraviolet and visible regions) and the formation of protonated SALO (H_3L^+), which becomes significant at concentrations of 0.5 to 0.7 M acid. In the copper-SALO study, a pH value of around 4 was found to be suitable, since all of the ligand is in the H_2L form at this pH value, and no side reactions occur.

Interference by inorganic complexes of Fe(III) was minimized by the use of perchlorate salts and perchloric acid, A.R.-grade materials being used throughout. The ionic strength was adjusted with lithium perchlorate, and the spectra were recorded on a Beckman Acta MIV spectrophotometer.

RESULTS

a. LOADING TESTS

The results of the loading tests for various mixtures of KELEX 100 and 8-hydroxyquinoline are given in Figure 1. The uppermost curve in Figure 1 represents the reagent mixture that contains KELEX 100 in the form in which it is received from the manufacturers, so that the 2 per cent 8-hydroxyquinoline, reported in Figure 1, is only an approximate value [8].

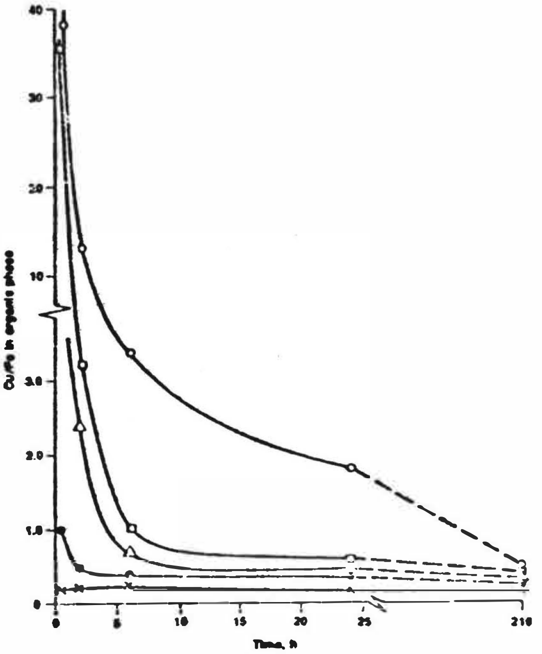

FIGURE 1

The effect of 8-hydroxyquinoline in KELEX 100 on the selectivity of the reagent for copper(II) over iron(III). $[Cu^{2+}]$ = 4.39 g/l, $[Fe^{3+}]$ = 4.48 g/l. Total ligand = 0.10 M, Initial pH value = 2.00. Mole percentage 8-hydroxyquinoline = 100 (x), 40 (●), 16 (Δ), 8 (□), and 2 (O).

The results show clearly that commercial KELEX 100 owes its selectivity for copper over iron to kinetic phenomena. After half-an-hour of extraction, the ratio of copper to iron in the organic phase is 38. However, after 216 hours, it can be seen that this ratio has fallen to 0.5. As the contact time between the phases is generally less than 5 minutes in normal plant operation, excellent selectivities can be expected.

The other curves in Figure 1 represent reagent mixtures containing a higher percentage of 8-hydroxyquinoline, and they show that the copper-iron separation factor decreases as the proportion of 8-hydroxyquinoline in the reagent mixture increases. In fact, in the case of pure 8-hydroxyquinoline, there is a reversal of selectivity and, even after very short contact times, the copper-to-iron ratio in the organic phase is about 0.1.

The results for various mixtures of LIX 65N and salicylaldoxime are given in Table 2. These results show that LIX 65N and salicylaldoxime and any mixture of the two, are selective for copper over iron, and that this situation does not change appreciably over a period of 18 days.

TABLE 2

The Extraction of Copper(II) and Iron(III) from Aqueous Nitrate Media by Various Reagent Mixtures of LIX 65N and Salicylaldoxime in Chloroform

$[Cu^{2+}]$ = 4.39 g/l, $[Fe^{3+}]$ = 4.48 g/l
Total ligand concentration = 0.10 M, initial pH value = 2.00

Reagent Composition (Mole %)		Metal Extracted (%) as a Function of Time							
LIX 65N	Salicylal-doxime	1.5 h		3.0 h		22.0 h		428.0 h	
		Cu	Fe	Cu	Fe	Cu	Fe	Cu	Fe*
100	0	20	2	26	1	38	2	40	1.9
80	20	29	2	39	1	44	2	45	2.1
60	40	39	1	37	3	48	1	49	1.4
40	60	44	2	46	2	50	1	52	0.8
20	80	50	2	51	2	52	2	55	0.3
0	100	59	1	60	1	57	3	61	0.1

* Analysed by stripping of iron from the organic phase with 20 per cent sulphuric acid, and determination of the iron in the stripping solution.

b. TESTS ON IMPREGNATED RESINS

A comparison of the performance of conventional impregnated resins and solvent-modified impregnated resins is given in Figure 2 for LIX reagents and in Figure 3 for KELEX 100. Some selectivity data from these two figures are summarized in Table 3. An XAD-2 matrix with a large surface area was used in the preparation of a conventional impregnated resin; a matrix with good swelling properties, XE-305, was chosen for the diluent-modified impregnated resins.

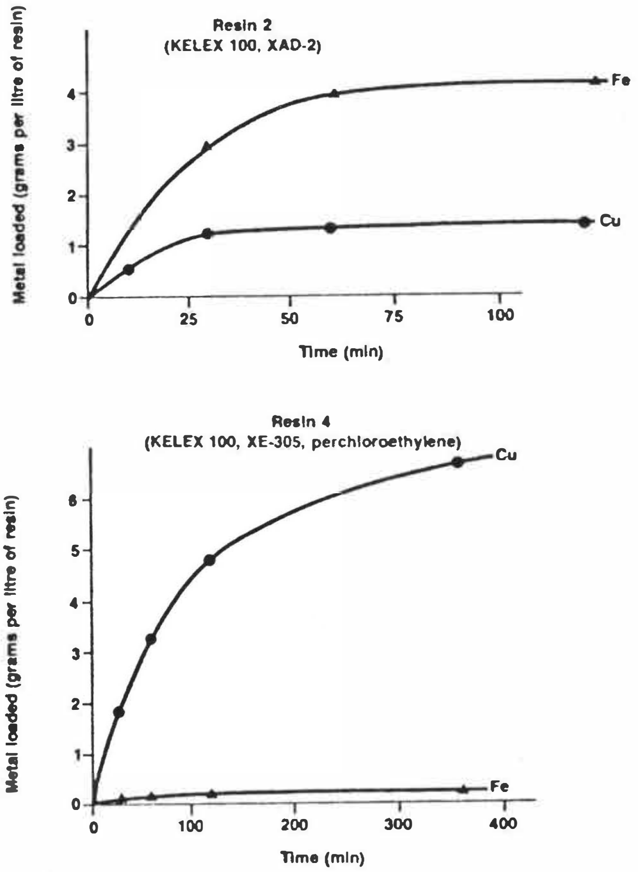

FIGURE 2

The effect of diluent on loading on KELEX impregnates

TABLE 3

Selectivity of Impregnated LIX and KELEX for Copper(II) over Iron(III)

Resin	Type	$\alpha_{Cu/Fe}$
1	LIX XAD-2	13
3	LIX XE-305 perchloroethylene	200
5	LIX XAD-2 perchloroethylene	250
2	KELEX XAD-2	0.1
4	KELEX XE-305 perchloroethylene	70

When impregnated resins are loaded, they rapidly (i.e., in less than 10 minutes) attain a pseudo-equilibrium state dictated by kinetic factors. Thereafter, the metal concentration on the resin may change slowly as the true thermodynamic selectivity emerges. It is the pseudo-equilibrium that is referred to in Table 3.

The improved selectivity for copper over iron, which is imparted by the diluent, is clearly shown for the LIX and the KELEX reagents. In fact, for KELEX 100 there is a reversal of selectivity that is consistent with the results for experiments on loading during solvent extraction shown in Figure 1.

These results were obtained for the pregnant solution containing sul-

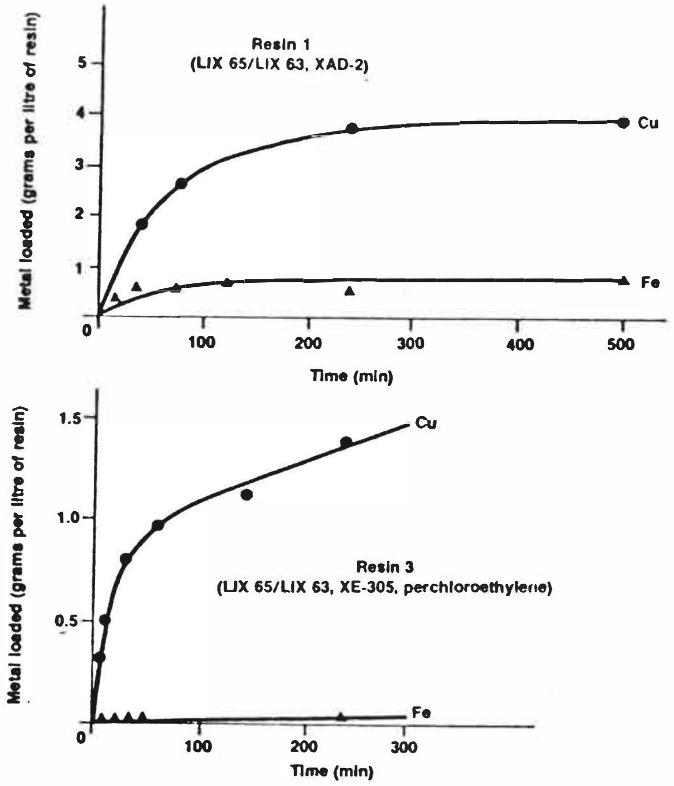

FIGURE 3

The effect of diluent on loading on LIX impregnates

phate ions. The formation of fairly stable ferric sulphate complexes (which do not load into LIX or KELEX solvents) is therefore likely to influence the copper-iron selectivity of the reagents. As a test of this suggestion, the experiments on impregnated resins were repeated with a pregnant solution containing nitrate ions. The results are presented in Table 4.

TABLE 4

The Effect of the Anion in Solution on the Selectivity of Impregnated Resins

Resin	Type	Anionic Medium	$\alpha_{Cu/Fe}$	Loading Time (h)
1	LIX XAD-2	Sulphate	17	4
			17	24
			16	72
		Nitrate	9	4
			3	24
			1.7	168
3	LIX XE-305 perchloroethylene	Sulphate Nitrate	$\approx$200 $\approx$ 70	4 4

Separation factors are substantially reduced when loading takes place from a nitrate medium in which there is no competition between the resin and the solution for ferric ions. It is of interest that the results for resin 1 in a nitrate feed suggest that a kinetic effect is operative under these conditions.

c. EXPERIMENTS ON STABILITY CONSTANTS

The detailed results and experimental methods are not reported here since they are to be published elsewhere [9]. This paper is concerned primarily with the selectivities of oxine and oxime reagents for copper over iron, and the possible influence of the stabilities of the complexes on these selectivities. Therefore, only the calculated stabilities of the complexes formed are reported in the tables below.

(i) Copper-salicylaldoxime (SALO)

Only one copper-SALO species was observed, and Job's method established it as the $Cu(SALO)_2$ complex. The spectrum exhibited two absorption maxima and two isosbestic points, indicating the presence of two absorbing species, SALO and the complex. The spectrum did not change as the ratio of copper to SALO was varied from 0.08 to 50.

The observed reaction is:

$$Cu^{2+} + 2H_2L \rightleftharpoons Cu(HL)_2 + 2H^+ . \qquad (2)$$

$$\beta_2^* = \frac{[Cu(HL)_2][H^+]^2}{[Cu^{2+}][H_2L]^2} = \frac{[Cu(HL)_2]}{[Cu^{2+}][HL^-]^2} \times \frac{1}{K_a^2} = \frac{\beta_2}{K_a^2} , \qquad (3)$$

where K_a is the acid dissociation constant for the phenolic proton of SALO

$$H^+ + HL^- = H_2L. \qquad (4)$$

Values for various mixtures of dioxane and water are presented in Table 5.

TABLE 5

Formation Constants for the $Cu(SALO)_2$ Complex in Various Media. Ionic Strength = 0.1 ($NaClO_4$), pH Value = 4.20

Dioxane	$\frac{\beta_2^*}{[H^+]^2} \times 10^{-8}$	β_2^*	Log K_a	Log β_2
75.0	2.3 ± 0.4	0.916	10.70†	21.35 ± 0.07
67.0	2.2 ± 0.6	0.876	10.46	20.86 ± 0.10
57.0	0.49± 0.14	0.195	10.20	19.69 ± 0.10
46.4	0.18± 0.01	0.072	9.80	18.45 ± 0.02
0	0.0063‡	0.0025	8.9‡	15.2‡

† Reference 10

‡ Values obtained by extrapolation

Comparison of the values from the literature is possible only with the values for 75 per cent dioxane. The log β_2 value of 21.35 can be compared with 23.8 (potentiometric technique [11])and 21.5 (spectrophotometric technique [10]).

(ii) Iron-SALO

Immediately upon the mixing of iron and SALO in a solution of dioxane and water, a broad band is formed with an absorption maximum at about 580 nm. Once again, Job's method was used for identification of this species as the 1:1 complex $Fe(SALO)^{2+}$. The spectrum did not change as the ratio of SALO to iron was increased from 1 to 600.

The broad band at 580 nm undergoes a slow change to form a new species, the final spectrum of which is characterized by a broad band with a peak at 520 nm. The half-life of this reaction is of the order of several hours. The peak at 520 nm is very similar to the spectrum of $Fe(SALO)_3$ in an organic solvent, so it may be speculated that the product of the slow reaction in dioxane and water is $Fe(SALO)_3$. However, it has not yet been possible for formation constants to be derived for either of the two higher complexes.

The observed rapid reaction is

$$Fe^{3+} + H_2L \rightleftharpoons Fe(HL)^{2+} + H^+ , \qquad (5)$$

where

$$\beta_1^* = \frac{[Fe(HL)^{2+}][H^+]}{[Fe^{3+}][H_2L]} = \frac{[Fe(HL)]^{2+}}{[Fe^{3+}][HL^-]} \times \frac{1}{K_a} = \frac{\beta_1}{K_a} .$$

Values for the formation constant in a mixture of 75 per cent dioxane and 25 per cent water at three different acid concentrations are presented in Table 6.

TABLE 6

Formation Constant for the $Fe(SALO)^{2+}$ Complex at an Anionic Strength of 0.3 M ($LiClO_4$)

$[H^+]$ (M)	$\frac{\beta_1^*}{[H^+]}$	β_1^*	log K_a	log β_1
0.1	28.8	2.88	10.70†	11.16
0.2	11.1	2.22	10.70	11.05
0.3	7.0	2.10	10.70	11.02

† Reference 10

DISCUSSION

There can be little doubt that KELEX 100 owes its selectivity for copper over iron to kinetic factors. Results showing that the separation factor for copper and iron changes with time have been presented before [5], and further evidence is presented here in Figure 1. Moreover, the results presented here suggest that this selectivity is a function of the insolubility of the reagent in aqueous solutions and of the presence of an inert organic diluent. In the first instance, this evidence is provided by the reversal in the selectivity of copper over iron in extractions by 8-hydroxyquinoline, the water-soluble analogue of KELEX 100. In the second instance, the evidence is provided by the KELEX 100-impregnated resins where a copper-iron separation factor of 70 is reduced to less than 1, merely by removal of the inert diluent from the resin matrix.

Studies on the kinetics of iron extraction by 8-hydroxyquinoline [8, 12] and KELEX 100 [13] have shown that the former reaction is diffusion controlled, whereas the latter is chemically controlled. It has been shown that copper extraction by both KELEX 100 [14] and 8-hydroxyquinoline [15] is diffusion controlled. On this basis it can be concluded that the selectivity of KELEZ 100 for copper over iron originates in the slow chemical reaction between iron and KELEX 100. On the other hand, 8-hydroxyquinoline extracts copper and iron by diffusion-controlled reactions, and therefore little kinetic selectivity (based on the relative rates of diffusion of the two complexes) can be expected. In this case, the stability of the metal complex becomes the most important criterion in the determination of the separation factor, and a selectivity for iron over copper can be predicted [1]. This is adequately borne out by the results for pure 8-hydroxyquinoline, presented in Figure 1.

It is interesting to speculate on the mechanism of the slow iron-KELEX 100 reaction. The observation that the selectivity for copper depends on the low solubility of the reagent in the aqueous phase and on the presence of an inert organic diluent indicates that the reactions between KELEX 100 and copper or iron take place either at the interface or in an aqueous zone close to the interface. This is consistent with current thinking on the location of the zone of chemical reaction in solvent-extraction systems [7], and also with the known low solubility of KELEX 100 in aqueous solutions [16].

Iron-substitution reactions are known to be several orders of magnitude slower than copper-substitution reactions in a homogeneous aqueous environment. Moreover, in solvent extraction, a prerequisite for extraction is that the neutral chelate must be formed, and therefore the rate of formation of this species and not that of any intermediate complex becomes the most important criterion in the determination of extraction rates. In the case of trivalent iron, three substitution reactions must take place, and it is probable that each substitution reaction is slower than the one preceding, due to the successive reduction of charge on the metal ion. The possibility therefore exists that thermodynamically stable intermediate species (FeK^{2+} or FeK_2^+) may be formed fairly rapidly in competition with copper, i.e., for 8-hydroxyquinoline, $\log \beta_2(Cu) = 23.0$ and $\log \beta_2(Fe) = 26.3$ [1]. However, whereas the neutral copper complex is extractable, the charged iron complex is not.

The results for the impregnated resins provide evidence for such intermediate species. Thus, Warshawsky's [17] work indicates that the surface area of the resin is covered by approximately one monolayer of reagent in an impregnated resin that contains no inert diluent. Under these conditions, the requirements pertaining to neutral species in the organic phase disappear, and the extracted species can be either charged or neutral, i.e., the hydrophilic functional groups of the reagent will orientate in the aqueous phase and a hydrated, charged metal ion can approach and interact with such functional groups to form an extracted species that may be only partially substituted. The concentration of KELEX 100 at the aqueous KELEX interface will be infinitely large for a monolayer coverage of reagent, and therefore, by analogy with the 8-hydroxyquinoline results, diffusion-controlled kinetics for copper and iron can be expected. Under these conditions, thermodynamics becomes the most important criterion in the determination of the separation factor, and a selectivity for iron over copper can be predicted - a prediction borne out by the results given in Figure 3.

In the impregnated resins modified with diluent, the situation is similar to that in solvent extraction, since the concentration of KELEX 100 in the reaction zone is very low. Therefore, the concentration of partially substituted iron complexes in the reaction zone will also be low and any iron in the organic phase will be the fully substituted neutral chelate, which will have undergone slow chemical reaction. The selectivities should therefore be similar to those found in solvent extraction.

The results given in Table 2 show that LIX 65N and salicylaldoxime are selective for copper over iron and that this situation does not change noticeably over a period of 428 hours. This indicates that the selectivity is thermodynamic in origin, which agrees with the conclusions reached by earlier workers [2,6]. The study on impregnated resins sheds further light on these observations. Thus, results given in Table 3 show that, in the diluent-modified impregnated resins, a selectivity of more than 200 can be achieved. However, in the absence of inert diluent, this selectivity is reduced by a factor of 15. By analogy with KELEX 100, it is proposed that, in the diluent-modified impregnated resins, a prerequisite for extraction is the formation of neutral chelates in the reaction zone whereas, when the diluent is removed, the extracted species can be either charged or neutral. In the first case, the selectivity is therefore determined by the relative stabilities of the CuL_2 and FeL_3 complexes whereas, in the second case, the relative stabilities of the intermediate species CuL^+, FeL^{2+}, and FeL_2^+ also become important.

The data on the stability constants for salicylaldoxime are interesting in this context. Thus, the results show that the neutral complex, CuL_2, is far more stable than the 1:1 species CuL^+, - so much so that, even at a copper-to-ligand ratio of 50, the latter complex is undetectable. The extra stability associated with the CuL_2 species is almost certainly due to the formation of a hydrogen-bonded macrocyclic structure, as proposed by Price and Tumilty [6].

Whereas the neutral copper species is readily extractable into an organic solution, the dominant species (kinetically metastable) in the iron-salicylaldoxime reaction is apparently the charged 1:1 intermediate FeL^{2+}, which is clearly not extractable under solvent-extraction conditions.

However, in an impregnated resin, both species would be extractable. In fact, the results presented in Tables 5 and 6 indicate that, in a perchlorate medium, iron ($\beta_1^* = 2.4$) should be extracted in preference to copper ($\beta_2^* = 0.92$). Similar results could be expected in a nitrate medium, whereas in a sulphate medium the formation of strong ferric sulphate complexes will reduce the value of β_1^*. These predictions are adequately borne out by the results presented in Table 4. The kinetic component to the selectivity in a nitrate medium, under these conditions, is interesting, since it implies that the reaction to form FeL^{2+} at the LIX-monolayer surface is not sufficiently fast to be controlled by diffusion, as was apparently the case with KELEX 100.

Finally, it could be argued that the changes in selectivity of impregnated resins are due to steric constraints imposed by the solid resin matrix on the chelation of copper, and that these constraints are absent in a diluent-modified impregnated resin or in a solvent-extraction system. Militating against steric effects, however, is the fact that the same diluent-induced changes in selectivity are observed in a macroporous resin with very good swelling properties (XE-305) as in a non-swelling resin (XAD-2) with a large surface area (see Table 3).

CONCLUSIONS

Under solvent-extraction conditions, the selectivity of KELEX 100 for copper over iron originates in the slow chemical reactions between iron and

KELEX 100 to form the neutral chelate in the interfacial zone. However, at an aqueous-KELEX interface (in impregnated resins, for example) the KELEX concentration is sufficiently high for the kinetic reactions of the iron-KELEX reaction to be controlled by diffusion. Under these conditions, the separation factor is determined by thermodynamic factors and a selectivity for iron over copper is observed.

The selectivity of LIX 65N for copper over iron is thermodynamic in origin. Under solvent-extraction conditions, the separation factor is determined by the relative stabilities of the neutral chelates, CuL_2 and FeL_3, in the interfacial zone ($\alpha \approx 200$ for sulphate medium). In impregnated resins, however, the separation factor is determined by the relative stabilities of the species CuL_2 and FeL^{2+}, and α is reduced to about 17 for a sulphate medium.

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INVESTIGATION OF THE CATALYTIC MECHANISM IN THE EXTRACTION OF COPPER WITH MIXTURES OF THE PURE ACTIVE HYDROXYOXIME ISOMERS OF LIX64N

L. Hummelstedt, E. Paatero, T. Nyberg
and L. Rosenback

Laboratory of Industrial Chemistry
Åbo Akademi

SF-20500 ÅBO FINLAND

ABSTRACT

The catalytic effect of the *anti* isomer of 5,8-diethyl-6-hydroxy-7-oximinododecane on the extraction of copper from sulphate solutions with the *anti* isomer of 2-hydroxy-5-nonylbenzophenone oxime has been studied both in a Lewis cell and in a dispersion cell. The results are quantitatively explained in terms of a model assuming interfacial equilibrium involving positively charged reaction intermediates which are strongly oriented at the interface. In the Lewis cell the physical reorientation of these intermediates is rate-limiting, while the kinetics of the addition of the second ligand begins to affect the overall extraction rate in the dispersion cell. Numerical values are reported for the rate and equilibrium constants included in the model.

INTRODUCTION

In previous papers (1,2) from our laboratory an approximate model was presented for the catalytic action of 5,8-diethyl-6-hydroxy-7-oximinododecane (DEHOD) on the extraction of copper with 2-hydroxy-5-nonylbenzophenone oxime (HNBPO). These two compounds are the active components of the well-known commercial copper extractant LIX64N. Our model contained experimental mean aggregation numbers for the extractants as parameters and provided a qualitative explanation for the diluent effects on the observed reaction orders and the apparent activation energy of the extraction. The catalytic mechanism proposed was based entirely on kinetic data from the literature. We have now performed kinetic copper extraction studies using both a stirred cell with quiescent interface and a dispersion cell with vigorous agitation. Chloroform was chosen as the diluent because of the low aggregation tendency of the extractants in this solvent (1). In most cases, copper was extracted from sulphate solutions, but for the sake of comparison some experiments were also performed using aqueous chloride media. Only *anti*-HNBPO (also called (E)-HNBPO; denoted RH in the following) and *anti*-DEHOD ((E)-DEHOD; denoted BH) were used as extractants, the inactive *syn* (or Z) isomers being excluded by careful purification of commercial extractants. Care was also taken to exclude other interfering components such as nonyl phenol.

It was found that the previously suggested catalytic mechanism (1,2) did not explain the kinetic results satisfactorily. In the present paper, a new model is presented which describes the experimental data in a quantitative manner.

THEORY

Extraction in stirred cells with quiescent interface. When the extraction is performed using stirred cells with a plane interface, the following mechanism is assumed for the extraction of copper with RH only:

$$Cu^{2+} + RH_i \rightleftarrows CuR^+_i + H^+ \qquad (1)$$

Subscript i denotes species at the organic interface. For simplicity the hydrated copper ion is denoted Cu^{2+} and the charged intermediate CuR^+_i is also assumed to contain some water of hydration. While CuR^+_i can only exist at the interface, equation (2) is assumed to describe the equilibrium between the interfacial concentration $[RH]_i$ and the bulk concentration $[\overline{RH}]$ of the extractant:

$$[RH]_i = K_2[\overline{RH}](1 - a\,[CuR^+]_i) \qquad (2)$$

The symbol a stands for the interfacial area occupied by one mole of CuR^+_i and the equation implies that RH cannot compete successfully with CuR^+_i for space at the interface. It is recognized that K_2 may not be constant over a wide range of conditions. For example, the interfacial tension caused by RH has been reported to change with the pH of the aqueous solution in contact with the organic phase (3).

Equilibrium is assumed to be maintained in reaction (1), the equilibrium constant K_1 being given by the expression

$$\frac{[CuR^+]_i\,[H^+]}{[Cu^{2+}][\overline{RH}](1 - a[CuR^+]_i)} = K_1\,K_2 \qquad (3)$$

The charged intermediate CuR^+_i is likely to be strongly oriented with the partially hydrated copper ion pointing toward the aqueous phase. If this is a sulphate solution the water of hydration is not efficiently displaced by other coordinating species in the aqueous phase, and further reaction with RH in the organic phase is sterically hindered. The rate-limiting step in the extraction is therefore assumed to be a physical reorientation with a rate directly proportional to the surface concentration $[CuR^+_i]$. The proportionality constant k_4 depends on the hydrodynamic conditions but may be expected to be constant at a constant rotation frequency of the stirrers used in the experiments. With these assumptions, equation (3) yields the following expression for the copper extraction rate N:

$$N = \frac{k_4 K_1 K_2 [Cu^{2+}][\overline{RH}]}{[H^+] + K_1 K_2 a [Cu^{2+}][\overline{RH}]} \qquad (4)$$

When the product term in the denominator is much smaller than $[H^+]$, equation (4) predicts that the extraction rate should be first order in $[Cu^{2+}]$ and $[\overline{RH}]$ while it should be inversely proportional to $[H^+]$. This agrees with many of the results reported in the literature (2). It is also interesting to note that a constant maximum rate N_{max} should be reached at high pH values:

$$N_{max} = \frac{k_4}{a} \qquad (5)$$

Equation (5) explains why the extraction rate becomes independent of the hydrogen ion concentration in the pH region 3-4. Thus it is not necessary to assume that pH gradients are formed at the interface, as suggested earlier (1,2).

When copper is extracted with mixtures of RH and BH the following equilibrium is rapidly established at the interface:

$$CuR^+_i + BH_i \rightleftharpoons CuRBH^+_i \tag{6}$$

The catalytically active component BH is much less acidic than RH and it is therefore assumed to react in the molecular form in the pH region ≤ 2. At high BH and copper concentrations and low pH this compound has been shown to transfer $CuSO_4$ and $Cu(HSO_4)_2$ to the organic phase (1). According to van der Zeeuw and Kok (4), BH collects more strongly than RH at the interface, and it is therefore assumed to be able to displace CuR^+_i at the interface. The equilibrium between BH at the interface and in the bulk of the organic phase is thus given by the simple expression

$$\frac{[BH]_i}{[\overline{BH}]} = K_7 \tag{7}$$

In this case, the corresponding equilibrium for the less interfacially active extractant RH is written as

$$[RH]_i = K_2[\overline{RH}](1 - a[CuR^+]_i - b[CuRBH^+]_i - cK_7[\overline{BH}]) \tag{8}$$

where b and c are the areas covered by monomolecular layers of one mole of $CuRBH^+_i$ and BH_i, respectively. The equilibrium expression of reaction (1) then takes the form

$$\frac{[CuR^+]_i\ [H^+]}{[Cu^{2+}][\overline{RH}](1 - a[CuR^+]_i - b[CuRBH^+]_i - cK_7[\overline{BH}])} = K_1\ K_2 \tag{9}$$

Using the equilibrium constant K_6 of reaction (6) and expressing $[BH]_i$ by means of equation (7), one obtains expressions for the interfacial concentrations $[CuR^+]_i$ and $[CuRBH^+]_i$. Since the copper ion in CuR^+_i probably looses its residual water of hydration in the reaction forming $CuRBH^+_i$ this new intermediate is likely to reorient itself faster than CuR^+_i. However, the reorientation step is assumed to be rate-limiting in this case also. The rate N_{cat} of the BH-catalyzed copper extraction can thus be described by equation (10):

$$N_{cat} = k_4[CuR^+]_i + k_{10}\ [CuRBH^+]_i =$$

$$= \frac{K_1K_2[Cu^{2+}][\overline{RH}](1-cK_7\ [\overline{BH}])}{[H^+]+K_1K_2(a+\ bK_6K_7[\overline{BH}])[Cu^{2+}][\overline{RH}]}\left(k_4 + k_{10}\ K_6K_7[\overline{BH}]\right) \tag{10}$$

At equal concentrations of copper and RH a comparison of the rates for catalyzed and uncatalyzed extraction, respectively, yields the expression

$$\frac{N_{cat}}{N} = \frac{([H^+]+aK_1K_2[Cu^{2+}][\overline{RH}])(1-cK_7[\overline{BH}])}{[H^+]+K_1K_2(a+bK_6K_7[\overline{BH}])[Cu^{2+}][\overline{RH}]}\left(1+\ \frac{k_{10}\ K_6K_7}{k_4}\ [\overline{BH}]\right) \tag{11}$$

At low acidity (pH ≥ 3.5) equation (11) may be simplified to the following form, which is useful for comparison with experimental rate data:

$$\left(\frac{N_{cat}}{N}\right)_{pH \geq 3.5} = \frac{a(1 - cK_7[\overline{BH}])}{a + bK_6K_7[\overline{BH}]}\left(1 + \frac{k_{10}K_6K_7}{k_4}[\overline{BH}]\right) \qquad (12)$$

The previous treatment is valid for extraction in stirred cells of the Lewis type, where the agitation is so mild that a plane interface is maintained. Under such conditions the physical reorientation of the positively charged intermediates CuR_i^+ and $CuRBH_i^+$ limits the extraction rate and thus the subsequent reaction steps

$$CuR_i^+ + \overline{RH} \underset{k_{-13}}{\overset{k_{13}}{\rightleftharpoons}} CuR_{2i} + H^+ \qquad (13)$$

and

$$CuRBH_i^+ + \overline{RH} \underset{k_{-14}}{\overset{k_{14}}{\rightleftharpoons}} CuR_{2i} + BH_i + H^+ \qquad (14)$$

do not affect the kinetics of the extraction. Interfacial tension measurements in the literature (5) indicate that CuR_2 is less interfacially active than RH, therefore the equilibrium

$$CuR_{2i} \rightleftharpoons \overline{CuR_2} \qquad (15)$$

should be well displaced to the right. At low concentrations far from extraction equilibrium CuR_2 is thus not expected to displace other reaction components from the interface.

Extraction in dispersion cells with vigorous agitation. When the agitation is increased, the reorientation rate constants k_4 and k_{10} may be expected to increase until reactions (13) and (14) become the rate-limiting steps in the extraction process. This gradual transition results in an increased reaction order for RH, as reported by van der Zeeuw and Kok (4) and confirmed by us. In a dispersion, the interfacial area is unknown and only the product SN of the area S and the extraction rate N can be measured. When only RH is present sufficiently vigorous agitation should yield an extraction rate following equation (16), which

$$SN = \frac{k_{13}K_1K_2[Cu^{2+}][\overline{RH}]^2}{[H^+] + K_1K_2a[Cu^{2+}][\overline{RH}]} \qquad (16)$$

is obtained from equation (4) by replacing the reorientation rate constant k_4 by the product of the reaction rate constant k_{13} and the extractant concentration $[\overline{RH}]$ according to reaction (13). In the presence of BH the corre- rate expression is easily obtained from equation (10):

$$SN_{\mathrm{cat}} = \frac{K_1 K_2 [\mathrm{Cu}^{2+}][\overline{\mathrm{RH}}]^2 (1 - cK_7[\overline{\mathrm{BH}}])}{[\mathrm{H}^+] + K_1 K_2 (a + bK_6 K_7 [\overline{\mathrm{BH}}])[\mathrm{Cu}^{2+}][\overline{\mathrm{RH}}]} \left(k_{13} + k_{14} K_6 K_7 [\overline{\mathrm{BH}}]\right) \qquad (17)$$

At equal copper and RH concentrations equations,(17) and (16) yield the following ratio:

$$\frac{SN_{\mathrm{cat}}}{SN} = \frac{([\mathrm{H}^+] + K_1 K_2 a[\mathrm{Cu}^{2+}][\overline{\mathrm{RH}}])(1 - cK_7[\overline{\mathrm{BH}}])}{[\mathrm{H}^+] + K_1 K_2 (a + bK_6 K_7 [\overline{\mathrm{BH}}])[\mathrm{Cu}^{2+}][\overline{\mathrm{RH}}]} \left(1 + \frac{k_{14} K_6 K_7}{k_{13}} [\overline{\mathrm{BH}}]\right) \qquad (18)$$

Equation (18) differs from equation (11) only with respect to the rate constants but it seems likely that the ratio k_{14}/k_{13} is considerably smaller than k_{10}/k_4. From equation (18),retarding effects such as those reported by van der Zeeuw and Kok (4) therefore appear possible. It should be pointed out that equations (16)-(18) imply that equilibrium is maintained at the interface in spite of the increased extraction rate in the dispersion cell. This is not necessarily the case.

EXPERIMENTAL

Solvents and chemicals. All aqueous solutions were prepared using distilled water which was further deionized with a Milli-Q$^{\mathrm{RM}}$ Water Purification System. All other solvents and chemicals were of p.a. quality except for the *anti* isomers of HNBPO and DEHOD, which were isolated from the commercial extractants LIX65N and LIX63, respectively.

For isolation of *anti*-HNBPO,the oxime was first precipitated with aqueous sodium hydroxide from a solution of LIX65N in hexane. After washing it with hexane,the sodium salt was dissolved in ether by shaking with aqueous sulphuric acid. The free *anti* isomer was then converted into the copper complex by saturating the ether solution with copper at pH 4.0, whereafter the solid copper complex was precipitated by gradually replacing the ether with methanol under reduced pressure. Analysis of the solid copper complex showed it to be of the normal 1:2 type, but some variations in the composition were observed, as has also been reported in the literature (6). Because the *syn-anti* equilibrium for HNBPO is established relatively rapidly in solution (7) the isolated *anti* isomer was stored as the solid copper complex, solutions in chloroform being freshly prepared by stripping with aqueous sulphuric acid

The *anti* isomer of DEHOD was isolated from LIX63 according to the nickel method developed by Tammi (8).

Apparatus and experimental technique. The modified Lewis cell was a double-walled cylindrical glass vessel with an internal diameter of 60 mm. Internal mixing in the phases was provided by two independently variable two-bladed turbine stirrers, of which the lower one was driven magnetically. The stirrers rotated in opposite directions. The tip-to-tip dimension of the stirrers was 25 mm and the width of the blades 7 mm. The rotation frequency was accurately measured with a digital photo tachometer, a constant frequency of 3.75 s^{-1} being used for both stirrers on the basis of preliminary studies of the dependence of the extraction rate on the stirring frequencies. An immobile circular disc was mounted at the interface in the center of the vessel in order to prevent vortex formation and reduce the differences in agitation intensity between different parts of the interface, which had an area of 23.2 cm^2. The construction material was glass or PTFE except for the stainless steel spindle of the bottom stirrer which was only exposed to the organic phase.

The organic phase was continuously pumped from a bottom outlet through a VARIAN 634 UV-Visible spectrophotometer equipped with a chart recorder. Calibration showed the copper complex of *anti*-HNBPO in the organic phase to follow the Lambert-Beer law, and no spectral interference from added *anti*-DEHOD was observed at the wavelength used (669 nm).

During extraction the pH of the aqueous phase was kept constant to within 0.005 unit by addition of gaseous ammonia. A Radiometer PHM64 pH meter with a GK2401C combined electrode was used for monitoring the acidity of the aqueous phase. Extraction at constant pH gives linear absorbance curves with slopes directly proportional to the extraction rate.

When testing the effect of increasing additions of *anti*-DEHOD to the organic phase, injection of several small portions of a strong solution during the same run was found to give the best reproducibility. In all runs with the Lewis cell, the phase volume ratio was 1.0 (150 cm^3 of each phase) and the temperature 25.0 °C.

The double-walled dispersion cell had the same dimensions as the Lewis cell. A six-bladed impeller (tip-to-tip diameter 31.5 mm, blade width 11 mm) was run at 11.9 s^{-1}, which was the highest vibrationfree rotation frequency with the apparatus in question. The vessel was equipped with four vertical baffles.

During extraction 5-cm^3 samples of the dispersion were taken through the bottom outlet, and the organic phase was analyzed for copper using the spectrophotometer previously mentioned. The phase volume ratio and the temperature were the same as in the experiments with the Lewis cell.

RESULTS AND DISCUSSION

Extraction with RH alone. In the experiments designed to clarify the extraction mechanism with RH alone pH, [$\overline{RH}$] and [Cu(II)] were varied one at a time while keeping the other two variables constant. Equation (4) contains four constants which it should be possible to derive from the experimental results. The starting point was equation (5) which gave a value close to 10^{-4} mol/m^{2}s for the ratio k_4/a. As an approximation for a, we used the value $8.7 \cdot 10^5$ m^2/mol reported by Yagodin et al. (9) for RH in toluene on the basis of measurements by Al-Diwan et al. (3). The aggregation tendency of RH is low both in toluene and in chloroform (1) and the area covered by the charged intermediate CuR_i^+ should primarily be determined by the bulky ligand. Using data from extraction experiments at constant [Cu(II)] (400 mol/m^3) and [$\overline{RH}$] (50 mol/m^3) but different pH values, the following set of constants were found to give good agreement between the experimental rates and the rates calculated by equation (4):

$$a = 8.7 \cdot 10^5 \ \text{m}^2/\text{mol}$$

$$k_4 = 77.4 \ \text{s}^{-1}$$

$$K_1 K_2 = 3.1 \cdot 10^{-9} \ \text{m}$$

The agreement between theory and experiment achieved using these constants is illustrated in Table 1, where the free [$\overline{RH}$] is calculated by subtracting twice the concentration of extracted copper from the original [$\overline{RH}$] value.

The free copper ion concentration [Cu^{2+}] in the aqueous phase was roughly estimated using the model of Whewell and Hughes (10) although the authors state that such calculations will give trends rather than definitive answers. The model is valid for mixtures of $CuSO_4$ and H_2SO_4 only, and the neutralization with ammonia during extraction therefore introduces some uncertainty. Also, the model was in many cases used at higher pH values and Cu(II) concentrations than investigated by Whewell and Hughes ($1.1<pH<2.5$;$[Cu(II)]\leq 100$ mol/m^3). Thus the results can not be considered very reliable. However, the need to correct for the formation of the $CuSO_4$ complex is clearly shown by Fig.1, where the logarithm of the experimental extraction rate is plotted against the logarithms of the total aqueous copper concentration [Cu(II)] and the estimated free copper ion concentration [Cu^{2+}]. The latter plot gives a line with a slope of 1.03 which is not too much higher than one would expect from equation (4), since [H^+] in most experiments was considerably larger than the product term in the denominator. The reasonable agreement with theory in Table 1 in spite of large variations in [Cu(II)] provides the strongest indication of the soundness of the approach.

TABLE 1. Comparison of experimental extraction rates for RH only in the Lewis cell with rates calculated according to equation (4) using [Cu^{2+}] values estimated according to (10).

pH	$[\overline{RH}]$ mol/m^3	[Cu(II)] mol/m^3	[Cu^{2+}] mol/m^3	$N_{calc}\cdot 10^5$ mol/m^2 s	$N_{exp}\cdot 10^5$ mol/m^2 s	$\frac{N_{calc}}{N_{exp}}$
3.50	49.0	400	26.9	8.17	8.36	0.98
2.96	47.6	400	28.0	6.82	6.52	1.05
2.49	46.9	400	29.1	4.73	4.35	1.09
2.00	45.3	400	32.4	2.52	2.09	1.20
1.70	45.0	400	36.2	1.61	1.34	1.20
1.47	44.7	400	40.0	1.11	0.92	1.21
3.50	22.7	400	26.9	7.46	7.11	1.05
2.85	21.1	400	28.2	4.74	4.68	1.01
2.42	20.3	400	29.6	2.66	3.09	0.86
2.00	19.7	400	32.4	1.31	1.62	0.81
1.48	19.6	400	39.8	0.532	0.627	0.85
2.00	49.9	20.0	4.97	0.558	0.578	0.97
2.00	49.6	46.0	8.85	0.942	0.920	1.02
2.00	49.1	96.3	14.2	1.40	1.51	0.93
2.00	48.3	190	21.2	1.93	2.43	0.79
2.00	46.1	353	30.2	2.43	3.60	0.68
2.00	44.6	591	40.2	2.90	4.85	0.60

The extraction of copper with RH only was also studied in the dispersion cell at pH 1.75 and [Cu(II)] = 50 mol/m^3. When the extractant concentration $[\overline{RH}]$ was varied from 3.0 mol/m^3 to 15 mol/m^3, the initial rates yielded the plot in Fig. 2. Under these conditions, the product term in the denominator of equation (16) can be neglected compared to [H^+] and the reaction order for RH should therefore be 2.0. The observed slope of 1.45 indicates that the reorientation mechanism described by equation (4) plays a major role in the dispersion cell also at the rotation frequency used (11.9 s^{-1}).

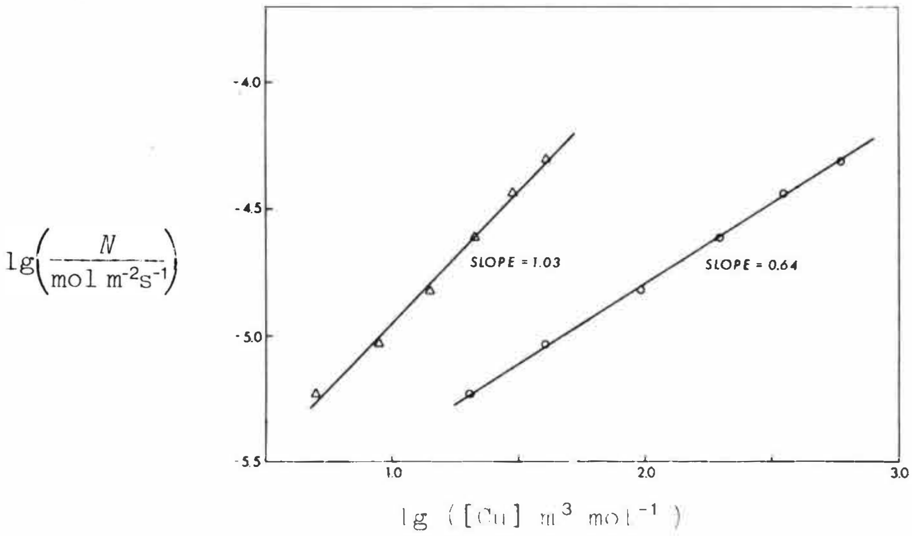

FIG. 1
The extraction rate in the Lewis cell at pH 2.00 as a function of [Cu(II)] (0) and $[Cu^{2+}]$ (Δ). ($[\overline{RH}]_o$ = 50 mol/m^3).

Extraction with mixtures of RH and BH. When treating the data obtained the Lewis cell with addition of BH to RH the constants *b* and *c* in equation (10) were obtained from the same sources as *a* (9,3). For the molar area *c* of BH_i the value $10.2 \cdot 10^5$ m^2/mol measured in toluene was used. The corresponding area for $CuRBH_i^+$ was taken as the sum of the areas for RH_i and BH_i in toluene, a value of $19 \cdot 10^5$ m^2/mol being obtained. Insertion of experimental data in equations yielded the following additional constants:

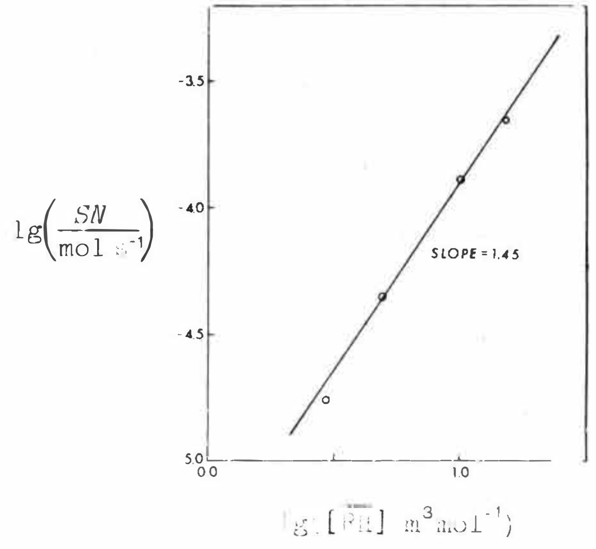

FIG. 2
The initial extraction rate in the dispersion cell as a function of the extractant concentration $[\overline{RH}]$ (pH = 1.75, [Cu(II)] = 50 mol/m^3).

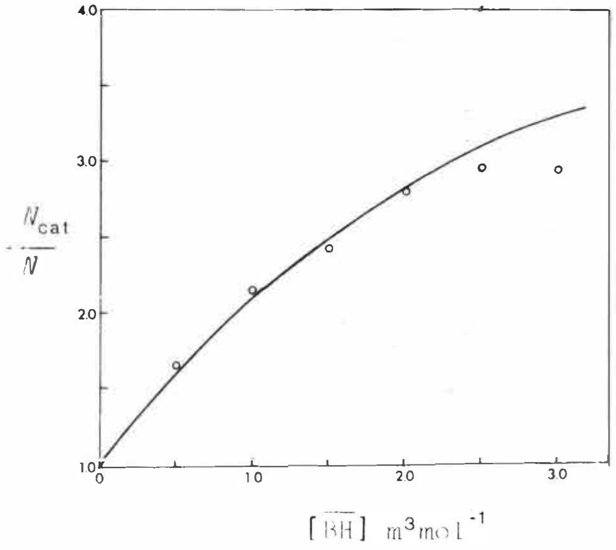

FIG. 3
Relative extraction rate in the Lewis cell as a function of $[\overline{BH}]$ (curve theoretical, points experimental). pH = 2.00, $[\overline{RH}]_o$ = 48.4 mol/m^3, [Cu(II)]= 400 mol/m^3, $[Cu^{2+}]$ = 32.4 mol/m^3.

$K_6 = 1.6 \cdot 10^6\ m^2/mol$
$K_7 = 6.4 \cdot 10^{-8}\ m$
$k_{10} = 1090\ s^{-1}$

As shown in Fig. 3 these constants give good agreement between theory and experiment. Further support for the theory is obtained from the comparison presented in Table 2.

TABLE 2. Comparison of experimental extraction rates with mixtures of RH and BH in the Lewis cell with rates calculated according to equation (10) using [Cu^{2+}] values estimated according to (10). ([Cu(II)] = 400 mol/m^3)

pH	[$\overline{BH}$] mol/m^3	[$\overline{RH}$] mol/m^3	[Cu^{2+}] mol/m^3	$N_{calc} \cdot 10^5$ mol/m^2 s	$N_{exp} \cdot 10^5$ mol/m^2 s	N_{calc}/N_{exp}
4.00	3.0	46.9	27.3	22.4	21.8	1.03
3.27	3.0	44.6	27.3	20.7	18.4	1.13
2.46	3.0	43.0	29.4	14.1	14.1	1.00
2.00	3.0	41.1	32.4	8.52	8.36	1.02
1.50	3.0	40.2	39.6	4.20	3.18	1.32
4.00	1.0	47.6	27.3	16.2	17.5	0.93
3.33	1.0	46.1	27.1	14.9	14.8	1.01
2.46	1.0	44.6	29.4	9.19	9.87	0.93
1.99	1.0	43.8	32.4	5.20	5.60	0.93
1.69	1.0	43.0	36.2	3.33	2.93	1.14
1.46	1.0	42.5	40.0	2.30	1.59	1.45

Equation (12) gives for [$\overline{BH}$] = 3.0 mol/m^3 a value of 2.56. Interpolation of the experimental rates in Table 2,gives a value of about $20 \cdot 10^{-5}$ mol/m^2 s at pH 3.50, where Table 1 gives the rate $8.36 \cdot 10^{-5}$ mol/m^2 s. The ratio thus becomes about 2.4, in good agreement with equation (12).

For the sake of comparison,some extraction experiments in the Lewis cell were performed using aqueous solutions containing chloride instead of sulphate. The extraction rate was then found to be independent of pH at least in the range 1.5 - 2.8, and addition of BH did not increase the extraction rate with RH (11). The reaction order for RH was close to one, a decrease being observed with increasing chloride concentration. Further, the rate of extraction was considerably higher in chloride media than in sulphate media, as has also been reported by Ellender and Lawson (12). The lack of pH dependence indicates that no interfacial equilibrium is established in the chloride system. Since copper forms chloride complexes,an uncharged intermediate such as CuClR can be formed. This may then undergo a fast homogeneous reaction in the organic phase. It is interesting to note that a similar kinetic behaviour has recently been reported by Pratt and Tilley (13) for the homogeneous reaction between $Cu(ClO_4)_2$ and RH in ethanol.

Addition of BH to RH (10 mol/m^3) at pH 1.75 in the dispersion cell (at [Cu(II)] = 50 mol/m^3) produced a linear increase in the relative extraction rate to 1.83 at [$\overline{BH}$] = 0.9 mol/m^3. The slope of the line was thus 0.92 m^3/mol which can be compared to the slope 1.44 calculated for equation (11). The accelerating effect of BH is thus smaller in the dispersion cell than in the Lewis cell. If k_{14} is smaller than k_{13} (see reactions (13) and (14)) the addition of BH would decrease the extraction rate in a dispersion cell provided that no part of the charged intermediates react according to equation (10).

If both mechanisms are of importance (as indicated by a reaction order for RH between 1 and 2) a retarding effect at low [BH] may well change into an accelerating effect at higher $[\overline{BH}]$, as reported for 2-hydroxy-5-tert-octylphenylheptyl ketoxime (4).

The findings reported in the present paper also emphasize the importance of the mixing operation in industrial copper extraction.

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COPPER PRECIPITATION FROM LOADED KELEX 100 BY REACTION WITH HYDROGEN

G.P. Demopoulos and P.A. Distin

Dept. of Mining and Metallurgical
Engineering
McGill University, 3450 University St.
Montreal, Canada

ABSTRACT. Tests were conducted to determine the possibility of precipitating copper by reaction between hydrogen and the commercial extractant KELEX 100 (i) loaded with copper, as an alternative route to the conventional stripping and electrowinning processes.

Current work shows that KELEX 100 (an alkylated 8-hydroxyquinoline) loaded with copper may be reacted rapidly with hydrogen to precipitate metal with no apparent organic decomposition. The precipitate is massive and readily filterable while only minor plating was observed on metal surfaces within the reactor assembly.

The present investigation examines the kinetic effects of temperature, pressure and the amount of copper powder present on the reduction of copper-loaded KELEX 100 by hydrogen. Particle size distribution and chemical properties of the copper powder product were also examined. In addition, the composition and behaviour of the organic solvent under the experimental conditions were studied by gas-liquid chromatography.

INTRODUCTION

Solvent extraction is now widely used in the recovery of certain base metals, particularly copper. A conventional solvent extraction circuit (loading and stripping) is often associated with the energy intensive recovery step of electrowinning, while deleterious impurities are sometimes present in the electrowon product.

For those extractants which are loaded and stripped by 'cation exchange' one possible way of avoiding the stripping and subsequent electrowinning steps is to precipitate metal and regenerate organic by reaction with hydrogen.

Studies by earlier investigators (1)(2)(3)(4) have shown that several metals may be precipitated by reaction between hydrogen and loaded carboxylic or alkyl-phosphoric acids. Besides the organic acids, oximes and 8-hydroxyquinolines are also extractants normally stripped by 'cation exchange' with an aqueous acid. Regarding two extractants of particular practical significance (LIX 64 N (ii) and KELEX 100), it has been reported (1) that loaded LIX 64N (a substituted benzophenone oxime) is not amenable to direct reduction with hydrogen due to decomposition of the organic extractant - a result

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(i) Sherex Chemical Co., Ltd. (ii) General Mills Chemicals, Inc.

confirmed in the present study. However, current work shows that KELEX 100 (an alkylated 8-hydroxyquinoline) loaded with copper may be reacted with hydrogen to precipitate metal and regenerate the extractant.

After promising results obtained with preliminary work on KELEX 100, a thorough investigation was initiated to examine the kinetics of copper precipitation and the physical and chemical properties of the copper powder product.

EXPERIMENTAL

The organic solvent consisted of (in volume %) 15 KELEX 100 diluted in a low vapour pressure kerosene containing no aromatic compounds. In initial experiments, 10% decyl alcohol was used as modifier in the organic solvent to facilitate stripping of the analytical samples before analysis by atomic absorption spectrophotometry. Subsequently, the decyl alcohol was removed from the reaction system since a simpler analytical method for copper was used (5) in which the samples were diluted with methyl iso-butyl ketone (MIBK) and analysed directly by atomic absorption. Independent measurements of the copper contents of organic samples taken during the reaction were also determined by diluting the samples with kerosene and analysis with a UV-Visible spectrophotometer (5).

Batch reduction tests were carried out in a standard 2 litre Parr autoclave using 1200 cc of organic solvent loaded from copper sulphate solution to give organic feed containing 11 g.p.l. (0.175 M) copper. Samples of organic solution were removed periodically during the reduction reaction for copper analysis. The autoclave was purged with high purity nitrogen before heating began. The hydrogen (maximum 5 p.p.m. O_2) was then admitted when the working temperature had been reached and the hydrogen pressure was kept constant throughout the test. Gas was introduced through an inlet tube immersed in the solvent. Agitation was provided to promote gas dispersion and suspension of the copper powder.

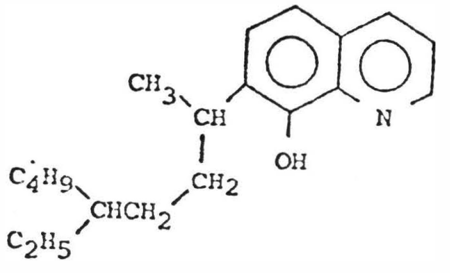
Oxygen, hydrogen and carbon contents of the copper powder product were measured using LECO analysers. For particle size analysis of the copper precipitates, a MICROMETRICS Sedigraph was used.

The composition of the KELEX 100 - kerosene solvent was examined by Gas-Liquid Chromatography. The KELEX 100 samples were silylated with bisilyltrifluoroacetamide (BSTFA) before chromatographic analysis so that clearly defined peaks for individual components were obtained.

RESULTS AND DISCUSSION

COMPOSITION AND CHEMICAL STABILITY OF KELEX 100

Since 1976, the process for KELEX 100 manufacture has been changed giving as the major product a C_{11}-alkylate of 8-hydroxyquinoline instead of a C_{12}-alkylate product (5)(6). A gas chromatographic analysis of a sample of this more recent KELEX 100 shows that in addition to the active component (i.e. C_{11}-alkylate of 8-hydroxyquinoline: peak 4) a number of other products are also present (Figure 1). Peak number 1 corresponds to the parent compound 8-hydroxyquinoline.



C_{11}-alkylate of 8-hydroxyquinoline

As received KELEX 100 showed excellent thermal stability and resistance to hydrogenation. A 15 volume % KELEX 100 in kerosene solution was heated to 573°K (300°C) and was held for 3 hours under 2.862 MPa (415 p.s.i.) hydrogen. A comparison of the gas chromatograms before and after the test showed no detectable change.

The change in the chromatogram of KELEX 100 due to loading with copper is shown in Figure 2. Peaks 1, 3, 6, 8, 9, 10 do not appear, which implies that compounds corresponding to these peaks take part in the loading reaction. Peak 4 represents the unloaded C_{11}-alkylate of 8-hydroxyquinoline, and is therefore smaller than the corresponding peak shown in Figure 1.

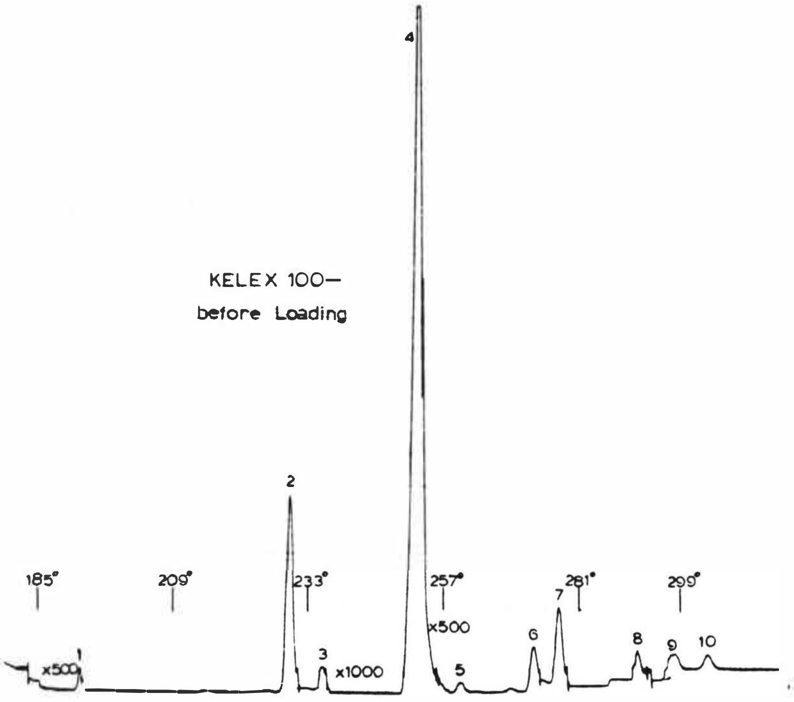


FIG. 1
Gas chromatogram of KELEX 100 before loading with copper. (The numbers with x are attenuator settings; temperatures are in °C.)

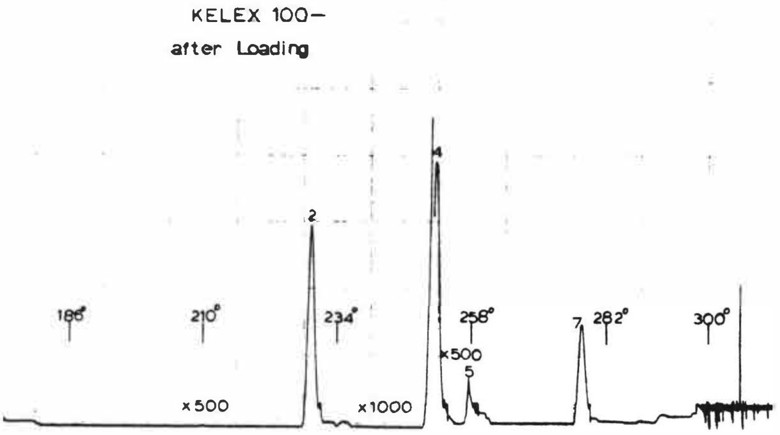


FIG. 2
Gas chromatogram of KELEX 100 after loading with copper.

Reduction of an 11 g.p.l. copper in KELEX 100 - kerosene solvent at 473°K (200°C) and 1.414 MPa (205 p.s.i.) hydrogen resulted in 90% metal precipitation within 2 hours. The chromatogram of this final solution is shown in Figure 3. A comparison of Figures 1 and 3 shows that after reduction with hydrogen, the organic solvent was regenerated with all the initial components reappearing in the chromatogram, except the parent compound 8-hydroxyquinoline (peak 1). The absence of this latter constituent may be due to insolubility of the copper-8-quinolinate in the kerosene diluent (6). Regenerated organic was recycled eight times without loss of loading capacity.

At temperature and hydrogen pressures approaching the maximum at which the reaction rate can be measured with reasonable precision, there is occasional evidence of organic degradation. A chromatogram of the solvent after degradation is shown in Figure 4. The conditions of the reduction test were the same as those of Figure 3 except that hydrogen pressure was 2.793 MPa (405 p.s.i.). This effect appears to be associated with traces of oxygen, either in the form of air trapped in the autoclave or as entrained droplets of aqueous. In these circumstances, several effects on reaction characteristics were noted. Firstly, the copper product contained an increased amount of carbon (Table 2). Secondly, an adherent copper deposit formed on the glass liner in addition to the minor plating on internal metallic surfacesobserved for all tests. Thirdly, while the loading capacity of recycled KELEX 100 appeared unaffected, phase separation was slower than experienced following an 'oxygen-free' copper precipitation test. Lastly, comparison of Figures 3 and 4 shows that the chromatograms of organic solvents following copper precipitation with and without degradation differ

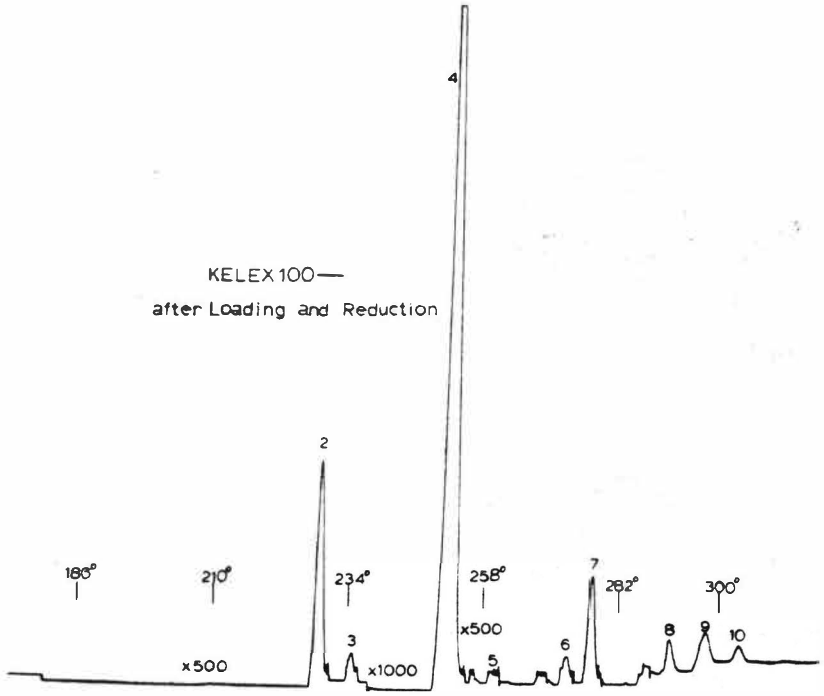


FIG. 3
Gas chromatogram of KELEX 100 after loading and reduction (see text for reduction conditions).

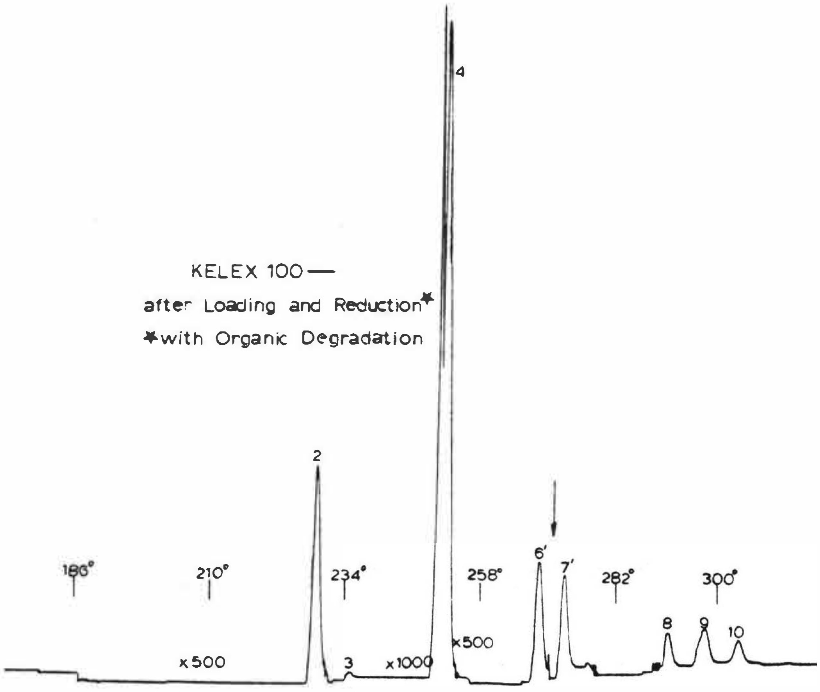
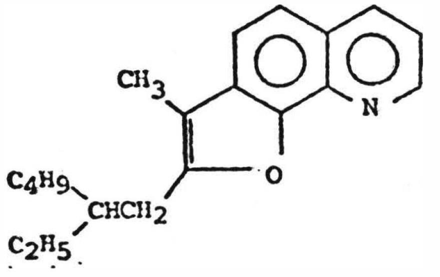
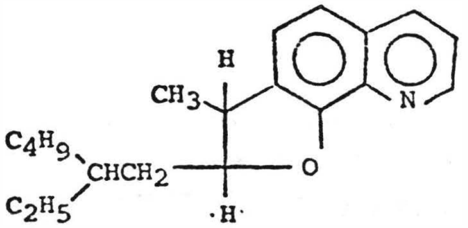


FIG. 4
Gas chromatogram of KELEX 100 after loading and reduction:- with organic degradation.

slightly. In particular, peaks 6 and 7 of Figure 4 (with degradation) are closer to peak 4 than is the case in Figure 3 (no degradation). Peaks 6 and 7 in Figure 3 are believed to correspond to furoquinoline and dihydrofuroquinoline respectively (5). The 5-membered ring in these compounds is known



Furoquinoline



Dihydrofuroquinoline

to be highly vulnerable to oxidation, although the presumed oxidation products represented by peaks 6 and 7 in Figure 4 have not been identified.

REACTION STOICHIOMETRY

Before determining reaction stoichiometry, hydrogen solubility was checked by holding 15 vol. % KELEX 100 in kerosene for 1 hour at 473°K with an initial hydrogen pressure of 2.793 MPa. There was no detectable drop in hydrogen pressure.

Subsequently, at constant temperatures of 463°K and 473°K, tests were performed in which copper-loaded organic solvent was held in a closed system of known gas volume containing initially 2.793 MPa hydrogen. Samples of organic were removed periodically and analysed for copper, while corresponding hydrogen pressures were noted. These measurements showed that, within 5% error, the precipitation reaction can be represented by:

$$R_2Cu + H_2 \rightarrow 2RH + Cu \qquad [1]$$

where R_2Cu and RH are loaded and regenerated KELEX 100 respectively.

REACTION KINETICS: 1.EFFECT OF MODIFIER

In initial tests, 10 volume % decyl alcohol was used as a modifier so that organic samples could be readily stripped for analytical purposes. As discussed previously, subsequent copper analyses were performed directly on the organic and the modifier was removed from the reduction system. Figure 5 shows that the presence of decyl alcohol had no significant effect on reaction kinetics.

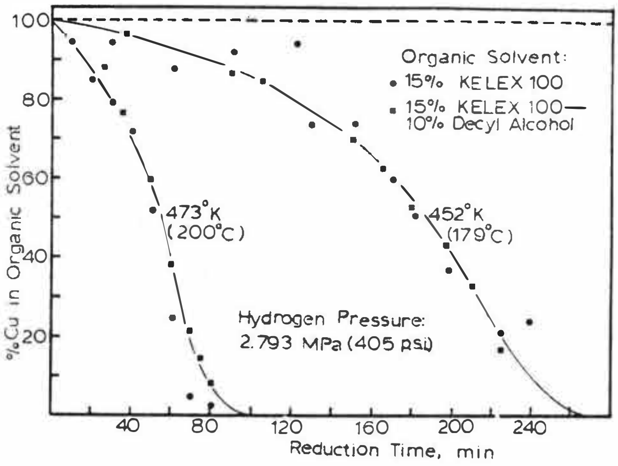


FIG. 5
Effect of modifier on reaction rate.

2. EFFECTS OF TEMPERATURE AND HYDROGEN PRESSURE

The reaction rate was found to be strongly dependent on temperature. For example, with 2.793 MPa hydrogen, precipitation becomes unacceptably slow at below 443°K, while at above about 483°K the reaction becomes too fast for accurate measurement (Figure 6).

Typical results for dependence of reaction rate on hydrogen pressure are shown in Figure 7, which refers to a reaction temperature of 473°K. In general, reaction rates are more sensitive to temperature than pressure.

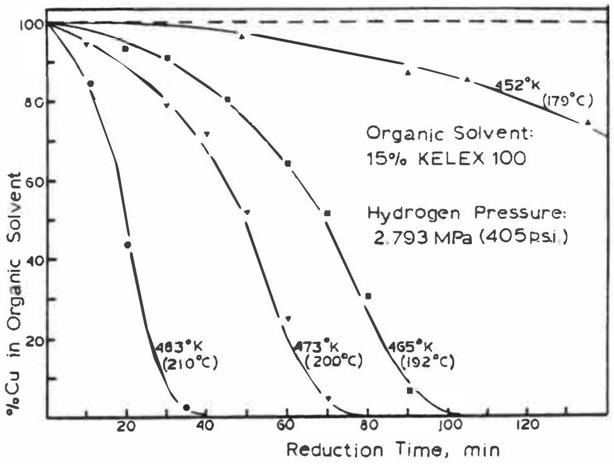


FIG. 6
Effect of temperature on reaction rate.

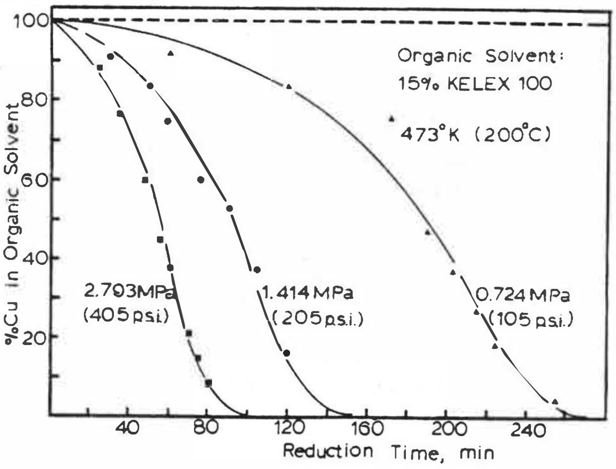


FIG. 7
Effect of hydrogen pressure on reaction rate.

For example, about 95% copper precipitation is obtained in 70 minutes with 0.724 MPa hydrogen at 483°K while this precipitation rate requires nearly a fourfold increase in hydrogen pressure (to 2.793 MPa hydrogen) at 473°K.

The curves of Figures 6 and 7 are characterized by initial acceleration of reaction rates during precipitation of about 70% of the copper followed by decelerating rates towards the end of the reaction. This increase in precipitation rates corresponds to an autocatalytic reaction in which copper particles act as nuclei for further precipitation. More detailed analysis of data typified by Figures 6 and 7 showed that the curves were closely parabolic to about the 70% copper precipitated level in that linear plots of % copper in organic solvent against the square of time were obtained. This behaviour would be expected where the precipitation rate is directly proportional to the number of nuclei present whose rate of formation is constant. The decrease in reaction rate in the final stages of reaction could be due to either depletion of dissolved copper, growth of particles to the point where they are no longer held in suspension, or to particle agglomeration such that the surface area decreases.

3. EFFECT OF RECYCLING PRECIPITATES

A series of recycle tests was carried out to study the effect on reaction rates of the amount of copper precipitate present, and the extent of particle growth. After an initial run, the copper product was retained in the autoclave. The copper-depleted organic was reloaded and, along with fresh organic to compensate for sampling losses, used for a recycle test. This procedure was repeated for three further recycle tests and the copper precipitate from the fourth recycle was retained for particle size analysis. The tests were performed with 1.414 MPa hydrogen at 473°K, and the results are given in Figure 8.

It is apparent that, while the initial run was characterized by the accelerating kinetics also shown in Figures 6 and 7, this pattern was not observed for the recycle tests. The results for all the recycle runs are best represented by a common straight line at least to the point where 70% of the copper had precipitated. A constant precipitation rate would be obtained if hydrogen transfer into the solvent controlled reaction rates. Alternatively, linear kinetics might be expected if the total surface area of copper powder in the reaction zone remains constant. This condition could be approached if under the prevailing agitation conditions, particles fall to the bottom of the autoclave once a critical size is reached. In fact, comparison of particle size analyses of the products from recycle 4 and a duplicate of the initial run shows negligible particle growth (Table 1).

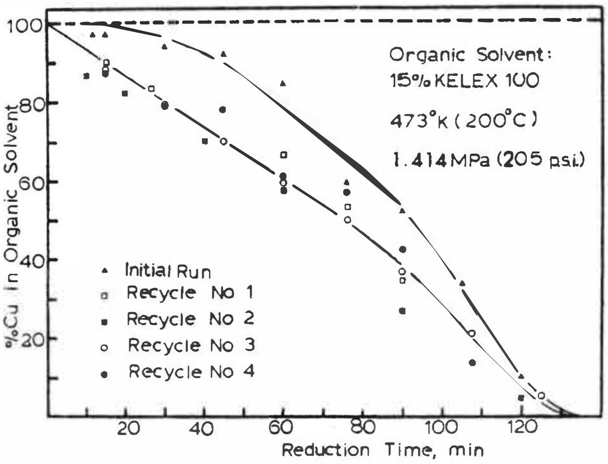


FIG. 8
Effect of recycling precipitates on reaction rate.

4. PROPERTIES OF THE PRECIPITATES

Massive precipitates were obtained with good filtration properties.

The particle size analysis given in Table 1 for powder produced at 473°K with 1.414 MPa hydrogen shows that about 90% of the precipitate was between 1 μm and 20 μm in size. It was observed that an increase in temperature at constant hydrogen pressure produces a finer precipitate. This would follow if with increasing temperature, the rate of nuclei formation increases more rapidly than their rate of growth. Conversely, an increase in hydrogen pressure at constant temperature results in coarsening of the precipitate. This would occur if, with increasing hydrogen pressure, the growth rate for existing particles increases faster than the nucleation rate.

TABLE 1. Particle size analysis of copper precipitates formed with 1.414 MPa hydrogen at 473°K.

Size Fraction μm	Initial Run wt%	Recycle No. 4 wt%
+ 20	5	2
-20 + 10	10	5
-10 + 5	30	33
- 5 + 2	40	50
- 2 + 1	10	7
-1	5	3

The major contaminants in the copper product are oxygen, carbon and hydrogen. Table 2 gives the ranges of impurity levels measured. Most of the oxygen contamination probably results from surface oxidation, since protective measures to prevent this were not adopted during filtration and subsequent handling of the powder. It is believed that the measured carbon and hydrogen contents result mainly from traces of organic entrained in the powder after filtration. The relatively viscous organic solvent was washed from the precipitate using a high vapour pressure solvent (acetone) and allowed to air dry. For those experiments where some organic degradation was observed, as noted previously, the carbon content of the product increased to between 0.30 and 1.03% carbon.

TABLE 2
Chemical analysis of copper powder.

	wt%
O	0.120-0.155
H	0.008-0.015
C	0.195-0.212 (0.30-1.03)$^+$

\+ organic degradation

CONCLUSIONS

Copper may be precipitated from loaded KELEX 100 - kerosene solvents by reaction with hydrogen at pressures between 0.724 MPa and 2.793 MPa, and temperatures from 443°K to 483°K. Essentially complete copper recovery may be obtained within 2 hours. The reaction is autocatalytic, and is initiated without addition of external seed, while the solvent is regenerated with no loss of loading capacity. Minor plating on metallic parts inside the autoclave was observed.

Under the experimental conditions, recycle of powder to further reduction tests produced a linear reaction rate, which did not increase with continued precipitate recycling. This constant rate and the lack of particle growth through repeated recycling suggest that, in these tests, hydrogen transfer controlled reaction kinetics, while only particles below a certain maximum size were suspended in the reaction zone.

About 90% of the precipitate formed using 1.414 MPa hydrogen at 473°K was between 1 μm and 20 μm in diameter. An increase in hydrogen pressure or temperature gave an increase or decrease in particle size respectively. Oxygen, carbon and hydrogen contamination was thought to be due mainly to powder handling procedures rather than side reactions during the precipitation process.

In general, the results show that the present system is a technically feasible alternative to stripping and electrowinning, although the physical form of the copper product is unconventional.

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STUDIES ON THE SOLVENT EXTRACTION OF COPPER(I) FROM SULFATE AND CHLORIDE MEDIA

D.M. MUIR*, M.D. BENARI and J.S. PRESTON

Mineral Chemistry Research Unit,
Murdoch University

Murdoch, Western Australia, 6153.

ABSTRACT

An investigation into possible solvent extractants for copper(I) has been carried out using commercially available extractants. A comparison is made between the extraction of copper(I) present as $CuC\ell_2^-$ in 3 M $NaC\ell/H_2O$ and the extraction of copper(I) present as $Cu(CH_3CN)_3^+$ (as sulfate) in 1 M and 6 M CH_3CN/H_2O. TBP readily extracts copper(I) chloride from brine solution but not from aqueous acetonitrile. Conversely, mixtures of D2EHPA and nonyl phenol are suitable to extract copper(I) from CH_3CN/H_2O but not from $NaC\ell/H_2O$. Copper(II) chelating extractants Kelex 100 and Lix 34 extract copper(I) from both media around pH 3-5 depending upon the activity of copper(I) in solution.

INTRODUCTION

Whilst the solvent extraction of copper (II) with various chelating and cation exchange (acidic) extractants is well documented, the solvent extraction of copper(I) has received scant attention. Normally the copper(I) ion is unstable in water and readily disproportionates or precipitates as insoluble salts but in the presence of certain ligands like chloride ion or acetonitrile, stable complexes like $CuC\ell_2^-$ or $Cu(CH_3CN)_3^+$ (as sulfate) are formed in high concentrations in neutral and acidic solutions. Recently several hydrometallurgical processes have been proposed in which these complex ions are formed in solution (1 - 5). Solvent extraction of copper from these process streams require copper(I) to be oxidised to copper(II) prior to extraction. Copper(II) is subsequently stripped with acid and reduced to copper by electrowinning (3). The direct solvent extraction of copper(I) from these process streams and the reduction of copper(I) to copper would conserve energy and extend the applications of processes which produce dilute solutions of the copper(I) ion.

Copper(I) can be solvent extracted from brine solutions with solvating extractants. It has been reported that copper(I) chloride is extracted from chloride media as the complex $CuCl_2^-$ ion by tri-n-octylamine (6), by tri-alkyl-(aryl) phosphites (7) and by tri-n-butyl phosphate (8). But when the organic phase is stripped with water, a white suspension of insoluble CuCl is formed which presents a practical problem. A novel method of recovering CuCl is to extract CuCl, rather than $CuCl_2^-$, using azeotropic acetonitrile, allowing pure CuCl to be recovered by stripping the volatile solvent (8). However, this approach is only suitable for leach solutions which contain high concentrations of chloride ion and copper(I) ion.

There has been no practical study of the solvent extraction of copper(I) other than from chloride media and no study of other potential solvent extractants. This paper therefore examines the solvent extraction of copper(I) from chloride and sulfate media using commercial reagents employing the principles of selective solvation, complex anion-ion exchange, chelation and cation exchange.

EXPERIMENTAL

Reagents

Acetonitrile (B.P. Chemicals) was distilled over $KMnO_4$ to remove acrylonitrile and the middle fraction (B.pt 81°; S.G. 0.7796) was retained. Otherwise all other reagents except Kelex 100 were used as supplied.

Kelex 100 (Ashland Chemicals) was found to have a molecular weight of 326 ± 4 (calc. 318) by potentiometric titration with standard perchloric acid in glacial acetic acid. G.C. and T.L.C. analysis showed it to contain a fluorescent impurity of about 4% oxine. Prior to use, Kelex 100 was shaken with 10% v/v H_2SO_4 to remove much of this oxine impurity. Primene J.M.T. was found to have a molecular weight of 267 ± 1 when titrated against standard HCl in methanol (methyl red indicator).

A stock solution of Cu_2SO_4 was prepared by stirring 0.5 moles $CuSO_4.5H_2O$ (A.R.) with excess copper powder in 1 litre of 30% v/v CH_3CN in water at pH 2. The colourless solution was stored under nitrogen and diluted with deoxygenated CH_3CN/H_2O for extraction studies. A stock solution of CuCl in 3 M NaCl was prepared from pure CuCl which had been freshly washed with SO_2 water.

Copper(I) was analysed by titration against standard $KMnO_4$. The titre was corrected for a solvent blank which had been contacted with the organic phase. Copper(II) and total copper were analysed by atomic absorption.

Measurements of pH were carried out using a Radiometer pH M26 standard pH meter using a combined glass calomel electrode. Density measurements were determined with an Anton Paar Precision density meter model DMA 02D.

Extraction of copper

All extractions of copper(I) were carried out in separating funnels under an atmosphere of nitrogen using deoxygenated solvents and 1 M NaOH or 1 M H_2SO_4 to adjust pH. Equal volumes of each phase were shaken at 25 ± 1° for 5 minutes to ensure equilibration. The extraction systems that were studied exhibited fast kinetics and are reported to reach equilibrium with

Cu^{2+} in less than 2 minutes. Extraction of copper(II) was carried out in air using the AKUVE solvent extraction apparatus (9) equipped with a Metrohm automatic titrator which was set up to deliver concentrated NaOH or H_2SO_4 and to monitor pH.

Extraction of acetonitrile

The transfer of acetonitrile from water into hexane, toluene and various kerosene diluents was determined by taking precise density measurements of the two phases before and after mixing. From these measurements it was possible to estimate the distribution of acetonitrile between water and the organic phases used.

Table 1: Distribution of CH_3CN between aqueous and organic phases.
(Aqueous = 6 M CH_3CN)

Organic Phase	K_D	Organic Phase	K_D
Toluene	1.0	20% D2EHPA/Shellsol T	0.05
Solvesso 150 (97% aromatic)	0.30	20% D2EHPA/5% Nonyl Phenol/ Shellsol T	0.06
Escaid 100 (20% aromatic)	0.04	10% Lix 34/Escaid 100	0.05
Shellsol T (<0.5% aromatic)	0.02	10% Kelex 100/5% Nonyl Phenol/Escaid 100	0.07
Hexane	≤0.02		

Table 1 shows that the extraction of acetonitrile into the organic phase is largely determined by the aromatic content of the solvent. Only a little is transferred when the kerosene diluent is non-aromatic and this may be recovered by washing the organic phase with water. The extraction of acetonitrile into 10% Lix 34/Escaid 100 is about 5 times greater than the extraction of ammonia into 10% Lix 65N/Escaid 100 (10).

RESULTS AND DISCUSSION

(a) Extraction of copper(I) by selective solvation using TBP or organic nitriles

In chloride media, copper(I) forms the complex ion $CuCl_2^-$ which is readily extracted by tri-n-butyl phosphate (TBP), (Table 2). TBP replaces water in the first hydration shell of the ion and selectively solvates the ion. However, when CuCl is dissolved in aqueous acetonitrile, it is not extracted by TBP. This is because acetonitrile is a stronger ligand for copper(I) than is chloride ion (10,11) so that CuCl is extensively ionised as $Cu(CH_3CN)_3^+$ and Cl^- in solution. But whereas TBP is unable to replace acetonitrile in the solvation sphere of $Cu(CH_3CN)_3^+$ other immiscible organic nitriles like benzonitrile are able to replace acetonitrile and extract CuCl.

Water immiscible organic nitriles, like benzonitrile offer a small favourable free energy change when Cu^+ transfers from aqueous acetonitrile to an organic nitrile rich phase (11). This allows copper(I) salts to be extracted when the change in free energy of the accompanying anion is small. Thus whilst CuCl and $CuNO_3$ are readily extracted from aqueous acetonitrile by benzonitrile, copper(I) sulfate is not extracted because the sulfate counter anion is more strongly solvated by water. For SO_4^{2-}, ΔH of hydration - 1144 kJ mol^{-1}. It exhibits a large negative free energy change on transfer from water to most organic solvents.

Table 2: Extraction of copper(I) salts into TBP or organic nitriles

Copper(I) salt	Distribution Coefficient		
	TBP	BN	AN
$Na^+CuC\ell_2^-/H_2O$	30 [a,j]	-	< 0.1 [c,j]
$CuC\ell/CH_3CN/H_2O$	< 0.01	13 [b,k]	1.6 [c,j]
$CuNO_3/CH_3CN/H_2O$	< 0.15[d]	10 [e,k]	2 [d]
$Cu_2SO_4/CH_3CN/H_2O$	< 0.01[f]	< 0.01[g,k]	< 0.01[f]
$CuHSO_4/CH_3CN/H_2O$	< 0.01[h]	0.3 [h]	1.1 [h]

Key: $[Cu^+]$ = 0.25 M; $[CH_3CN]$ = 4 M; pH 3; 25°; unless stated otherwise.
TBP = Tri-n-butyl phosphate; BN = benzonitrile;
AN = azeotropic acetonitrile (85% w/v CH_3CN/H_2O)

Additional salts or conditions as follows: (a) 3.5 M $CaC\ell_2$, 0.5 M Cu^+; (b) 1.3 M $NaC\ell$; (c) 3.5 M $NaC\ell$, 0.5 M Cu^+; (d) 4 M $NaNO_3$, 0.5 M Cu^+; (e) 1.3 M $NaNO_3$; (f) 0.4 M Na_2SO_4; (g) 1.3 M Na_2SO_4; (h) 1.0 M Na_2SO_4, pH 0.7; (j) reference (8); (k) reference (13).

Rather than use benzonitrile, however, a two phase nitrile-rich and water-rich system is conveniently produced by adding inorganic salts like $NaC\ell$, $NaNO_3$ and $(NH_4)_2SO_4$ to solutions of aqueous acetonitrile. Azeotropic acetonitrile (85% w/v CH_3CN/H_2O) salts out as an immiscible layer on addition of salts and carries with it, copper(I) as chloride or nitrate. Although the distribution coefficient is less than that given with benzonitrile (Table 2) it is possible to extract 95% of the copper(I) from brine solutions by extraction with acetonitrile using a 4-stage counter current extraction procedure (8).

The problem with the extraction of $CuC\ell$ is the subsequent stripping and recovery of the copper. The stripping of $CuC\ell_2^-$ from TBP with water results in solid $CuC\ell$ dispersed over the two phases. To recover copper from benzonitrile it is necessary to oxidise Cu^+ to Cu^{2+} with air before stripping with dilute acid (12). However to recover $CuC\ell$ from azeotropic acetonitrile it may be preferable to strip the solvent by distillation (B.pt 78°) to leave pure $CuC\ell$ (8).

(b) Extraction of sulfate complexes using Primene JMT

A brief investigation into the possible extraction of copper(I) as $CuSO_4^-$ was carried out using the primary alkyl amine Primene JMT (Rohm and Haas) which readily extracts the anionic sulfate complex of iron(III), i.e. $Fe(SO_4)_2^-$. This investigation was prompted by the fact that silver(I) forms a weak complex anion, $AgSO_4^-$, in water (log K = 1.3) which is partly extracted by Primene JMT (Table 3). However, under conditions where iron(III) is completely extracted and silver(I) is partly extracted from water, there was no extraction of copper(I) or silver(I) sulfate from aqueous acetonitrile (Table 3). It appears that the activity of the silver(I) and copper(I) ion is lowered by solvation with acetonitrile which inhibits ion-pairing with sulfate ion.

Table 3: Extraction of sulfate complexes Fe^{3+}, Ag^+ and Cu^+ into Primene JMT[a]

Metal species	log K for complex anion	Distribution coefficient
$Fe(SO_4)_2^-$	1.3[b]	> 20[c]
$AgSO_4^-$	1.3[d] 0.25[e]	0.3[c] < 0.05[f]
$CuSO_4^-$	-	< 0.05[f]

a. Organic phase is 0.4 M Primene JMT in Shellsol T; Aqueous phase is 0.005 M metal sulfate; 0.1 M Na_2SO_4 at pH 3; b. Equilibrium constant for $Fe(SO_4)^+ \rightleftarrows Fe(SO_4)_2^-$; c. Extraction from water. d. Zero ionic strength (reference 14) e. In 3 M $NaClO_4$ (reference 14) f. Extraction from 6 M CH_3CN/H_2O.

(c) Extraction of copper(I) with Kelex 100 and Lix 34

The extraction of copper(II) by hydroxyoximes is well established, but these reagents do not extract copper(I) from chloride media (3) nor from sulfate media in the presence of acetonitrile. Extractants like 8-hydroxyquinoline which extract a wide range of metals, including Ag^+ (15), were therefore considered.

Kelex 100 (a β-alkenyl hydroxy quinoline) and Lix 34, (8-alkyl aryl sulfonamido-quinoline (16,17)), are commercially available derivatives of 8-hydroxyquinoline which were found to extract copper(I) from both chloride and sulfate media. Figures 1 and 2 show the effect of pH on the extraction of 0.1 M copper(I) as chloride and as sulfate using 10% Kelex 100 and 10% Lix 34 in Escaid 100. It was found necessary to choose a diluent containing at least 15% aromatics or 5% nonyl phenol to prevent third phase formation when using Kelex 100, or to prevent precipitation of a black copper complex when using Lix 34.

For comparison, the extraction of copper(II) from 6 M CH_3CN/H_2O is also plotted in figures 1 and 2 to show that a good separation of Cu^+ and Cu^{2+} is achieved with both extractants under the same conditions. The extraction isotherm for copper(II) from 6 M CH_3CN/H_2O is very similar to that from water but a precise study of the effect of acetonitrile or chloride ion is yet to be carried out. Comparative studies on the extraction of copper(II) with Lix 64N from chloride and sulfate media (18,19) and on its extraction with Kelex 100 from chloride solutions (20) have shown only small changes in the extraction - pH isotherms in 3 M chloride rather than sulfate media. Much larger changes in $pH_{\frac{1}{2}}$ are observed with the extraction of copper(I) when the composition of the aqueous phase is changed.

FIG. 1

pH extraction isotherms for Cu^{2+} and Cu^{+} using Kelex 100. (0.1 M, 25° Cu^{2+} from 6 M CH_3CN/H_2O).

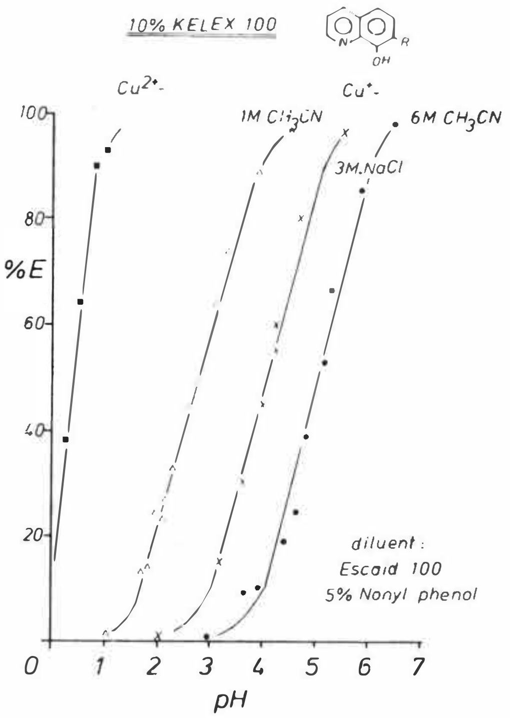
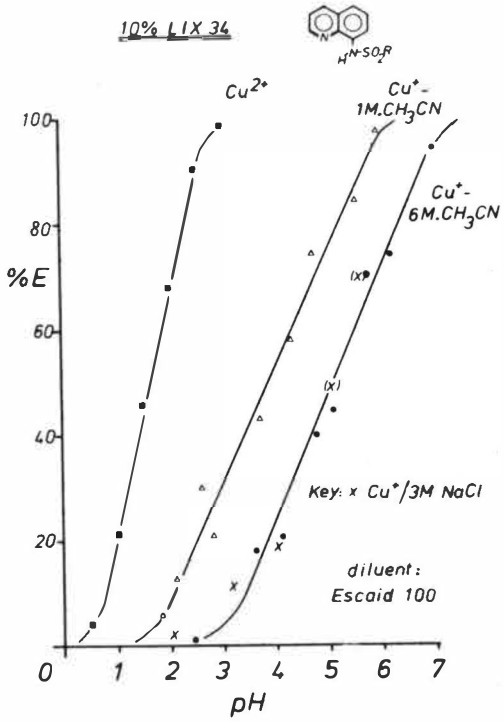


FIG. 2

pH extraction isotherms for Cu^{2+} and Cu^{+} using Lix 34 (conditions as figure 1)



Both Kelex 100 and Lix 34 are stronger ligands for copper(II) than copper(I) and extract copper(II) at a lower pH than copper(I). Under comparable conditions Kelex 100 extracts both copper(II) and copper(I)at a lower pH than does Lix 34. The precise $pH_{\frac{1}{2}}$ values for copper(I), however, vary significantly with acetonitrile concentration. These changes largely reflect changes in the activity of copper(I) in the aqueous phase. As shown in Table 4 there is a close correlation between $pH_{\frac{1}{2}}$, $E^{o}(Cu/Cu^{+})$, and the pH of hydrolysis of copper(I) in the aqueous phases studied. Copper(I) has a higher activity in 1 M CH_3CN than in 6 M CH_3CN; and its activity in 3 M NaCℓ lies between that in 1 M and 6 M CH_3CN.

Table 4: Effect of aqueous composition on $pH_{\frac{1}{2}}(Cu^{+})$, $E^{o}(Cu/Cu^{+})$, and pH(CuOH)

Aqueous phase (0.09 M Cu^{+})	E^{o} Cu/Cu^{+}(nHe)	$pH_{\frac{1}{2}}$ [c]	pH(CuOH)
1 M CH_3CN - SO_4^{2-}	180 mV[a]	2.8	4.9
6 M CH_3CN - SO_4^{2-}	52 mV[a]	5.0	7.8
1 M NaCℓ - $Cℓ^{-}$	145 mV[b]	-	5.8
3 M NaCℓ - $Cℓ^{-}$	90 mV[b]	4.1	7.0

(a) ref Hg_2SO_4 (b) ref calomel (c) 10% Kelex 100 (figure 1)

A slope analysis of figures 1 and 2 indicates that Kelex 100 and Lix 34 form 1 : 1 complexes with Cu^+. Log D varies by no more than 1 unit per unit change in pH. The slope of log D vs pH is certainly less than 1 using Lix 34 (figure 2).

Both Cu^{2+} and Cu^+ formed dark complexes with Kelex 100 and Lix 34 which could not be distinguished spectroscopically. However about twice as much copper is loaded into the organic phase with Cu^+, than with Cu^{2+}, in the aqueous phase. A solution of 10% v/v Lix 34 in Escaid 100 loads about 3 gl^{-1} copper when contacted three times with a solution of 0.1 M Cu^{2+} at pH 4, but loads about 6.5 gl^{-1} copper when contacted three times with a solution of 0.1 M Cu^+ in 1 M CH_3CN maintained at pH 6. Likewise, 10% v/v Kelex 100-5% nonyl phenol in Escaid 100 loads 7 gl^{-1} copper from solutions of Cu^{2+} and about 11.8 gl^{-1} copper from solutions of Cu^+. The loading of Cu^{2+} into Lix 34 and Kelex 100 agrees with that reported by Kordosky et al (17), and by Ritcey and Lucas (21) respectively. Thus the increased loading of Cu^+ also suggests that both Kelex 100 and Lix 34 form 1 : 1 complexes with Cu^+ rather than a 2 : 1 complex with Cu^{2+}.

Although high loadings of copper in the organic phase may be economically attractive, there are practical limitations to the amount of copper which can be loaded into Kelex 100 and Lix 34. With Kelex 100, increasing the copper concentration above 10 gl^{-1} produced a stable third phase requiring the addition of further nonyl phenol to ensure good phase separation. Whilst with Lix 34, high copper loadings from chloride media brought about disproportionation of Cu^+ in the organic phase and formation of copper powder. It would seem that like ethylene diamine (22), Lix 34 forms a much more stable complex with Cu^{2+} than with Cu^+ allowing disproportionation of $CuC\ell$ from brine solution. Disproportionation was not observed when copper(I) was extracted from aqueous acetonitrile with Lix 34, presumably because small amounts of acetonitrile transfer to the organic phase and stabilise the complex.

The recovery of copper(I) from the loaded Kelex 100 and Lix 34 organic phases was readily accomplished by stripping with 0.5 M H_2SO_4 in water containing 4 M CH_3CN. Acetonitrile was present to prevent disproportionation of the stripped copper(I) sulfate. Titration of the strip solution against $KMnO_4$ typically showed over 80% theoretical recovery of copper(I) under laboratory conditions; the remainder being oxidised to Cu^{2+} during successive shake out tests. Any copper present as the Cu^{2+} complex was retained in the organic phase until it was stripped, as Cu^{2+}, with 2 M H_2SO_4.

Thus whilst Kelex 100 and Lix 34 extract Cu^{2+} by chelation, forming a 2 : 1 complex, Cu^+ is extracted by cation exchange via a 1 : 1 complex. This difference in the chemistry of extraction enables Cu^{2+} and Cu^+ to be readily extracted at different pH and stripped with different concentrations of acid.

(d) Extraction of copper(I) by cation exchange with D2EHPA

Copper(I) is not extracted from chloride solutions with Versatic Acid 911S (a branched long chain carboxylic acid) even at pH 6 (23), nor from sulfate solutions containing acetonitrile. However we find that Di-2-ethyl hexyl phosphoric acid (D2EHPA) readily extracts copper(I) from 1 M CH_3CN/H_2O at $pH_{\frac{1}{2}} = 4.0$ and from 6 M CH_3CN/H_2O at $pH_{\frac{1}{2}} = 5.5$ (figure 3). By comparison copper(II) is extracted from 6 M CH_3CN/H_2O at $pH_{\frac{1}{2}} = 2.3$ (figure 3) which again is similar to that reported from pure water (24). Acetonitrile does not affect the extraction of Cu^{2+} but rather affects the activity of Cu^{+} and hence $pH_{\frac{1}{2}}$. For practical use however, D2EHPA is not suitable for extractions above pH 4 due to the formation of stable third phases and formation of sodium salts of the acid. Possible modifiers and synergists for copper(I) were therefore sought.

FIG. 3

pH extraction isotherms for Cu^{2+} and Cu^{+} using D2EHPA (conditions as figure 1)

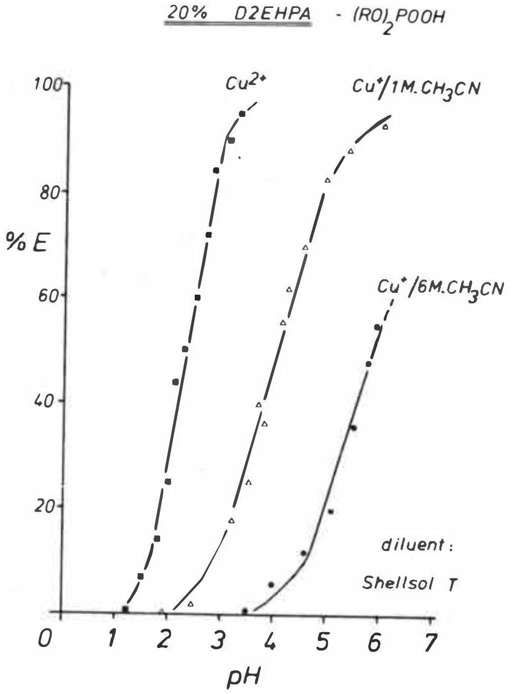
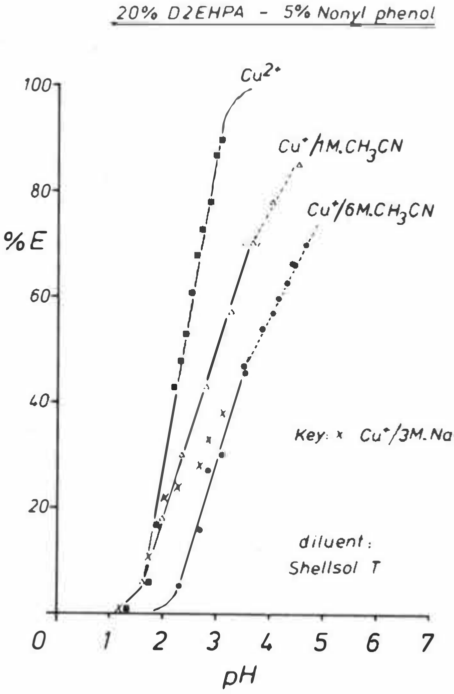


FIG. 4

Effect of added nonyl phenol to D2EHPA on pH extraction isotherm (conditions as figure 1; dashed line indicates formation of Na salt of D2EHPA)



Following a report (25) that combinations of D2EHPA and 4-sec-butyl-2(α methylbenzyl)phenol (BAMPH) extracts silver(I) from water at pH 2, further experiments were carried out using decanol and nonyl phenol as synergists. It was found that whilst decanol had little effect, the addition of 5% nonyl phenol brought about large changes in the extraction isotherms for copper(I), without changing that for copper(II) (figure 4). When figure 3 is compared with figure 4 it can be seen that $pH_{\frac{1}{2}}$ for copper(II) remains at 2.35 whilst that for copper(I) from 1 M CH_3CN/H_2O falls from 4.0 to 3.0 and from 6 M CH_3CN/H_2O falls from 5.5 to 3.5 . Further experiments established that nonyl phenol had little effect on the extraction of zinc(II) and iron(II), thus it would appear that phenols are specific synergists for copper(I) and silver(I). Presumably phenols are able to replace water in the solvation sphere of copper(I) and silver(I), but not from the strongly aquated divalent cations.

When Log D is plotted vs. pH using the data from figure 4, good straight lines are obtained with slopes near 2 and 1 for the extraction of copper(II) and copper(I) from aqueous acetonitrile. But as evident from figure 4, the extraction of copper(I) from 3 M NaCℓ/H_2O is not ideal above pH 2 due to the formation of sodium salts of D2EHPA. The sodium salt is formed at low pH values when the aqueous phase contains high concentrations of NaCℓ making D2EHPA-nonyl phenol mixtures not suitable extractants for copper(I) in chloride media stabilised by NaCℓ. Such mixtures may be considered only suitable for copper(I) in sulfate media containing low concentrations of acetonitrile.

Again, as found with Kelex 100 and Lix 34, copper(I) was readily stripped and recovered quantitatively from the D2EHPA phase by contacting with 4 M CH_3CN containing 0.5 M H_2SO_4.

CONCLUSIONS

Copper(I) stabilised as $CuCℓ_2^-$ in chloride media or as $Cu(CH_3CN)_3^+$ in sulfate media can be solvent extracted with Kelex 100, Lix 34 or, D2EHPA containing nonyl phenol in the absence of high concentrations of sodium salts. In general the extraction chemistry of copper(I) is similar to that of silver(I). Copper(I) is extracted 1-2 pH units higher than copper(II) allowing selective extraction of copper(II) from its mixture. The complex ion formed by copper(I) in the aqueous phase makes little difference to $pH_{1/2}$ with these extractants. Rather it is the activity of Cu^+ which appears to determine $pH_{1/2}$.

Kelex 100 appears to be the most suitable extractant for copper(I) from brine solutions but both Kelex 100 or D2EHPA may be used to extract copper(I) from aqueous acetonitrile. For the optimum recovery of copper(I) it would be necessary to extract and strip in sealed vessels under an inert atmosphere.

ACKNOWLEDGEMENTS

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SOLVENT EXTRACTION AND DIRECT HYDROTHERMAL PRECIPITATION OF CUPROUS OXIDE FROM LOADED CARBOXYLIC ACID

Lung Tsuen-ni & Chen Cheng-kaung
Mining Research and Service Organization
Industrial Technology Research Institute
Hsin-chu, Taiwan, China.

When solvent extraction is applied in a hydrometallurgical process for achieving separation of metals from one another, the metals extracted into the organic phase are normally stripped back into aqueous phase with mineral acid to prepare a suitable solution for the final recovery of metal by chemical precipitation or electrolytic deposition. The objective of this paper is to present the investigation results of recovery of solid form cuprous oxide directly from loaded organic phase by hydrothermal precipitation reaction at the temperature range of 150°C to 200°C under autoclaving conditions. A highly-branched synthetic tertiary carboxylic acid is selected, owing to its thermal stability, as extractant and used with a low aromatic content diluent in all experiments reported here. The rate of precipitation of cuprous oxide from the loaded carboxylic acid is a function of temperature in the temperature range investigated. FIG.1 shows the reaction rate increased sharply with increasing the reaction temperature. At 150°C, only about 65% of the totally loaded copper is precipitated after 2 hours of reaction, but at a reaction temperature of 200°C, almost 100% precipitation is attained within 25 minutes. Because reduction of copper occurred during the hydrothermal reaction, a certain amount of degradation of extractant is found. The percentage of degradation of the extractant for a given reaction time depends on the reaction temperature and shows a linear relation with the amount of cuprous oxide precipitated. The physical and chemical properties of the precipitated cuprous oxide generally meets the industrial specification of pigment for paint manufacturing.

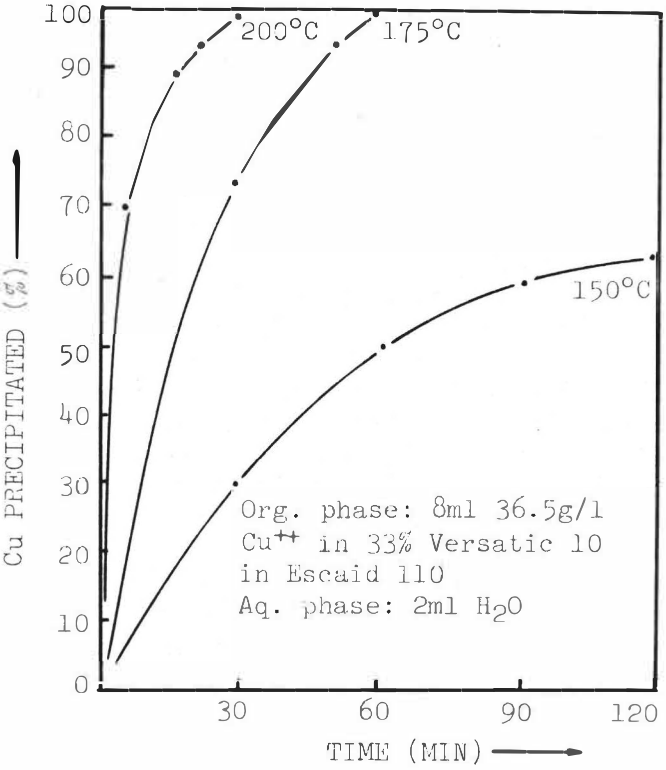

FIG.1
Rates of hydrothermal precipitation of Cu_2O

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THE BEHAVIOUR OF *SYN*-2-HYDROXY-5-NONYLBENZOPHENONE OXIME IN THE EXTRACTION OF COPPER WITH LIX65N AND LIX64N

E. Paatero and L. Hummelstedt

Laboratory of Industrial Chemistry
Åbo Akademi

SF-20500 ÅBO FINLAND

The commercial extractant LIX65N is known to contain both the active *anti* and the inactive *syn* isomers of 2-hydroxy-5-nonylbenzophenone oxime (HNBPO). Osmometric measurements of the aggregation of *syn*-HNBPO in CCl_4 and $CHCl_3$ proved that it has a greater tendency for aggregation than the *anti* isomer. The mean aggregation number for a 100 mol/m^3 solution of *syn*-HNBPO is 2.0 in CCl_4 and 1.27 in $CHCl_3$. For *anti*-HNBPO the corresponding values are 1.45 and 1.10. Osmometric measurements of *syn*-HNBPO in mixtures with *anti*-HNBPO and with the copper complex of *anti*-HNBPO in $CHCl_3$ revealed no tendency of *syn*-HNBPO to associate with these other components present in the bulk of the organic phase. However, addition of *syn*-HNBPO to a Cu-*anti*-HNBPO solution has a slight influence on the visible spectrum.

The kinetics of the conversion of the isomers of HNBPO was studied at 25 °C during 10 months by following with an infrared spectrophotometer the change in composition of initially pure *anti*-HNBPO and initially pure *syn*-HNBPO in CCl_4, respectively. The conversion of the *syn* isomer was also studied in CCl_4 solutions which were continuously stirred in contact with aqueous phases at different pH. All the samples reached the same equilibrium. In the absence of an aqueous phase the *syn*-HNBPO followed the kinetics of a first order reversible reaction with the forward rate constant $8.7 \cdot 10^{-7}$ s^{-1} and the reverse rate constant $0.45 \cdot 10^{-7}$ s^{-1}. The half-life was 10 days. In the presence of an aqueous phase the reaction reached equilibrium much later (at pH 2 the half-life was 19 days) than in the absence of an aqueous phase. The rate of conversion was approximately second order with respect to the oxime concentration and showed only sligth pH-dependence. It can be concluded that in this case the reaction occurs mainly at the interface and that two oxime dimers are involved in the rate-determining step. At low pH the parallel reaction in the bulk is negligible. We suggest that the interfacial intermediate is a tetrameric anion. In a solvent such as $CHCl_3$ it would probably be a dimeric anion.

The effect of *syn*-HNBPO on the rate of copper extraction was studied in a Lewis cell and in a dispersion cell. The retardation reported by Whewell et al. (Proc. ISEC'77 p. 185) was observed in sulphate media in both cases. In the Lewis cell, however, the retarding effect seemed to increase strongly with time. In corresponding experiments in chloride media *syn*-HNBPO did not seem to have an effect on the extraction rate. The results imply that the retarding effect is mainly due to the association of a *syn*-HNBPO anion to an interfacial intermediate Cu-*anti*-HNBPO$^+$. The reorientation of this charged species is the rate-limiting step in the extraction of copper in sulphate media (Hummelstedt et al., ISEC'80). Addition of small amounts of LIX63 was partly able to overcome the retarding effect of *syn*-HNBPO.

COLLOIDAL SILICA IN THE SOLVENT EXTRACTION OF COPPER WITH OXIMES

Jorge Menacho Llaña

Centro de Investigación Minera y Metalúrgica

Santiago, Chile

Extractant behavior in phase separation was studied for LIX 64N, SME 529 and ACORGA P5100 on solution having levels of between 4 and 6 gpl SiO_2, obtained from conventional acid vat leaching.

It was found, for concentrates of the three extractants equivalent to a 40 % vol dilution in Tridecano (a Chilean Diluent), that abnormally high levels of crud were formed, in some cases producing an almost total emulsification of the organic phase. Under whatever operational conditions, the crud produced to an O/W emulsion are strongly stabilized by the colloidal silica.

So as to minimize levels of crud formation, two approaches are discussed:

1) Silica removal through the use of specific flocculants, such as polyglycols, that allow eliminating over 90 % of the silica with a dosage of 150 ppm for levels of 4 gpl SiO_2.

2) Silica dissolution inhibition through a leach procedure employing acid curing techniques. Thus, reduction of silica dissolution to 10-20 % of the original level is possible allowing for operation with normal crud levels in solvent extraction.

Lastly, considering that even under the best of conditions a certain level of crud is inevitably produced, a simple and economical method is proposed for recovering organic from the crud, making use of phase-continuity-inversion techniques. Its efficiency compares favorably with established methods for treating cruds having a high physico-chemical stability.

THE INFLUENCE OF THE STRUCTURE OF OXIME DERIVATIVES OF 2-HYDROXY-5-ALKYLBENZALDEHYDE ON COPPER EXTRACTION FROM ACID DILUTED SULPHATE SOLUTIONS

Danuta Stępniak-Biniakiewicz
and Jan Szymanowski

Institute of Chemical Technology,
Politechnika Poznańska,

Poznań, Poland

Spectrophotometric and extraction measurements, made as in our previous work [1], prove that 2-hydroxy-5-alkylbenzaldehyde oximes (I) and 2,6-diformyl-4-alkylphenol dioximes (II) (FIG.1) form copper complexes with mole ratios of ligands to metal equal to 2:1 and 1:1, respectively.

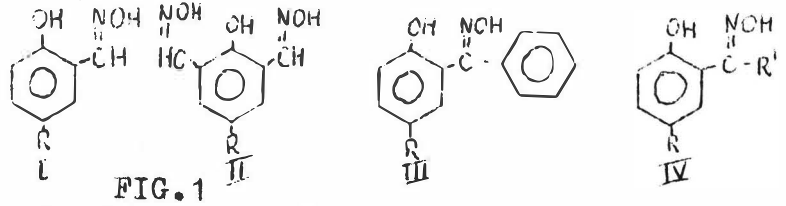

FIG.1

The structure of the examined hydroxyoximes.

II can extract copper from more acidic aqueous solutions than I can and with better efficiency, especially at pH < 2.2. However, when compared with 2-hydroxy-5-alkylbenzophenone oximes (III) and (2-hydroxy-5-alkylphenol)-alkyl ketone oximes (IV) I is a stronger extractant and can extract copper from more acidic aqueous solutions.

The length of the alkyl chain (C_4-C_{12}) of I and its structure (normal or branched) do not significantly influence the extraction of copper. However, the solubility of I in water depends upon the length of the alkyl chain, and when the chain contains 4, 8 or 12 carbon atoms the solubility is equal to 46 ppm, 9 ppm and 1.5 ppm, respectively.

Diluents have a great effect upon the extraction of copper by I, although the effect depends upon the pH equilibrium and the ratio of the extractant to the copper concentration. The examined diluents can be arranged as follows: isooctane = octane > xylene > ethylene dichloride.

The interpretation of the extraction curves (lgD vs pH) shows that slopes equal to the theoretical value (2) are obtained when the association of I is considered along with the solvation of copper complexes with hydroxyoximes. These results are consistent with the IR spectra of I which suggest a dimer structure of the oxime, but they are in disagreement with the cryoscopic measurements of the molecular masses and the association degrees.

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COPPER EXTRACTION STUDIES USING PURIFIED LIX34

G. Sandström and L. Hummelstedt

Laboratory of Industrial Chemistry
Åbo Akademi

SF-20500 ÅBO FINLAND

The active component in the commercial extractant LIX34 is an 8-(alkarylsulfonamido)quinoline having an average molecular mass of 438. LIX34 offers a possibility of comparing the hydroxyoximes now dominating industrial copper extraction with an extractant of a different chemical structure. A fundamental study of copper extraction with LIX34 is not complicated by the *syn-anti* isomerism characteristic of the hydroxyoximes.

The pure 8-(alkarylsulfonamido)quinoline, here denoted ASAQ, was isolated from commercial LIX34 by precipitating it with NaOH in hexane. The sodium salt was reconverted to the quinoline by dissolving it in ether and shaking with acid. After evaporation of the ether the purified ASAQ was obtained as a yellowish viscous liquid.

Gas chromatographic and mass spectrometric analyses of ASAQ showed it to be a mixture of eight components each having a molecular mass of 438. This suggests the existence of eight different isomers of the alkaryl substituent.

Since aggregation has a considerable influence on the performance of an extractant osmometric studies were made to explore the aggregation behaviour of ASAQ in different solvents. Marked aggregation occurs in iso-octane while the mean aggregation number is very close to one in benzene, carbon tetrachloride and chloroform. In the following studies chloroform was used as diluent in order to avoid complications arising from aggregation.

The interfacial tension of ASAQ in chloroform / water systems was measured with a ring balance. Comparison of the intefacial tension of ASAQ with that of the *anti*-isomer of 2-hydroxy-5-nonylbenzophenone oxime (the active component in LIX65N), here denoted *anti*-HNBPO, showed ASAQ to be much less surface active than the *anti*-HNBPO under equal conditions.

In order to determine the ligand to metal ratio for the copper chelate the dependence of the copper distribution ratio on the pH of the aqueous phase was studied. A log*D* vs pH plot gave a straight line with a slope of 2.0. This confirms that the ligand to metal ratio is 2:1 which is to be expected according to the stoichiometry $2\,RH + Cu^{2+} \rightleftharpoons CuR_2 + 2\,H^+$. The value of the extraction constant is about 0.16 at 25 °C.

The rate of extraction of copper from sulphate solutions with ASAQ was studied in a stirred cell with quiescent interface. The extraction rate for ASAQ was found to be about one order of magnitude lower than for *anti*-HNBPO under equal conditions. The effect of extractant concentration and pH on the extraction rate of ASAQ is similar to that of the extraction rate of *anti*-HNBPO (Hummelstedt et al., ISEC'80). In that mechanism the physical reorientation of a charged intermediate at the interface is the rate controlling step. The low rate of extraction with ASAQ as compared to *anti*-HNBPO appears to be attributable to the large size of the molecule which makes the reorientation of its charged copper intermediate at the interface very slow and to its low surface activity which decreases the interfacial concentration.

EXTRACTION OF COPPER FROM SULPHATE AQUEOUS SOLUTION BY OXIME TYPE EXTRACTANTS.

Z. Maksimovic, A. Ruvarac,
A. Kostic-Pulek and J.A.J. Tumilty*
"Boris Kidrič" Institute - Vinča
Yougoslavia (*Acorga Ltd., England).

The extraction process of copper from sulphate solutions with two chelate extractants of the oxime class has been investigated. The used extractants were produced by the Acorga Comp. (England) and their trademarks are P-17 and P-50.

The experimental results obtained in this work were used for the determination of the stoichiometry of the extracted complex and of its stability constants. From extraction isotherms obtained at 293 K, 303 K and 323 K, the thermodynamic equilibrium constants were calculated. The aqueous phase, in these experiments, was made by $CuSO_4$ and H_2SO_4 in such a way to obtain the constant ionic strenght of 0,0125 M. For the various organic phases the obtained $\underline{K}^{o}_{ex}$ values are listed below :

0,025 M P-17 in CCl_4	$\underline{K}^{o}_{ex} = 5{,}75$
0,025 M P-17 in hexane	$\underline{K}^{o}_{ex} = 9{,}55$
0,025 M P-50 in CCl_4	$\underline{K}^{o}_{ex} = 91{,}3$
0,025 M P-50 in hexane	$\underline{K}^{o}_{ex} = 100{,}0$

According to the obtained results it seems that hexane as a diluent of oxime in organic phase extracts greater amounts of copper ions than in the case with CCl_4.

Extraction and reextraction isotherms of the process were obtained and they were used for continual copper extraction in a mixer-settler apparatus. The calculations of the number of theoretical stages needed were carried out first by using the Mc-Thiele method. The determined numbers of theoretical stages necessary for the quantative extraction and reextraction of copper were confirmed by the experimental runs using leaching copper solutions from the copper-mine "Bor".

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Co-chairmen : H. Freiser (University of Arizona, Tucson, Arizona, U.S.A.)
F. Adams (University of Antwerpen, Belgium)

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80-129 The extraction of variety-ligand complexes of some metals with metallochrome indicators and N-containing organic reagents.
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A.K. De and B.K. Pal, Visva-Bharati University, Santiniketan, India.

ORGANOTIN SUBSTANCES AS EXTRACTANTS FOR OXO ANIONS. CHEMISTRY OF SOLVENT EXTRACTION AND ANALYTICAL APPLICATIONS

B.Ya.Spivakov, V.M.Shkinev,
Yu.A.Zolotov

Vernadsky Institute of Geochemistry
and Analytical Chemistry, Academy of
Sciences, Moscow 117334, U.S.S.R

ABSTRACT Properties of dialkyltin salts as extractants for phosphate, arsenate and other oxo anions have been examined. These salts extract oxo anions of polybasic acids much better than other extractants. They make it possible to extract phosphate and arsenate from large volumes of aqueous solutions. Metal cations are not extracted. The extraction power of the extractants is explained by formation of coordination bonds of tin-anion oxygen. The extractants were used in various methods of determining arsenic and phosphorus.

Extraction of phosphate, arsenate and other oxo anions is an important practical problem. Widely used extractants usually weakly extract oxo anions of polybasic acids. Phosphate and arsenate are satisfactory extracted by primary amines, alcohols and as heteropoly acids. However, solvent extraction by using such systems is not always convenient whether because it is necessary to introduce foreign components into the solution or to maintain strict extraction conditions, or because of low selectivity.

Bock et al (1-3), Schweitzer and McCarty (4) have shown that triphenyltin and triphenyllead hydroxides can be used to extract phosphate, arsenate, selenite and other oxo anions as well as halide ions. However, oxo anions are extracted by these extractants over a narrow pH range. The extractants are not sufficiently stable with respect to acids and oxidants, and appreciably soluble in acid aqueous solutions.

We have examined dialkyltin (DAT) salts $(C_nH_{2n+1})_2SnA_2$, where $7 \leq n \leq 12$ and A=anion of mineral or organic acid. Different DAT salts, including commercially available ones, have been examined. Dialkyltin dinitrates (DATDN) have proved to be convenient for some practical purposes. These extractants are very slightly soluble in water, stable with respect to acids and oxidants, non-toxic, available. They are well dissolved in chloroform, octyl alcohol, methylisobutylketone; slightly soluble in dichloroethane, nitrobenzene; insoluble in o-xylene, kerosene, cyclohexane. Such additives as tributyl phosphate (TBP), trioctylphosphine oxide (TOPO) or high alcohols (octanol, butanol) significantly increase the solubility of the compounds in inert solvents and make it possible to work not only with acid but also with neutral aqueous solutions. In order to dissolve a portion of DATDN in a solvent, it is necessary to use two-fold or higher excess of TBP (or another additive) molar concentration with respect to the extractant concentration.

If DATDN solutions in organic solvents are equilibrated with alkaline aqueous solutions as well as solutions of some acids or salts, precipitation occurs in the organic phase. Thus, precipitates form after equilibration of 0.1 M solution of dinonyltin dinitrate (DNTDN) in chloroform with H_2SO_4 and HCl solutions if their concentrations are higher than 1.5 M. Nitric and perchloric acids do not cause any visible changes in the organic phase. The application of some organic acid salts instead of the dinitrates makes it possible to work with neutral aqueous solutions at pH 7-8.

Using radioactive isotopes, we have studied the extraction of perrhenate, molybdate, tungstate, selenite, selenate sulphate, arsenate, and phosphate ions. The data on extraction of oxo anions with DNTDN chloroform solutions, containing 25% TBP, from aqueous solution (pH 2) are presented in Fig.1. The extraction increases in the order $ReO_4^- < MoO_4^{2-}$, $WO_4^{2-} < SeO_3^{2-}$, $SeO_4^{2-} < AsO_4^{3-}$, PO_4^{3-}. Arsenate and phosphate are extracted with high distribution ratios which are several hundred times as high as those for monocharged perrhenate

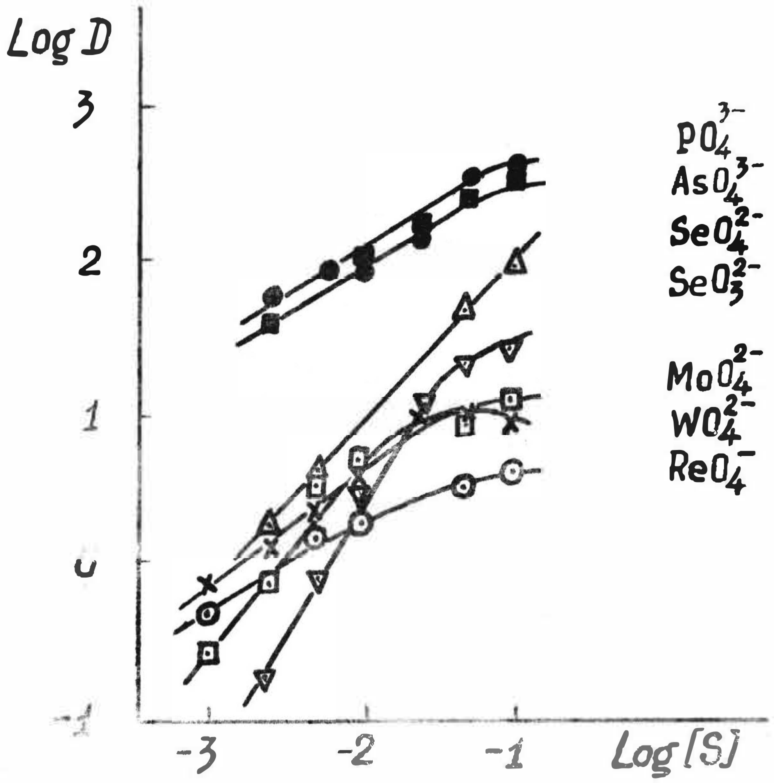

FIG.1

The extraction of oxo anions by dinonyltin dinitrate in chloroform, containing 25% vol. TBP, as a function of extractant concentration

ions. The order of anion extraction is unusual for anion exchange extraction. A reverse order is usually observed for such extractants as tertiary amines and quaternary ammonium salts, i.e. monocharged anions are extracted better than anions of di- and tribasic acids.

A comparative study has been made on solvent extraction power of the organotin compounds and a quaternary ammonium salt-trialkyl(C_7-C_9)benzylammonium chloride (TABAC) with respect to selenate ions. A comparative study has also been made on extraction power of dialkyltin dinitrates and a primary amine with respect to phosphate and arsenate. The extraction was performed under optimal conditions for the corresponding amines: pH 6 for TABAC and pH 6-7 for dodecylamine nitrate. These comparative data (Figs 2, 3) show that dinonyltin and dioctyltin dinitrates extract selenate and phosphate better than conventional extractants for anions.

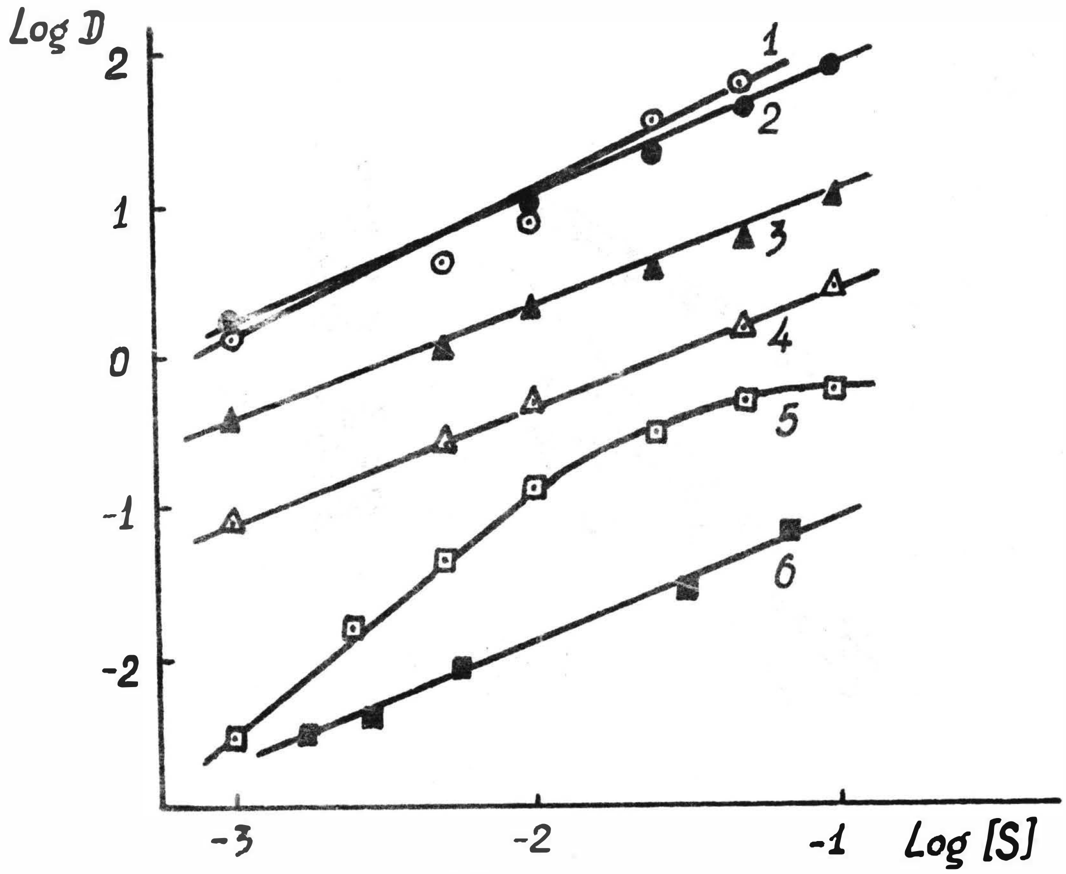

FIG.2

The extraction of selenate by trialkylbenzylammonium chloride, dinonyltin and dioctyltin dinitrates from aqueous solution of pH 6; 1-DNTDN in chloroform+25 vol.% TBP, 2 - DNTDN in o-xylene+25% TBP, 3 - DOTDN in chloroform+25% TBP, 4 - DOTDN in o-xylene+25% TBP, 5 - TABAC in o-xylene, 6 - TABAC in chloroform

The investigation of the effect of mineral acids on the extraction of arsenate, phosphate, and selenate with DNTDN has shown that these anions are extracted over a wide acidity range; phosphate and arsenate are extracted from more acidic solutions than selenate. Phosphorus(V) and arsenic(V) can be quantitatively extracted from 5 M HNO_3 while selenium is extracted at HNO_3 concentration $\leq$ 0.5 M. Fig.4 illustrates the extraction of arsenate, phosphate, and selenate by 0.1 M DNTDN in chloroform containing 25 vol.% TBP. The distribution ratios for all oxo anions decrease in the order: $HClO_4 \leq HNO_3 \leq H_2SO_4 \leq HCl$.

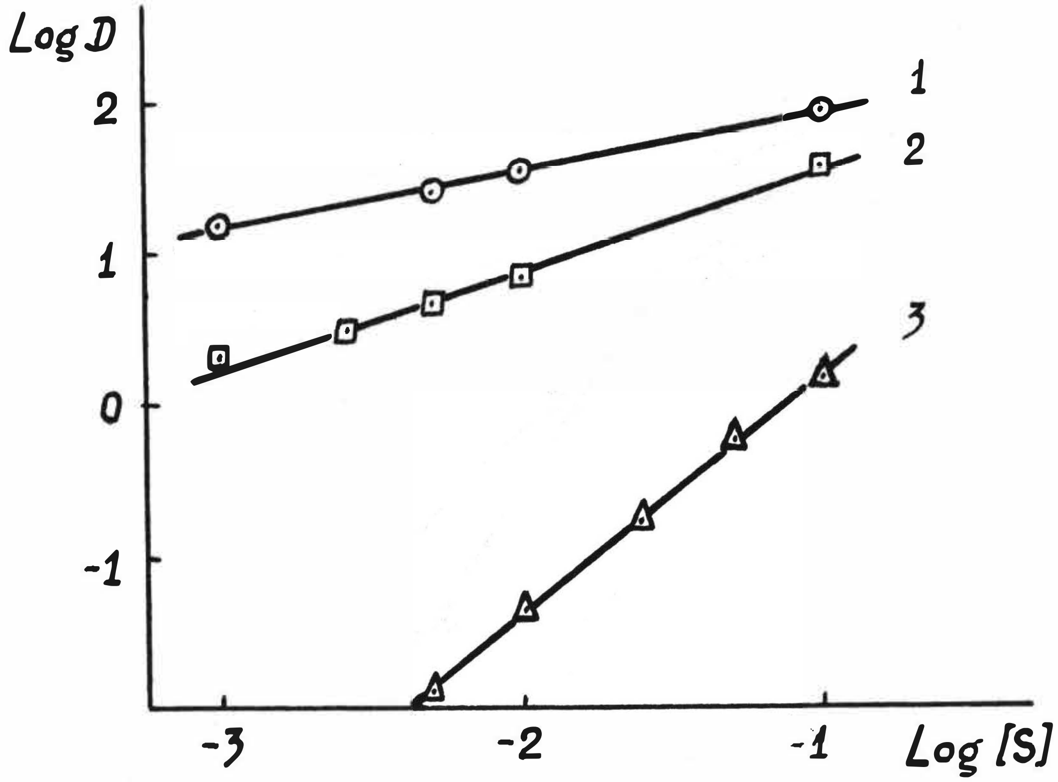

FIG.3

The extraction of arsenate (1) and phosphate (2) by DNTDN in chloroform+25 vol.% TBP and phosphate by dodecylamine nitrate in chloroform (3) from aqueous solution of pH 6-7

Very high distribution ratios for arsenate and phosphate ensure their extraction from large aqueous solution volumes. Thus, in the extraction from 0.05 M HNO_3 by 0.1 M DNTDN solution in chloroform, phosphate is extracted by 99.4% and arsenate by 99.2% at the ratio of organic and aqueous phase volume 1:20. The concentration may be also carried out by stripping the oxo anions with hydrochloric acid; 1.5 M HCl completely back-extracts all the elements studied.

The change in the alkyl radical length from C_7 to C_{12} does not cause significant changes in the distribution ratios for phosphate and arsenate in the extraction from nitric and perchloric acid solutions. Dicharged anions, e.g. SeO_3^{2-}, SeO_4^{2-} are better extracted by the organotin compounds with longer alkyl radicals.

Most cations, e.g. sodium, cadmium, zinc, vanadyl ca-

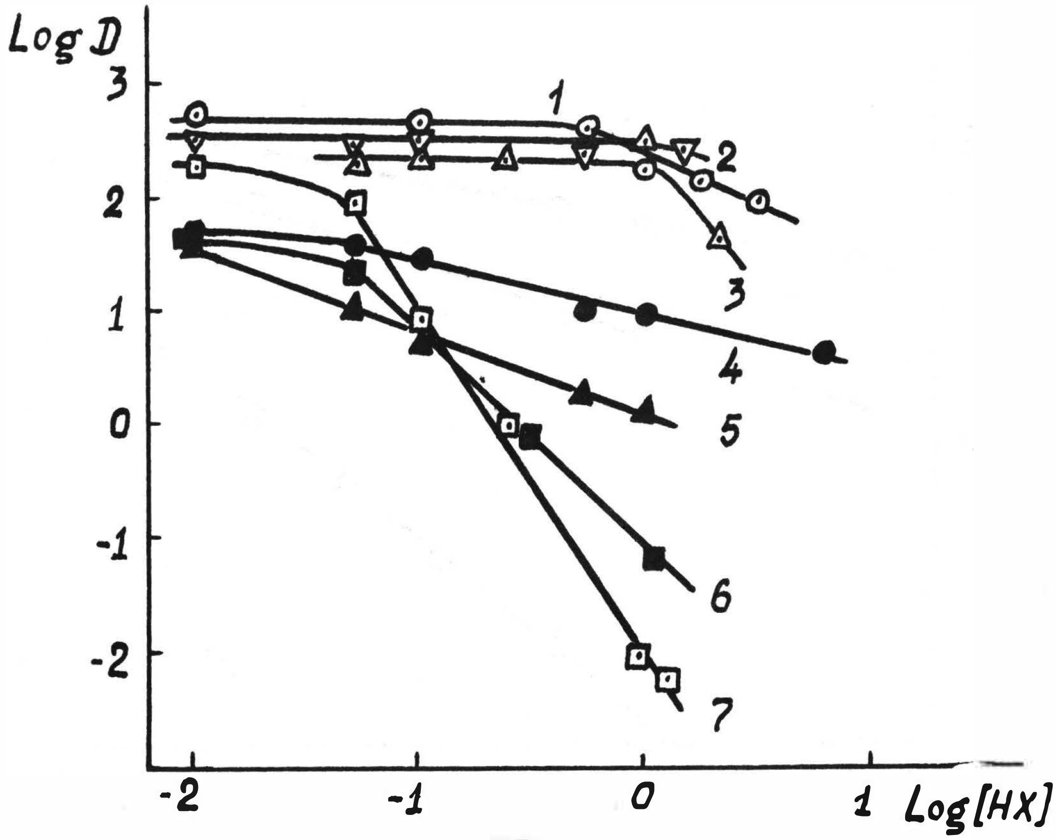

FIG.4

The effect of mineral acid concentration on the extraction of oxo anions by 0.1 M DNTDN in chloroform+25 vol.% TBP; 1 - extraction of phosphate from HNO_3 solutions, 2 - phosphate from H_2SO_4, 3 - arsenate from HNO_3, 4 - selenate from HNO_3, 5 - selenate from H_2SO_4, 6 - selenate from HCl, 7 - phosphate from HCl

tions, practically have no effect on the extraction of phosphorus(V) and arsenic(V). Large amounts of iron(III) somewhat decrease the extraction that is probably due to high stability of phosphate and arsenate complexes of iron(III). The separation factors for phosphate or arsenate and various cations are 10^4-10^5.

To investigate the state of the extractants and extracted species and to account for unusually high extracting ability of the organotin salts, extraction methods, infrared and Mössbauer spectroscopy studies have been made. Solid DATDN are polymerized. The polymer structure is only partially destructed during dissolution in chloroform and the dinitrate molecules exist in a solution as separate polymer fragments.

Equilibration of DATDN solutions with neutral or weakly acidic aqueous solutions causes a partial hydrolysis of the extractants due to which hydroxyl groups are substituted for the nitrate ones. Further hydrolysis causes the formation of DAT oxides which are insoluble in organic solvents. The above mentioned precipitate formation in the organic phase during equilibration of extractant solutions with alkaline aqueous solutions is a result of such hydrolytic transformation of DAT salts.

Addition of donor additives to an inert solvent results in not only an increase in DAT salt solubility but also to some stabilization of extractant solutions and extracts in the work with neutral aqueous solutions. This is due to the formation of adducts because of entering donor additive molecules the inner coordination sphere of the tin. The adducts do not tend to polymerization as much as non-solvated DAT salts. Significant displacements of the valency vibrational frequencies due to the $P \rightarrow O$ groups of the donor-active additive (40-60 cm^{-1} for TOPO and 35-45 cm^{-1} for TBP), observed by infrared studies of DAT salt solutions in inert diluents containing an additive, have confirmed that the tin atom coordinates the additive molecules. In the case of the dinitrates, adducts of a $R_2Sn(NO_3)_2L_2$ type (L=TBP, TOPO) form which have trans-R-configuration. The extracted species, containing phosphorus(V) and arsenic(V) have the same configuration of the alkyl groups.

The composition of the compounds being extracted and the degree of their aggregation in the organic phase depend on the nature of the anion extracted and the additive and on concentration of salts and acids in the aqueous phase. The observed isomer shifts and quadrupole splittings, obtained from the Mössbauer spectra of the extractants, their solutions in organic diluents, blank extracts and arsenic-, phosphorus-, selenium-containing extracts, have shown that the coordination number of tin is six in all the cases. The extracted oxo anions enter the inner coordination sphere of the tin, the bonds tin-anion oxygen being responsible for the compound formation. Thus, the dialkyltin salts can be considered as a new class of extractants,the extraction power of which is due to ability of the extractant central atom to form donor-acceptor bonds with oxygen atoms. Depending on extraction conditions, arsenic(V) and phosphorus(V) are extracted as HMO_4^{2-} or $H_2MO_4^-$ anions. Oxo anions of dibasic acids (selenite, selenate, sulphate, molybdate, tungstate) are mainly extracted as 1:1 compounds.

The results obtained suggest that the DAT salts can be successfully used to solve various practical problems which demand selective extraction of oxo anions, particularly arsenic(V) and phosphorus(V) anions. As examples, it is worth to mention some methods developed: extraction-spectrophotometric determination of phosphorus and arsenic in various materials; neutron-activation determination of arsenic based on substoichiometric separation; extraction-atomic-absorption determination of arsenic using flame and graphite furnace atomizers.

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THE EXTRACTION OF MIXED-LIGAND COMPLEXES OF SOME METALS WITH METALLOCHROME INDICATORS AND N-CONTAINING REAGENTS.

M.I. Shtokalo, M.S. Ostrovskaya and
V.L. Ryzhenko
Technological Institute for Food
Industry, Analytical Chemistry Dept.,
Vladimirskaya Street, 66
Kiev, USSR.

The complex formation of Al, Fe(III), Zr, Mg with a series of metallochrome indicators in the presence of various organic reagents was studied. The formation of mixed-ligand complexes was observed during this process. Some of them are good analytical species for extraction-photometric determination of metals.

Some of the most sensitive reagents for spectro-photometric determination of metals are acidic dyes of the metallochrome indicator type. Binary metal complexes with these reagents are not extracted by organic solvents in most cases. However, it is well known that liquid extraction favours the increase of sensitivity and selectivity of analytical reactions.

For the improvment of extracting properties we used the formation of mixed-ligand complexes with metallochrome indicators and some additional reagents.

The formation of complexes between aluminium, iron, zirconium and magnesium and a number of metallochrome indicators such as arsenazo III, xylenol orange (XO), methyl thymol blue (MTB), pyrocatechol violet (PV) and eriochrome black-T (ECB-T) was investigated. Various organic reagents (many of which are drugs) and some chelate-forming reagents, such as N-benzoyl-phenylhydroxylamine (N-BPhHa) and 8-oxyquinoline were used as additional ligands. In most cases, the formation of complex multicomponent compounds takes place. This is testified by a batochrome shift of the binary complex absorption bands and by a hyperchrome effect.

Aluminium complexes absorption bands with PV in the presence of some N-containing reagents are presented as an example in Figure 1.

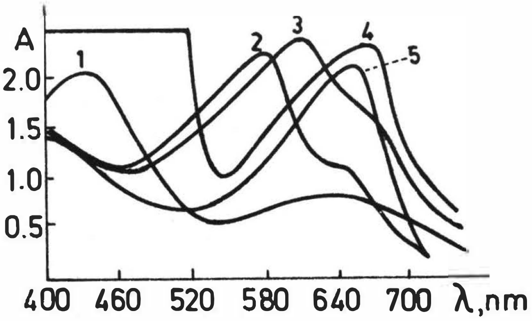

FIG. 1

Absorption bands of PV and its complex with aluminium(III) in the presence of cardiamine (3), rivanol (4) and phenanthroline (5).

Some of the compounds produced by complexation can be separated as a non-miscible phase by the addition of higher spirits (e.g. Al-Pv-rivanol). The surface films produced are easily dissolved in acetone with the formation of intensively coloured solutions. Similar systems can be used for extraction-photometric determination of elements, as well as amines.

Mixed-ligand complexes, which can be extracted by organic solvents, are of special interest for photometric analysis. Such a complex, which can be extracted in chloroform, is formed in the system zirconium-XO-papaverine (Papav)-perchlorate ion. The absorption spectra of this complex and of the papaverine compounds with XO are presented in Fig. 2.

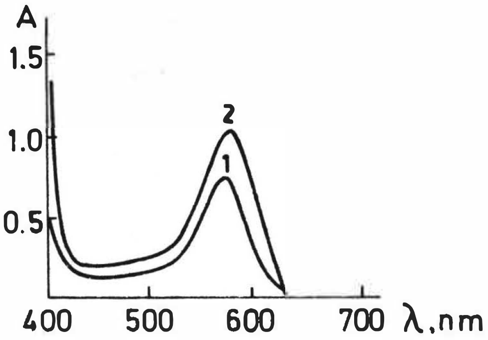

FIG. 2

Absorption spectra of chloroform solutions of zirconium complex with XO (1) and papaverine (2) in the presence of perchlorate ions, pH 1.6-1.8.

A binary zirconium-XO complex is not extracted by organic solvents. However, with the introduction of papaverine into the system, a coloured compound is extracted into chloroform and the appearance of an intensively violet colour is observed. The complex separates partially during the extraction. The addition of perchlorate ions to a Zr-XO-Papav complex promotes the quantitative extraction. This is indicative of the participation of the ions ClO_4^- in the complex formation process.

The dependence of the extracts optical density on concentration conditions and on the pH is presented in fig. 3.

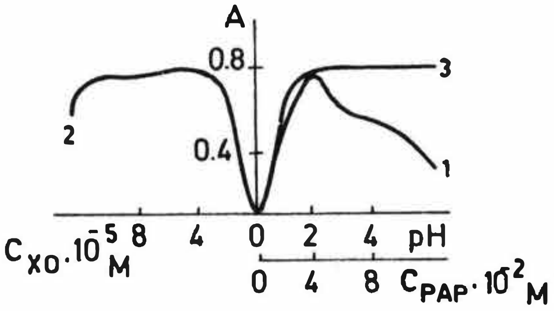

FIG. 3

The influence of pH (1), XO (2), and papaverine (3) concentration on complex extract light absorption.

The optimal conditions for mixed-ligand complex formation and extraction for $C_{Zr} = 2.10^{-5}$ mole/l are : $C_{XO} = 4.10^{-5}$mole/l ; $C_{papav} = 5.10^{-2}$ mole/l ; $C_{ClO_4} = 1.10^{-2}$mole/l ; pH = 1.6-1.8.

The components ratio in the complex Zr:XO:papav.:ClO_4 is 1:2:2:1 as determined by means of the balance shift and isomolar series methods.

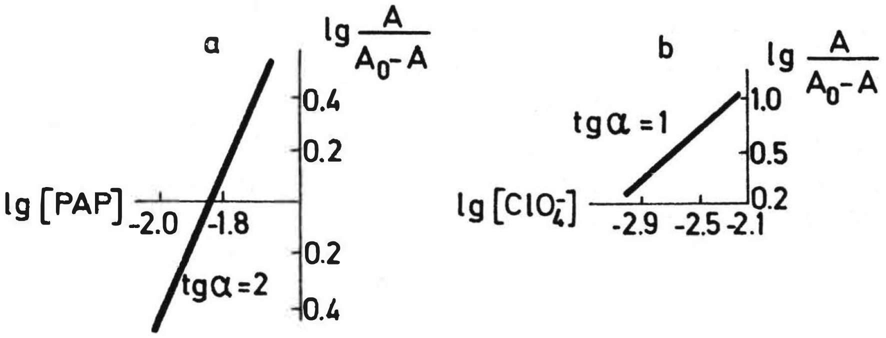

FIG. 4

Determination of components ratio in the complex by means of a balance shift method.

Relying on the method described in reference (1), it is concluded that $Zr(OH)^{3+}$ is a coordinating ion (2).

Electromigration tests demonstrated the cation complex presence. It seems likely that a zirconium cation, a papaverine molecule and a XO molecule are forming a inner sphere complex, while perchlorate ions neutralize the residual charge of Zr, thus staying in the outer sphere.

The reaction is characterized by high contrast ($\Delta\lambda$ = 180 nm) and sensitivity ($\varepsilon = 5.1x10^4$). The following ions do not interfere with Zr determination : Al, Cr(III), Mn(II), Ni(200),Ca(100), Zn, Ga(50). The following ions interfere with the Zr determination : Fe(III), Pb, Nb(V), Ti(IV).

The possibility of zirconium determination by means of its extraction in the form of diantipyrilpropylmethanerhodanide complex with the subsequent introduction of arsenazo III into a non-aqueous phase is of great interest. Zr forms complexes with diantipyrilpropylmethane : $Zr(DAPM)^{4+}$ and $Zr(DAPM)_2^{4+}$ with stability constants of $(5.0 \pm 0.60).10^8$ and $(3.8 \pm 0.36).10^{12}$ respectively. The presence of rhodanide ions leads to the formation of precipitates, which can be dissolved in organic solvents. The optimal conditions for complex extraction from the medium 2N HCl are C_{DAPM} = 0.03 mole/l, C_{SCN} = 0.2 mole/l, $C_{ars} = 1.6x10^{-3}$ mole/l.

A method denoted here of "two reagents" allows to increase the sensitivity of the determination of Zr in the presence of arsenazo III. In 2N HCl-medium a molar absorption coefficient of 1.10^5 was measured. This coefficient is considerably larger than the value determined under analogous conditions, but without preliminary Zr extraction in the form of Zr-DAPM-SCN-complex ; it approaches the absorption molar coefficient previously obtained in 9 to 11N HCl medium (3). It is noteworthy that equimolar quantities of Th, Ti(IV), and Fe(III) (5), Ce(IV) (10), La(50) do not interfere with the reaction course.

Mixed-ligand complexes are most easily extracted with BPhHa, as the second reagent, which is widely used for extractive separation and metal determination. BPhHa promotes the extraction of Zr complexes with XO and MTB.

Figure 5 illustrates the absorption spectrum of zirconium complex with MTB and BPhHa.

The influence of pH and concentration conditions on mixed-ligand complexes ectraction was studied. Experimental data for a system with MTB are presented in Figure 6.

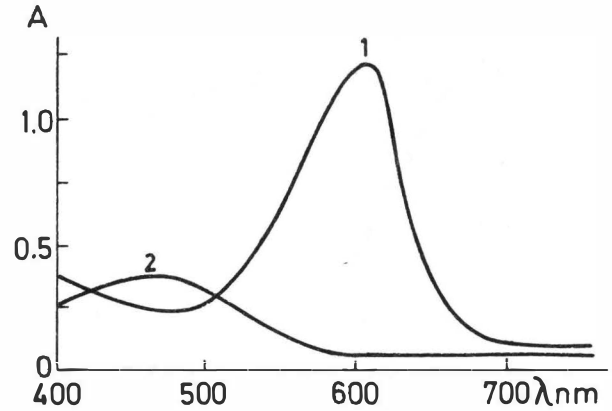

FIG. 5

Absorption bands of Zr-MTB-BPhHa (1) and MTB-BPhHa (2).

The optimal conditions for the formation of the Zr-MTB-BPhHa complex and for the extraction of zirconium when its concentration amounts to 4.10^{-5} mole/l are as follows : $C_{BPhHa} = 1.10^{-3}$ mole/l ; $C_{MTB} = 8.10^{-5}$ mole/l ; pH = 1.1-2.0. If the optimal concentration of BPhHa is exceeded, an optical density decrease is observed. It is connected with mixed-ligands destruction because of the competing action of BPhHa.

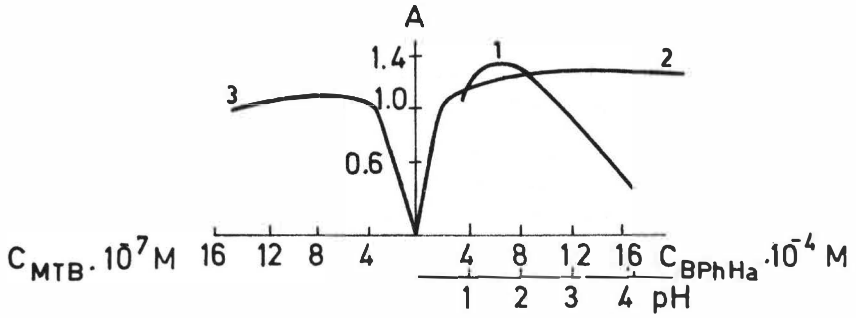

FIG. 6

The influence of pH (1), BPhHa (2) and MTB (3) concentration on the absorption of Zr mixed-ligand complexes.

The components ratio Zr : MTB(XO) : BPhHa in the extracted complex is 1:1:2 as determined by the balance shift and isomolar series methods.

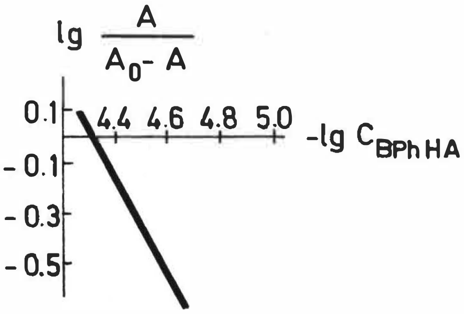

FIG. 7

Components ratio determination by the balance shift method.

Electromigration experiments demonstrated that a neutral complex is formed. Both ligands could possibly belong to an inner coordinative sphere.

Molar light absorption coefficients are 3.0×10^4 (at 600 nm) and 3.5×10^4 (at 580 nm) for MTB and XO respectively. The following ions do not interfere with the determination of zirconium : Al(200), In, Ga, Ti(IV), Nb(V), Cr(III), Ca and Pb(50). Hf and Fe(III) interfere but influence of the latter can be removed by ascorbic acid.

In the case of the arsenazo III reagent the "method of 2 reagents" was used. Zr was extracted from an aqueous solution by a BPhHa chloroform solution ; then arsenazo III was introduced into the organic phase. The Zr complex with arsenazo III seems stronger than with BPhHa because an exchange reaction takes place in the solution and the extensive blue-green colour of the Zr complex with arsenazo III develops. The extract spectral characteristics coincide with the binary complex data.

It is to be noted that BPhHa extracts Zr from strongly acidic media, while thorium and rare-earth elements, which interfere with the determination of Zr with arsenazo III, are not extracted.

According to a metal indicator method (4), Zr complexes with metallochrome indicators related to BPhHa can be arranged into the following series depending on their stability :

arsenazo III > arsenazo I > XO > MTC

A mixed-ligand complex of magnesium with ECB-T and BPhHa, which is extracted with butanol in alcali media, was also studied. The molar absorption coefficient is 2.5×10^4 at 560 nm.

A less stable complex of calcium with ECB-T is destroyed by the introduction of the BPhHa. This allows the determination of Mg in the presence of Ca.

The above systems are suitable for analytical purposes,they are used for extraction-photometric determination of metals in a variety of materials.

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COMPLEXONES FOR EXTRACTIVE SEPARATION PROCESSES OF RARE EARTH ELEMENTS BY AMINES.

A.A. Kopyrin, V.D. Murashov

Lensovet Institute of Technology

Leningrad, USSR.

The extraction distribution and separation of rare earth elements from a concentrated lithium nitrate solution by tertiary amines in organic diluents have been studied as a function of the composition and structure of a series of polyaminopolyacetic acids. The optimum conditions for the separation of rare earth have been determined.

Selectivity in the extraction separation of rare earth elements (REE) by amines is dependent upon the extractant structure, the nature and concentration of salting out agent, the presence of additional complexing agents, the pH of the aqueous solution and some other factors. The efficiency of the REE separation may be essentially increased with the addition of organic complexing agents to the extraction system.[1-4] This efficiency is primarily dependent upon the ratio of the complexonates stability constants.

It is well known that REE extraction by amines takes place only when considerable amounts of salting out agents are present. The description of the REE distribution and separation processes by extraction in the presence of chelating agents, requires the knowledge of the stability constants of the lanthanide complexes in the concentrated salting out solution. These data do practically not exist in the literature.

We investigated the influence on the separation of REE by trio-n-octylamine nitrate (TOA) in p-xylene extraction from concentrated lithium nitrate aqueous solutions, for the following chelating agents : iminodiacetic (IDA),2-oxiethyliminodiacetic (OIDA), nitrilotriacetic (NTA), ethylenediaminotetraacetic (EDTA), diethylenetriaminopentaacetic (DTPA), 1,2-diaminocyclohexanetetraacetic (CDTA) and citric acids (H_3Cit). Fig. 1 and 2 show the results obtained for the distribution and separation of europium and promethium trace quantities from 8,035 M aqueous lithium nitrate solution containing various complexones (10^{-3}M) with 0,2 M TOA in ethylbenzene as a function of the equilibrium pH of the aqueous phase.

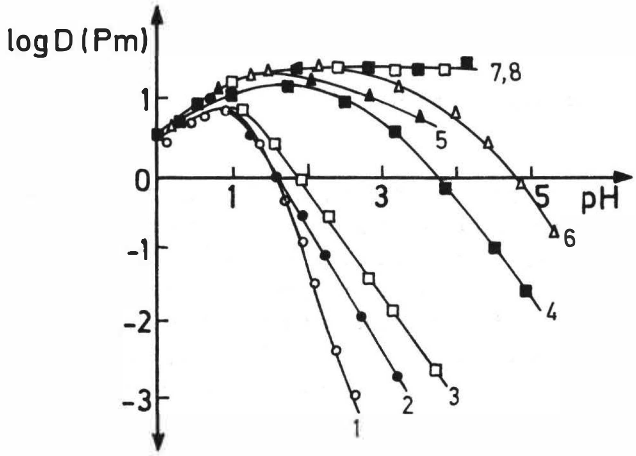

Fig. 1

Variation of the distribution ratio of Pm with the pH of the aqueous phase. 1-DTPA ; 2-CDTA ; 3-EDTA ; 4-NTA ; 5-H_3Cit ; 6-OIDA ; 7-IDA ; 8 - in the absence of complexone.

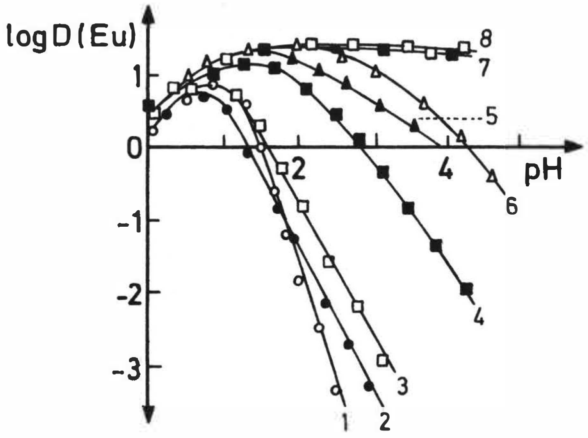

Fig. 2

Variation of the distribution for Eu with the pH of the equilibrium aqueous phase. 1-DTPA ; 2-CDTA ; 3-EDTA ; 4-NTA ; 5-H_3Cit ; 6-OIDA ; 7-IDA ; 8 - in the absence of complexone.

Addition of any complexone with the exception of IDA decreases the extraction of the studied elements, but in a different degree.

It is shown in figs. 1-2 that by increasing the stability of complexation of the organic ligand, the pH at the origin of the complex formation shifts to a more acidic region and the decrease of the extraction of promethium and europium takes place more sharply. It is clear that the fraction of Pm and Eu chelated with DTPA, CDTA or EDTA is greater than with the other complexones.

The separation factor for the Pm-Eu pair at various pH of the aqueous phase was calculated from the experimental data (fig. 3).

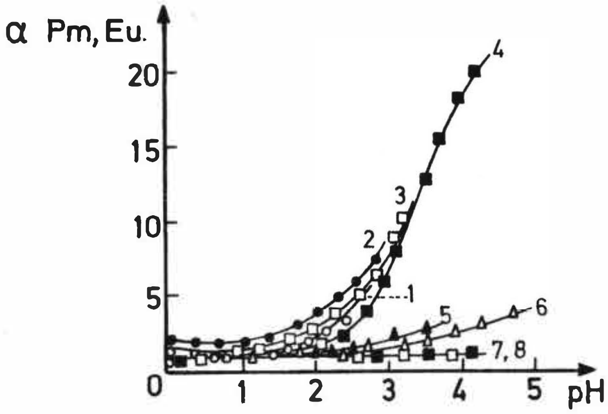

Fig. 3

Variation of the separation for the Pm-Eu pair with the equilibrium pH of the aqueous phase. 1-DTPA ; 2-CDTA ; 3-EDTA ; 4-NTA ; 5-H_3Cit ; 6-OIDA ; 7-IDA ; 8 - in the absence of complexone.

Practically no separation of the Pm-Eu pair can be achieved with IDA ; the separation can be increased by the addition of H_3Cit and OIDA to the extracting system. The variation of α Pm/Eu with the equilibrium pH of the aqueous phase for NTA, EDTA, CDTA, DTPA is rather similar. These complexones behave similarly with respect to the separation of Pm and Eu.

A more detailed study was undertaken concerning the extraction of REE with amines in the presence of DTPA or EDTA.

In order to predict the effect of these chelating agents, the stability constants of the REE complexes with the complexones under the experimental conditions of extraction are required.

Complexation of REE with EDTA or DTPA in concentrated lithium nitrate solutions was studied by means of extraction and potentiometric methods.$^{3-4}$

The determination of the "conditional" stability constants of REE with EDTA or DTPA by the extraction method with tertiary amines is based on a correlation between the distribution ratio of the REE, the equilibrium pH of the aqueous phase and the equilibrium concentration of the complexone.

The relationship between the distribution ratio of the REE and the equilibrium pH of the aqueous phase for the extraction of REE by tertiary amines from concentrated solutions of lithium nitrate containing complexone is described by the Eq. (1)

$$D = \frac{D^{o}}{F} \qquad (1)$$

where F represents the distribution function of REE complexes by :

$$F = 1 + \frac{C_L}{A} \sum_{i=0}^{i=n} \beta_i \, [H]^i \qquad (2)$$

C_L : equilibrium concentration of the complexone in the aqueous phase. A depends on the equilibrium pH of the aqueous phase and is given (for DTPA) by the following equation :

$$\frac{[H]^5}{K'_{a_5} \cdot K_{a_4} \cdot K_{a_3} \cdot K_{a_2} \cdot K_{a_1}} + \frac{[H]^4}{K'_{a_5} \cdot K_{a_4} \cdot K_{a_3} \cdot K_{a_2}} + \frac{[H]^3}{K'_{a_5} \cdot K_{a_4} \cdot K_{a_3}} +$$

$$\frac{[H]^2}{K'_{a_5} \cdot K_{a_4}} + \frac{[H]}{K'_{a_5}} + \frac{1}{\beta_{Li}} + [Li] = A \qquad (3)$$

where K_{a_i} - dissociation constants of the complexone,

β_{Li} - stability constants for the complex of lithium with the complexone ($Li\,L^{4-}$),

β_i - conditional stability constant of REE with the complexone

$$\frac{[M\ L\ H_i]}{[M]\,[L]\,[H^{1-}]^i} = \beta_i$$

The conditional stability constants of the REE may be obtained by Leden's method based on the dependence of the F function with the pH of the aqueous phase. However, this requires the determination of the dissociation constants of EDTA or DTPA by pH-titration in concentrated solutions of lithium nitrate.

Analysis of the dependence of the F function with pH shows that for EDTA it may be represented by an equation of the first order ; while for DTPA it is one of the second order in terms of H^+-ion concentration ; β_i values are conditional stability constants for the REE-EDTA complexes, LnL^-, $LnHL$, and for the REE-DTPA complexes, LnL^{2-}, $LnHL^-$, LnH_2L.

The complexation of REE with EDTA or DTPA in concentrated lithium nitrate was also determined by pH-metric titration.

The pH-metric titration curves were treated by Schwarzenbach's method. The calculation of the conditional stability constants was carried out in a pH region where the formation of H-containing complexes is very weak.

The conditional stability constants determined by various physico-chemical methods are in good agreement.

The average values for the conditional stability constants for the complexes of Ce, Pm and Eu with EDTA and DTPA are given in tables 1 and 2 :

Table 1.

Average conditional stability constants for REE complexes with EDTA.

REE	C_{LiNO_3}	β_o	β_1
Ce(III)	5M	$(2.2\pm0.3)\ 10^{12}$	$(1.4\pm0.6)\ 10^{16}$
	6M	$(5.0\pm0.4)\ 10^{11}$	$(1.5\pm0.7)\ 10^{15}$
	8M	$(1.0\pm0.1)\ 10^{10}$	$(7\pm3.2)\ 10^{13}$
Pm	5M	$(2.5\pm0.2)\ 10^{13}$	$(5\pm2.7)\ 10^{16}$
	6M	$(4.2\pm0.3)\ 10^{12}$	
	8M	$(1.5\pm0.2)\ 10^{11}$	$(3\pm1.6)\ 10^{14}$
Eu	5M	$(3.5\pm0.3)\ 10^{13}$	$(4\pm1.9)\ 10^{17}$
	6M	$(8.1\pm0.8)\ 10^{12}$	$(8\pm4.9)\ 10^{16}$
	8M	$(2.4\pm0.3)\ 10^{11}$	$(5\pm2.9)\ 10^{15}$

Table 2.

Average conditional stability constants for REE complexes with DTPA.

REE	C_{LiNO_3}	β_o	β_1	β_2
Ce(III)	5M	$(2.6\pm0.3)\ 10^{14}$	$(3\pm2.4)\ 10^{16}$	$(1.3\pm0.9)\ 10^{19}$
	6M	$(5.1\pm0.5)\ 10^{13}$	$(4\pm3.1)\ 10^{15}$	$(9\pm7.1)\ 10^{17}$
	8M	$(1.1\pm0.1)\ 10^{12}$	$(1.0\pm0.7)\ 10^{14}$	$(7\pm3.9)\ 10^{16}$
Pm	5M	$(3.1\pm0.3)\ 10^{15}$	$(2.2\pm0.9)\ 10^{17}$	$(1.5\pm0.9)\ 10^{20}$
	6M	$(4.2\pm0.4)\ 10^{14}$	$(1.3\pm0.7)\ 10^{16}$	$(1.8\pm0.9)\ 10^{19}$
	8M	$(2.1\pm0.3)\ 10^{13}$	$(3\pm1.8)\ 10^{15}$	$(2.1\pm0.9)\ 10^{18}$
Eu	5M	$(1.4\pm0.2)\ 10^{16}$	$(1.8\pm0.9)\ 10^{18}$	$(3\pm1.7)\ 10^{21}$
	6M	$(2.0\pm0.2)\ 10^{15}$	$(1.0\pm0.5)\ 10^{17}$	$(5\pm3.2)\ 10^{19}$
	8M	$(6.6\pm0.5)\ 10^{13}$		$(4\pm2.1)\ 10^{17}$

The conditional stability constants were calculated for the various concentration of lithium nitrate 5, 6 and 8M.

The conditional stability constants for REE complexes with DTPA were used to determine the optimum conditions and to calculate the separation factors of REE in extraction systems with tertiary amines.

The separation factor of elements 1 and 2 in their extraction with amine nitrate in the presence of a complexone is :

$$\alpha_{1,2} = \frac{D_1}{D_2} = \frac{D_1^o}{D_2^o} \cdot \frac{F_2}{F_1} = \alpha_{1,2}^o \cdot \frac{F_2}{F_1} \qquad (4)$$

D_1^o and D_2^o : distribution ratios of elements 1 and 2 in the absence of a complexone ;

F_1 and F_2 : formation functions of elements 1 and 2 in the presence of complexone ;

$\alpha_{1,2}^o$: separation factor of elements 1 and 2 in the absence of complexone.

The determination of the optimum conditions and the calculation of the separation factors can be reduced to the analysis of the dependence of F_2/F_1 on the equilibrium concentrations of complexone and REE.

It may be seen that calculated and experimental values for the separation factors are in a good agreement.

Equation (4) can be written for the amine extracting system with DTPA (the existence of three complexes of LnL^{2-}, $LnHL^-$ and LnH_2L is assumed) :

$$\alpha_{1,2} = \alpha_{1,2}^o \cdot \frac{1 + ({}^2\beta_o + {}^2\beta_1[H] + {}^2\beta_2[H]^2) \cdot \frac{C_L^o}{A}}{1 + ({}^1\beta_o + {}^1\beta_1[H] + {}^1\beta_2[H]^2) \cdot \frac{C_L^o}{A}} \qquad (5)$$

As a rule,`the extraction separation of REE in the presence of complexones was carried out under conditions where

$$\beta_o + \beta_1 [H] + \beta_2 [H]^2 >> 1 \qquad (6)$$

Therefore,

$$\alpha_{1,2} = \alpha_{1,2}^o \; \frac{{}^2\beta_o + {}^2\beta_1 [H] + {}^2\beta_2 [H]^2}{{}^1\beta_o + {}^1\beta_1 [H] + {}^1\beta_2 [H]^2} \qquad (7)$$

The separation factors for the pairs of lanthanides Ce-Pm, Pm-Eu, Ce-Eu and the conditions, under which they have been obtained, are shown in tables 3 and 4.

Table 3.

Separation factors for the Ce-Pm pair with 0,2M TOA from solutions of lithium nitrate in the presence of EDTA.

$C_{(Li)NO_3}$	α^o factor in the absence of complexone	$\alpha_{exp.}$	$\alpha_{calc.}$	$pH_{exp.}$	$pH_{calc.}$
5M	3.0	26	30.6	3.0	3.0
6M	3.0	26	28.5	2.5-3.0	3.0
8M	3.1	30	29.3	2 -2.3	2.3

Table 4.

Separation factors for certain REE pairs with 0,2M TOA from solutions of lithium nitrate (6M) in the presence of DTPA.

Pair	Separation factor in the absence of complexone	$\alpha_{exp.}$	$\alpha_{calc.}$	$pH_{exp.}$	$pH_{calc.}$
Cm-Pm	3.0	28	24.7	2.4-2.5	2.4-2.5
Pm-Eu	1.4	6.3	6.2	2 -2.5	1.9-2.5
Ce-Eu	5.8	140	152	2.3-2.4	2 -2.5

It may be seen from table 4 that the calculated and experimental values of the separation factors for Ce-Pm, Pm-Eu and Ce-Eu are in good agreement.

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EXTRACTION AND DETERMINATION OF RUTHENIUM, PALLADIUM AND IRIDIUM WITH N-α-(5-BROMOPYRIDYL)-N'-BENZOYL THIOUREA IN ORGANIC PHASE

S.C.SHOME AND P.K.HALDER
Chemistry Department,
Presidency College
Calcutta 73, INDIA

ABSTRACT

N-α-(5-bromopyridyl)-N'-benzoyl thiourea has been employed as a chelating agent in the solvent extraction and subsequent spectrophotometric determination of ruthenium, palladium and iridium. Considerable excess of diverse ions do not interfere with the procedures. The molar absorptivities of the platinum metal chelates studied are in the 10^4 range.

Although alkyl, aryl and - NHR substituted thioureas (1,2) offer sensitive colour reactions with the platinum metals, they, however, suffer from lack of selectivity. The introduction of an acyl group on one of the nitrogen atoms of the thiourea molecule and a pyridyl group on the other gives rise to reagents of increased sensitivity and selectivity towards platinum metals (3,4,5). The sensitivity of the colour reactions of the thiourea derivatives is further improved by substituting a bromine atom in the 5-position of the pyridine ring. The present communication deals with the extraction and subsequent spectrophotometric determination of ruthenium, palladium and iridium with N-α-(5-bromopyridyl)-N'-benzoyl thiourea (Br-PBT) in the organic phase. Br-PBT forms a brown complex with Ru(III), a yellow complex with Pd(II) and an orange yellow complex with Ir(III) in acetate buffer medium. The Pd complex is formed instantaneously at room temperature, whereas the Ru and Ir complexes are obtained by heating on the water bath for 15 minutes and 30 minutes respectively.

EQUIPMENTS AND REAGENTS

A Carl Zeiss PMQ II spectrophotometer equipped with 1-cm quartz cells was employed for the absorbance measurements. A Cambridge pH meter (Bench model) was used to measure the acidity of the aqueous layer.

Ru(III), Pd(II) and Ir(III) solutions were prepared by dissolving their respective chlorides (J. Mathey, London) in distilled water containing hydrochloric acid. The solutions were standardised by DMG for Pd and hydrolytic precipitation method for Ru and Ir. A 10% sodium acetate solution and 4N hydrochloric acid were used for the regulation of acidity of the solutions. A 0.01M ethanolic solution of Br-PBT was employed for complex formation. All the reagents used were of A.R. quality.

SOLVENT EXTRACTION OF METAL CHELATES

To study the effect of organic diluents on the extraction of Ru, Pd and Ir chelates, thorough survey experiments were performed. A set of solutions, each containing a definite amount of Ru(III), were adjusted to the same acidity, excess of Br-PBT solution added, warmed and the resulting metal complex was extracted separately with various organic diluents of the same volume. The absorbance of each extract was measured at wave lengths ranging between 300 nm and 400 nm. Experiments were then carried out by adjusting the Ru(III) solutions to varying acidities, other conditions remaining the same. The same shape of the absorbance curves obtained using different diluents indicated that the extraction mechanism was similar irrespective of the extraction media. Moreover, the pH range for the maximum extraction of the metal complex remained the same when the extractant was changed. Survey experiments performed with Pd(II) and Ir(III) solutions showed similar results.

In determining the distribution ratio (D) and per cent extracted (E) values of Ru(III), Pd(II) and Ir(III), each metal chelate was extracted with the organic diluent of the same volume as that of the aqueous layer in a single step under optimum conditions. The metal contents of the aqueous layers were measured by standard methods. The results (Table I) indicated that Ru(III), Pd(II) and Ir(III) could be quantitatively extracted with Br-PBT when chloroform or isobutyl methyl ketone was employed as an extractant. The addition of ethanol (20% of organic phase) facilitated the extraction of the metal chelates in chloroform in a single step, whereas for the other diluents no

TABLE I

EFFECT OF DILUENTS ON EXTRACTION OF METAL CHELATES

Solvent	Ru(III)		Pd(II)		Ir(III)	
	D	%E	D	%E	D	%E
Isobutyl methyl ketone	65.80	98.50	35.05	97.23	40.68	97.60
Benzene	1.01	58.18	0.76	43.30	1.01	50.13
Carlon tetrachloride	0.71	41.88	0.65	39.23	0.82	45.15
Ethyl acelate	2.34	70.06	1.40	58.38	2.05	67.23
Dichloroethane	3.94	79.75	2.18	68.53	3.29	76.70
Chloroform	168.00	99.40	599.00	99.82	154.80	99.40
Chloroform-ethanol (4:1)	3039.00	99.95	3099.00	99.98	1796.50	99.95

such single step extraction was possible.

SPECTROPHOTOMETRIC STUDIES OF THE METAL CHELATES IN CHLOROFORM

The spectral absorbance of the chloroform extracts of Ru, Pd and Ir chelates was studied in the range of wavelengths from 300 nm to 400 nm. The absorbance curves (Fig 1) indicated that the maximum absorption occurred at 355 nm for each of the metal chelates. The colour of the extracts of the metal chelates was found to be stable for more than 48 hours.

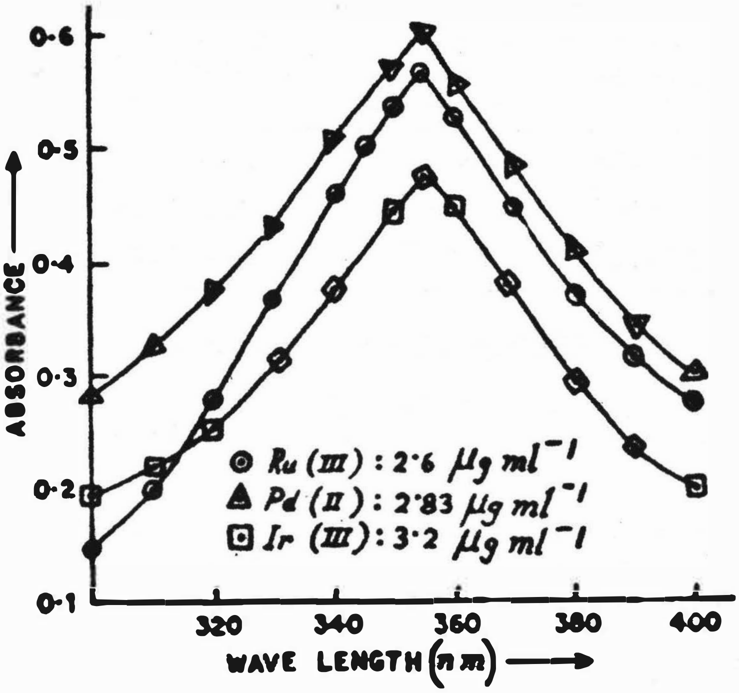

FIG. 1

ABSORBANCE CURVES OF CHELATES OF Ru(III), Pd(II) and Ir(III)

The extraction of the metal chelates in chloroform depended largely upon the acidity of the aqueous phase. The optimum pH ranges for complete extraction of Ru, Pd and Ir chelates were determined and found to be 4.7 to 6.4, 3.8 to 6.1 and 4.9 to 6.2 respectively. Ru, Pd and Ir metal ions were quantitatively extracted with Br-PBT in chloroform when the molar ratios of the organic reagent to metal ions were 6:1, 4:1 and 10:1 respectively.

The conformity to Beer's law by Ru, Pd and Ir chelates was studied by extracting the respective metal chelate from the aqueous layers containing varying concentrations of the metal under optimum experimental conditions. The chloroform extracts of the metal chelates obeyed Beer's law at 360nm over the concentration regions 0.65 to 3.90μg ml^{-1} for Ru(III), 0.47 to 3.77μg ml^{-1} for Pd(II) and 0.64 to 5.10μg ml^{-1} for Ir(III).

The empirical formulae of the Ru, Pd and Ir chelates formed with Br-PBT were determined spectrophotometrically by the mole-ratio method as described by Meyer and Ayres(6). The results showed that the molar ratios of the organic reagent to the metal ion in the complexes were 2:1 for Ru, 1:1 for Pd and 3:1 for Ir, which were verified by the conventional slope-ratio method. The dissociation constants of the metal complexes were calculated from their mole-ratio curves using the equation given by Harvey and Manning(7) and found to be 2.97×10^{-11}, 1.80×10^{-6} and 2.40×10^{-17} for Ru, Pd and Ir complexes respectively.

The characteristics of the methods for the extraction and determination of Ru, Pd and Ir are shown in Table II.

TABLE II

Metal ion	Molar absorptivity(litre mole^{-1}cm^{-1})	Sensitivity (μg cm^{-2})	Optimum concentration range(μg ml^{-1})	Relative mean error(%)	coefficient of variation (%)
Ru(III)	1.98×10^4	5×10^{-3}	1.02-3.57	0.26	0.51
Pd(II)	2.07×10^4	5×10^{-3}	1.03-3.59	0.21	0.46
Ir(III)	2.70×10^4	7×10^{-3}	1.34-4.70	0.21	0.34

EFFECT OF DIVERSE IONS

The effect of a number of diverse ions on the extraction and the photometric determination of Ru(III), Pd(II) and Ir(III) with

TABLE III

EFFECT OF DIVERSE IONS ON EXTRACTION AND DETERMINATION OF Ru(III), Pd(II) AND Ir(III) WITH Br-PBT

Foreign ion added	Amount tolerated(mg) in the determination of Ru(81.6μg)	Pd(59.1μg)	Ir(80.1μg)
Co(II)^b	3.00	3.00	3.00
Ni(II)^a	2.00	3.00	2.00
Mn(II)^b	3.00	5.00	2.00
Cd(II)^a	1.00	2.00	1.00
Hg(II)^a	0.50	1.00	1.00
Pb(II)^b	1.00	2.00	2.00
Cu(II)^a	1.00	2.50	1.50
Fe(III)^a	2.00	2.00	1.50
Au(III)^a	0.20	1.00	0.51
Ga(III)^b	1.50	1.00	2.00
Tl(III)^b	1.50	1.00	2.00
Th(IV)^b	2.50	5.00	3.00
Ti(IV)^c	0.50	2.00	1.50
Mo(VI)^b	2.00	2.00	1.00
W (VI)^b	1.50	1.50	1.00
U (VI)^b	2.50	5.00	3.00
Ru(III)	-	0.50	0.32
Rh(III)	0.20	0.82	-
Ir(III)	0.20	0.80	-
Pt(IV)	0.30	0.99	0.30
Os(VI)	0.10	0.38	0.30
Pd(II)	0.25	-	0.24

a-In presence of EDTA; b-In presence of tartrate;
c-In presence of fluoride.

Br-PBT was investigated. The tolerance limits (i.e., concentrations causing the error less than 2%) for the foreign ions are recorded in Table III.

In the determination of Ru(III), the interference of Pd(II) was overcome by its prior extraction with Br-PBT in chloroform at room temperature. The separation of Ru(III) from Pt(IV) and Os(VI) was effected by preliminary extraction of the latter metal ions with the organic reagent in chloroform at pH 2.2. Rh(III) and Ir(III) were removed by extracting with Br-PBT in chloroform in the presence of hydroxylamine hydrochloride, which reduced Ru(III) to the bivalent state. Ru(II), which remained in the aqueous phase, was then oxidised to the trivalent state by adding nitric acid, extracted as the metal chelate with Br-PBT in chloroform and determined spetrophotometrically.

Pd(II) could be easily separated from the other platinum metals and determined, as the latter metal ions did not form extractable complexes with Br-PBT at room temperature.

Ir(III) was seperated from Pd(II) by first extracting the latter metal with Br-PBT in chloroform at room temperature and Ir(III) was subsequently determined spectrophotomatrically in the organic phase. The separation of Ir(III) from Pt(IV) and Os(VI) was achieved by preliminary extraction of these intereffering metal ions with Br-PBT in the organic solvent at pH 2.2. The interference of Ru(III) was avoided by its prior reduction to the bivalent state with hydroxylamine hydrochloride.

The commonly associated base metals produced no interference in the extraction of Ru(III), Pd(II) and Ir(III), with Br-PBT in chloroform in the presence of suitable masking agents such as EDTA, tartrate and fluoride ions (Table III).

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SOLVENT EXTRACTION SEPARATION OF SOME TRANSITION METALS IN MALONATE SOLUTIONS WITH SELECTED LIQUID ANION EXCHANGERS.

Madhuri A. Sawant and S.M. Khopkar

Department of Chemistry
Indian Institute of Technology

Bombay-400 076, India.

Abstract

The solvent extraction separation of uranium(VI), scandium(III), zirconium(IV) and thorium(IV) was carried out with 1.0×10^{-2} M of Amberlite LA-1 in xylene from $1.0\text{-}7.0 \times 10^{-4}$ M malonic acid between pH range of 2.5-5.5. The stripping was carried out with 0.5-2 M hydrochloric acid and they were determined spectrophotometrically. These elements were separated from alkali and alkaline earths, thallium(I), iron(II), silver, arsenic(III), tin(IV) by selective extraction. Metals like zinc, cadmium, nickel, copper, cobalt, chromium, aluminium and lead were separated by selective stripping. Other elements were separated in chloride, sulphate and nitrate media.

The solvent extraction studies of transition metals like uranium(VI), scandium(III), zirconium(IV) and thorium(IV) have sulphate, nitrate or chloride and with few exceptions, it has not been studied extensively in the organic acid media, e.g. uranium was extracted from oxalate and acetate media (1-3) ; scandium was generally studied in sulphate media (4-6) ; zirconium(IV) was mainly studied in oxalate solutions (7,8) and thorium(IV) was largely studied with Amberlite LA-1,2 in nitrate media (9,10). This paper presents systematic studied in malonic acid media with Amberlite LA-1 as an extractant.

Experimental.

Apparatus and Reagents : Spektromom-204 spectrophotometer with 10 mm quartz cells ; Wrist action flask shaker ; Digital pH meter (ECIL, India, Model pH 822) ; Sicospec Model 100 colorimeter. The stock solutions of uranium, scandium, zirconium and thorium were prepared by dissolving respectively 5.70 g of uranyl nitrate, 0.73 g of scandium oxide in 40 ml nitric acid, 2.0 g of zirconium nitrate and 1.312 g of thorium nitrate in 500 ml of distilled water. The solutions were standardised complexometrically. The dilluted solutions containing 51.8 µg/ml uranium, 45 µg/ml of scandium, 25 µg/ml zirconium and 51 µg/ml of thorium were prepared by appropriate dilutions. The colorimetric reagents such as 4-(2-pyridylazo) resorcinol, Alizarin Red S, Arsenazo III and Thoron were prepared as usual.

General Procedure.

An aliquot of solution containing either uranium, scandium, zirconium or thorium was taken. Then an appropriate amount of malonic acid was added to it. The pH of the solutions was adjusted to a known value. The total volume was made to 25 ml in a separatory funnel and then 10 ml of a 4 % Amberlite LA-1 in xyle was added to it. The solution was shaken on the Wrist flask shaker for about 5 minutes. The solution was allowed to settle and separate. The aqueous phase was discarded and the metal from the organic phase was stripped back with a suitable stripping agent, its pH was adjusted and the metal concentration in the aqueous phase was determined colorimetrically with PAR for uranium at 530 nm, Alizarin Red S for scandium at 525 nm, Arsenazo III for thorium at 665 nm and thoron for thorium at 545 nm.

Results and Discussion.

Effect of pH : - The studied relealed that uranium can be quantitatively extracted at pH 2.5-4.0, scandium at pH 2.5-5.5, zirconium at pH 2.25-5.5 and thorium at pH 3.0-4.5 with 4 % Amberlite LA-1 in xylene in the presence of 5.10^{-4}-10.10^{-4} M malonic acid (Table 1).

Effect of Stripping Agent : - The systematic studies with various stripping agents showed that uranium can be stripped with 0.01 M sodium hydroxyde, scandium with 0.5 M hydrochloric acid, zirconium with 2 M hydrochloric acid and thorium with 1 M hydrochloric acid. Nitric and sulphuric acid can also be used for the purpose of stripping.

Effect of Malonic Acid Concentrations : - The variation in the concentration of malonic acid during extraction for complex formation in the range (Table 1) from 5.10^{-4} to 1.10^{-2} M showed that the optimum concentration of malonic acid as indicated in table, was adequate for complexation of metals.

Effect of Diluents : - The study of various diluents for liquid anion exchangers (Table 2) showed that xylene was the best diluent while benzene and toluene produced slight turbidity and chloroform and carbontetrachloride gave emulsions. Kerosene, hexane and cyclohexane were poor diluents.

Effect of Various Liquid Exchangers : - The study with different liquid anion exchangers (Table 3) showed that Amberlite LA-1, LA-2 ; Aliquot 336 S generally are good extractants. Alamine 336 S and triisooctylamine were poor extractants. Primene JMT was good but it produced emulsions.

Effect of Variation of Exchanger Concentration : - The variation in the concentration of the echanger from 4 - 10 % in xylene i.e. (0.1 - 10) 10.10^{-2} M.(Table 4) showed that 4 % or 1.10^{-2} was adequate for the quantitative extraction of the metals.

Period of Equilibration : - The shaking period was varied from 2-20 minutes on Wrist action flask shaker. It was seen that a 5 minutes period of equilibration was sufficient for the quantitative extraction of these elements.

Nature of Species Extracted : - The studies of log(extractant) versus log D for various metals at fixed pH indicated that the species formed are ... $(R_2NH_2)_6$ $[Sc(malonate)_3]_2$ or $(R_2NH_2)_2$ $ZrO(malonate)_2$ and $(R_2NH_2)_2$ $Th(malonate)_3$.

Effect of Diverse Ions : - Various elements like alkali and alkaline earths thallium(I), iron(II), silver, arsenic(III), tin(IV), yttrium(III) which could not form malonate complexes were not extracted along with metal in question and were thus separated (Table 5).

Metals like zinc, cadmium, nickel, copper, cobalt, chromium, aluminium and lead formed relatively weak complexes which after extraction were stripped with water leaving behind any of the elements under study in the organic phase thus facilitating their separation (Table 6).

The behaviour of certain metals to for anionic complexes with mineral acids at a specific molarity of acid was exploited for certain separations. As such complexes were reextracted with a liquid anion echanger and are not forming anionic complex was released in solution (Table 6). Thus elements were separated in chloride, sulphate and nitrate media. The methods were extended to analysis of the elements in minerals.

The methods are rapid, simple, selective and reproducible. The standard deviation is ± 1.5 %.

Table 1

Effect of Malonic Acid Concentration

Malonic acid conc. 1×10^{-4}	% Extraction U(VI)	Sc(III)	Zr(IV)	Th(IV)
0.3	-	-	-	50.0
0.5	-	0	-	67.0
0.6	-	-	-	79.4
0.7	-	-	-	86.1
0.8	-	-	-	94.0
0.9	-	-	-	97.4
1.0	64.0	22.0	60.0	99.8
1.2	-	-	-	99.8
1.5	-	-	-	-
2.0	88.0	58.0	87.9	-
2.5	-	-	-	-
3.0	96.0	78.0	95.0	-
4.0	97.5	91.5	97.5	-
5.0	98.5	95.0	98.6	-
6.0	99.1	97.8	99.0	-
7.0	99.1	100.0	99.6	-
8.0	-	100.0	99.6	-

Table 2

Effect of Diluents 4% Amberlite LA-1

Diluent	Dielectric(ε) constant	% Extraction U(VI)	Sc(III)	Zr(IV)	Th(IV)
Benzene	2.28	98.5	99.0	99.5	99.8
Toluene	2.38	97.0	98.8	99.0	96.0
Xylene	2.38	99.1	100.0	99.6	99.8
Chloroform	4.80	81.5	99.5	92.0	99.7
Carbontrachloride	2.24	98.5	95.1	75.0	88.5
Hexane	1.89	-	66.0	66.0	87.0
Cyclohexane	2.05	-	44.5	60.0	85.2
Kerosene	(2)	-	66.0	77.4	92.0
Nitrobenzene	-	-	-	-	91.2

Table 3

Effect of Different Types of Liquid Anion Exchangers

Liquid anion exchanger	Diluent	% Extraction			
		U(VI)	Sc(III)	Zr(IV)	Th(IV)
Amberlite LA-1	Benzene	98.5	99.0	99.5	99.8
	Xylene	99.1	100.0	99.6	99.8
	Chloroform	81.5	99.5	92.0	87.0
Amberlite LA-2	Benzene	98.5	-	99.2	99.5
	Xylene	99.0	99.5	99.6	99.8
	Chloroform	80.0	-	90.0	85.2
Primene JMT	Benzene	54.0	-	99.1	99.8
	Xylene	-	99.7	99.7	99.8
	Chloroform	89.0	-	86.2	84.0
Aliquat 336	Benzene	-	-	99.6	98.2
	Xylene	-	-	99.6	98.8
	Chloroform	-	-	94.2	92.0
Alamine 336.5	Benzene	-	-	84.2	93.5
	Xylene	-	-	94.0	95.0
	Chloroform	-	-	63.0	71.0
TIOA	Benzene	-	-	30.0	40.0
	Xylene	-	16.0	32.0	40.0
	Chloroform	-	-	18.0	25.5

Table 4

Effect of Amberlite LA-1 Concentration

Amberlite Conc. 1×10^{-2} M	U(VI)	Sc(III)	Zr(IV)	Th(IV)
0.10	70.0	10.0	-	--
0.25	89.0	54.5	-	-
0.50	96.0	90.3	29.0	14.0
0.75	98.5	7	-	33.1
1.0	99.1	100.0	60.0	75.0
1.5	-	100.0	78.0	-
2.0	99.1	100.0	87.0	-
3.0	-	100.0	93.4	-
4.0	99.1	100.0	97.6	-
6.0	-	100.0	99.6	90.0
8.0	99.1	100.0	99.6	99.8
10.0	-	100.0	99.6	99.8

Table 5

Effect of Non-transition Elements on Extraction

Foreign ion	Tolerance limit mg			
	U(VI)	Sc(III)	Zr(IV)	Th(IV)
Tl^{+}	0.26	0.51	0.5	1.5
Tl^{3+}	-	0.22	0.5	1.0
In^{3+}	-	0.13	0.26	0.5
Ga^{3+}	-	0.11	0.25	1.0
As^{3+}	0.27	0.28	0.50	1.2
Sb^{3+}	0.13	0.19	0.40	1.0
Bi^{3+}	0.51	0.25	0.25	1.0
Al^{3+}	0.52	0.50	0.60	2.5
Sn^{2+}	0.50	0.45	0.40	1.0
Be^{2+}	0.53	0.51	1.0	2.5
Mg^{2+}	-	1.0	1.5	3.0
Ca^{2+}	1.20	1.0	1.5	3.0
Sr^{2+}	1.20	1.0	1.5	2.5
Ba^{2+}	0.51	0.41	0.55	2.0
Li^{+}	5.2	4.5	5.0	6.0
Na^{+}	5.2	5.0	5.0	6.0
K^{+}	5.18	5.0	5.0	5.0
Rb^{+}	1.04	1.0	2.0	4.5
Cs^{+}	1.00	1.0	2.1	2.5
Pb^{2+}	0.25	-	-	-

Table 6

Effect of Transition Metals on Extraction

Foreign ion	Tolerance limit mg			
	U(VI)	Sc(III)	Zr(IV)	Th(IV)
Ag^+	0.5	0.5	1.0	0.4
Cu^{2+}	0.25	0.99	0.95	2.2
Cd^{2+}	0.50	0.51	0.52	2.5
Hg^{2+}	-	-	0.20	0.5
Pt^{4+}	0.26	0.28	0.25	1.5
Fe^{2+}	0.53	0.48	0.48	2.5
Fe^{3+}	0.13	0.20	0.28	1.0
Cr^{3+}	0.53	0.22	0.25	0.9
Ti^{4+}	-	0.05	0.12	0.6
Th^{4+}	0.06	0.05	0.13	-
U^{+6}	-	0.11	0.25	0.5
Y^{3+}	0.11	0.50	0.50	1.2
La^{3+}	-	0.23	0.20	1.0
Ce^{4+}	-	0.13	0.20	0.5
Mn^{2+}	0.26	0.25	0.25	2.0
Co^{2+}	0.52	0.50	0.63	2.5
Ni^{2+}	0.55	0.52	0.48	2.5
Au^{3+}	0.25	-	-	-
Sc^{3+}	0.11	-	-	-
Zr^{4+}	0.11	0.10	-	0.8
V^{4+}	0.11	-	-	-
Zn^{2+}	0.53	-	-	-

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SEPARATION OF Pr AND Nd IN HIGH PURITY (99.9%) BY COUNTER CURRENT EXCHANGE EXTRACTION AND ITS MECHANISM.

Hsu Kwang-Hsien, Huang Ch'un-Hui,
King Tien-Chu and Li Piao-Kuo
Department of Chemistry,
Peking University
Peking, The People's Republic of
China.

ABSTRACT : As far as the authors are aware, the separation of Pr and Nd in high purity by extraction has not been reported in the literature. D.J. Bauer used a counter-current extraction system of 20 stages to separate a mixture of Pr and Nd with a pull-push system, but the purity of Nd obtained was only 92%. In the present investigation, we have succeeded to separate a mixture of 75% $Nd(NO_3)_3$ and 25% $Pr(NO_3)_3$ to obtain 99.9% $Nd(NO_3)_3$ and 99.9% $Pr(NO_3)_3$ in a continuous counter-current extraction system of 20 stages with recirculations at both extraction and stripping sections. The yield of both metals was greater than 99%. The extractant used was a quarternary alkylammonium nitrate $R_3CH_3N^+NO_3^-$ (0.65M) in xylene as diluent. The mechanism of the extraction process was also investigated.

EXPERIMENTAL

1. Reagents : The extractant used is trialkyl-methyl-ammonium nitrate, $R_3CH_3N^+NO_3^-$, where R is an alkyl group containing 8 to 10 C atoms. The commercial reagent contains more than 95% quarternary ammonium salt, less than 5% tertiary amine R_3N, and has an average molecular weight of 450, and a specific gravity d = 0.89. It was preequilibrated with an aqueous solution of proper pH and containing an approximate amount of salting out agent before use. Diethylenetriamino-pentaacetic acid (DTPA) is an analytical reagent of Peking Chemical Works. The purity of Nd_2O_3 and Pr_6O_{11} used is 99%. The diluent xylene is of C.P. Grade.

2. Analyses : Total concentration of rare earths was determined by EDTA titration. The concentrations of Pr and Nd in rare earth mixtures were determined by a spectrophotometric method, while trace amounts of Pr in Nd or Nd in Pr were determined by emission spectroscopy.

RESULTS AND DISCUSSIONS

I. Mechanism of Extraction of Nd by trialkyl-methyl-ammonium nitrate.

Since the quarternary ammonium salt usually exists in polymerized form (3) and since the distribution ratio D_c is independent of pH within the pH range 2.5-5.5, we assume the extraction reaction to be :

$$M^{3+} + 3L^{-} + x(R_4N^{+}L)_n = ML_3.xnR_4N^{+}L^{-} \qquad (1)$$

where M^{3+} represents the rare earth ion, L^{-}, the nitrate ion, $(R_4N^{+}L^{-})_n$, the quarternary ammonium nitrate. The stoichiometry of the extracted species was determined by the saturation method as shown in Table 1, where Cs is the formal concentration of the extractant $R_4N^{+}L^{-}$, $(M)_{org}$ is the molar concentration of the rare earth ion in the saturated organic phase. The result is xn = 3.

Table 1. Determination of xn

Cs	$(M)_{org}$	$xn = Cs/(M)_{org}$
0.050 F	0.0171 M	2.94
0.100 F	0.0333 M	3.01
0.200 F	0.0663 M	3.02

In a medium of constant ionic strenght of $LiNO_3$ 3M, the concentration equilibrium constant of reaction (1) may be assumed constant, i.e.,

$$K_{ex} = \frac{(ML_3.xnR_4N^{+}L^{-})_{org}}{(M^{3+})(L^{-})^3((R_4N^{+}L^{-})_n)^x_{org}} = \frac{D_c}{(L^{-})^3((R_4N^{+}L^{-})_n)^x_{org}} \qquad (2)$$

$$\begin{aligned}\log D_c &= \log 27\ K_{ex} + x \log ((R_4N^{+}L^{-})_n)_{org} \\ &= \log 27\ K_{ex} + x \log \frac{Cs - 3(M)_{org}}{n} \\ &= \log 27\ K_{ex} - x \log n + x \log(Cs - 3(M)_{org}) \\ &= K' + x \log (Cs - 3(M)_{org})\end{aligned}$$

We varied Cs, measured the concentration of the rare earth in the organic phase $(M)_{org}$ and the distribution ratio D_c ; the experimental results are summarized in Table 2 and plotted in Fig. 1, where we find that the slope is x = 1.52 or 3/2. Hence n = 3/1.5 = 2, and the extraction reaction may be expressed by :

$$M^{3+} + 3L^{-} + 3/2(R_4N^{+}L^{-})_{2\ org} = ML_3.3R_4N^{+}L^{-}_{org} \qquad (3)$$

Next we investigated the effect of concentration of $LiNO_3$, (C_{LiNO_3}), on D_c and found the following empirical equation :

$$D_c = 0.292(Cs - 3(M)^{3/2}_{org}(C_{LiNO_3})\ 4.26 \qquad (4)$$

Since the nitrate ion takes place in reaction (3) and also acts as a salting-out agent, so the distribution ratio D_c is proportional to the 4.26 power of C_{LiNO_3}.

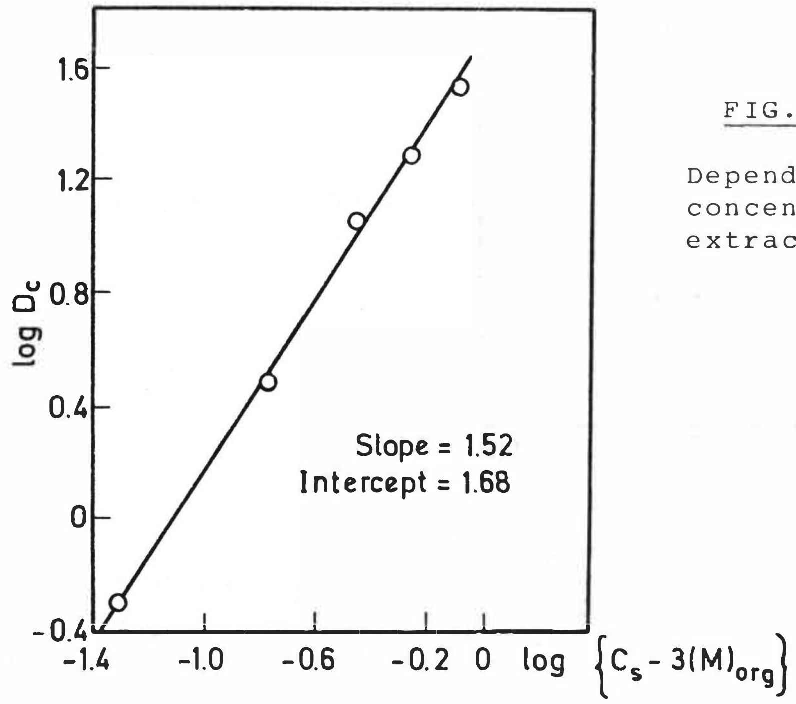


FIG. 1

Dependence of (D_c) on the concentration of free extractant.

Table 2. : Effect of concentration of free extractant on the distribution ratio (C_{LiNO_3} = 3M, pH = 4.3 to 5.3).
C°_M = initial aqueous concentration of $Nd(NO_3)_3$=0.05M
C_M = aqueous concentration of Nd^{3+} after extraction
$(M)_{org}$ = concentration of Nd in the organic phase.

Cs,M	C_M,M	$(M)_{org}$;M	D_c	log D_c	log $(Cs-3(M)_{org})$
0.950	1.47×10^{-3}	4.85×10^{-2}	34.3	1.535	- 0.0947
0.696	2.32×10^{-3}	4.77×10^{-2}	20.1	1.303	- 0.258
0.496	4.12×10^{-3}	4.59×10^{-2}	11.1	1.045	- 0.446
0.299	10.4×10^{-3}	3.96×10^{-2}	3.03	0.481	- 0.745
0.0998	33.3×10^{-3}	1.67×10^{-2}	0.502	-0.299	- 1.303

II. Separation factor $\alpha^{\circ}_{Pr/Nd}$.

The effect of pH on the separation factor $\alpha^{\circ}_{Pr/Nd}$ for the extraction system

$$\begin{array}{l|l|l} Pr(NO_3)_3 \ 0.150M & LiNO_3 \ 3M & R_3CH_3N^+NO_3^- \text{ in xylene} \\ Nd(NO_3)_3 \ 0.150M & pH \text{ varied} & Cs = 0.65M \end{array}$$

was investigated. The result is shown in Fig. 2. It may be seen that $\alpha^{\circ}_{Pr/Nd}$ increases with decreasing pH.

The effect of $LiNO_3$ concentration and initial rare earth concentration on $\alpha^{\circ}_{Pr/Nd}$ are shown in Tables 3 and 4.

In Tables 3 and 4, θ is the degree of saturation of the organic phase, which is defined by the following expression

$$\theta = \frac{(Pr)_{org} + (Nd)_{org}}{Cs/3} \qquad (5)$$

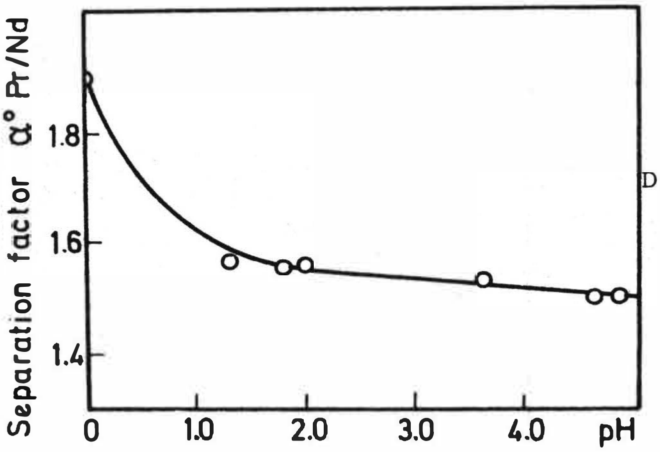


FIG. 2

Dependence of $\alpha^\circ_{Pr/Nd}$ on pH

Table 3. Effect of C_{LiNO_3} on $\alpha^\circ_{Pr/Nd}$
Cs = 0.65M, pH = 4, $C_{Pr} = C_{Nd}$ = 0.150M.

C_{LiNO_3}	$D_c Pr$	$D_c Nd$	$\alpha^\circ_{Pr/Nd}$	θ
2M	1.80	0.633	1.71	0.634
3M	1.60	1.07	1.50	0.790
4M	2.20	1.70	1.30	0.920

Table 4. Effect of initital rare earth concentration
C°_M on $\alpha^\circ_{Pr/Nd}$
$LiNO_3$ 3M, pH = 3, Cs = 0.65M, $C^\circ_{Pr} = C^\circ_{Nd} = 1/2C^\circ_M$

C°_M	$D_c Pr$	$D_c Nd$	$\alpha^\circ_{Pr/Nd}$	θ
0.100 M	15.9	8.19	1.94	0.425
0.200 M	3.24	1.99	1.63	0.660
0.300 M	1.59	1.10	1.45	0.789
0.400 M	1.01	0.690	1.42	0.836
0.500 M	0.725	0.534	1.36	0.886

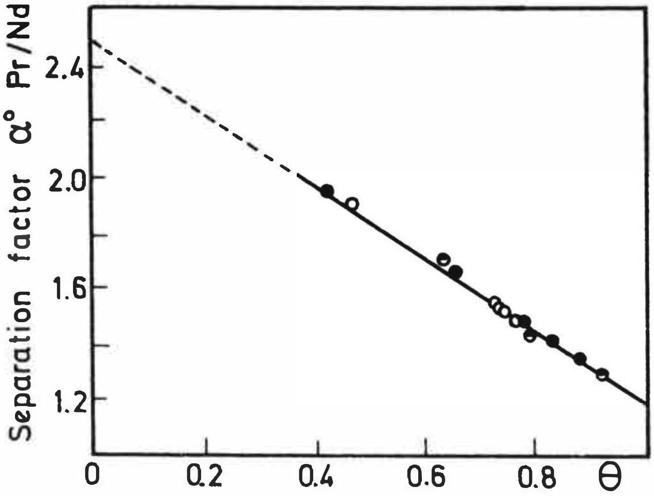


FIG. 3

Dependence of $\alpha^\circ_{Pr/Nd}$ on θ

When $\alpha^{\circ}_{Pr/Nd}$ was plotted against θ(Fig. 3), a straight line was obtained which may be expressed by :

$$\alpha^{\circ}_{Pr/Nd} = 2.51 - 1.30\ \theta \tag{6}$$

so the less saturated the organic phase is, the greater the separation factor will be. But in order to increase the production in an industrial extraction process, we have to increase the loading capacity of the organic phase by taking a value of θ not too small. If we choose $\theta = 0.85$, for example, then $\alpha^{\circ} = 1.40$. This separation factor is too small to separate Pr and Nd effectively, so we use a chelating agent (DTPA) to increase the separation factor.

III. Separation factor $\alpha_{Pr/Nd}$ in presence of DTPA (H_5L).

The chelating agent DTPA anion L^{5-} forms very stable complexes with Pr^{3+} and Nd^{3+} having stability constants equal to

$$\beta_{(Nd)} = \frac{(NdL^{=})}{(Nd^{3+})(L^{5-})} = 3.98 \times 10^{21}$$

$$\beta_{(Pr)} = \frac{(PrL)}{(Pr^{3+})(L^{5-})} = 1.17 \times 10^{21} \tag{7}$$

Since they are non-extractable complexes, the separation factor $\alpha^{\circ}_{Pr/Nd}$ in presence of DTPA will be equal to

$$\alpha_{Pr/Nd} = \frac{\dfrac{(Pr)_{org}}{(Pr^{3+}) + (PrL^{=})}}{\dfrac{(Nd)_{org}}{(Nd^{3+}) + (NdL^{=})}} \tag{8}$$

while in absence of DTPA, the separation factor is

$$\alpha^{\circ}_{Pr/Nd} = \frac{(Pr)_{org}/(Pr^{3+})}{(Nd)_{org}/(Nd^{3+})} \tag{9}$$

Substituting (7) and (9) into (8), we have

$$\alpha_{Pr/Nd} = \alpha^{\circ}_{Pr/Nd}\ \frac{1 + \beta_{(Nd)}(L^{5-})}{1 + \beta_{(Pr)}(L^{5-})} \tag{10}$$

Since DTPA is a penta-basic acid, we have

$$C_L = \sum_{j=0}^{5} (H_jL) = (L^{5-})Y \tag{11}$$

$$Y = C_L/(L^{5-}) = 1 + \sum_{j=i}^{5} Q_j\ (H)^j \tag{12}$$

where

$$Q_j = \frac{(H_jL)}{(L^{5-})(H)^j} \tag{13}$$

The numerical values of Q_j are : $\log Q_1 = 10.58$, $\log Q_2 = 19.18$, $\log Q_3 = 23.51$, $\log Q_4 = 26.06$, $\log Q_5 = 27.86$. We define the apparent stability constant

$$\beta'_M = (ML)/(M)C_L \qquad (14)$$

then

$$\beta'_M = K_M/Y \qquad (15)$$

and

$$\alpha_{Pr/Nd} = \alpha^{\circ}_{Pr/Nd} \cdot \frac{1 + \beta'(Nd)C_L}{1 + \beta'(Pr)C_L} \qquad (16)$$

Table 5 shows the values of β'_M of some of the rare earths at different pH values.

If we take $C_L = 0.1M$, it may be seen from Table 5 that at pH $\geqslant$ 2.8, $\beta'_{Nd}C_L >> 1$, $\beta'_{Pr}C_L >> 1$, so that from equation (16),

$$\alpha_{Pr/Nd} \cong \alpha^{\circ}_{Pr/Nd} \cdot \frac{\beta'_{Nd}}{\beta'_{Pr}} = 3.40\ \alpha^{\circ}_{Pr/Nd} \qquad (17)$$

Table 5. : Apparent stability constants β'_M

M	β_M	β'_M						
		pH=1.0	pH=1.2	pH=1.4	pH=1.6	pH=1.8	pH=2.0	pH=2.8
La	3.02×10^{14}	0.00036	0.0033	0.030	0.25	1.9	14	1.4×10^{4}
Pr	1.17×10^{21}	0.014	0.13	1.2	9.7	72	530	5.3×10^{5}
Nd	3.98×10^{21}	0.048	0.43	4.01	33	250	1700	1.7×10^{6}
Sm	2.18×10^{22}	0.25	2.4	22	180	1400	9800	9.8×10^{6}

thus increasing the separation factor by a factor of 3.4. But at lower pH values, say pH = 1, $\beta'_{Nd}C_L << 1$, $\beta'_{Pr}C_L << 1$, then

$$\beta_{Pr/Nd} \cong \beta^{\circ}_{Pr/Nd} \qquad (18)$$

there is no enhancement of separation factor at all.

The experimentally determined $\alpha_{Pr/Nd}$ at different pH values are shown in Table 6. It has a maximum value of 4.92 at pH 3.3 in agreement with with equation (17). At pH > 5, $\alpha_{Pr/Nd}$ decreases due to the decrease of $\alpha^{\circ}_{Pr/Nd}$.

Table 6. Dependence of $\alpha_{Pr/Nd}$ on pH.
$C^{\circ}_{Pr} = 0.090M$, $C^{\circ}_{Nd} = 0.270M$, $C_L = 0.223M$, $C_{LiNO_3} = 2.0M$, $C_s = 0.65M$.

pH	E_{Pr}	E_{Nd}	$\alpha_{Pr/Nd}$
0.86	2.90	1.48	1.96
1.24	2.60	1.08	2.40
1.39	2.33	0.889	2.61
1.56	1.81	0.525	3.46
1.75	1.50	0.385	3.90
3.31	1.37	0.279	4.92
3.33	1.31	0.273	4.80
5.00	1.00	0.278	3.60
5.30	0.96	2.291	3.04

Table 7 shows the dependence of $\alpha_{Pr/Nd}$ on the DTPA concentration C_L and the extractant concentration Cs.

Table 7. Dependence of $\alpha_{Pr/Nd}$ on C_L and Cs

$C^{\circ}_{Pr} = 0.090M$, $C^{\circ}_{Nd} = 0.270M$, $C_{LiNO_3} = 2.0M$, O:W = 2.1

Cs	C_L	pH	E_{Pr}	E_{Nd}	$\alpha_{Pr/Nd}$
0.702	0.13	2.92	3.63	0.825	4.41
0.702	0.16	2.96	2.73	0.588	3.97
0.702	0.19	2.96	1.78	0.414	4.50
0.702	0.22	2.97	1.47	0.323	4.56
0.702	0.24	2.97	1.31	0.286	4.58
0.702	0.27	2.96	0.95	0.205	4.74
1.067	0.13	2.93	4.81	1.06	4.54
1.067	0.16	2.96	3.86	0.777	4.97
1.067	0.19	2.95	2.78	0.543	5.12
1.067	0.22	2.96	2.17	0.414	5.25
1.067	0.24	2.96	1.68	0.323	5.20
1.067	0.27	2.95	1.12	0.238	4.71

Since the diluent xylene is toxic, we tried to use kerosene as diluent for the tetra-alkyl ammonium nitrate with the addition of TBP (18 %) in order to increase the solubility of the extracted species in kerosene. We also used NH_4NO_3 (4 to 7M) as salting-out agent instead of the more expensive $LiNO_3$. Then we determined the separation factors in this more practical extraction system as follows :

$\alpha_{Pr/Nd} = 3.5$ to 4.5, $\alpha_{La/Pr} = 30$ to 50, $\alpha_{Nd/Sm} = 15$ to 20

so that this extraction system is very effective for separation of light rare earths.

IV. <u>Recovery of pure Nd and DTPA from the raffinate</u>

The raffinate from continuous counter-current extraction of Pr and Nd contains a DTPA complex of pure Nd (> 99.9%) and salting-out agent NH_4NO_3. The raffinate is acidified by adding HNO_3 up to pH = 1, then the apparent stability constant β'_{Nd} will be much less than 1 (see Table 5), and the rare earth metal will mainly exist in the form of Nd^{3+}, which may easily be extracted by the quarternary ammonium salt in presence of the salting-out agent NH_4NO_3. The dependence of the percentage of extraction of La, Pr, Nd, Sm on pH is shown in Fig. 4 and Table 8.

The data in Table 8 may also be calculated from the apparent stability constants β'_M and the distribution ratio of rare earth in quarternary ammonium nitrate-6M NH_4NO_3 in the absence of DTPA. The deviations of the calculated pH from the experimental ones are within 0.3 pH units.

Thus pure $Nd(NO_3)_3$ may be removed from the raffinate by a counter-current extraction with 5 or more stages. The raffinate containing DTPA in the acid form H_5L is neutralized with NH_4OH up to pH = 8-9 and recirculated as stripping solution.

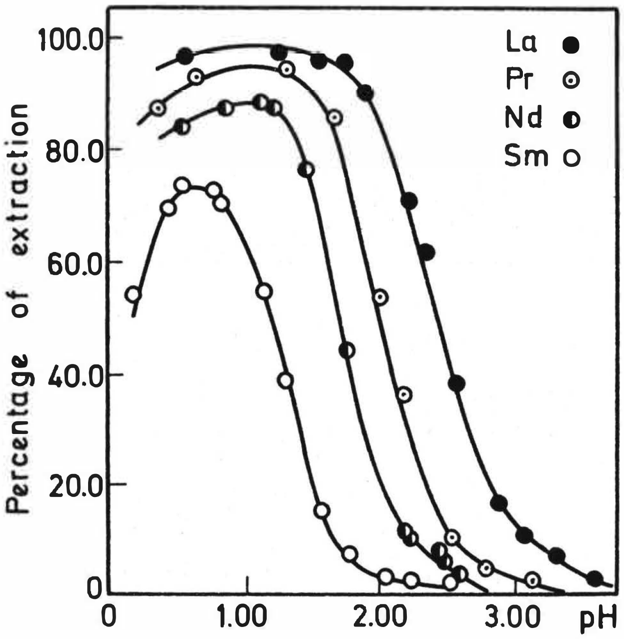


FIG. 4

Dependence of percentage of extraction on pH

Aq. solution : rare earth nitrate 0.18M, DTPA 0.18M, NH_4NO_3 6M

Organic extractant : 0.918M quarternary ammonium nitrate : 1.08M, MIBK and kerosene as diluent

Phase ratio : O:W = 3:1

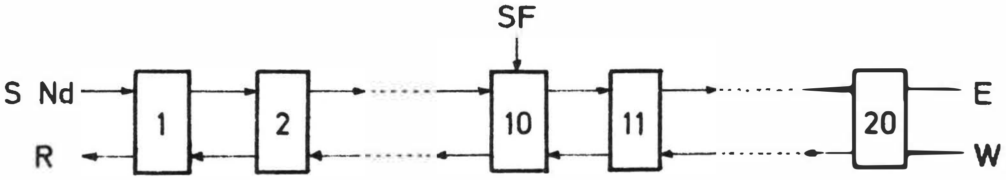
Table 8. Effect of pH on percentage of extraction.

Rare earth nitrate 0.18M NH_4NO_3 6M, DTPA 0.18M O:W=3:1 $R_3CH_3N^+NO_3^-$ 0.916M MIBK 1.08M, kerosene

% Extraction	pH			
	La	Pr	Nd	Sm
90	1.91	1.60	-	-
80	2.10	1.74	1.46	-
70	2.23	1.84	1.56	0.89
60	2.36	1.92	1.64	1.09
50	2.47	2.01	1.73	1.20
40	2.58	2.10	1.82	1.28
30	2.70	2.23	1.94	1.38
20	2.86	2.39	2.10	1.52
10	3.12	2.60	2.29	1.72
5	3.42	2.80	2.50	1.92

V. Separation of Pr and Nd by counter-current extraction.

Separation of Pr and Nd by counter-current extraction was first carried out batch-wise using separating funnels as shown in the following flow diagram :



SF is 100 ml of organic feed solution containing a mixture of 0.075M $Nd(NO_3)_3$ and 0.025M $Pr(NO_3)_3$. W is 75 ml of stripping solution containing 0.2M DTPA, 1M NH_4OH and 6M NH_4NO_3, the pH is in the range 8-9. R is 75 ml of raffinate containing 0.2M $NdL^=$ complex and 6M NH_4NO_3, pH = 3 to 4. S Nd is 75 ml of organic extractant containing 0.1M $Nd(NO_3)_3$, which is obtained from the 50 % recirculation of the extracted raffinate R. E is 175 ml of extract containing 0.0143M pure $Pr(NO_3)_3$.

The purity of both products $Nd(NO_3)_3$ and $Pr(NO_3)_3$ were analyzed by emission spectroscopy to be 99.9 %. Higher purities (say 99.99 %) of products could be obtained by doubling the number of extraction and stripping stages.

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SOLVENT EXTRACTION OF COPPER FROM AQUEOUS THIOCYANATE SOLUTIONS BY 4-(5-NONYL) PYRIDINE AND SUBSEQUENT DETERMINATION IN WATER, SOILS, LUBRICATING OILS AND PLANT MATERIALS BY ATOMIC ABSORPTION SPECTROSCOPY.

MOHAMMAD EJAZ

Applied Science Department,Engineering
College,King Abdulaziz University,
P.O.Box-1540, Jeddah, Saudi Arabia.

We have studied the extraction behaviour of certain high molecular weight pyridine amines (1). Of the compounds investigated, 4-(5-Nonyl) pyridine has been found the most versatile extractant because it extracts through solvation and/or ion-pair formation, depending on experimental conditions. This study is part of a comprehensive programme concerned with the solvent extraction of halides and pseudohalides of bivalent first transition-series metal ions with long chain alkyl pyridine derivaries.

The characteristics of the pyridine, the equipment used for radiochemical assay and atomic absorption measurements, and the procedure for extraction were described previously(2). $HNO_3+H_2O_2$ procedure was used for opening out soil samples, lubricating oils were first charred and then converted into clean solution by 1:1 HNO_3+HClO_4.

Copper (II)($<10^{-6}$M) is not extracted from 0.01 -10M solutions of HCl, HNO_3 or H_2SO_4 by 0.1M NPy in benzene, However, quantitative extraction is obtained from these acids up to 0.1M containing 0.02M KSCN. Extremal partition coefficient are obtained from HCl (0.01M), HNO_3 (0.01-0.25M), and H_2SO_4 (0.01-0.5M) solutions containing 0.05-0.5M KSCN. Quantitative extraction can also be achieved from simple water containing 0.1MKSCN. Slope analyses and loading ratio data for different concentrations of the acids indicate the extraction of $Cu(NPy)_2(SCN)_2$. The addition of neutral chloride, nitrate and sulphate ions added to the corresponding solutions of constant acidity does not affect the extraction. The results show that the pyridine is an excellent reagent for the extraction of toxic metals as a group from most of the associated base metals. 1:100 organic: aqueous ratios do not have significant effect on the extraction efficiency.

For atomic absorption measurements copper was extracted into the 0.1M NPy/benzene phase from aqueous solutions. 20µl sample size was selected for injection into the graphite tube. All determinationswere made with background compensation in use. Copper was measured with good accuracy down to p.p.b. levels in the above mentioned matrices.

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EXTRACTION OF COBALT-4-(2-THIAZOLYLAZO)RESORCINOL COMPLEXES

M. Široki, Lj. Marić and M.J. Herak

Laboratory of Analytical Chemistry
Faculty of Science, University of
Zagreb

Strossmayerov trg 14, 41000 Zagreb,
Yugoslavia

4-(2-Thiazolylazo)resorcinol (TAR) is known as a sensitive but a rather non-selective reagent which, like 4-(2-pyridylazo) resorcinol (PAR), gives intensively coloured chelates with many metal ions. Some metal chelates of PAR and TAR can be directly extracted into appropriate polar solvents. Extraction efficiency is sometimes much improved if the extraction is carried out in the presence of an organic base or an organophilic quaternary salt.

In this work, the extraction of the cobalt-TAR complexes with tetraphenylphosphonium, tetraphenylarsonium and triphenylmethylarsonium salts has been studied and compared with the extraction behaviour of cobalt-PAR complexes. By means of these extractants, the cobalt-TAR complexes can be efficiently extracted into chloroform, dichloromethane and dichloroethane over a wide pH range, from a slightly acidic, to a slightly basic aqueous solution. Maximum and constant extraction was achieved in the pH region between 5 - 10. The best reproducibility was obtained at pH 6-8, with the buffered media. The extraction in chloroform is practically complete with all the three extractants. With tetraphenylphosphonium and arsonium chloride more than 99%, and with triphenylmethylarsonium iodide about 98% of cobalt is transferred into the organic phase by a single extraction with a phase volume ratio 1:1.

The composition of the extracted complexes has been determined spectrophotometrically in solution and by characterization of isolated compounds. The molar ratio of the extractant to cobalt to TAR in the organic phase is 1:1:2 for all extraction systems studied. Since the complex formation and extraction is carried out in the pH region in which the p-hydroxyl group of TAR is ionized $[Co(II)(TAR)_2]^{2-}$ and $[Co(III)(TAR)_2]^{-}$ species (TAR refers to deprotonated ligand) are to be expected in the aqueous solution in agreement with the previous investigations. The molar ratio value shows that the anionic cobalt(III)-TAR complex bearing one negative charge is predominantly extracted, forming associated ion-pairs with the cation of the extractants.

The solid compounds isolated from the chloroform extract correspond to this composition. They were found to be diamagnetic, confirming the Co(III) oxidation state.

SOLVENT EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF MERCURY (II) AT MICROGRAMME LEVEL

Anil K. De and Bata K. Pal

Visva-Bharati

Santiniketan, W.Bengal, India

Mercury is a well-known source of water pollution in some industrial belts. Hence its detection and determination at ppm level is of considerable significance in water pollution control programmes. This paper describes two solvent extraction methods for Hg(II) followed by spectrophotometric determination in the organic phase. The methods are based on the extraction of coloured ternary complexes of mercury (II) iodide with cationic dyes, viz. Malachite Green (MG^+) and Methyl Violet (MV^+) at pH 4.5 - 7.5 into benzene and toluene, respectively. These complexes have absorption peaks at 630 nm and 600 nm respectively. The Hg-I-MG system obeys Beer's law up to 50 μg of Hg in a total organic phase of 25 ml while Hg-I-MV system, up to 60 μg of Hg in 25 ml toluene. The Sandell sensitivity values are 0.002 μg Hg cm^{-2} (MG system) and 0.003 μg Hg cm^{-2} (MV system) respectively and the corresponding molar absorptivities are 8.7×10^4 and 7.1×10^4 mol^{-1} cm^{-1}. The sensitivity is comparable with that for dithizone system. Mercury (II) can be conveniently estimated in presence of commonly associated water pollutants e.g. Cu(II), Cd(II), Pb(II), Zn(II) etc.

The proposed methods are relatively fast requiring single extraction only and relatively free from interferences compared to the previous methods reported in the literature.

Membrane Extraction

Session 12

Co-chairmen : M. Hafez (Imperial Oil Ltd., Sarnia, Canada)
S. Wajc (University of Brussels, Beglium)

80-90	Coupled transport membranes for uranium recovery. W.C. Babcock, R.W. Baker, D.J. Kelly and E.D. LaChapelle, Bend Research, Inc., Bend, Oregon, U.S.A.
80-230	Extraction of copper from aqueous solutions using a liquid membrane process : a model to simulate the process. T.P. Martin and G.A. Davies, University of Manchester, Manchester, U.K.
80-144	A new concept for mass transfer in liquid surfactant membranes. A. Kopp, R. Maar and J. Wilhelmer, Technische Universität Graz, Graz, Austria.
80-88	Removal of toxines from plasma and blood with liquid surfactant membranes. W. Halwachs, W. Völkel and K. Schügerl, University of Hannover, Hannover, Germany.
80-89	Membranes in extraction, a state of the art review. M.M. Hafez, Imperial Oil Limited, Sarnia, Ontario, Canada.

COUPLED TRANSPORT MEMBRANES FOR URANIUM RECOVERY

W.C. Babcock, R.W. Baker, D.J. Kelly, and
E.D. LaChapelle
Bend Research, Inc.
64550 Research Road
Bend, Oregon 97701
USA

ABSTRACT

A new membrane separation process called "coupled transport" is described. The process was developed for use in the recovery of metals from hydrometallurgical leach solutions. Results of laboratory studies with synthetic uranium leach solutions are presented that demonstrate clean separation of uranium from common impurity metals. Based on these results, an economic analysis is presented that demonstrates that coupled transport would be competitive with other recovery processes, such as solvent extraction or ion exchange.

I. INTRODUCTION

In recent years, hydrometallurgical processing of ores has become increasingly important, replacing the more polluting and energy-intensive pyrometallurgical techniques. Hydrometallurgical leach solutions contain low concentrations of the desired metal ion as well as impurity metal ions. Present methods for product recovery from these solutions include solvent extraction, ion exchange, and precipitation.

Since 1975, Bend Research has been developing an alternative recovery process that utilizes coupled transport membranes. These are liquid membranes consisting of a water-immiscible, liquid complexing agent, held by capillary forces within the pores of a thin microporous polymeric support. When the membranes are placed between a hydrometallurgical leach solution and another aqueous solution, metal ions from the leach solution are extracted into the membrane and diffuse across it as a neutral organic complex. Under suitable conditions, diffusion can occur "uphill", i.e., against the metal ion concentration gradient of the aqueous solutions. The energy for concentrating metal ions is provided by the coupled diffusion of a second ionic species. By using conventional solvent extraction agents in the membranes, it is possible to combine the high selectivity and ability to concentrate ions of solvent extraction with large throughputs and continuous processing capability of modern membrane technology. A major advantage of the process over solvent extraction is that problems associated with phase separation and solvent entrainment are eliminated.

The process is illustrated in Figure 1 for the coupled transport of uranyl sulfate anions by a tertiary amine. Here, "feed solution" refers to the leach solution and "product solution" is the concentrate from which yellow cake would be precipitated. On the feed side of the membrane, the uranyl sulfate anion plus two hydrogen ions are extracted into the membrane via the reaction

$$2H^{+}_{(aq)} + UO_2(SO_4)_{2(aq)}^{--} + 2R_3N_{(org)} \rightleftharpoons (R_3NH)_2UO_2(SO_4)_{2(org)}, \quad (1)$$

where (org) and (aq) refer to species soluble only in the organic membrane phase or aqueous phase, respectively. The uranium-amine complex diffuses across the membrane to the product side where the reverse reaction in Equation (1) occurs (due to the low H^+ concentration on the product side), releasing the uranyl sulfate anion and two hydrogen ions to the aqueous phase. The free amine then diffuses back across the membrane and the process is repeated. Thus, uranyl sulfate anions are transported from left to right (in Figure 1), and electrical neutrality is maintained by the coupled transport of hydrogen ions in the same direction. In this way, uranyl sulfate anion can be chemically pumped up its concentration gradient as hydrogen ion diffuses down its concentration gradient in the same direction.

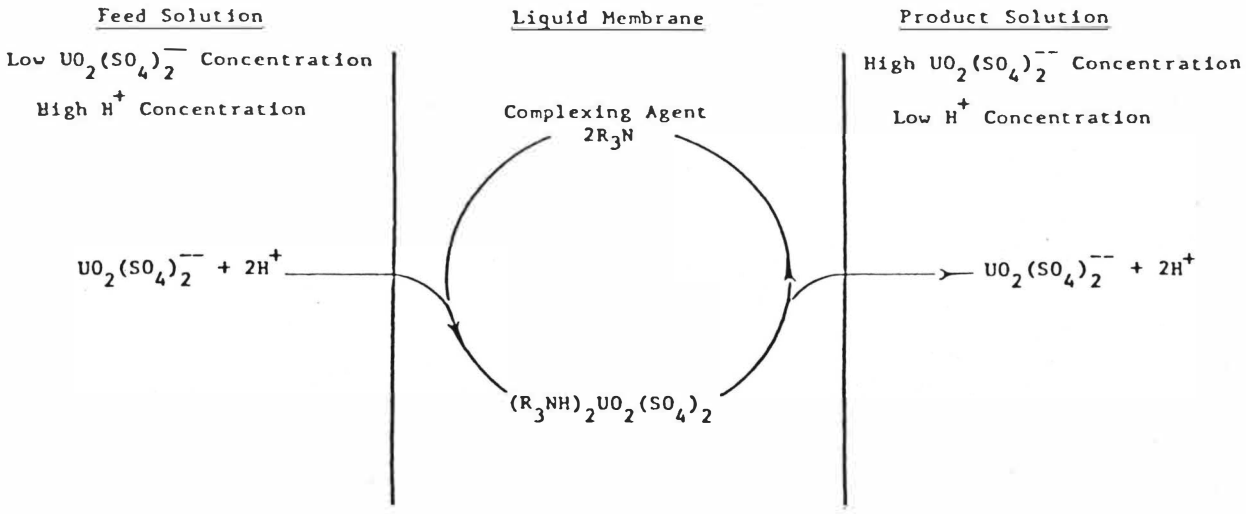

FIG. 1

Coupled transport of uranium across a liquid membrane.

II. DEMONSTRATION OF THE PROCESS

The process described in Figure 1 was demonstrated in the laboratory with a simple two-compartment permeation cell.(1) The cell consisted of a feed solution chamber (100 ml) separated from a product solution chamber (100 ml) by a liquid membrane having an area of 20 cm^2. The feed and product solutions were well stirred, and the temperature was maintained at 30°C.

The organic phase of the liquid membrane consisted of a tertiary amine, Alamine 336 (Henkel Corp., Minneapolis, MN), diluted to 30 vol% with a hydrocarbon diluent, Aromatic 150 (Exxon Corp., Houston, TX). This organic phase was incorporated into Celgard 2400 microporous polypropylene, a product of Celanese Plastics, Inc., Philadelphia, PA. Celgard is approximately

25 µm thick and has a porosity of approximately 38%. Liquid membranes were prepared by submerging the microporous sheet in the organic solution for several minutes, leading to quantitative filling of the pores by capillary action.

To demonstrate uphill diffusion, an experiment was performed in which the feed and product solutions initially contained equal uranium concentrations. The pH of the feed solution was 1.0, representative of the pH of hydrometallurgical leach solutions, while the pH of the product solution was maintained at a high value with 200 g/l Na_2CO_3. The results are presented in Figure 2, which shows the concentration of uranium in the feed and product solutions with time. The concentration of uranium in the feed solution decreased and the concentration of uranium in the product solution increased. After about 500 minutes, the uranium concentration of the feed solution was

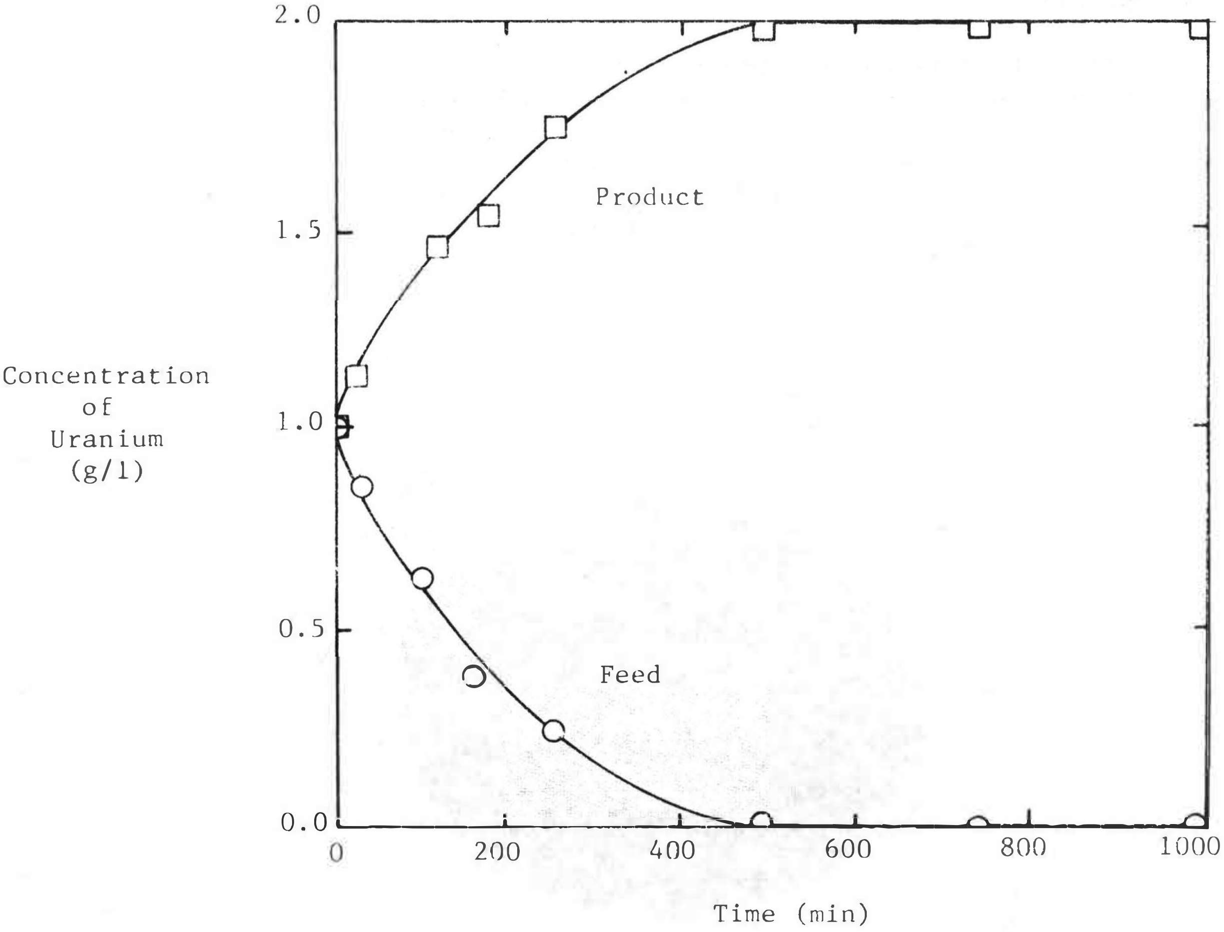

FIG. 2

Uranium concentration in the feed and product solutions vs. time.

Membrane: 30 vol% Alamine 336 in Aromatic 150 held in Celgard 2400.

Initial Feed Solution: 1.0 g/l uranium, pH 1.0 with H_2SO_4.

Initial Product Solution: 1.0 g/l uranium, 200 g/l $NaCO_3$.

below detectable limits, i.e., less than about 1 ppm. The final concentration factor, defined as the ratio of the product to the feed concentration, was greater than 2000.

III. PROCESS SCALE-UP WITH HOLLOW FIBER MEMBRANES

The way in which membranes are modularized bears strongly on both the operation and the economics of the process. One possible design would be a simple plate-and-frame module using the microporous polypropylene membranes used in our laboratory test cells. However, plate-and-frame units are unlikely to be the optimum membrane configuration for large-scale plants because of their relatively high cost per unit area. A potentially more economical configuration uses hollow fiber membranes in a tube-and-shell configuration.

For coupled transport applications, we have made hollow fibers from polysulfone because of its excellent chemical resistance to acids, bases, and a wide variety of organic compounds. A scanning electron micrograph of a cross section of a representative fiber is shown in Figure 3. Permeation occurs not only through the fingerlike voids visible in the scanning electron micrograph, but also through much smaller pores, which are not visible at this magnification. Fibers such as these are incorporated into modules of the type illustrated in Figure 4. In operation, the organic complexing agent is incorporated into the walls of the fiber, the product solution flows on the outside of the fiber, and the feed solution flows down the fiber lumen.

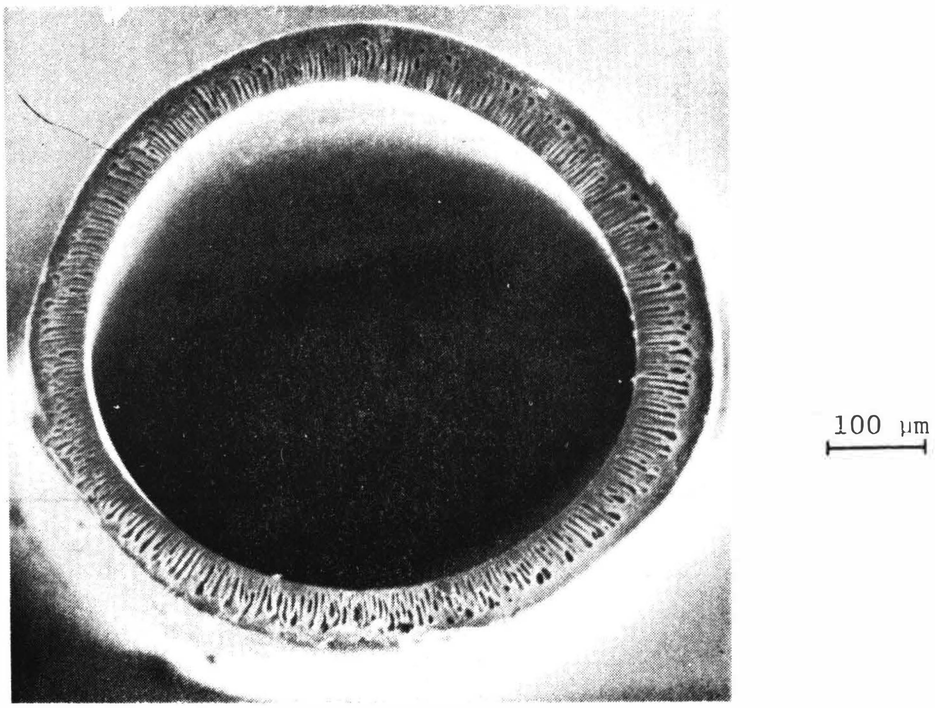

FIG. 3

A scanning electron micrograph of a polysulfone hollow fiber.

For large-scale processing, a number of modules must be arranged to permit the removal of most of the uranium from a continuous feed stream. Design studies, performed elsewhere, (2) have shown that a three stage "feed-and-bleed" configuration offers substantial advantages over other possible configurations. A schematic representation of this configuration is presented in Figure 5. A fixed feed volume is recirculated through each module, as indicated by the bold lines in the figure. Feed solution is continuously introduced into the recirculating volume of the first module and is bled off at the same rate. This "bleed" from the first module constitutes the feed for the second. The bleed from the second module constitutes the feed for the third. In operation, the concentration of uranium in the feed solution decreases as it flows from Module 1 to Module 3, with the final raffinate concentration depending on the feed-and-bleed flow rate. The product solution flows in series through the modules.

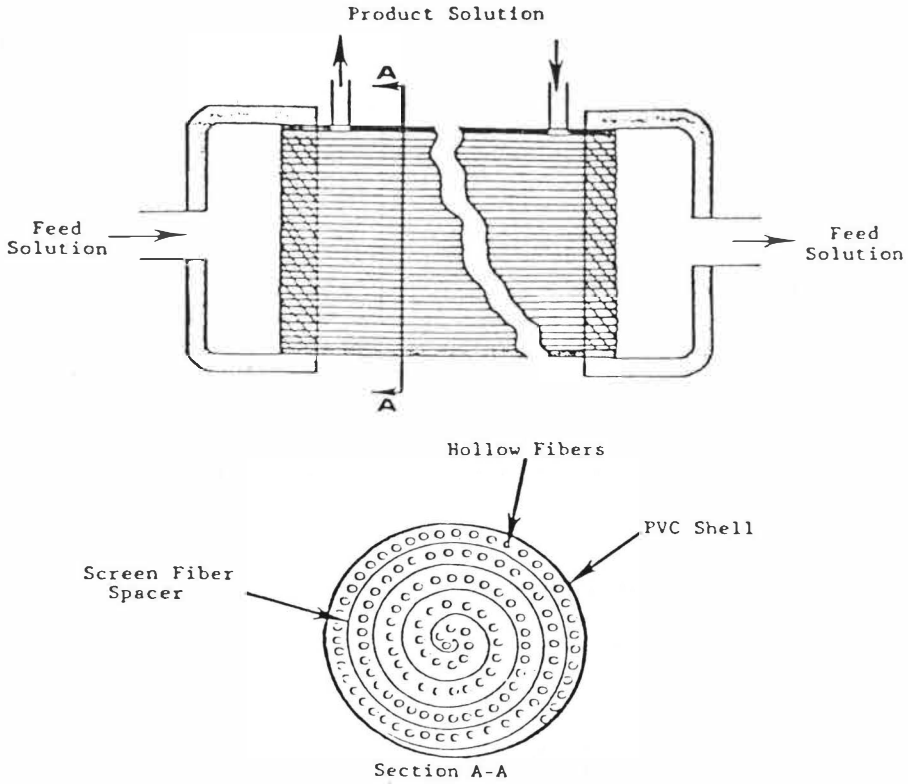

FIG. 4

Schematic representation of a hollow fiber module.

IV. SEPARATION OF URANIUM FROM A SYNTHETIC LEACH SOLUTION

The process scheme used to effect separation of uranium from vanadium, molybdenum, and iron (the major metal impurities present in acidic uranium leach solutions(3)), is shown in Figure 6. Vanadium and iron are rejected by the coupled transport membrane because they are present as cations and are not extracted by the amine carrier. Molybdenum, present as molybdate anion, is concentrated in the product solution along with uranium. Separation of uranium from molybdenum is achieved by selectively precipitating

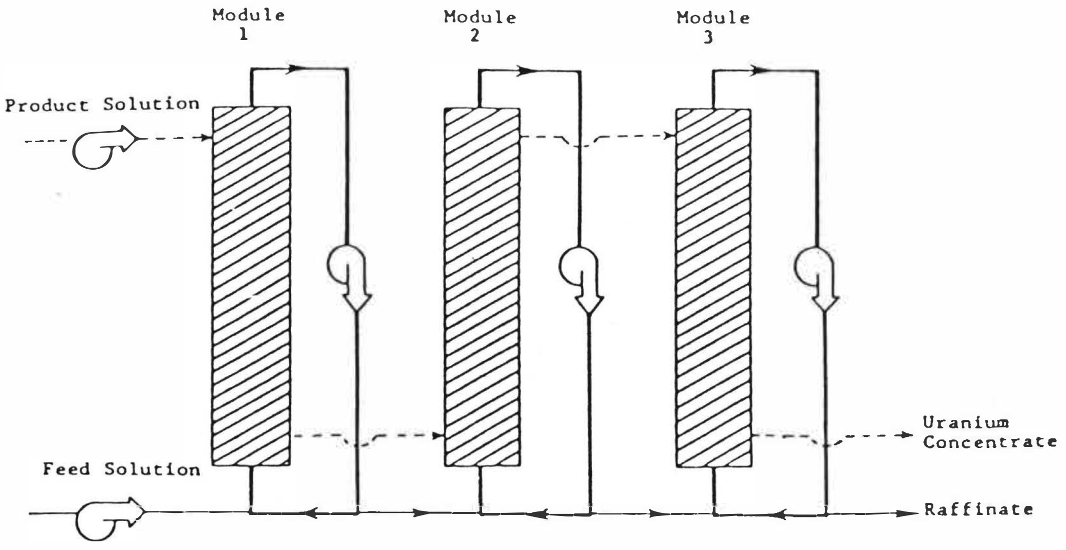

FIG. 5

Schematic representation of a coupled transport concentrator.

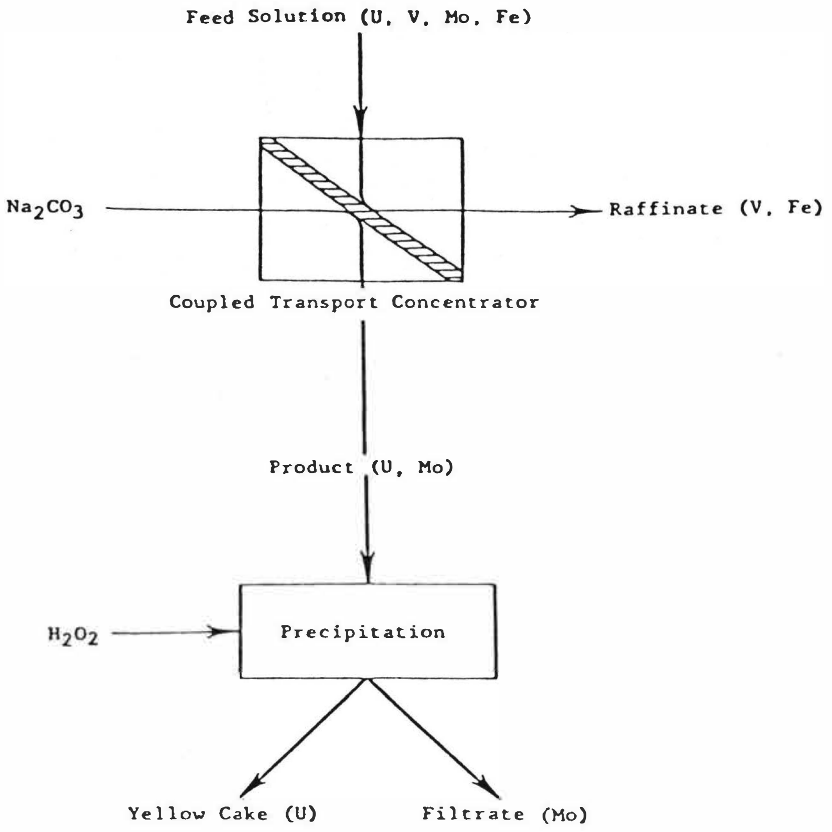

FIG. 6

Scheme for obtaining pure uranium yellow cake from an acidic leach solution.

the uranium with hydrogen peroxide. A separation of uranium from a synthetic leach solution was performed using this scheme with a bench-scale concentrator of the design shown in Figure 5. The results are described below.

A synthetic leach solution having the metal concentrations shown in the first row of Table I was used. The pH of the solution was 1.0, adjusted with sulfuric acid. The oxidation-reduction potential was lowered to 300 mV relative to the saturated calomel electrode. This was accomplished by adding 500 ppm ferric ion and 500 ppm ferrous ion to the solution and then dissolving iron filings until the desired oxidation-reduction potential was reached. At an oxidation-reduction potential of 300 mV, vanadium, initially present as VO_3^-, is reduced to V^{4+}.

The coupled transport concentrator contained three 0.25 ft^2 modules with a combined capacity for treating about two gallons of leach solution per day. The ratio of feed volume throughput to product volume throughput was fifteen to one. The compositions of the resultant raffinate and product are shown in Table I. Uranium recovery from the feed solution was greater than 99%, and uranium was concentrated by a factor of 2300 over the raffinate concentration. Most of the molybdenum was also recovered from the feed solution, while vanadium and iron were rejected to the raffinate.

	Concentration (ppm)			
	U	V	Mo	Fe
Feed Solution	2000	100	100	1140
Raffinate	13	100	3	1140
Product	30,000	<0.1	1500	<0.1

Table I.

Results of a coupled transport separation. Metals were added to the feed solution as UO_2SO_4, $NaVO_3$, Na_2MoO_4, $FeSO_4$, and $Fe_2(SO_4)_3$.

Selective precipitation of uranium yellow cake was accomplished by using hydrogen peroxide to oxidize uranium to insoluble UO_4 following established procedures.(4) The composition of the resultant yellow cake is shown in Table II. Also shown is the acceptable composition as specified by major purchasers of yellow cake for UF_6 production.(5) The yellow cake product in this experiment was well within the acceptable limits.

V. PROCESS ECONOMICS

Based on the above laboratory evaluation of coupled transport, we can compare the economics of coupled transport with the economics of solvent extraction and ion exchange. The key elements in this analysis are the transmembrane uranium flux and the capital and operating costs per square foot of membrane. The uranium flux, defined as the mass of uranium that crosses a unit area of membrane per unit time, is about 12 lb/ft^2-year under the experimental conditions described above.

For the cost of the membrane separator, we use the well established

	Composition (wt%)			
	U	V	Mo	Fe
Yellow Cake	78	0.00	0.04	0.00
Acceptable Composition	>60	<0.08	<0.12	Not Specified

Table II.

Results of precipitation of UO_4 from the product.

costs of reverse osmosis (RO) processing. Those membrane separators operate in a mode somewhat similar to ours, and as a first approximation, we feel that it is reasonable to assume that a coupled transport membrane processor would have a similar capital cost when expressed as cost per unit surface area of membrane. For hollow fiber RO units, this cost is currently well under $\$1/ft^2$ of membrane.(6) If we use $\$1/ft^2$ as a conservative figure, the capital cost of the membrane unit would be about 8¢/lb of uranium produced per year. This can be compared with the capital costs of solvent extraction and ion exchange units, which are reported to be about 20¢/lb of uranium produced per year.(3,7)

Because virtually no energy is consumed in the process, operating costs are due principally to membrane replacement, amortization, labor, and reagents. In reverse osmosis, membrane lifetimes of five years are obtained under favorable conditions. If equal performance is obtained in coupled transport, membrane replacement would cost only about 20¢/ft^2-year. The labor cost is difficult to define at this time. It will depend on the frequency at which it is necessary to replace the complexing agent in the membrane and on many other presently undefined factors. We could assume, again following the pattern established in reverse osmosis, that operating labor costs are comparable to membrane replacement costs. We would thus add 20¢/ft^2-year to the operating costs. The major reagent cost in the process is due to sodium carbonate consumption. For each pound of uranium produced, stoichiometry requires that about two pounds of sodium carbonate be consumed.(3) The current cost of bulk sodium carbonate is about 5¢/lb. With a flux of 12 lb/ft^2-year, this corresponds to an annual cost per square foot of membrane of $1.20.

Thus, the costs of a hollow fiber coupled transport membrane processor recovering 99% of the uranium from a 2 g/l feed stream can be summarized as follows:

	Annual Costs/Ft^2 of Membrane
Capital costs at $\$1/ft^2$, 25% interest and depreciation	$ 0.25
Membrane replacement, 5 year lifetime	0.20
Labor and maintenance	0.20
Reagent costs	1.20
Total Costs	$ 1.85

Using a uranium flux of 12 lb/ft^2-year, we obtain a cost of about 15¢/lb of uranium recovered. Recently reported costs of ion exchange and solvent extraction range from 20 to 40¢/lb.(7) Thus, the economics of coupled transport processing look favorable, based on a laboratory evaluation of the process.

VI. ACKNOWLEDGEMENTS

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EXTRACTION OF COPPER FROM AQUEOUS SOLUTIONS USING A LIQUID MEMBRANE PROCESS: A MODEL TO SIMULATE THE PROCESS

T.P. Martin and G.A. Davies

Department of Chemical Engineering
U.M.I.S.T.
University of Manchester
Manchester 1

ABSTRACT

A model is proposed to describe the transfer of copper from a dilute aqueous solution through an organic liquid membrane into sulphuric acid solution. The membrane contains a copper chelating agent; in this work Shell SME 529 was largely used. Therefore, this represents a case of facilitated transport through the membrane. The important parameters controlling the degree of extraction and rate of extraction of copper are shown to be rate of extraction and stripping reactions which are considered to take place at each interface between the aqueous, the concentration of reagent in the membrane, the initial copper concentration in the external aqueous phase and the hydrogen ion concentrations in the aqueous phase. The response of the model to these variables is considered and compared with experimental results. The limitations of the model are evident particularly in the sparcity of kinetic data which is available for the reactions involved. That the process is operated in an intermediate regime where both the rate of chemical reaction and diffusion across the membrane is important is shown by experiments in which a kinetic accelerator is added to the membrane. This is shown to improve the extraction performance.

An unexpected result is the sensitivity of the process to low levels of iron III in the external aqueous phase. With SME 529 the extraction rate of copper from the aqueous solution is reduced even at levels of iron III of only 10 ppm. At first sight this may appear to be a serious limitation of the process. However, the results using the kinetic accelerator perhaps indicate the future development work required since these results show not only an improvement on extraction performance but also a reduced sensitivity to iron III.

INTRODUCTION

In an earlier paper (1) the feasibility of applying a liquid membrane (L.M.) process to the extraction of copper ions from dilute aqueous solutions was demonstrated. The technique is based on selective transfer of a solute (copper) across a liquid membrane which separates the feed solution from an aqueous receptor phase, equivalent to a stripping solution in solvent extraction. The membrane is stabilised by a surface active agent and in the previous work contained a metal chelating agent, Shell SME 529, in a diluent of Napolean 470*.

In order to a) achieve the required membrane stability and b) a high interfacial area for mass transfer an emulsion technique, originally proposed by Li (2) and Hochhauser (3), was needed. In this the receptor phase is emulsified in the membrane phase to form, in this case an acid in oil emulsion. This emulsion was then contacted with the feed solution, to form globules of emulsion dispersed in the feed. In this way copper was transferred from the aqueous feed phase into the acid receptor phase in the emulsion. Full details are given in reference (1). Using this technique copper can be extracted from solutions containing less than 100 ppm Cu^{2+} to produce a concentrated electrolyte which can be processed by electro-winning to obtain metallic copper.

In the initial paper some of the important system and process variables were determined and the response characteristics considered. It was found, for example, that the extraction of copper ions from the feed solution obeys initially a first order rate process. The rate coefficient was shown to depend on such factors as the concentration of reagent (RH) in the membrane, the pH of the feed solution, the method of producing the emulsion and the contacting of the emulsion with the feed. Deviations from a first order process were evident when significant emulsion breakdown took place.

To examine the process further it was decided to study the emulsion properties in more detail and to develop a mathematical model for ion transfer in the system. The latter step may help in isolating and evaluating important system variables. In the first part of this paper a model to represent the process will be described.

MATHEMATICAL MODEL FOR FACILITATED TRANSPORT OF COPPER ACROSS A LIQUID MEMBRANE

Mass transfer of copper from a dilute copper sulphate solution through a liquid membrane into an acid receptor phase involves a chemical reaction between copper ions and an organic chelating reagent (alkyl aryl oxime) which takes place at both aqueous organic interfaces and diffusion of the organic metal chelate across the membrane. Simultaneously there takes place, as a result of the reaction, counter-current diffusion of the reagent across the membrane. This effectively transports countercurrently (to copper) hydrogen ions. It is the proton gradient across the membrane which represents the true driving force for the process. Therefore, for example, it is possible to transfer copper from solutions containing less than 50 ppm Cu^{2+} into electrolytes containing 3×10^4 ppm Cu^{2+}.

The basic reaction represented by the equation:

$$Cu^{2+} + 2RH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CuR_2 + 2H^+ \qquad (1)$$

is assumed in this model to take place at the surface or interface between the membrane and the aqueous solutions.

The next most important feature to consider is the geometry of the membrane. The acid or receptor phase droplets in the emulsion are between 1 and 3 μm diameter. The organic films forming the membranes are of the order of 0.7 μm. This is important to stress since one would not be justified in ignoring the size of the droplets and considering the dispersed phase for

*Trade mark of Kerr McGee.

example as made up of a distribution of infinitely small droplets (4). Therefore one cannot reduce the problem to effectively diffusion in a 'quasi-homogeneous' media.

The emulsion is more like the structure of a foam in which the membranes are interconnected through plateau borders (5). This structure may form the basis of a realistic representation (6).

The limiting cases are either to consider the emulsion made up of a very large number of infinitely small droplets dispersed in the continuous phase or to consider a planar membrane. The former has been criticised with respect to the relative dimensions of the membrane thickness and equivalent drop diameter. This becomes more serious when one considers the actual volume ratios used in the emulsions; for any effective separation to be obtained the capacity of the receptor phase for the solvent must be high and hence one cannot work at very low A/O phase ratios in the emulsion. The latter case can be criticised since it can only approximate the conditions at the outer surface of the emulsion globules and does not account for the basic interconnecting membrane structure. Nevertheless a planar membrane will be considered in this first approach to the problem. As we shall see, since some basic physical data is not available for the system this assumption is perhaps acceptable.

A diagram of the system and transfer processes involved is shown in Fig. 1. The membrane is assumed to have a mean thickness of δ separating the inner and outer phases (stripping and feed solutions), 1 and 3 respectively. The volumes of these phases are assumed to be constant and not vary with time. This will be discussed later. The concentration profiles in the membrane will be considered linear and it is assumed that there is no significant breakdown of the membrane or entrainment of phase 3 into the emulsion. Finally, it is assumed that the reactions take place at the interfaces between the phases.

Then under these conditions a mass balance with respect to copper in the system at steady state gives

$$\frac{D_c a_o}{\delta}(C_{C2e} - C_{C2i}) = -v_3 \frac{dC_{A3}}{dt} = n_A \qquad (2)$$

To distinguish between copper in the ionic form in aqueous solution, phases 1 and 3, from that in the chelate form in the membrane, phase 2, a subscript A and C is used respectively. The second subscript refers to the phase. In the membrane a third subscript is required to distinguish between the outer interface where extraction reaction is predominant, e, from the inner interface where stripping takes place, i. Equation (1) may be made dimensionless by introducing the initial concentration of copper in the feed solution, $C_{A3}|_{t=o}$. Thus:-

$$(X_{C2e} - X_{C2i}) = \frac{dX_{A3}}{dt} = N_A \qquad (3)$$

where X_{ij}, dimensionless concentration, $= \dfrac{C_{ij}}{C_{A3(o)}}$

T, dimensionless time $= \dfrac{t.D_c a_o}{\delta\, v_3}$

and N_A, dimensionless copper mole flux $= \dfrac{n_a . \delta}{C_{A3(o)} . D_c}$

The transfer flux of copper can also be expressed in terms of the differences in forward and reverse reaction rates at each interface, e and i. Thus:-

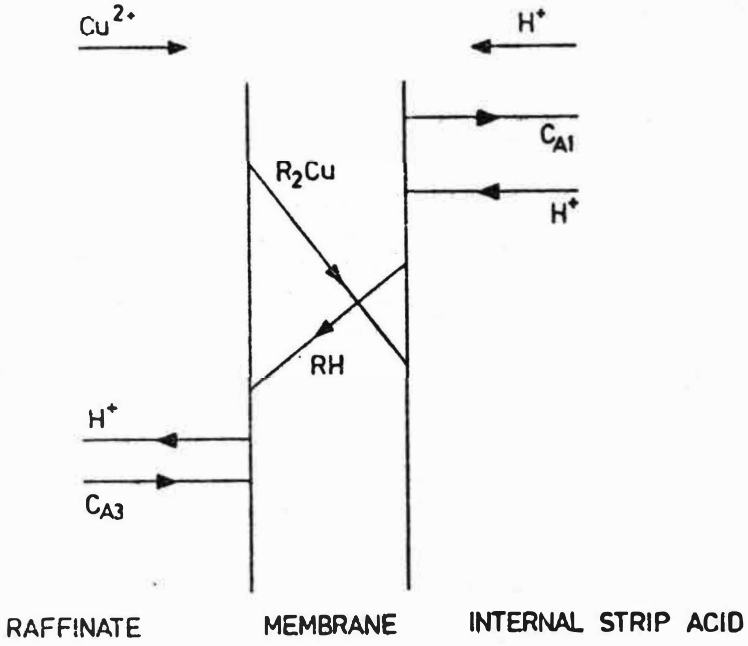


Figure 1.

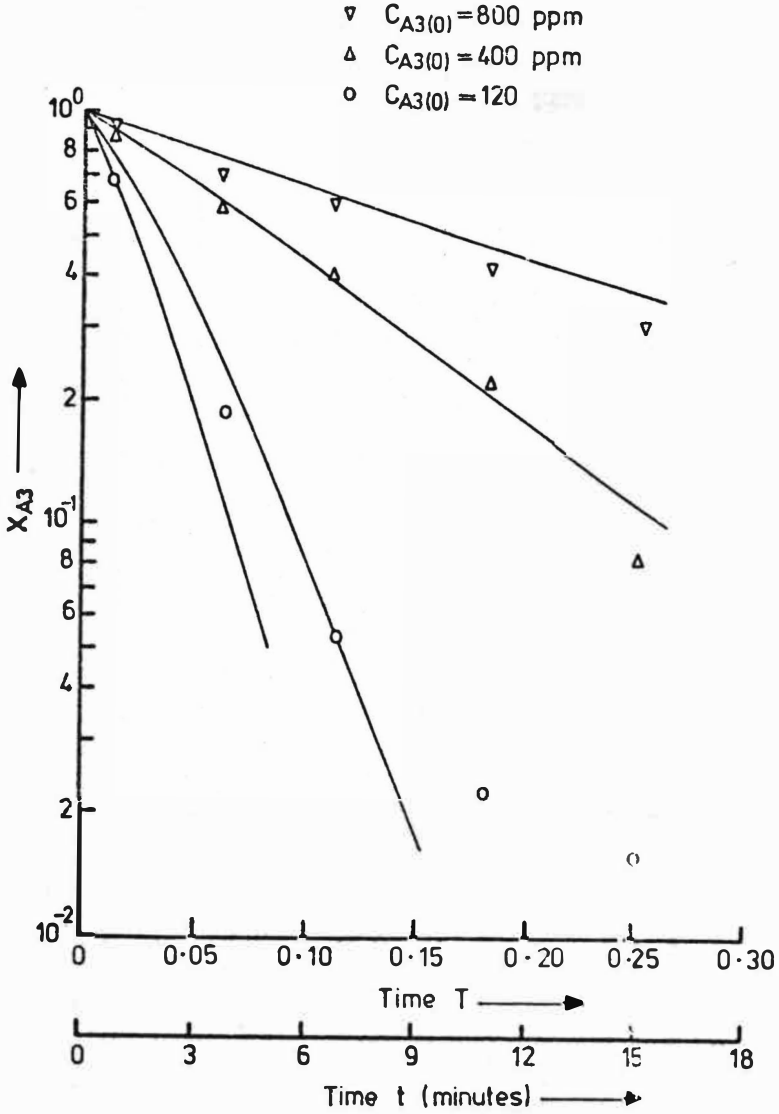


Figure 2

$$k_1\left[C_{A3}\right]\left[\frac{C_{E2c}}{2}\right] - k_2\left[C_{C2e}\right] \cdot \left[C_{D3}\right]^2 = n_A \tag{4}$$

Subscript E refers to the 'carrier' material, the chelate reagent, subscript D refers to the 'driver' material, hydrogen ions.

Also at the inner interface i

$$k_2\left[C_{C2i}\right] \cdot \left[C_{D1}\right]^2 - k_1\left[C_{A1}\right] \cdot \left[\frac{C_{E2i}}{2}\right] = n_A \tag{5}$$

The reaction is assumed to be first order with respect to the half molar concentration of the extractment (i.e. the dimer concentration).

In dimensionless form equations (4) and (5) become:-

$$K_1\left[X_{A3}\right] \cdot \left[X_{E2e}\right] - K_2\left[X_{C2e}\right] \cdot \left[X_{D3}\right]^2 = N_A \tag{6}$$

$$K_2\left[X_{C2i}\right] \cdot \left[X_{D1}\right]^2 - K_1\left[X_{A1}\right] \cdot \left[X_{E2i}\right] = N_A \tag{7}$$

where K_1 and K_2, dimensionless reaction rate coefficients, are

$$K_1 = \frac{k_1 . \bar{\delta}}{D_c} \cdot C_{A3(o)}$$

and $$K_2 = \frac{k_2 . \bar{\delta}}{D} \cdot C^2_{A3(o)}$$

They may be recognised as Damköhler groups of the second kind.

Mass balances based on the ion exchanges yield:-

$$X_{A1} = R_{31}(1 - X_{A3}) \tag{8}$$

$$X_{D1} = X_{D1(o)} - 2.R_{31}.(1 - X_{A3}) \tag{9}$$

$$X_{D3} = X_{D3(o)} + 2\ (1 - X_{A3}) \tag{10}$$

R_{31} is the volume ratio of the phase 3, 1, v_3/w_1. If there is no loss of reagent from the emulsion, then

$$X_{C2} + X_{E2} = \text{constant} \tag{11}$$

and $$X_{Ee} = X_{E(o)} - X_{Ce} \tag{12}$$

$$X_{Ei} = X_{E(o)} - X_{Ci} \tag{13}$$

The redundant subscript (2) is dropped from the equations involving only the membrane phase.

For convenience the degree of extraction, Y, can be introduced such that

$$Y = 1 - X_{A3} \tag{14}$$

The set of equations (3), (6) and (7) is of the form

$$X_{Ce} - X_{Ci} = N_A \tag{15i}$$

$$aX_{Ce} + b = N_A \qquad (15ii)$$

$$fX_{Ci} + d = N_A \qquad (15iii)$$

where a, b, etc., are appropriate combinations of other factors. This system has the general solution

$$N_A = \frac{a.d - b.f}{a.f - f + a} \qquad (16)$$

where $a = - K_1(1 - Y) - K_2(X_{D3(o)} + 2Y)^2$

$$b = K_1(1 - Y).X_{E2(o)}$$

$$d = K_1.Y.R_{31}.X_{E2(o)}$$

$$f = K_2(X_{D1(o)} - 2R_{31}Y)^2 + K_1.Y.R_{31}$$

The dimensionless flux is thus expressed as a ratio of two polynomials in Y with the system parameters K_1, K_2 etc., forming the coefficients.

Using equations (3) and (14)

$$- \frac{dY}{dT} = \frac{F_1(Y)}{F_2(Y)} \qquad (17)$$

where $F_1(Y) = a.d - b.f$

and $F_2(Y) = a.f - f + a$

The boundary condition is Y = 0, T = 0. Equation (17) could be integrated either analytically by first dividing one polynomial into the other and integrating term by term or numerically. Because of the complexity of various coefficients the latter was preferred. A computer programme was written to carry out the calculations. The inputs to the programme are: $X_{D1(o)}$, $X_{E2(o)}$, K_1, K_2, R_{31}, $X_{D3}(o)$. The outputs can either be values of X_{A3} v.s. T or coefficients of the analytical solution. The integrated expression is of the general form:-

$$T = g_o + g_1 Y + g_2 Y^2 + g_3 \ln (Y - \alpha) + g_4 \ln (Y^2 + \beta^2) + g_5 \tan (Y/\beta) \qquad (18)$$

The terms α and β come from the roots of the cubic equation $F_1(Y)$. This equation, for practical values of the inputs, always has one real and two imaginary roots. The real root (α) representes the equilibrium value of Y, i.e. the maximum degree of extraction possible. T tends to infinity as this root is approached.

Before examining the numerical solutions for X_{A3} v.s. T it is perhaps instructive to inspect two limiting cases. If the internal resistance is ignored, i.e. X_{D1} is large, Y is small and $X_{D3(o)}$ is zero, then equation (16) reduces to:-

$$N_A = \frac{K_1 X_{E2(o)} (1 - Y)}{K_1(1 - Y) + 1} \qquad (19)$$

Two limiting cases then arise from this:

a) Reaction rate much higher than the diffusion rate $K_1 >> 1$. Then

$$N_A \simeq X_{E2(o)} \quad (1 - Y) \qquad (20)$$

$$\simeq X_{E2(o)} \quad X_{A3} \qquad (21)$$

This is a pseudo first order rate process, diffusion controlled. It is interesting to note that under these conditions, the rate of extraction is proportional to the initial reagent concentration in the membrane.

b) $K_1 << 1$

Equation (19) becomes

$$N_A = K_1 X_{E2(o)} X_{A3} \qquad (22)$$

The extraction is now controlled by the chelating reaction step and again is a first order rate process with respect to copper ion concentration. Substituting for N_A and integrating equation (22) gives

$$\ln(X_{A3}) = -K_1 . X_{E2(o)} . T \qquad (23)$$

Putting this back into dimensional terms

$$\ln(\frac{C_{A3}}{C_{A3(o)}}) = -k_1 C_{E2(o)} . \frac{a_o}{v_3} . t \qquad (24)$$

shows that the extraction rate under these conditions is independent of membrane thickness, diffusion coefficient and even inlet copper concentration (except in as much as it is included in the limits of integration).

In both cases a) and b) if ln X_{A3} is plotted against T a straight line would result, in case a) the slope would be - $X_{E2(o)}$ and in case b) - $K_1XE2(o)$.

The important parameters from equations (16,17) are the dimensionless rate coefficients K_1 and K_2 and the following operating variables:-

i) initial solute concentration in the external phase, $C_{A3(o)}$,
ii) initial pH of the external phase,
iii) reagent concentration in the membrane, C_{E2},
iv) initial acid concentration in the internal phase, C_{D1},
v) properties of the emulsion - mean membrane thickness $\bar{\delta}$ and the interfacial area per unit volume between the emulsion and the external phase.

These parameters can now be investigated and the predictions of the model compared with the experiment.

RESULTS

The experimental procedures adopted for this work have been described in a previous paper(1). The additional information required from the experiments is values for the mean film thickness, $\bar{\delta}$, and the interfacial area a_o. The emulsion was produced under standard conditions using an Ultra Turrax homogeniser. This procedure was used throughout all of the experiments. To determine $\bar{\delta}$ photomicrographs of samples of the emulsion were taken and analysed to a Zeiss Endtler particle size analyser. From this the drop size distribution of the dispersed internal phase in the emulsion was measured, the reproducibility of the emulsions assessed and the mean film thickness of the membrane phase determined. The mean drop size varied between 1.5 - 1.8 micrometers, the standard deviation σ from 0.51 - 0.73 and the mean film thickness $\bar{\delta}$ = 0.7 micrometers.

a_o was determined by taking photographs of the emulsion mixture during mass transfer. A similar technique was used analysing the photographs with a Zeiss Endtler particle size analyser. Under the standard mixing conditions used a_o was determined from drop size measurements to be 29.8 ± 3.576 cm^2/cm^3.

1) Rate constants k_1, k_2. These are primary variables in the model and in order to achieve a complete quantitative comparison between theory and experiment accurate data on these for each reagent tested is necessary. Unfortunately, no such data exists in the literature. That which does exist has been measured in an Akuve contactor where it is impossible to assign an interfacial area to the operating conditions and hence impossible to disassociate $K_i a$. A more useful series of measurements from which k_1 and k_2 could be obtained would be possible from experiments using a Lewis cell. This work is now underway. Notwithstanding these comments some preliminary data is available from which estimates of k_1 can be made(7), this was used. Then, using the measured data on $\bar{\delta}$ and the Wilke-Chiang correlation to obtain estimates for the diffusivity D of the complex in the membrane(8) values for K_1 between 2 and 10 were obtained. The response of the model to values of K_1 covering this range can also be obtained for this case when computed for experimental conditions in which the metal copper concentration $C_{A3(o)}$ is 120 ppm in a solution at a pH of 2.5, using a membrane containing 5% wt/wt Shell SME 529 in Napoleum 470, emulsifier 1% Span 20 and phase ratio $R_{31} = 8.333$. The data is arbitrarily scaled in dimensionless time T so that the curve for $R_1 = 1.7$ passes through the point $X_{A3} = 0.05$, $T = 1$. The effect of increasing the dimensionless rate coefficient can be seen. The extraction rate is sensitive to K_1 up to about 20 above this value the curves converge to the limiting case, $K_1 \to \infty$. This represents the position of diffusion controlled mass transfer and corresponds to the region predicted in equation(21).

The opposite extreme, a kinetic controlled region anticipated in equation (23), can also be illustrated. In this case, when $K_1 < 0.1$ the extraction curves converge. The limiting curve is almost a straight line, and, after correction for the scaling factor, the slope is within 5% of the predicted value (-E).

At this stage no definitive value can be ascribed to the rate coefficients. The best estimate from inspection of the data using SME 529 reagent is that $K_1 \simeq 2$. Thus in the remainder of the work using the model a value of 2 was used. It is sufficient to observe at this time that the practical response is in a sensitive region. The experimental conditions do not correspond to either of the limiting cases.

2) Initial copper concentration, $C_{A3(o)}$. The variation in extraction rate with the initial copper concentration is illustrated in figure 2. As can be seen the theoretical model predicts a progressive increase in the negative slope of this graph as the initial concentration $C_{A3(o)}$ decreases. This is in line with the experimental results(1). The model is seen to fit fairly well at the higher concentrations $C_{A3(o)}$ 400 ppm but predicts a higher extraction rate and therefore greater overall extraction, Y, as the copper concentration decreases. Measurements have been made on the extent of emulsion breakdown. This was shown to increase with extraction time(1,9); the result is to reduce the degree of extraction measured and causes the measured extraction rate to decrease. Emulsion breakdown also has bigger observable effects in dilute solutions. Evidence for such breakdown can be seen in the experimental results for $C_{A3(o)} = 120$ ppm. The model does not allow for this. The quantitative fit for dilute solutions is poor.

3) The effect of the concentration of the reagent, SME 529, in the membrane phase is shown in figure 3. The model predicts a successive increase in the extraction rate as the reagent concentration increases, the curves are shown for concentrations varying from 1% w/v SME 529 up to 20% w/v SME 529. The

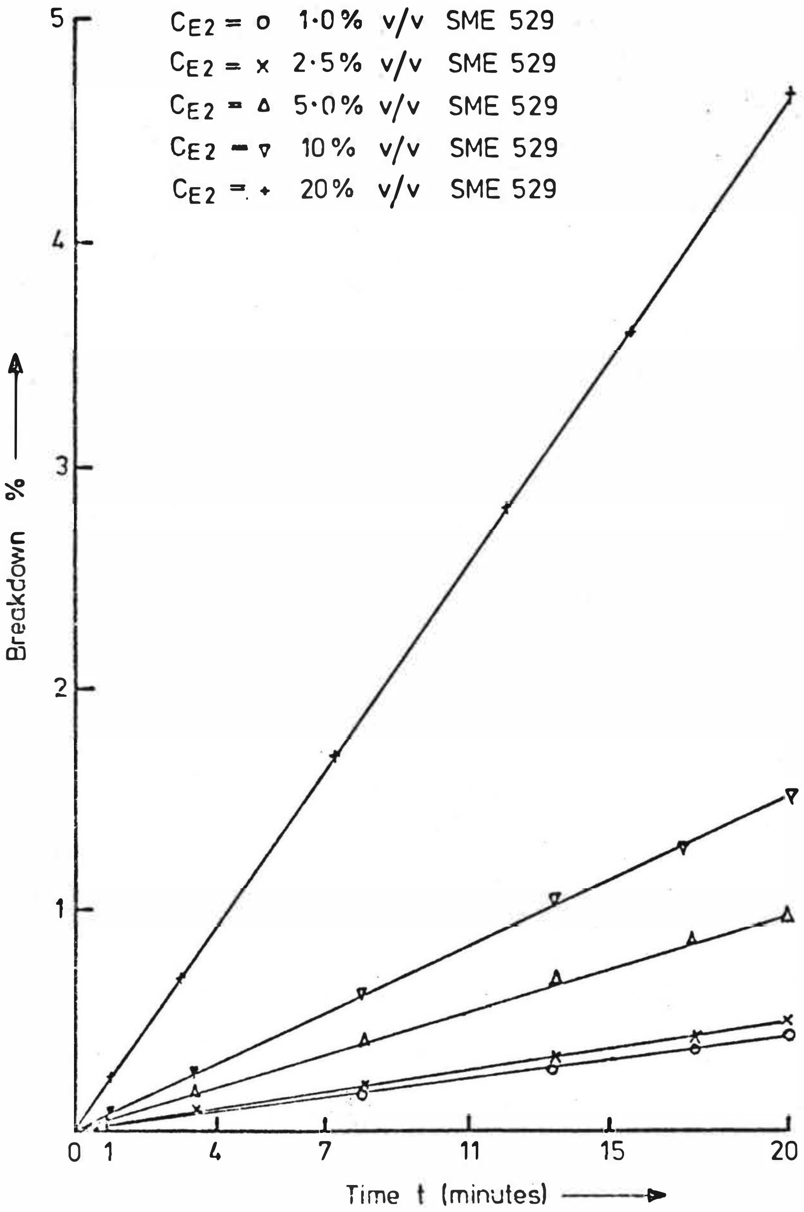


Figure 4.

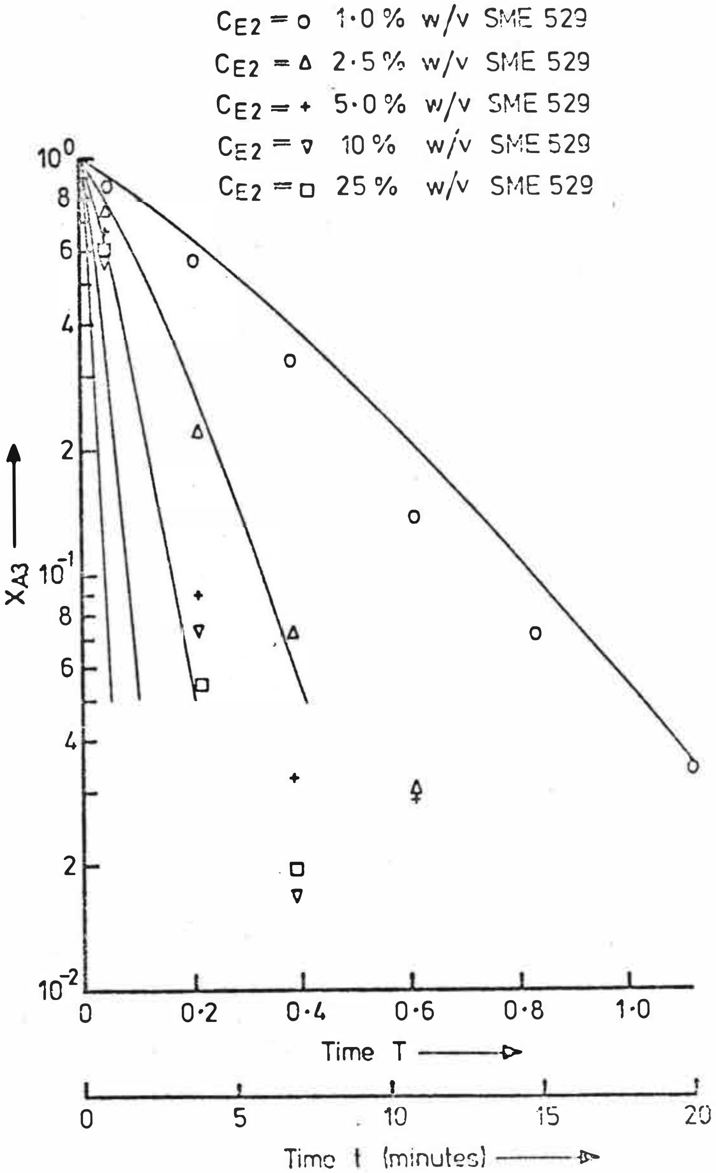


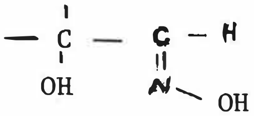
Figure 3.

curves start to converge at concentrations greater than 10% w/v, the largest effect being shown at the diluent end. The dependence is predicted from the influence on reagent concentration on reaction rate and on diffusion within the membrane, the reagent being the carrier for copper and hydrogen atoms in the organic phase. The experimental results under the same standard conditions covering the range of reagent concentrations are shown. A similar strong dependency on $X_{E2(o)}$ is evident with the highest sensitivity at the dilute end of the concentration range. The results at 1% and 2.5% w/v SME 529 are seen to fit the theoretical curves reasonably well up to contract times of 10 minutes. However, deviations between theory and experiment increase at the higher end of this range. The practical results do start to converge but the theory over-predicts the extraction achieved above 5% w/v SME 529. In this region breakdown of the emulsion was evident which became significant at contact times greater than 11 minutes. A typical set of breakdown-time curves is shown in figure 4. These were all determined for experiments carried out under identical conditions and illustrate the effect of increasing the reagent concentration, $X_{E2(o)}$, increases, the % breakdown of the emulsion of any particular contact time increases. It was found impossible to form stable emulsions in the present work, using Span emulsifiers, at reagent concentrations above 25% w/v. The degree of emulsion breakdown could be reduced by either increasing the concentration of emulsifier in the membrane or by using a different, more efficient emulsifier. Thus there are practical ways of overcoming this effect if long contact times are shown to be necessary.

The present model does not of course allow for emulsion breakdown. In addition to measurements made to follow the copper ion concentrations in the raffinate during extraction the internal acid phase was analysed for copper. The samples of emulsion removed during the extraction experiment were split into an oil and acid phase, these were separately analysed for copper. The variation in internal phase composition is shown in figure 5. First this shows the concentration that can be obtained. The lower curve, 120 ppm, rapidly reaches an asymtotic value; here most of the available copper has been extracted from the raffinate. Clearly no useful purpose is served in extending the contact once the asymtotic value has been approached; indeed, to do so would be detrimental since as is evident in figure 4 emulsion breakdown increases with time. These curves are useful in determining the contact time required for given conditions.

REAGENT ACCELERATORS

In part of this work the importance of reaction kinetics was assessed experimentally by adding 'kinetic accelerators' to the membrane. A compound developed by Shell International Chemicals for use with their reagent SME 529. given the code, RD 547 was used. This is an α hydroxyoxime, the active part of the molecule having the structure:-



$$-\underset{\substack{| \\ OH}}{\overset{|}{C}}-\underset{\substack{\| \\ N\diagdown OH}}{C}-H$$

It was used throughout the tests in a 10 mole per cent. solution in SME 529. Apart from the addition of this material all other conditions were kept constant. Results for raffinate copper concentrations v.s. time for two conditions, $C_{A3(o)}$ - 120 ppm and $C_{A3(o)}$ = 800 ppm Cu^{2+} are shown in figure 6. It can be seen that in both cases an improvement in extraction is obtained on addition of the accelerator. This lends support to conclusions regarding the operating region and points to future developments in reagents for membrane

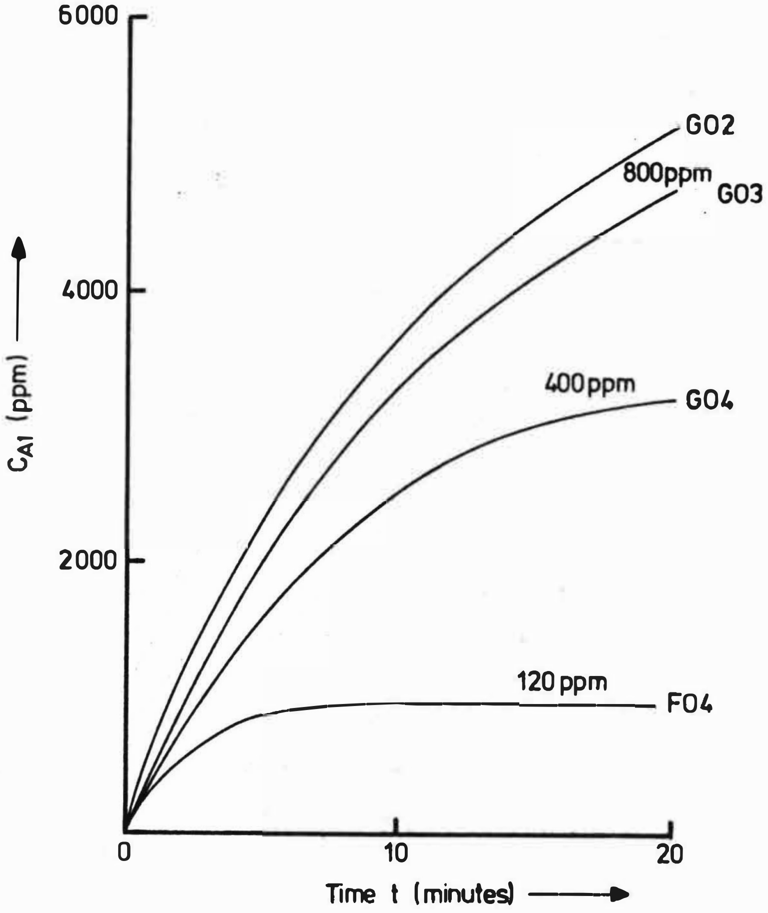


Figure 5

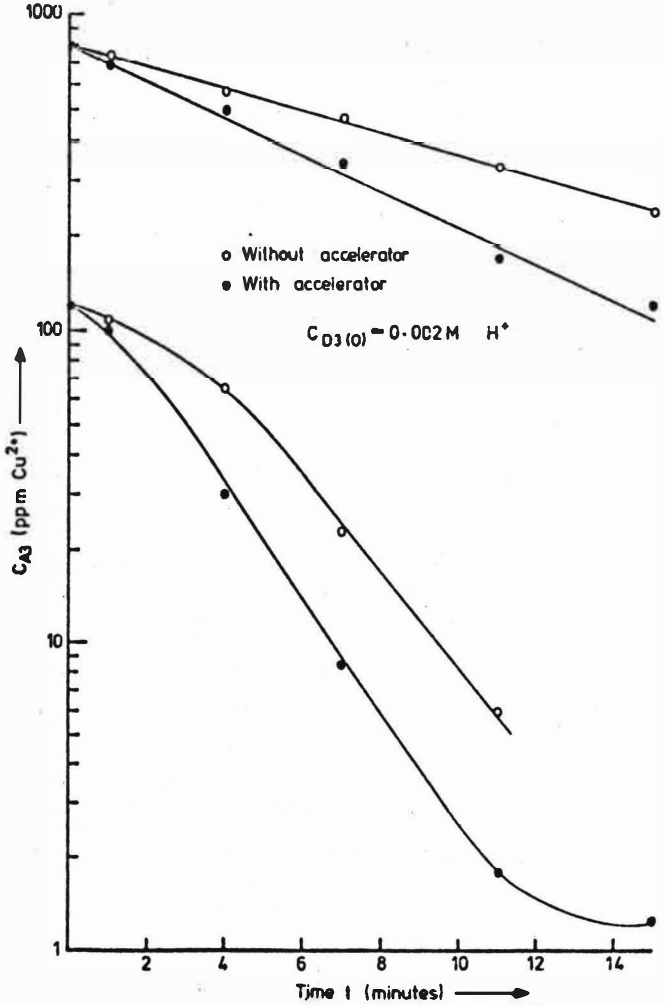


Figure 6.

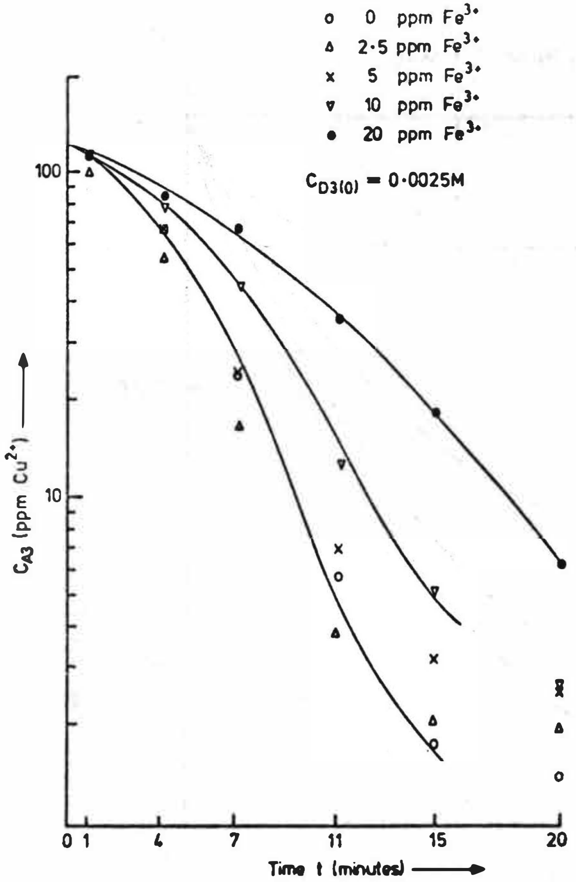


Figure 7

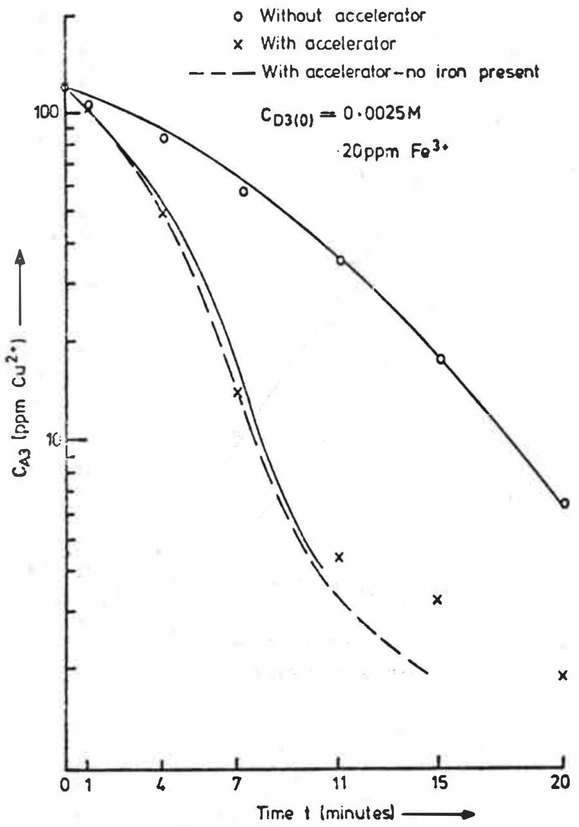


Figure 8.

systems. At both concentrations studied significant improvements in degree of extraction, Y, and the rate of extraction were obtained. Starting with a feed of 120 ppm Cu^{2+} a raffinate containing only 1.5 ppm Cu^{2+} was obtained after 11 minutes contact.

Improvements of this order may be commercially very significant in that it may reduce the number of contact stages required and thus lead to an immediate reduction in capital and operating costs. In this preliminary work no problems relating to emulsion stability when the accelerator was included were encountered.

THE EFFECT OF IRON, (Fe^{3+})

As ferric ions are present in most practical leachates at pH $<$ 2.6 it was decided to carry out preliminary work to investigate copper transfer in the presence of the co-ions Fe^{3+}. Experiments indicated that there were significant changes in the measured mass fluxes of copper through the membrane when ferric ions were present in the leachate and thus work was concentrated on determining the threshhold value for ferric ions at which an interaction was statistically significant. The results are shown in figure 7. These are for a membrane system containing SME 529 reagent. It can be seen that iron III affects the degree of extraction and mass flux, causing a reduction in both cases, at very low levels, 10 ppm.

Comparing this data with sllvent extraction it may be at first sight surprising but it must be remembered that this is a rate controlled, not an equilibrium controlled, process. Further work has recently been carried out into studying the selectivity of copper with respect to iron III in an L.M. process and reviewing the mechanism of iron/copper transfer. This work will form the subject of a future paper(10,11). It is interesting to compare the effect of iron when the accelerator RD 547 is present. This is shown in figure 8. It is seen that the membrane containing the accelerator is now much less sensitive to iron III at the 20 ppm level, this in spite of the fact that the equilibrium selectivity of the solutions containing RD 547 is inferior to that for SME 529 alone.

Clearly much more must be known about the mechanisms of these interfacial chemical reactions. The results thus far serve to illustrate that an L.M. process has potential; that the conditions pertaining to solvent extraction are not necessarily valid for membrane separations. This applies especially to the selection of or development of future reagents. The problems on simultaneous co-ion transport, selectivity and emulsion membrane properties may be partially resolved by reagent formulation.

ACKNOWLEDGEMENTS

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A NEW CONCEPT FOR MASS TRANSFER IN LIQUID SURFACTANT MEMBRANES

R. Marr, H.J.Bart, M. Siebenhofer

Institut für Grundlagen der Verfahrenstechnik, TU Graz, Kopernikusgasse 24

Graz, Austria

Liquid-membrane-permeation is a new unit operation which combines the advantages of extraction and common permeative methods. A new model to describe mass transfer in such multiple emulsions, was found. This paper gives a summary of experiments, made to prove the currency of this model and to find out its limitations.

1) INTRODUCTION

Beside already industrially used membranes for dialysis, hyper- and ultrafiltration a new type of membranes has been developed during the late sixties. The principle of this membrane is based on an invention of N.N.Li /1,2,3,4/. As Li found out it is possible to get a stable emulsion by dispersing a watery solution in a tensid containing oil phase. Stirring this emulsion in an other water solution by low velocity, causes the formation of a multiple emulsion with the phase sequence water I - oil II - water III (Fig.1). Phase III separates from the emulsion I in II when stirring is finished. Although there is a difference in the geometrical appearance, these multiple emulsions show a very similiarity to the mass transfer of ordinary membranes of the solubility type. On account of this it is possible, to transfer the principle of carrier transport, wellknown in biology, to synthetic membranes /6,7,8,9/. The coefficient of mass transfer is some ten to hundred times better than that of polymeric membranes /5/. The carrier solved in the liquid membrane fixes the species which has to be seperated on the one side of the membrane. Then the substance is brought to the other side of the membrane by diffusion and dissolves. The unloaded carrier goes back to start this rotation again. An other difference to ordinary membranes is given by the force which is not caused by a difference in pressure, as

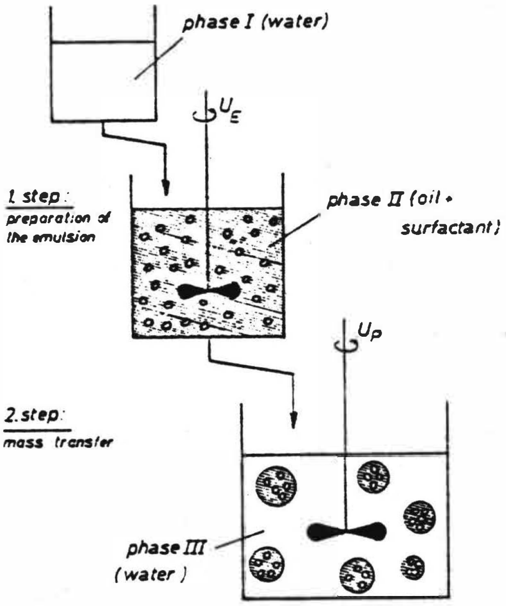


FIG. 1: Preparation of a liquid membrane by the method of multiple emulsion

usual for ordinary membranes. The reason for mass transfer and seperation by liquid membranes is caused by a very special chemism.

2) MECHANISM OF MASS TRANSFER

Various facilities of mass transfer have to be differend. The force for seperation is caused by a difference of the chemical potential between both sides of the membrane. Mass transfer is continued up to an equilibrium till there is no difference in the chemical potential to both sides of the membrane. The rate of mass transfer depends on the mechanism of mass transfer. Various mechenism are known.

These are:
- a) single permeation
- b) single permeation combined with a chemical reaction at the interface $F_{I/II}$
- c) single carrier-transport
- d) co-transport
- e) counter-transport

But there are only two mechanism of technological importance. These are the transportmechanism of co-transport and of counter-transport /10,11,12/ (Fig. 2).

If the seperation of a species A is linked with the transfer of a species B, permeation of A against its gradient of concentration is possible. This way of seperation is used in common seperation of anions and cations. When counter transport is used, A and B are seperated by the membrane. In this case both ions are either cations or anions. If an enrichment of A is

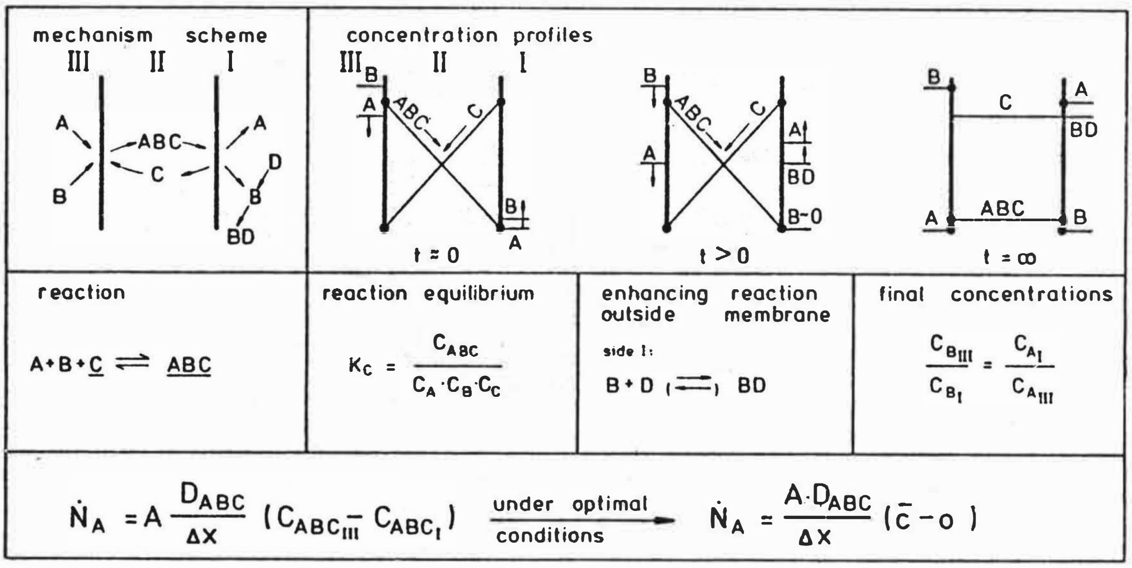


FIG. 2a: Co - transport

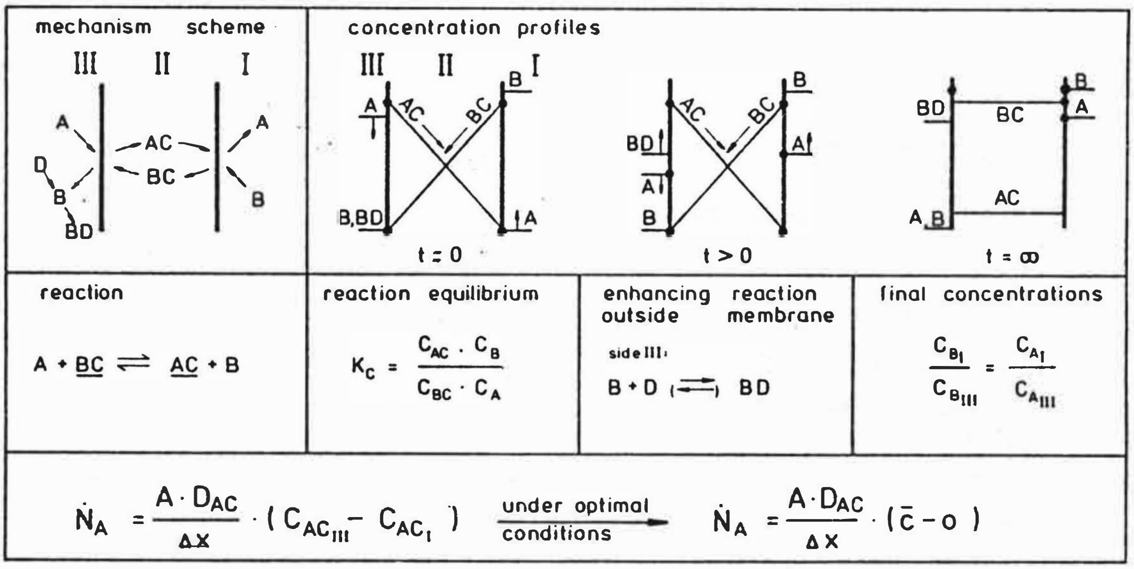


FIG. 2b: Counter - transport

wanted, B is given into phase I with rather high concentration. This causes shifting of the equilibrium. By this a good enrichment will be forced (FIG.3). Mass transfer is described by the following steps (see FIG 3). (For example: permeation of copper with carrier HX):

1. Diffusion of Cu^{++} to the interface III/II
2. Formation of copper-carrier-complex at the interface; $Cu^{++} + 2HX \rightleftharpoons CuX_2 + 2H^+$
3. Protons diffuse into phase III
4. CuX_2 passes the membrane by diffusion
5. Deloading of the carrier at the interface II/I

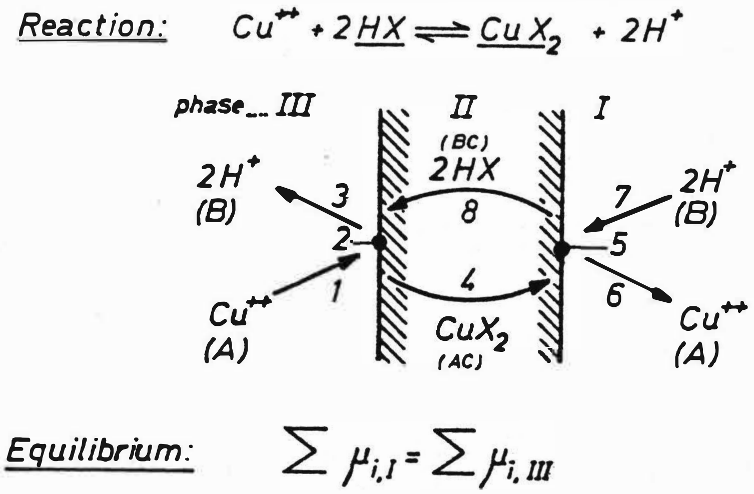
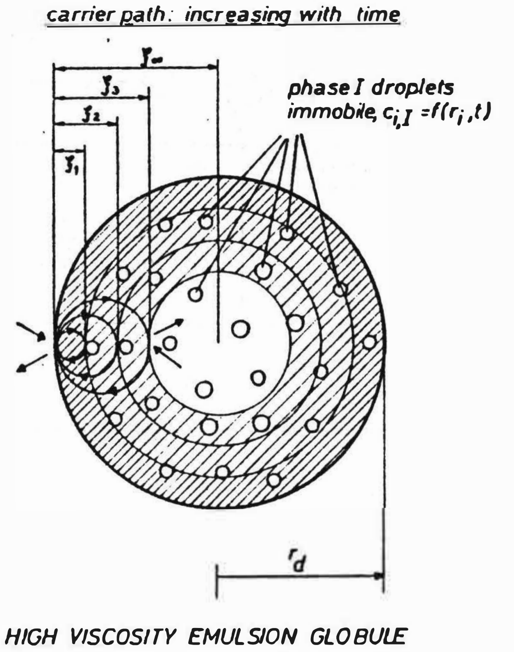


FIG. 3: Scheme of mass transfer (counter-transport)



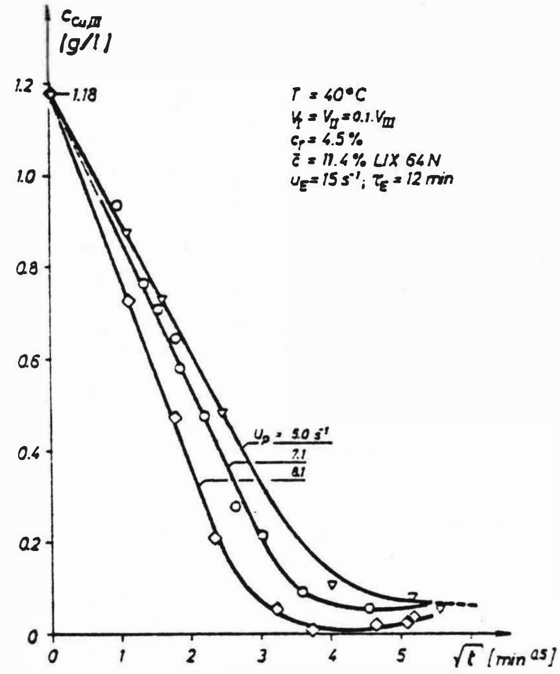


FIG. 4: High viscous emulsion

FIG. 5: Concentration of copper = f ($\sqrt{t}$)

$CuX_2 + 2H^+ \rightleftharpoons 2HX + Cu^{++}$

6. Cu^{++} diffuses into phase I
7. The carrier is loaded with H^+ again
8. HX permeates the membrane

If it is possible to disturb the equilibrium by removing the seperated species, quantitative seperation is possible. The mathematical description is given by the common mass transfer equation. But for practical use it is advantageous to use models.

The model of the hollow sphere /13,16,17/ derives from the experiments of N.N.Li with membrane bubbles. Although this model gives a good description for supported membranes it is unfit for the description of the behavior of multiple emulsions /17,18/. By this model the drop of emulsion is treated as a flat membrane with constant diameter (FIG.2). This opinion causes a cumulation of mistake. As mass transfer of liquid membranes is controlled by diffusion, description ensues by the laws of Fick. But the conditions of this model only tolerate to seize the order of magnitude.

The reaction site model is based on the conditions that the drops of phase I are symmetrically distributed and fixed in the emulsion drop. At these spots reaction of the species of permeation occurs /15,16,17,18/ (FIG.4). Instationary behavior of shrinking unsaturated phase I core is well described with 2nd Fick's law. At the surface of the emulsion the carrier is loaded with the species, which has to be seperated, at any time. The carrier is deloaded instantaneous when meeting a not saturated phase I drop. Saturation of the phase I drops ensues from the surface to the centre. Opposite to the model of a hollow sphere the contact surface is not defined by a strict distance, but continuous between the surface and the centre of the emulsion drop.
Between the zone of saturated and not saturated phase I droplets there has to exist a strict border at $x = \xi$, which already ensues through the emulsion drop. The diffusion of the loaded carrier between the surface of the emulsion drop and this border is described with 2nd Fick's law.

Taking into consideration the limiting conditions as followed,
$c_0 = c/2 = \text{constant}_{x=0}$ (at the surface of the emulsion drop).

$c = 0$ at $x = \xi$ (at the border of saturated phase I)
$t = 0 \quad \xi = 0$
$t > 0 \quad \xi > 0$
the solution of this system of equations solved by Hermans /19/ gives

$$c_0/S = 2\sqrt{\pi}\, z\, e^{-z^2} \int_0^z e^{-s^2} \cdot dS \quad \text{with } z = \xi/2\cdot\sqrt{Dt}$$

A. Kopp /16/ found, that $\xi/\sqrt{t} = \text{constant}$ if $t > 0$.
This solution is current for one dimension. If $\xi/r_d > 0.5$, the application of this equation is current for the globe too. The difference to the model of hollow sphere is given by:

a) $M_t = \xi F_{II/III} S_\infty$ and the consequence, that $-dc_c\ /dt = f(\sqrt{t})$

b) Mass transfer is not a linear function of the carrier concentration (degressive increase).

This condition depends on the opinion of an infinite number of well distributed phase I drops with an infinite small area. This relation, was verified by tests for copper permeation. As long as the carrier is saturated with copper at the surface of the emulsion drop, mass transfer is proportional to $\sqrt{t}$ (FIG.5). Essential importance has to be investigated now to find out the range of currency for this model.

3) PARAMETERS OF THE $\sqrt{t}$-LAW

Beside the composition of the membrane these parameters are given by the stirring velocity Up in the permeation vessel, the relation between duration and the velocity of emulsification t_E/U_E, and the rate between phase V_I and phase V_{II} (V_I/V_{II}).

The conditions for the preperation of the emulsion are of great importance. For to quantify the influence of the stirring velocity, mass transfer of membranes of the same composition was measured at various stirring velocities. The efficiency of the membrane becomes better, the higher the number of revolutions, or by given low number of revolutions by increasing duration of stirring (FIG. 6). Analogous the loss of protons from Phase I ceases. This contradicts the classical predictions of mass transfer resistance. Ordinary you expect that the loss of protons is bound to the transfer area $F_{I/II}$. But the better homogenisation of phase I in phase II, the better the stability of the membrane against not controllable acid loss. The quality of homogenisation is directly bound to stirring conditions.

As an influence of stirring velocity in the permeation vessel it was found, that increasing the stirring velocity causes a lower concentration of copper in phase III. A best possible stirring velocity was found. Increasing velocity above that increases masstransfer too, but the mechanical stress causes a lower working life. At these tests concentration of copper in phase III runs through a minimum.

Furthermore tests were made to find out the best phase relation between phase V_I and phase V_{II}. The end of the investigation was to find the maximum of mass transfer under the conditions of a maximum working life. The optimum lies between $0.5 < V_I/V_{II} \leq 1.0$ /14/. The capacity of a multiple emulsion is very correlated with its stability. Loss of stability is caused by swelling of the emulsion drop during the experiment. This appearance was proved during the experiments of copper permeation with LIX 64N as carrier /17/. Two main reasons caused emulsions going unstable, osmosis and occlusion of phse III. But a strict seperation of both effects is impossible. By investigation of the limits for the influence of osmosis, criterions were found. Two kinds of experiments were made to detect osmosis. On the one hand by watching the concentration at the start and the end of an experiment, on the other hand by continuous control of the concentration /14/. The phase relation $V_{I,t}/V_{E,t}$

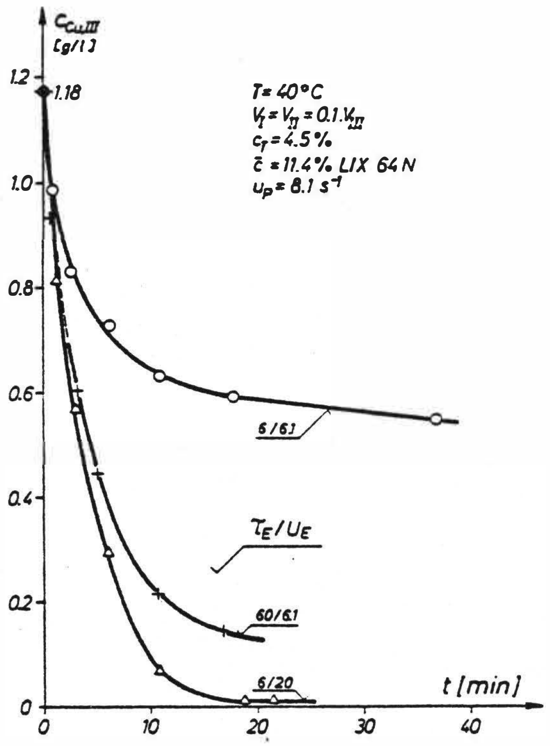


FIG. 6: Experimental investigation of the preparation

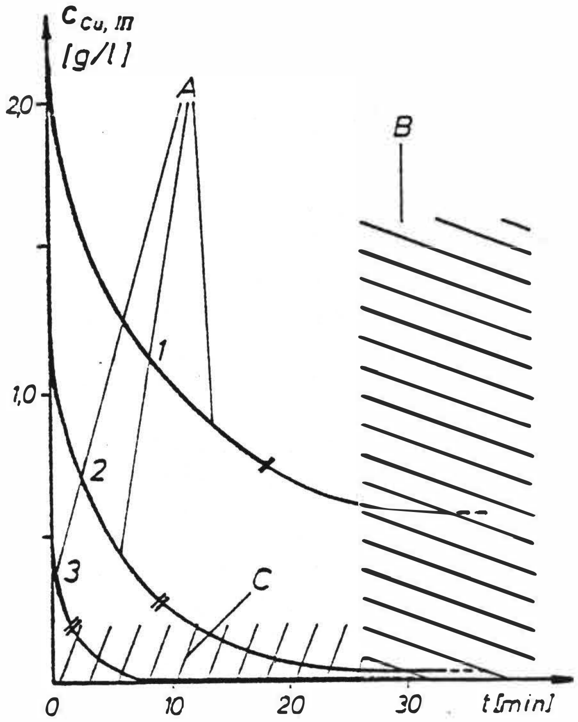


FIG. 7: Currency of the $\sqrt{t}$-law (experimental dates see FIG. 5)

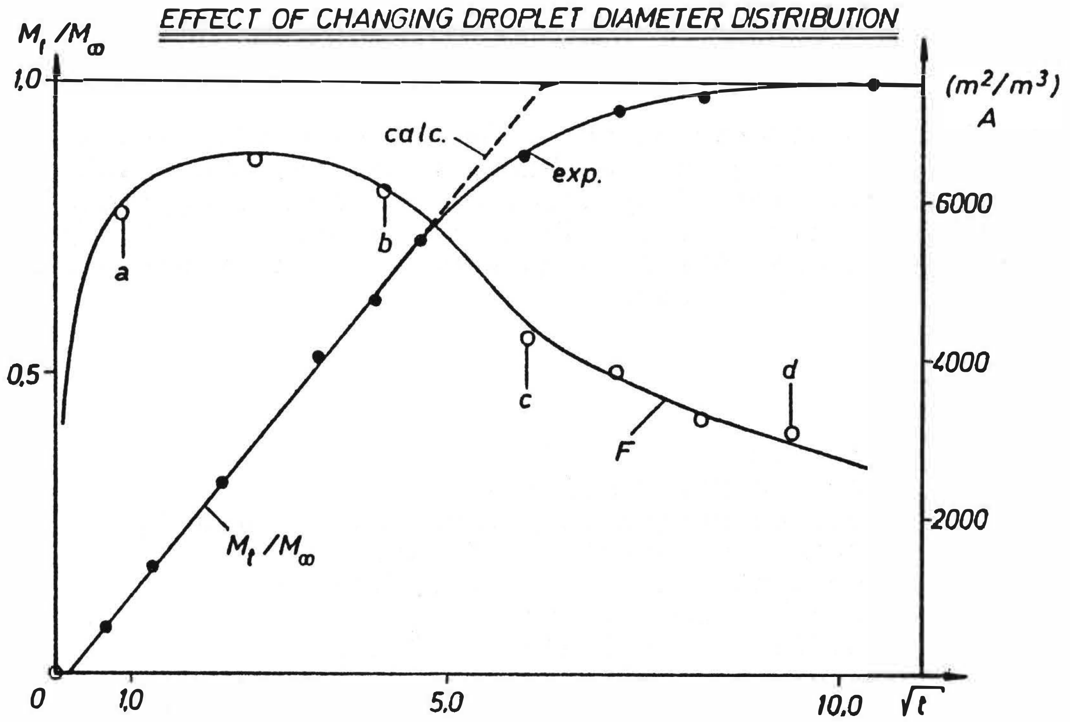


FIG. 8: Comparison of mass transfer and specific tansfer area II/III

was detected volumetric. As the occlusion of phase III at the end of an experiment is not reproduceable, the true influence of osmosis on the increase of membrane volume is hardly to detect. But increasing concentration of copper in phase III /14/ is typical for the effect of osmosis of water during an experiment.

4) CONCLUSION

Beside the very important information about the different influence of various parameters on the behaviour of multiple emulsions, the reaction site model was found current. The extent of currency was definitely limited.

Swelling was observed for the system Cu/LIX 64N (FIG.7, part C) and limits the residence time because of decreasing concentration of copper in phase I /16/.

If the concentration of copperions in phase III becomes less than the limit, the carrier cannot be loaded completely at the interface $F_{II/III}$. Proportionality between concentration of Cu^{++} in phase III and t is disturbed /16/ (FIG. 7, part C).

FIG.8 shows the quantification of the effect. On account of this, mass transfer is a strictly current function of $\sqrt{t}$ if the transfer surface is constant.
With lasting rise of the emulsion by osmosis and occlusion interfacial area decreases and differs from theoretical dates. At last this appearance leads to the tip of emulsion

SUMMARY

Taking into consideration the present scientific state of investigation on liquid membrane permeation, the results show promising facilities of application. Of course applicability will never be universal and limitations are given by economy. But economy is guaranteed, when seperation of materials of ppm-concentration is necessary.

NOMENCLATURE

A,B,C	species
AB, BD	compounds, complexes
c	concentration of permeating species (g/l)
$\bar{c}$	total concentration of carrier (g/l)
c_T	concentration of tensid (Vol %)
c_o	startconcentration
D	diffusioncoefficient (m^2/sec)
F (A)	area (cm^2, m^2)
K_c	equilibrium contact
M	transferred material
$\dot{N}$	transferred material/time
r	radius of i

S	concentration of immobile species
S_∞	saturation concentration of the emulsion
t,	time (min)
T	temperature (°C)
U	number of revolutions
V	volume
x	distance from the surface II/III
ξ	distance form the surface II/III to the border of saturated/not saturated phase I droplets
I,II,III	phase (II = oil phase)
I/II, II/III	interface

INDICES

A,B	species to be transferred
E	emulsion
P	permeation
t	time
o	start-
∞	equilibrium -
I,II,III	phase
d	drop

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REMOVAL OF TOXINES FROM PLASMA AND BLOOD WITH LIQUID SURFACTANT MEMBRANES

W. Halwachs, W. Völkel, K. Schügerl

Institut für Technische Chemie der
Universität Hannover
Hannover, W-Germany

ABSTRACT

At certain hepatic disease phenols are crucial compounds which occur in blood in an increased extent. This paper is an in-vivo study applying liquid surfactant membranes for toxine extraction. The phenol transport across the membrane is coupled with an enzymatic reaction within the emulsion globules to provide specifity of the process. After stating the problem and explanation of the extraction method and analytics results are given for the removal of phenol(s) from aqueous solutions, plasma and blood. An estimation of the relative reaction resistance in this coupled mass transfer/reaction process is supplied to avoid a useless excess of expensive enzyme activity.

INTRODUCTION

Phenols and mercaptanes are thought to be the most crucial toxines in coma hepaticum (1-3). They are detoxified normally by the liver. At coma, however, their concentrations in blood increase sharply. Together with increased fatty acids (4) the toxines are harming not only the brain but also the recreating liver in a synergistic effect. A removal of the toxines during coma hepaticum opens a chance to support the liver's self-regeneration (5). So this paper deals with the applicability of liquid membrane permeation on phenol detoxification of bovine plasma and blood. The extractant applied is an emulsion of paraffin oil acting as the liquid membrane and an enzyme solution ensuring the specifity of the method.

Commonly the elimination of lipophilic phenol compounds originating from the amino acid metabolism is accomplished by enzymatic reactions in the liver. UDPGA (Uridinediphosphoglucuronic acid) is linked by UDPGT (Uridinediphosphoglucuronyltransferase) to the phenols to be detoxified. The resulting conjugated phenols are hydrophilic and are eliminated by the kidneys.

HOW TO REMOVE THE LIPOPHILIC PHENOLS AND FATTY ACIDS?

The removal of the toxines in question should be a highly selective process so that other components in blood are not affected. The method we chose is a modified extraction process: the liquid-membrane technique (LMT), developed by Li (6).

LMT is a simultaneous extraction/stripping process using a dispersed emulsion instead of a pure solvent as the receiving phase (FIG. 1) (7). The term liquid membrane generally means a liquid component of a multi-emulsion which separates to other miscible liquids: the continuous phase from which the solute is to be removed and the dispersed phase which receives the solute. In special cases the transport of the solute may be vice versa. Generally the liquid membrane may be aqueous (if applied to organic solutions) or non-aqueous (if applied to aqueous solutions). The mass transfer velocities and selectivities of solutes are governed by their solubilities and diffusivities in the liquid membrane. Mass transfer and selectivity of the extraction may be enhanced by chemical reactions, which occur only in the dispersed phase consecutively to the mass transfer through the liquid membrane. This kind of LMT-process was chosen for phenol removal. The enzymatic reaction (linking active glucuronic acid to the phenols by UDPGT) is identical to the process which occurs in the liver.

EXPERIMENTAL

FIG. 1a shows a model scheme of an emulsion globule, in FIG. 1b the real habit is given. The emulsion used consisted of a droplet size spectrum in a range of some 0.1 - 1 mm droplet diameter dispersed in the continuous phase. Each emulsion globule itself consists of a drop collective of the dispersed phase encapsulated by the membrane. Droplet diameters of the dispersed phase are orders of magnitude smaller than globule diameters. Commonly, the size is determined by the conditions of emulsification (energy dissipated, surfactant concentration). The HLB value of the surfactant applied must be low (Span 80:4.3) in order to stabilize a water-in-oil emulsion.

The optimum composition of the liquid multi-phase system adapted for phenol detoxification of blood was obtained from a large amount of test series, because the stability of the multi-emulsion as well as the enzyme activity drop during encapsulation had to be considered carefully. Values are supplied below:

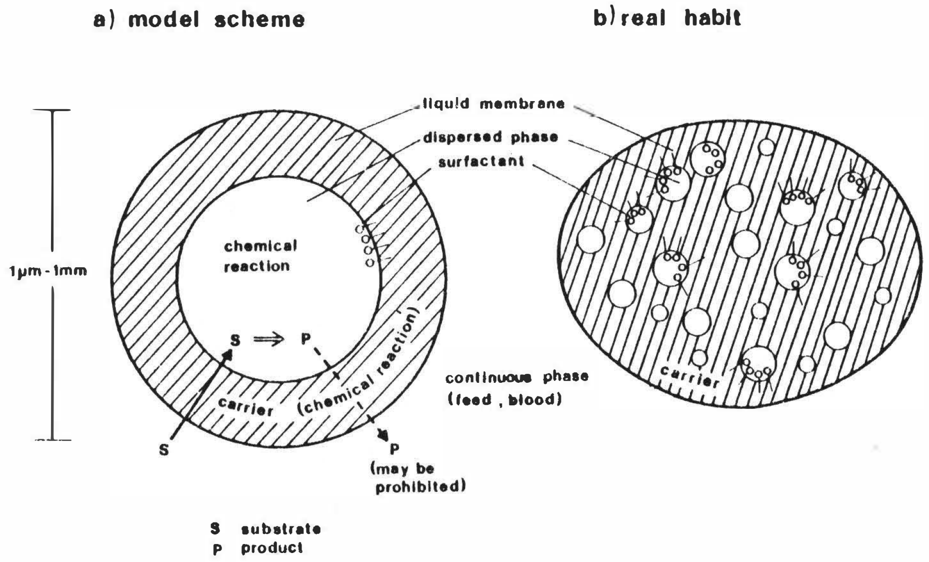

FIG. 1
Scheme of an emulsion globule, model and real habit

continuous phase	membrane	dispersed phase
plasma	90% paraffin oil	UDPGT
blood	(71 cP)	
albumine solution	5% dodecanol	UDPGA (0.1 M)
buffer	5% lecithin	heparin (1 mg/ml)
(alternatively)		$MgCl_2$ (1mM)
		pH 7.4

Typical volumes used for the emulsion treatment of plasma and blood were 100 ml continuous phase and 10 ml emulsion (phase ratio = 1). Rest activity of the enzyme after encapsulation with a high speed stirrer was in the range of 50-80%. The activity decreased according to a rate law of first order at a rate constant within a range of 10^{-5} ..... 10^{-4}/sec depending on the enzyme preparation.

The liquid surfactant membranes are prepared by emulsification of membrane and dispersed phase with a high speed stirrer or supersonic equipment (high energy dissipation). Employing an appropriate surfactant the emulsion is stable for hours or even days. The emulsion is then placed into a stirred device. Via the stirrer speed the mean value of the emulsion globule size distribution is adjusted within a range of 0.01 - 0.1 mm drop diameter. Samples may be taken from the continuous phase after passing a membrane by means of a peristaltic pump. The membrane filter prevents smaller emulsion globules from leaving the extractor (FIG. 2).

The preparation of phenol samples is very simple. Because

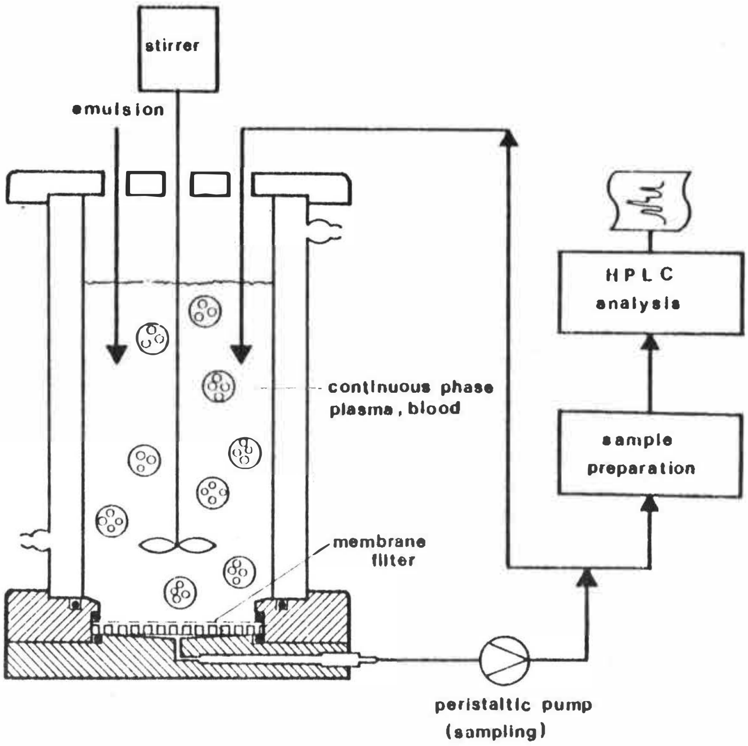

FIG. 2
Experimental set-up

they must be protein-free before injected into the HPLC (otherwise they would clog the chromatography column) protein is precipitated with a three-fold excess of methanol and centrifugated The phenol sample was processed on a 10 cm RP 18 column with a mobile phase of 40% methanol and 60% water. Flow rate was 1 ml/min, the pressure some 120 bar and the volume to be injected 10 µl. The peak retention increases with the lipophilic character of the toxine.

RESULTS

Some general remarks on mass transfer across liquid membranes followed by chemical reactions shall preceed the results section. With respect to the rate of extraction a limiting case prevails: If NaOH solutions are used as dispersed phase, the chemical reaction in the emulsion globules occurs instantaneously, that means the solute transport across the liquid surfactant membrane is mass transfer controlled. Hence experimental results obtained with encapsulated NaOH are of great importance for the estimation of the amount of enzyme needed because in mass transfer regime an increase of the enzyme protein content in the dis-

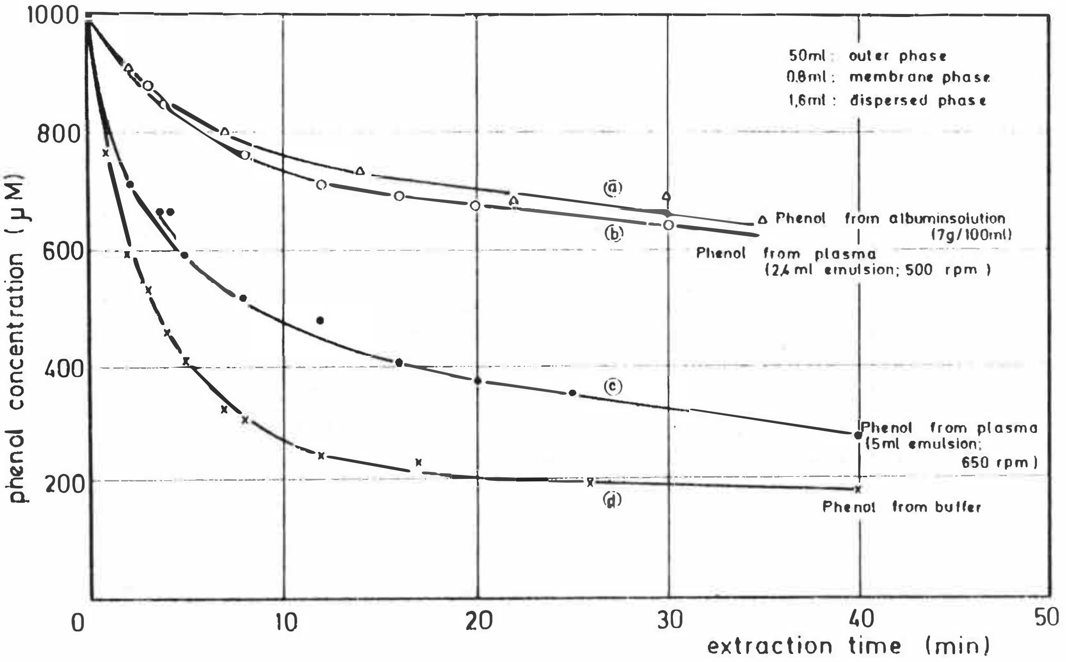

FIG. 3
Liquid membrane permeation employing NaOH as stripping agent for different types of continuous phases

persed phase may only effect a poor acceleration of the chemical reaction. As the enzyme/coenzyme system is the most precious component of the liquid surfactant membrane, the knowledge of the limiting case is of great economical importance.

The low-rate mass transfer limit is called the chemical reaction regime. If mass transfer across the liquid surfactant membrane is very fast, i.e. the mean membrane thickness is very small or the specific interface (per unit volume of continuous phase) is very large, the chemical reaction ought to be the rate determining step (chemical reaction regime). A small mean membrane thickness might be accomplished by a high ratio of dispersed phase volume to membrane volume. The experimental conditions in question put the permeation process right between both regimes. This is proved by the strong dependency of the extraction rate on the degree of dispersion as well as on chemical reaction rate (enzyme activity of UDPGT).

In FIG. 3 results of the phenol removal with a 0.1 n NaOH solution adapted as the dispersed phase are shown. Initial concentration is 1 mM, i.e. the concentration range of phenol in hepatic coma. The fastest extraction prevails for a buffer solution. Phenol drops below 20% in some 30 minutes (curve d). With respect to the same experimental conditions phenol is extracted from albumin or plasma only to an extent of some 25% (albumin concentration was 7 g/100 ml, see curve a and b). The strong decrease of the rate of extraction is due to an adsorption equi-

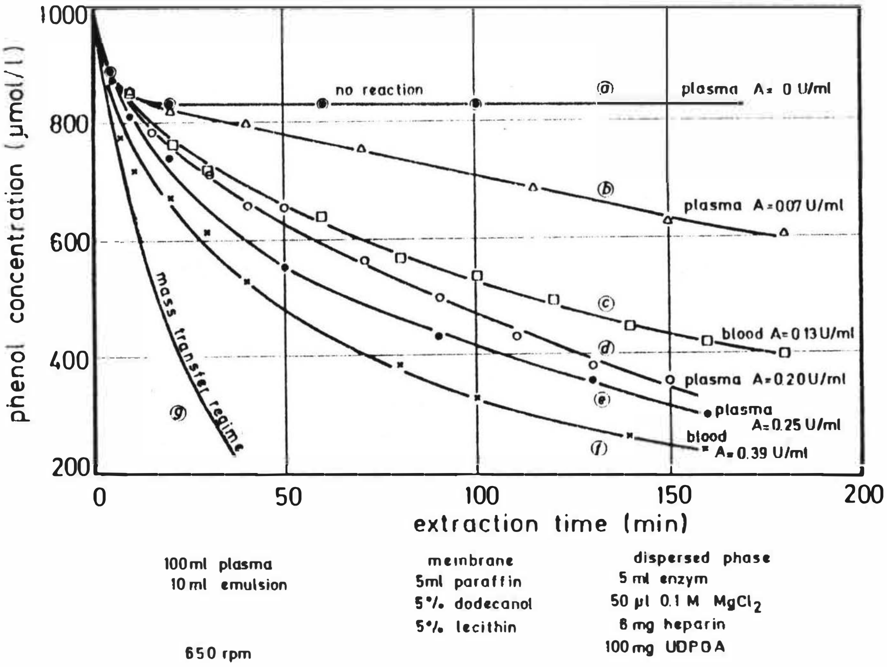

FIG. 4
Removal of phenol from bovine plasma and blood employing different enzyme volume activities

librium of phenol between albumin and water, preceeding the sorption of phenol into the liquid membrane. In that way free phenols in plasma are lowered. Hence the concentration gradient across the membrane which is responsible for the permeation rate is diminished, too.

If the degree of dispersion and the emulsion hold-up are increased via the stirrer speed (see curve c, 500 rpm 650 rpm) and the emulsion volume (1.6 5 ml), respectively, the extraction rate of phenol from plasma is enhanced considerably pointing to mass transfer control of the extraction process.

FIG. 4 shows the removal of phenol at different levels of immobilized UDPGT-activity. The extraction rate strongly increases with the enzyme activity pointing to reaction rate control. In the case of vanishing activity the sorption equilibrium between continuous phase and the liquid membrane causes a small extraction effect (A = 0 U/ml).

Comparing these results with the limiting case of mass transfer regime (see FIG. 4, curve g) it would be worth, obviously, to increase the enzyme activity because the extraction rate is still far away from strong mass transfer regime. But higher UDPGT volume activities than 0.40/ml could not be obtained at that time this work was done. Note that the enzyme activities given in FIG. 6 have been determined after finishing an extraction run. As a certain amount of active protein always denaturates during emulsification and extraction we have to direct

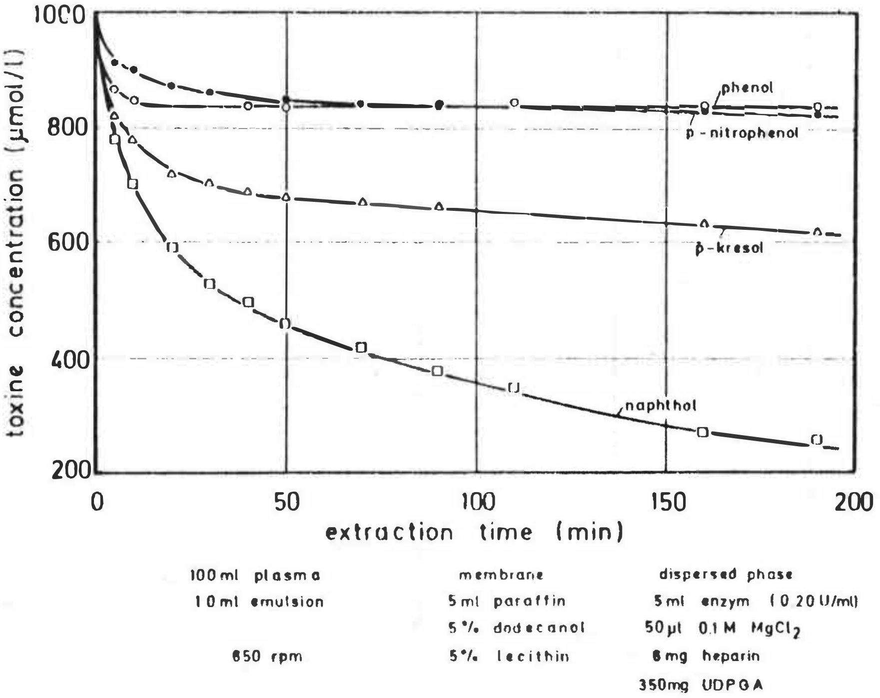

FIG. 5
Extraction of different phenols from plasma

our attention to highly sophisticated detergent compositions.

Courses of curve c and f in FIG. 4 in comparison with the others demonstrate that there is no different behaviour with respect to the extraction rate whether removing phenol from plasma or from blood.

FIG. 5 shows concentration time courses concerning the competitive removal of different phenols from plasma. The toxines are extracted with rather different rates due to their membrane solubility and chemical reaction rates. In a competitive process phenol is removed only by membrane sorption, no chemical reaction occurs in the dispersed phase, naphthol is removed with the highest extraction rate. Generally spoken, at short extraction times the overall permeation process is governed by membrane sorption (solubility). At high emulsion contact times the process is governed by a quasi-steady-state permeation coupled with enzymatic reaction. Hence the differential overall selectivities with respect to each of the phenols are varying with time. Overall selectivities (defined by the relative extraction rate) of phenol, p-nitrophenol, p-kresol and naphthol change from 0.21, 0.15, 0.29 and 0.35 at the beginning to 0.00, 0.09, 0.22 and 0.69 at high extraction times, respectively.

At quasi-steady-state the total molar flux with respect to a definite substrate depends on the rate of permeation and chemical reaction (principle of additive resistances). The later one implies a very high substrate selectivity. Maximum reaction rate referring to p-kresol and p-nitrophenol prevails when naphthol

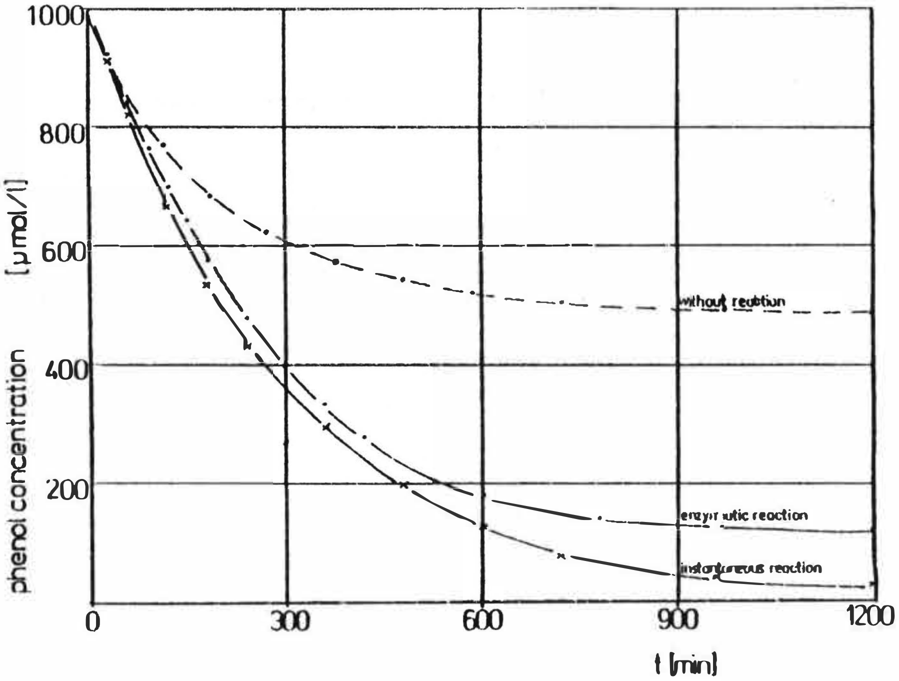

FIG. 6
Phenolpermeation across a solid supported liquid paraffin membrane

vanishes and for phenol when all the other substrates are conjugated. This effect proves to be a strong substrate competition.

HOW TO DESIGN AN OPTIMUM LIQUID MEMBRANE EMULSION?

Once the problem of enzyme and emulsion stability has been solved by choosing appropriate additives, stabilizers and membranes, the design of any enzyme-emulsion reactor is no longer a biochemical but a chemical engineering problem. Apart from preparing the emulsion and removing it from blood, the efficiency of the liquid surfactant membrane is a crucial parameter for extractor lay-out, as the overall extraction rate is limited by the membrane resistance. Hence it is very useful to know whether the transport across the liquid membrane or the chemical reaction is the rate limiting step in order to avoid a useless excess of expensive enzyme and coenzyme. (This problem has already been mentioned before).

According to the mass transfer resistance concept in reactive extraction we may write down

$$W_{tot} = \left(\frac{1}{k_L a} + \frac{x^2}{P} + \frac{c}{r}\right) \qquad (1)$$

with the overall resistance W_{tot}, k_La referring to continuous phase, the membrane thickness (length of diffusion path) x, the permeation coefficient P, the solute concentration c and the enzymatic reaction rate referring to the continuous phase solute concentration. Taking into account that k_La does not affect the emulsion efficiency the relative resistance of the enzymatic reaction within the emulsion comes up to

$$W_r = \left(1 + \frac{x^2}{P}\frac{r}{c}\right)^{-1} \qquad (2)$$

Note that the above equation should only be used for estimation purpose because it does not hold strongly for non-linear enzymatic reactions. Furthermore, the resistance according to equation (2) is time dependent because r(c) is a function of time. That is why the relative resistance of the enzymatic reaction increases with extraction time

Hence the emulsion efficiency may be estimated if x, P, c and r are known. r(c) is determined in a batch experiment. x and P can be obtained from the time-lag in a permeation cell with a solid supported liquid membrane of definite porosity. Results are suplied below:

$P = 0.89\ 10^{-6}$ $\mathrm{cm^2/s}$
$x = 0.0165$ cm
$c = 1\ 10^{-6}$ $\mathrm{mol/cm^3}$
$r = 5\ 10^{-9}$ $\mathrm{mol/cm^3/s}$

$W_r^{rel} = 40\%$

The relative resistance of reaction indicates that the main resistance (60%) is due to the mass transfer process. This prediction is confirmed by measurements shown in FIG. 6. Phenol permeation was carried under three conditions: Simple mass transfer without reaction, enzymatic reaction of definite reaction rate r and instantaneous reaction with an infinitely high rate employing 0.1 N NaOH as the stripping phase. These three cases are denoted in FIG. 6.

Of course maximum permeation prevails for instantaneous reaction, but it is interesting to see that even the slow enzymatic reaction shifts the overall process closer to mass transfer than chemical reaction regime (compare the relative location of the curves in FIG. 6), because the length of the diffusional path is high (0.0165 cm).

Applying the resistance concept to emulsions we may replace x by R/4 (R = 0.01 cm is the mean radius of the emulsion globules). Referring to the phenol removal in plasma and blood (FIG. 4) where a more viscous membrane was used ($p = 0.37 \cdot 10^{-6}$ $\mathrm{cm^2/s}$) and taking into account that the initial concentration of free phenol in plasma was $0.74\ 10^{-6}$ $\mathrm{mol/cm^3}$ the following values could be obtained for emulsion efficiency

			initial conc.
FIG. 4	curve b	W_r^{rel}	95%
	curve f		67%

What is obvious from the curves in FIG. 4 is now stated quantitatively: The reaction coupled mass transfer within the emulsion globules is reaction rate controlled and therefore it is worth to increase the enzyme volume activity to achieve a higher permeation rate.

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MEMBRANES IN EXTRACTION

A STATE OF THE ART REVIEW

Mahmoud M. Hafez

Research Department
Imperial Oil Limited

Sarnia, Ontario, Canada

ABSTRACT

Review of the use of membranes in solvent extraction indicates huge potential for increasing selectivity, reducing solvent usage and saving energy. Membrane extraction lends itself readily to processes such as metal extraction, waste water treatment and pharmaseutical and medical applications.

INTRODUCTION

The use of membranes in extraction is a new and promising approach to separation processes. It offers the advantages of low solvent requirement, improved selectivity and energy saving. Membrane extraction is still in the exploratory stage, but research activities are rapidly expanding.

This paper is a brief review of the state of the art. Its main purpose is to introduce to solvent extraction researchers the concept and and potential of this approach and to provide a few examples of extraction processes using the technique. It does not deal with liquid membranes, which are reviewed elsewhere.

To start, the general membrane process is described and the possibility of its use in solvent extraction is explored. Carrier mediated transport is further described being one important tool of membrane extraction (ME). Finally some examples are presented.

GENERAL MEMBRANE SEPARATIONS

Membrane Separations are those processes which depend on the properties of some membranes to bring about a separation of a mixture of molecules under a suitable driving force (1, 2, 3).

Despite being slow, a membrane separation process is attractive because it is very selective, and usually offers substantial energy savings compared with other conventional separations.

In most cases, membranes have been used as diffusion barriers (based on chemical nature) or microfilters (based on physical nature) or a combination of both. Based on this function, membranes have found a wide range of applications (4, 5, 6). Details of these are outside the scope of this paper. As such, however, membrane processes are limited by their inability to achieve complete separation, and are best used to supplement conventional separations.

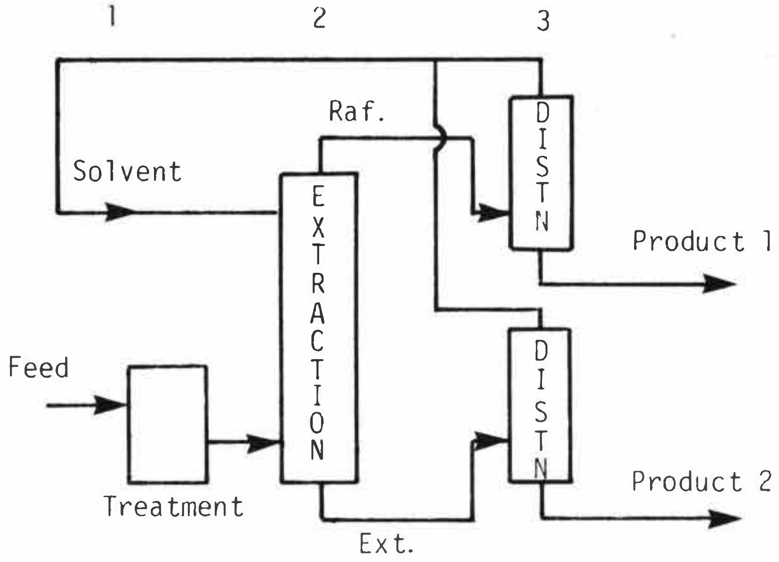
Recently, artificial membranes were shown to be made very selective by incorporating a mobile or semi-mobile carrier within the membrane matrix. The carrier chemically reacts or physically interacts with the permeant molecules, enhancing their permeation rate and improving the selectivity of the process. This process, known as carrier mediated transport, is more complicated and still in the early stages of development.

In the following discussion it will be shown that membranes as diffusion barriers could be indirectly used in extraction, while carrier impregnated membranes could be directly used as an extractant.

MEMBRANES IN SOLVENT EXTRACTION PROCESSES

Consider the general solvent extraction process (Figure 1). The feed is physically or chemically pretreated. Solvent and feed are countercurrently contacted in the extraction step proper, to produce an extract and raffinate phase. Finally, the solvent is recovered from the two phases by distillation.

FIG. 1



Typical Extraction Process

Membranes can be used in any of the above three steps of the process (treatment, extraction, recovery). The membrane function in the first two steps is essentially to avoid or minimize the use of solvent. In the last step, however, the membrane is mainly used to reduce the energy requirements of solvent recovery. In other words, the membrane process can be directly applied to the extraction step or can be indirectly used in the first or last steps of the process.

Indirect application of the membrane to the first step includes the case where the feed is chemically pretreated and the membrane used to replace the extractor. Thus in metal extraction, e.g. Cu from a mixture of other cations, the feed is treated under suitable conditions with a chelating agent. The Cu++ ions are alone complexed leaving other cations behind in solution. A membrane is then used to reject the larger size complex, while the small cations in solution permeate through the membrane (11, 12, 13).

Direct application of membranes to the second step of extraction is based on the principle of carrier mediated transport. This includes immobilizing the solvent in the membrane by impregnation (14, 15). Using the Cu++ extraction example again, the membrane is impregnated with the carrier (diluent plus complexing agent). Conditions (pH) on both sides of the membrane are adjusted so as to enhance complex formation on one side and complex decomposition on the other. The Cu++ ions are selectively transferred across the membrane. Here the membrane only supports the carrier and the system acts as a double extractor, pumping the Cu++ ions from one aqueous phase (containing other ions as well) to another aqueous system containing copper ions only.

Other ways of direct use of membranes in the second step include adding the carrier up or down stream of the membrane, rather than within. The process known as perstraction (16, 17) utilizes the carrier downstream of the membrane to sweep the permeated solute. In other instances the carrier, which is miscible with feed, is added upstream. It permeates through the membrane carrying the solute(s) to be extracted. In both cases the membrane's physical and chemical properties are actively involved in the extraction step.

Membrane application in the third step to recover the solvent from the extract or raffinate phases has not been reported in the literature. Although a very efficient method of reducing the energy requirements of the process, its treatment is outside the scope of this paper.

It can be seen from the above discussion that membranes can be used in extraction processes when:

1. the solute to be separated from a mixture of solutes is very large in size or can be made so by a specific complex reaction with a large (chelating) molecule. This enables size separation of the complexed molecules. In addition to being extremely useful for extracting ions (e.g. metals), it can also be used

for molecules (e.g. complexing acetic acid in waste water by secondary amines trioctylamine) (18). The advantages of this scheme are in reducing or eliminating the diluent and in simplifying the process (ultrafilters vs. cascades of mixer-settlers).

2. the solvent or complexing agent can be impregnated in the membrane matrix. The solute is transferred across the membrane with the help of the carrier, and is recovered downstream. This scheme is attractive because it considerably reduces the solvent inventory, which is usually large. It also combines both the extraction and stripping (or solvent recovery) in one step. Success of this technique depends, however, on the suitability of downstream solute recovery.

3. a membrane exists which is capable (by virtue of its chemical and/or physical properties and a carrier) of selectively permeating solute(s) to be extracted.

The most studied approach to membrane extraction is carrier mediated transport, and this will now be discussed in more detail.

EXTRACTION BY CARRIER MEDIATED TRANSPORT ACROSS MEMBRANES

Carrier mediated transport is the process in which a mobile or semi-mobile liquid or a solid is entrapped in the matrix of a suitable membrane, such that the carrier imparts to the membrane selectivity to and permeability of a certain solute(s). This is because only solute molecules can enter the membrane matrix by reacting or interacting with the carrier. Other components of the mixture cannot.

The carrier may be passive (e.g. just dissolving the solute molecules) or active (chemically bonding the solute molecules), while the membrane is usually non-reactive as its only function is to support the carrier.

Carrier transport has been known for some time in biological membranes where transfer is unusually fast and highly selective. To explain this behaviour, the concept of a molecular carrier reversibly reacting with the permeant was developed and experimentally established by Osterhaut (19, 20).

Various mechanistic models have been proposed to describe the process including molecular diffusion, passive and active transport. A model, based on diffusion accompanied by a reversible chemical reaction in a non-reactive membrane, was developed and analyzed by Goddard et Al (21, 22, 23).

They show that the permeant flux is the sum of its ordinary diffusion in the carrier and its diffusion rate as a complex form. Depending on the relative significance of the two processes, two operating regimes could be identified. A near diffusion [frozen] regime is characterized by small Damkohler numbers [kd^2/D]; which in the limit represents passive carrier transport. An equilibrium regime assumes reaction equilibrium within the membrane and is characterized by large Damkohler numbers. Permeation rate equations were developed which can be used to describe the extraction process in terms of solute transport numbers (obtained from equilibrium constant and reaction invarients), molecular diffusivities and overall concentration gradients.

CARRIERS IN CARRIER MEDIATED EXTRACTION

An important feature of carrier mediated extraction [CME] is the carrier and membrane choice (24, 25):

1. Besides being a good extracting solvent for the solute(s), carrier should be easy to entrap in the membrane matrix.

2. The carrier should be insoluble in both phases, on either side of the membrane, to minimize leaching.

3. The carrier and its complexes with the solute(s) should be mobile within the membrane to enable fast diffusion.

4. Active carriers forming complexes should be mild, and the reaction readily reversible. Goddard (22) showed that there is an optimum equilibrium constant of the reaction, such that the binding of solute is strong enough but the subsequent decomposition of complex is easy. The value of this constant is inversely related to the square of solute concentrations, upstream and downstream of the membrane.

5. The membrane should be able to support the carrier, be highly porous but thin and should not be affected by the system of the formed complexes.

EXAMPLES OF EXTRACTION PROCESSES USING MEMBRANES

Four examples of extraction processes that use membranes either directly or indirectly are summarized.

a) Direct Application to Copper Extraction (14)

    (i) The process; extraction of copper ions from aqueous solutions containing other metal ions.

    (ii) Pretreatment; the pH of the aqueous solution is adjusted to 1.5-2.0, to favour the complexion of Cu++ ions only.

    (iii) The carrier; LIX-64N in Esso Escaid.

    (iv) The membrane; cellulose acetate.

    (v) The impregnation process; direct impregnation of the membrane with carrier.

(vi) The stripping solution downstream of the membrane is water + acid (→ 250 g/L sulphuric acid).

b) Direct Application to Unsaturated Extraction (15)

(i) The process; extraction of unsaturated olefinic hydrocarbons (ethylene) from mixtures containing other saturates (ethane, methane).

(ii) Pretreatment; the pressure of the feed is raised to about 250 psi.

(iii) The carrier; aqueous solution of silver nitrate and glycerol, pH <5.

(iv) The membrane; hollow fibres made up from polymer mixture (60:40) formaldehyde alcohol modified 6:6 nylon and polyvinyl alcohol.

(v) The impregnation process; direct impregnation, no pressure used.

(vi) The stripping solvent downstream of membrane is n-hexane.

c) Indirect Application to Alkaline Earth Metal Ion Extraction (13)

(i) The process; extraction of alkaline earth metal ions (calcium) from aqueous mixtures containing Mg++ and other ions.

(ii) Pretreatment; the system is reacted with ethylene diamine-tetraacetic acid (EDTA) or ethylenebis(oxyethylene-nitrilo) tetraacetic acid (EGTA) at pH 6 to complex the Ca++ ions alone.

(iii) The membrane; asymetric cellulose acetate annealed at 85°C.

(iv) The ultrafiltration; continuous ultrafiltration loop at 200-300 psig. The Ca++ rejection is >95%.

(v) The recovery; changing the pH to reverse the reaction and free the complexing agent.

d) Indirect Application to Acetic Acid Extraction

(i) The process; extraction of acetic acid from waste water streams, which may or may not contain other contaminants.

(ii) Pretreatment; the system is reacted with di-tridecyl amine (Adogen 283-D) to complex acetic acid. Both the Adogen and its complex are water insoluble.

(iii) The membrane; polyamides and cellulose acetate membranes.

(iv) The ultrafiltration; continuous loop process at 100-300 psig. The acetic acid complex rejection is >98%.

(v) The recovery; by distillation.

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Recovery of valuable products from wastes
Session 13

Co-chairmen : G. Ritcey (CANMET, Ottawa, Canada)
J. Brach and M. Reginster (Sover S.A., Andrimont and Service de la Programmation Scientifique, Bruxelles, Belgium)

80-149	The recovery of molybdenum from spent mandrel acid by solvent extraction. D.S. Flett, J. Melling and D.W. West, Warren Spring Laboratory, Stevenage, U.K.
80-102	Controlled cycle liquid-liquid extraction of N-N dimethyl acetamide from aqueous solutions. W.M. Langdon, A. Bengali and G. Gavlin, Custom Organics Inc., Chicago, Illinois, U.S.A.
80-100	Industrial sludges processed by the use of solvents. J. Brach, J. Dewez and L. Rousseau, Laboratory CELAC, Chaineux, Belgium.
80-99	Solvent extraction of copper from smelter dust treatment liquors with Acorga P-5100. J.F. Spisak and R.J. McClincy, Federal-American Partners, Riverton, Wyoming and The Anaconda Copper Company, Denver, Colorado, U.S.A.
80-103	Recovery of mercury from wastes. J. Ortega and J. Gutiérrez, Junta de Energia Nuclear, Madrid, Spain.
80-157	Extraction from biological fluids. G.A. Yagodin, Yu. M. Lopukhin, E.V. Yurtov and V.I. Sergienko, Moskovskij Khimiko-Teckhnologicheskij Institut after D.I. Mendeleev, Moscow, U.S.S.R.

THE RECOVERY OF MOLYBDENUM FROM SPENT MANDREL ACID BY SOLVENT EXTRACTION

D.S. Flett, J. Melling and D.W. West

Warren Spring Laboratory

Stevenage, England

ABSTRACT

The treatment of spent mandrel acid has always presented problems to lamp manufacturing companies. The application of solvent extraction to this problem, with recovery of molybdenum from the spent acid and recycle of the acid raffinate solution, has been considered. The extractant chosen, di-2-ethylhexyl phosphoric acid (DEHPA) was shown to be stable in contact with the strongly oxidising spent acid. Isotherms have been developed which show that high molybdenum recovery should be achieved in about three countercurrent stages with the molybdenum being stripped from the loaded organic phase with alkali. Tungsten was coextracted with the molybdenum. Attempts to improve the purity of the molybdenum product by selective scrubbing/stripping were unsuccessful. However, the molybdenum product was upgraded in a further solvent extraction step in which hydrogen peroxide was added to the acidified strip liquor from which the molybdenum was selectively extracted from tungsten with TBP. An outline process flowsheet is proposed.

INTRODUCTION

In lamp manufacture, molybdenum is leached from a tungsten filament with a mandrel acid (50% HNO_3, 15-25% H_2SO_4). After leaching, the spent acid contains up to 120 gl^{-1} Mo and up to 1 gl^{-1} W at a total acidity of around 12N. In addition the spent acid contains some free oxides of nitrogen. The treatment of this spent mandrel acid has always presented problems to lamp manufacturing companies. The usual practice has been to treat the mandrel acid with lime and discharge the clarified liquor to sewer. This results in levels of sulphate and molybdenum, in the liquor discharged, above the new limits set by the Regional Water Authorities and in the loss of molybdenum and acid values. Each year, in excess of 15 tonnes of molybdenum are lost in this way within the United Kingdom. There is, therefore, an obvious need for a process which will recover the molybdenum and permit recycle of the nitric and sulphuric acids to mandrel dissolution. It is necessary, if revenue from the sale of the molybdenum product is to be maximised, that the Mo:W ratio in the product exceeds 5,000. The use of solvent extraction as part of such a process was considered attractive. Accordingly, testwork has been carried out which has provided the basis of a flowsheet for recovery of a high grade molybdenum oxide and recycle of the acid.

SOLVENT SELECTION

On acidification of the familiar oxy molybdenum VI anions (molybdates) with sulphuric or nitric acids, molybdenyl cations are formed. Isoelectric points in the pH range 0.8-2.0 have been reported for sulphate solutions (1). The major cationic species are MoO_2^{2+} and $Mo_2O_5^{2+}$, but more highly polymeric cations have been indicated. At 3 to 6 M H_2SO_4 equilibrium exists between the monomer MoO_2^{2+} and the dimer $Mo_2O_5^{2+}$.

Most of the published data on molybdenum extraction from highly acid solutions relates to the use of phosphorus-containing extractants. Phenolic oximes (2) and amines (3,4) have also been suggested but were considered unsuitable in the present application. Di-2-ethylhexylphosphoric acid has been used to extract molybdenum from strong nitric acid (5) and sulphuric acid solution (6,7). Within the range 0-12 M H_2SO_4, the greatest extraction was found from the strongest acid solution (7). Monoalkyl phosphoric acids have also been cited (5,8). Monohexadecyl phosphoric acid is the preferred reagent for solutions with an acid content of up to 10N H_2SO_4 or HNO_3 or a mixture of both (8). Tungsten is not extracted.

At intermediate concentrations of sulphuric acid, molybdenum is extracted by tributyl phosphate as a $MoO_2SO_4.2TBP$ complex (1). From the graphical data in the paper a distribution coefficient value of about 0.3 is indicated at $\sim$500 g l^{-1} H_2SO_4. As the sulphuric acid concentration increases to 7-8M a slight minimum occurs in the plot of the distribution coefficient versus sulphuric acid concentration which is attributed to the formation of anionic sulphate complexes $[MoO_2(SO_4)_2]^{2-}$. A sharp increase in the D value is obtained at sulphuric acid concentrations in excess of 9 M. The separation of molybdenum and iron by extraction using tributyl phosphate from nitric or sulphuric acid solution has been reported by Zelikman et al (9). In the presence of H_2O_2, optimum condition for molybdenum extraction from sulphuric acid solutions was given as 3-4N H_2SO_4.

Synergistic effects in molybdenum extraction are known to exist. Thus considerable enhancement in the extraction of molybdenum from sulphuric acid solution with DEHPA has been found (5) by addition of TBP or dibutyl butyl phosphonate (DBBP). It is claimed that by means of these mixed extractant systems, in particular DBBP + DEHPA, molybdenum can be extracted in quantitative amounts from solutions containing up to 600 g l^{-1} H_2SO_4. Urbanski et al (7) found that the extraction rate with DEHPA was enhanced by the addition of TBP.

The chemistry of tungsten is very similar to that of molybdenum and heteropolymolybdates containing tungsten are known in dilute acid solution (10). The tendency to form cationic species in acid solution is less marked than with molybdenum, and tungsten-containing cations are not well characterised. Very little information has been published on the extraction of tungsten from sulphuric or nitric acid solutions, but some tungsten is extracted (11) from strong sulphuric acid ($D \approx 0.15$) and strong nitric acid ($D \approx 0.03$) solutions with TBP.

From this survey, only acidic phosphorus-containing extractants, perhaps in combination with other extractants, emerge as potentially suitable reagents for molybdenum extraction from spent mandrel acid.

The only readily available acidic extractant of this type is di-2-ethylhexylphosphoric acid (DEHPA) and this was selected for this study alone and in combination with other extractants.

EXPERIMENTAL

The aqueous feed solutions used were samples of spent mandrel acids from production plants and are described in Table 1. Samples S and A were yellow in colour whilst samples B and C were deep red. Sample S contained 4.74M $SO_4^=$ and 7.0M NO_3^-. Sample A was obtained using a dissolving acid containing 7.9M HNO_3 and 4.7M H_2SO_4, whilst samples B and C were obtained using an acid containing 7.9M HNO_3 and 2.8M H_2SO_4. The as-received solutions contained considerable quantities of free nitrogen oxides, which were removed by air blowing before analysis and solvent extraction tests, to minimise the possibility of solvent oxidation. Diluents containing aromatic fractions discoloured in contact with the feed solutions and heptane was therefore used as diluent for the screening tests. This would not be suitable commercially and so before further tests the ability of a number of diluents to withstand attack from the feed liquor was ascertained, by stirring a sample with an equal volume of the feed liquor (sample S) for 24 hours. Odourless kerosene, MSB 210 (both Shell), Isopar M and Escaid 110 (Exxon) were all attacked by the acid with the liberation of nitrogen oxides. The final organic phase was pale yellow in colour. No reaction was observed in a comparable test with n-heptane, and since Escaid 110 and MSB 210 were known to have some aromatic content (1.0 and 2.5% respectively), the reaction was attributed to the nitraton of aromatic hydrocarbons. The organic phases were readily decolourised by treatment with silica gel and the treated diluents showed a much reduced reaction on further contact with the feed liquor. Treated Escaid 110 which showed no further reaction, was used in tests with sample S. In tests with samples A, B and C, Escaid 110 and Escaid 200 (Exxon) which is also low in aromatics, were used as-received without noticeable effect on the behaviour of the system. The extractants di-2-ethylhexylphosphoric acid - DEHPA, tributyl phosphate - TBP (both BDH Ltd), trioctyl phosphine oxide - TOPO (Eastman Kodak) and an alkane phosphonic acid ester of molecular weight 250 which corresponds to dibutylbutyl-phosphonate - PO 212 (Farbwerke Hoechst AG), were used as-received. The acidic feed liquors and organic phases were contacted in stirred baffled beakers (or separating funnels for the screening tests) for five minutes, except for tests in which the effect of contact time was examined and later tests on the selective recovery of molybdenum from strip solutions with TBP. All experiments were carried out at room temperature, with the exception of the alkaline stripping tests. Aqueous solutions were analysed for molybdenum and tungsten by atomic absorption spectrophotometry and X-ray fluorescence respectively. The accurate determination of low levels of tungsten in the presence of high levels of molybdenum proved difficult.

TABLE 1. Composition of Aqueous Feed Solutions

Sample	Mo, g l^{-1}	W, g l^{-1}	Total acidity, N
S	25.1	0.1	16.8
A	78	1.85	14.6
B	100	0.96	13.2
C	120	0.63	12.6

RESULTS

Screening Tests

Preliminary screening tests were carried out with sample S and organic phases containing 0.5M DEHPA, TBP, TOPO and PO 212 alone and in combination in heptane at an organic to aqueous ratio (O/A) of 1. With DEHPA, 77% of the molybdenum was extracted. This level was increased to 85% on the addition of TOPO but reduced to around 65% by the addition of TBP and PO 212. This reduction contradicts earlier results (5) showing a synergic effect on molybdenum extraction with DEHPA in the presence of TBP and dibutylbutylphosphonate. When DEHPA was absent no extraction occurred with TBP and PO 212 but some molybdenum was extracted with TOPO.

Development of Extraction Isotherms

In further tests with DEHPA and mixtures of DEHPA with TBP or TOPO, maximum extraction from sample S was obtained within 5 min with DEHPA and within 2 min with the mixed extractants. The extractant strength found in the screening tests, i.e. DEHPA + TOPO > DEHPA > DEHPA + TBP was confirmed. However, with TOPO the organic and aqueous phases after contact gave off nitrogen oxides on standing, suggesting that some oxidation process had taken place and so no further work was carried out with this mixed extractant. The extraction isotherms for sample S and both 0.5M DEHPA and 0.5M DEHPA + 0.5M TBP are shown in Fig. 1, and indicate that it should be possible to obtain a raffinate containing about 0.5 g l^{-1} Mo in three stages, using 0.5M DEHPA in countercurrent operation at an O/A of 1.0, but that more than three stages would be needed using the DEHPA/TBP mixture.

Further extraction isotherms were obtained for more concentrated solutions typical of current arisings (samples A, B and C). For these and subsequent tests the DEHPA concentration was increased to 1M (32 v/o). These isotherms are shown in Fig. 2 and indicate that it should be possible to achieve very low levels of Mo in the raffinate using three stages at an O/A of around 2. For one series of tests tungsten concentrations were also determined. The resultant tungsten isotherm is shown in Fig. 3. The full results for this series of tests are given in Table 2.

TABLE 2. Extraction Isotherm for Molybdenum and Tungsten Removal from Spent Acid by 1M DEHPA in Escaid 200

Initial aqueous phase: Sample C, Mo/W = 190

Phase ratio	Final metal ion distribution				Ratio
	aqueous phase		organic phase		Mo:W
$\frac{A}{O}$	Mo g l^{-1}	W g l^{-1}	Mo g l^{-1}	W g l^{-1}	in organic
0.125	0.8	<0.02	14.2	0.08	178
0.25	3.5	<0.02	28.8	0.14	206
0.5	22.6	0.03	49.6	0.28	177
1.0	62	0.10	60.0	0.52	115
2.0	86	0.26	60.8	0.64	95
4.0	105	0.45	61.5	0.63	98

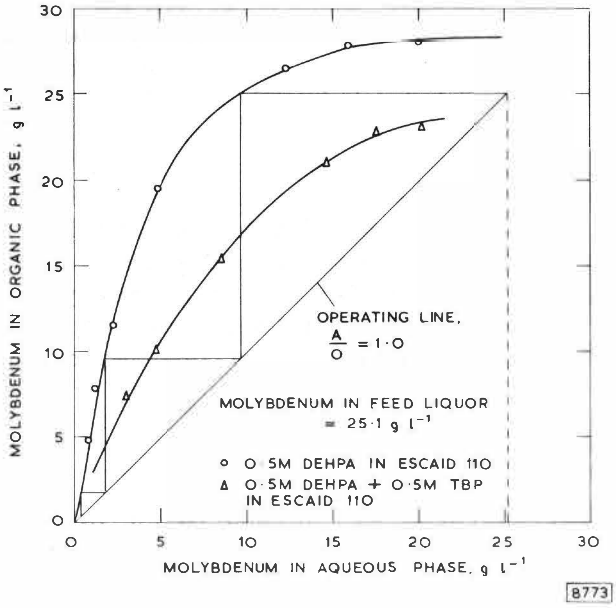

FIG. 1 EXTRACTION ISOTHERMS OF MOLYBDENUM FROM THE FEED LIQUOR USING DEHPA AND DEHPA + TBP

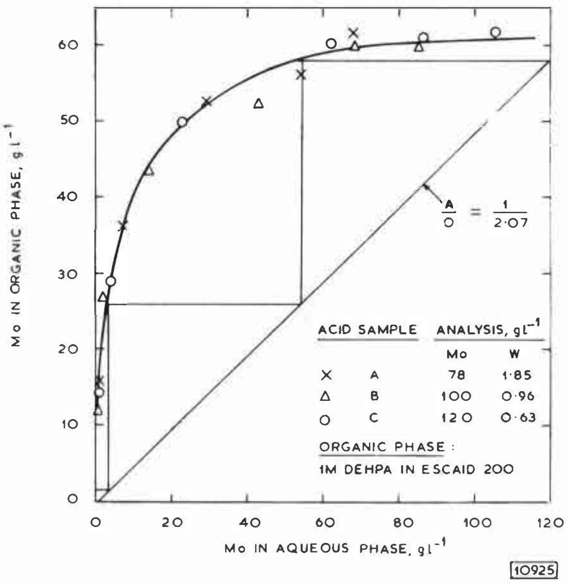

FIG. 2 EXTRACTION OF MOLYBDENUM FROM SPENT ACID BY DEHPA: EFFECT OF PHASE RATIO

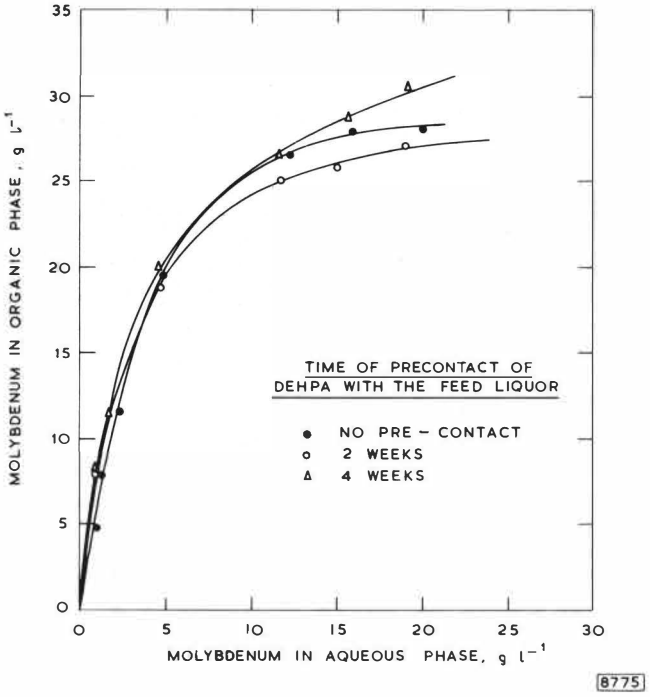

FIG. 4 EXTRACTION ISOTHERMS OF MOLYBDENUM EXTRACTION SOLVENT DEGRADATION STUDY

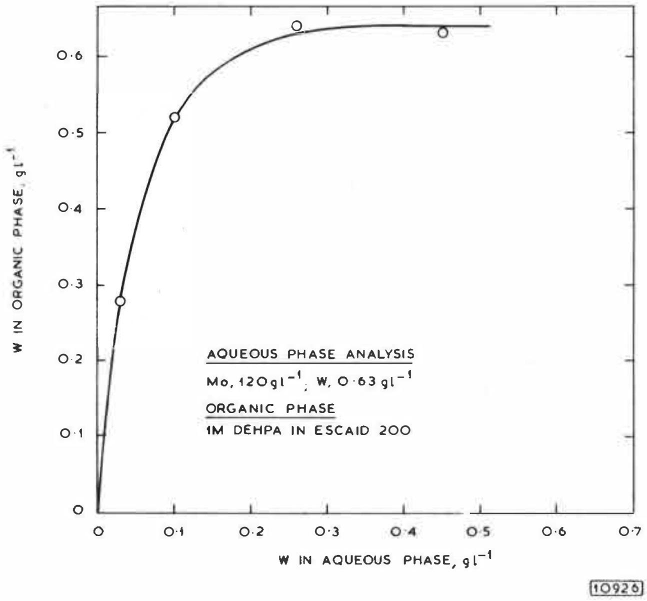

FIG. 3 EXTRACTION OF TUNGSTEN FROM SPENT ACID BY DEHPA: EFFECT OF PHASE RATIO

These results do not indicate any selectivity for molybdenum over tungsten and there is a suggestion that the solvent may be slightly selective for tungsten. The molybdenum loading from solutions A, B and C averaged 60.8 g l^{-1} Mo with 1M DEHPA, compared with an average loading of 28.3 g l^{-1} Mo from sample S using 0.5M DEHPA. These values can be explained by assuming a mixture of complexes of the type $(MoO_2)R_2$ and $(Mo_2O_5)R_2$ in the organic phase, in the ratio of 2.7 to 1 (1M DEHPA) or 4.6 to 1 (0.5M DEHPA).

Solvent Stability

It was important to establish that the DEHPA was sufficiently stable for continuous operation. This was done by determining the extraction isotherms shown in Fig. 4 with fresh solvent and with solvent previously contacted with the spent acid for up to four weeks. From these results it would seem unlikely that extractant stability would have a serious impact on process costs or operation.

Acid Scrubbing of Loaded Organic Phases

As no selectivity for molybdenum over tungsten was demonstrated in the extraction tests, attempts were made to produce a purer molybdenum solution by acid scrubbing. Selective scrubbing of tungsten into a weakly acid solution was expected because of the reduced tendency for tungsten to form cationic complexes. It was also considered that tungsten scrubbing might be further enhanced by addition of hydrogen peroxide to the scrub solution, since addition of hydrogen peroxide to weakly acid solutions containing molybdenum and tungsten has been shown (11,12,13) to allow selective extraction of molybdenum impurity from tungsten-containing solutions using TBP. This selectivity is obtained by the action of H_2O_2 in breaking up the heteropolymolybdates to give mono-nuclear metal complexes. The results of contacting loaded organic phases with acid at O/A of 1.0 are shown in Table 3.

TABLE 3. Removal of Molybdenum and Tungsten from Loaded Organic Phases (1M DEHPA) by Acid Scrubbing

Analysis of loaded organic phase solutions	Acid used in loading organic
I Mo, 59.5; W, 0.96 g l^{-1}; Mo/W, 62.0	B
II Mo, 59.4; W, 0.55 g l^{-1}; Mo/W, 108	C
III Mo, 60.0; W, 1.05 g l^{-1}; Mo/W, 57.1	A

Test No	Organic phase	Scrub solution	Final metal ion distribution				$\frac{Mo}{W}$ in scrub liquor	Metal removed %	
			aqueous		organic				
			Mo g l^{-1}	W g l^{-1}	Mo g l^{-1}	W g l^{-1}		Mo	W
13	I	H_2SO_4, 0.1N	11.6	0.1	49	0.78	116	19.7	10.4
14	"	" 1N	12.5	0.05	48	0.87	250	21.2	5.2
15	"	" 2N	19.3	0.06	42	0.92	322	32.7	6.3
16	"	" 4N	18.7	0.06	42	0.92	312	31.7	6.3
17	"	" 6N	17.9	0.07	39	0.91	256	30.3	7.3
18	"	" 8N	18.6	0.06	42	0.94	310	31.5	6.3
24	II	H_2SO_4, 0.1N + H_2O_2	17.0	0.08	42	0.47	213	28.6	14.5
7	III	HNO_3, 0.1N	6.1	0.09	53	0.89	68	10.2	8.6
25	II	HNO_3, 0.1N + H_2O_2	13.5	0.14	46	0.41	96	22.7	22.5

Contrary to expectations the molybdenum was scrubbed selectively, up to a third being recovered with 2-8 N H_2SO_4 to give a solution with a Mo:W ratio of about 300. Addition of hydrogen peroxide to 0.1N acid scrub solutions increased the amount of both molybdenum and tungsten scrubbed but appeared to have little effect on selectivity. The final organic phases in these tests were deep orange, suggesting a change in the molybdenum complex.

Based on the results of Fig. 1, it was thought that increased amounts of molybdenum would be scrubbed by acid if the solvent also contained TBP. Scrubbing of a loaded organic phase containing 1M TBP in addition to 1M DEHPA in Escaid 110 at an O/A of 1.0 was therefore examined, with the results given in Table 4.

TABLE 4. Removal of Molybdenum and Tungsten from Loaded Organic Phases Containing 1M DEHPA + 1M TBP by Acid Scrubbing

Organic phase: 48.7 g l^{-1} Mo, 0.46 g l^{-1} W, Mo:W = 106
Acid sample used in preparing solution: C

H_2SO_4 concn. N	Final metal distribution				$\frac{Mo}{W}$ in scrub liquor	Metal removed %	
	aqueous phase		organic phase				
	Mo g l^{-1}	W g l^{-1}	Mo g l^{-1}	W g l^{-1}		Mo	W
0.1	6.6	<0.01	42.1	>0.45	> 660	13.6	<2.2
1.0	11.0	<0.01	37.7	>0.45	>1,100	23.0	"
2.0	14.7	<0.01	34.0	>0.45	>1,470	30.2	"
4.0	20.4	0.01	28.3	0.45	2,040	41.9	2.2
6.0	18.0	0.01	30.7	0.45	1,800	37.0	2.2
0.1 +H_2O_2 (3%)	20.6	0.02	28.1	0.44	1,030	42.3	4.3

Very little tungsten was scrubbed and the scrub solutions showed a much higher Mo:W ratio than with DEHPA alone, but molybdenum recovery was not high. The low levels of tungsten scrubbed are surprising in view of the results of Chiola et al (14) who, using a solvent containing 23 v/o DEHPA and 6 v/o TBP in kerosene, found tungsten distribution coefficients from 0.01-0.05, compared to values for molybdenum close to 2 in the pH range 1-3. The addition of hydrogen peroxide to 0.1N H_2SO_4 increased the amount of both molybdenum and tungsten scrubbed. It is possible that these amounts could be increased still further at other values of acid and hydrogen peroxide concentration but this possibility was not investigated.

A comparison of these two series of tests shows that scrubbing of molybdenum was not markedly affected by the inclusion of TBP in the solvent but scrubbing of tungsten was considerably reduced and the scrub liquor produced was very much purer with respect to tungsten. In tests in which hydrogen peroxide was added to the strip solution, increased amounts of both molybdenum and tungsten reported in the strip liquor but no effect on selectivity was apparent.

Alkaline Stripping of Molybdenum from Loaded Organic Phases Containing DEHPA

In view of the failure to selectively acid scrub molybdenum or tungsten from DEHPA containing organic phases (Table 3) alkaline stripping was examined with a view to producing a pure molybdenum product from the resultant strip solution. A series of tests was carried out with mixtures of ammonia and ammonium sulphate to recover molybdenum from a 0.5M DEHPA solution in Escaid 110 at an O/A of 1.0 and a temperature of 40°C. A temperature above ambient was required as fairly stable emulsions formed at room temperature. A strip isotherm was developed using 3M NH_4OH + 1M $(NH_4)_2SO_4$ and the results are given in Table 5.

TABLE 5. Stripping of Molybdenum from a Loaded Organic Phase (0.5M DEHPA) by Ammoniacal Ammonium Sulphate Solutions: Effect of Phase Ratio

Concn of Mo in loaded organic phase = 24.5 g l^{-1}
Acid sample used in preparing organic phase: S

Test No	Stripping Agent	Phase Ratio, A/O		Final Distribution of Mo		Final pH of Aqueous Phase
		Initial	Final	Aqueous, g l^{-1}	Organic, g l^{-1}	
5	$(NH_4)_2SO_4$, 1M)	1.0	(0.79)	29.0	0.54	9.36
6	+NH_4OH, 3M)	0.5	(0.41)	58.0	0.06	8.63
7	"	0.33		71.3	0.39	6.05
8	"	0.25	(0.21)	93.0	0.83	4.32

Recovery of Molybdenum from Ammoniacal Strip Liquors

One method of producing a pure molybdenum product from the alkaline strip liquors could be through a further solvent extraction step utilising the method proposed by Zelikman et al (11,12,13) in which molybdenum is selectively extracted over tungsten with TBP, after addition to the solution of sufficient hydrogen peroxide to complex all the contained molybdenum and tungsten, and addition of nitric acid to adjust the pH to 0.4-0.9. This approach was adopted using a feed solution prepared by fully loading 1M DEHPA in Escaid 110 with Mo and W using sample C, stripping the loaded organic phase with ammoniacal NH_4NO_3, acidifying the strip solution with HNO_3, adding sufficient 100 volume hydrogen peroxide to convert all the contained Mo and W to their peroxide complexes (2 mol g atom^{-1} Mo + W), followed by further nitric acid until the solution pH value was 0.6.

An extraction isotherm for the removal of Mo from this solution by neat TBP using a contact time of 10 min is shown in Fig. 5. The results of these tests, which are also given in Table 6, show a very effective separation of

TABLE 6. Separation of Molybdenum and Tungsten by Solvent Extraction with TBP

Feed solution analysis: Mo, 55.0; W, 0.54 g l^{-1}

Test No	Phase ratio	Final metal ion distribution				$\frac{Mo}{W}$	Metal removed %	
		aqueous		organic				
	$^A/_O$	Mo g l^{-1}	W g l^{-1}	Mo g l^{-1}	W g l^{-1}	in organic	Mo	W
1	0.2	10.5	0.74	8.2	<0.01	> 820	74.5	
2	0.4	14.0	0.66	14.8	<0.01	>1,480	67.2	
3	1.0	24.5	0.60	25.8	0.01	2,580	46.9	1.9
4	2.5	40.0	0.53	33.2	<0.01	>3,320	20.5	

molybdenum from tungsten. Although, in the absence of data points at lower molybdenum concentrations, it is not possible to accurately determine stage requirements it should be possible to recover over 80 per cent of the molybdenum in the feed solution in three stages at an O/A of 1.33.

PRELIMINARY FLOWSHEET DEVELOPMENT

On the basis of the results obtained in this study a provisional process flowsheet can be proposed (Fig. 6). While the separation of molybdenum from tungsten requires optimisation and further work is necessary to provide a satisfactory means of tungsten recovery, there is little doubt that technically the process as proposed would work. Molybdenum can be readily recovered from the strip liquor as an ammonium molybdate compound. No economic data are available at present. The flowsheet would be much improved if a solvent system was found that permitted selective scrubbing of the tungsten from the loaded organic phase, thus avoiding the two-step solvent extraction flowsheet presented here.

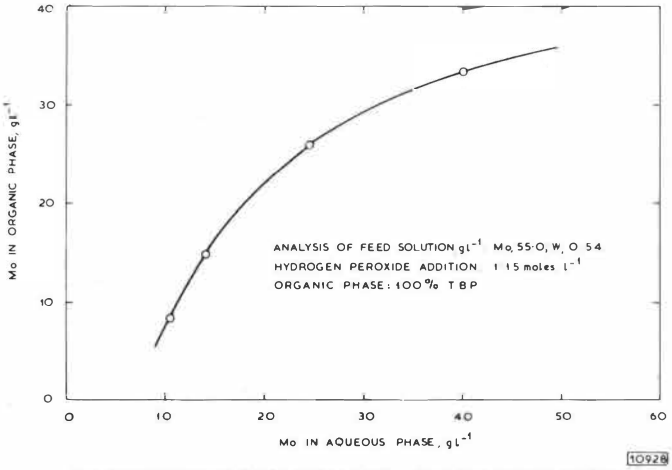

FIG.5 EXTRACTION OF MOLYBDENUM FROM A MIXED MOLYBDENUM, TUNGSTEN SOLUTION BY TBP

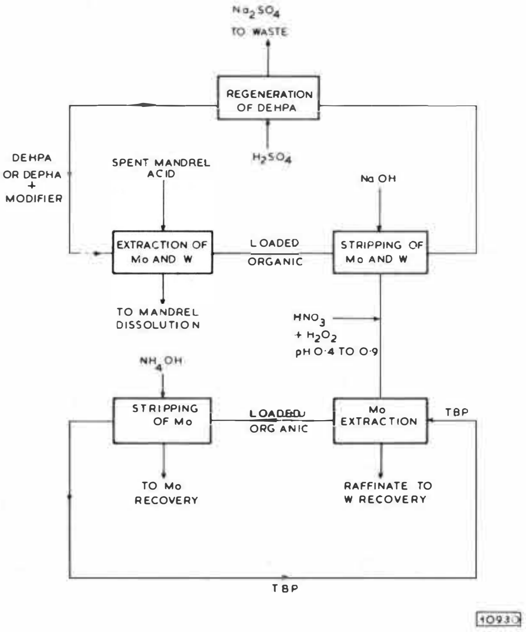

FIG.6 FLOWSHEET FOR RECOVERY OF MOLYBDENUM FROM SPENT MANDREL ACID

CONCLUSIONS

DEHPA is an effective extractant for the recovery of molybdenum directly from spent mandrel acid, thus permitting recycle of the molybdenum-free acid. Addition of TOPO and TBP to the solvent showed that molybdenum extraction decreased in the order DEHPA + TOPO > DEHPA > DEHPA + TBP. Although molybdenum extraction was faster in the presence of TOPO or TBP, the TOPO-containing organic phase appeared to be unstable in contact with the acid. The stability of DEHPA was demonstrated. Tungsten was extracted with the molybdenum and attempts to improve the molybdenum product purity by selective scrubbing were unsuccessful. A considerable improvement in product purity was effected by alkaline stripping of the loaded DEHPA phase followed by selective extraction of molybdenum from the acidified strip solution to which hydrogen peroxide was added using TBP. The process flowsheet shown in Fig. 6 is suggested as the basis for further development.

An alternative approach might be to use a solvent containing DEHPA and TBP for extraction of molybdenum from the spent mandrel acid followed by selective acid stripping of the molybdenum.

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CONTROLLED CYCLE LIQUID-LIQUID EXTRACTION OF N-N DIMETHYL ACETAMIDE FROM AQUEOUS SOLUTIONS

W.M.Langdon,Abid Bengali,and Gilbert Gavlin

Custom Organics Inc.
1445 W. 42nd Street
Chicago, Illinois 60609

ABSTRACT:

The controlled cycle, liquid-liquid extraction process (1,3) has been evaluated in recovering dimethyl acetamide (DMAC) from aqueoue potassium acetate solutions using methylene chloride as the extractant. At actual to minimum extractant to raffinate ratios of 1.7 and 1.8, the number of overall raffinate transfer units were 6.4 and 9.7. The overall extraction process will recover over 95 percent of the entering DMAC compared to 90 percent for the current distillation process, will reduce the energy requirements by one fourth, and the processing time by one-half.

INTRODUCTION

Controlled cycle extraction allows the raffinate and extractant phases to flow alternately in opposite directions through a series of contactors with a settling period in between. The complete cycle is usually 1 minute with any part adjustable from zero to ½ minutes. The extractor used in this investigation (Fig. 1) consisted of 5 contactors, each 6 in I.D. and packed with 4 ft of ½ in Intalox saddles. The contactors are set side by side and piped in series, i.e. top of one to bottom of next. The heavy phase is introduced at one end of the train of contactors and is sparged successively into the top of each contactor. The light phase is introduced at the other end and sparged successively into the bottom of each contactor. Gravity decantors are placed at both ends of the train to return any carryover of the opposite phase before removing the net raffinate or extract product streams.

The flow of the phases during this controlled cycle extraction differs from steady state, counter current, extraction. In the latter, the volumes of light and heavy phase vary continuously along the extractor. In the former the net light and heavy phase varies stepwise along the train. However, the total volume of liquid in each cycle to every contactor must be constant. The decrease or increase in a particular phase is compensated by the recycling of the other phase. In this investigation the removal of 45 and 29.5 percent DMAC results in a light product to light feed volume ratio of 0.52 and 0.68, respectively.

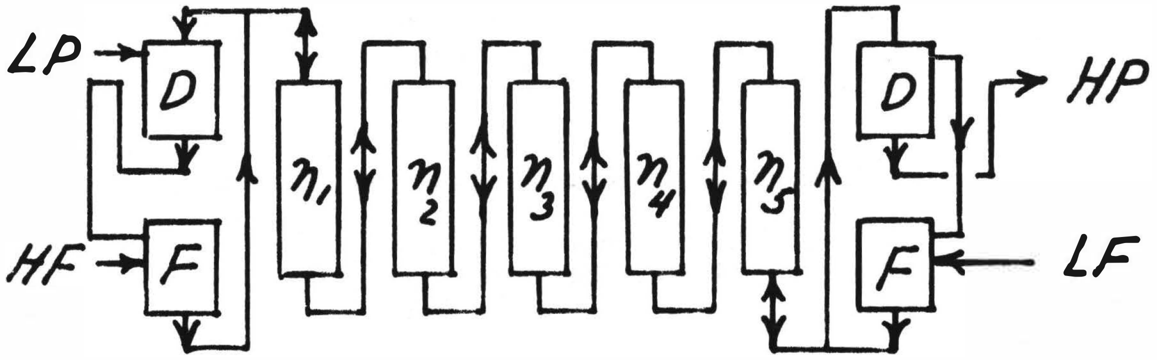

FIG. 1

CONTROLLED CYCLE EXTRACTOR

Current recovery practice involving distillation requires six steps with an overall energy requirement of 1.4 pounds of steam per pound of DMAC product. Extraction with methylene chloride requires only 3 steps and an energy requirement under 1.1 pounds of steam per pound of DMAC product. The current overall DMAC loss of 10 percent should be reduced several fold.

EXPERIMENTAL

The feed streams (Table 1) were 45 and 29.5 weight percent aqueous waste material neutralized with potassium hydroxide. The raffinate phase in all cases contained ∽17 weight percent potassium acetate. Two runs, A at 25-28°C and B at 12-16°C, were made with light feed rates of 33 and 24 gph. Extractant to raffinate (E/R) weight ratios were 2.5 and 2.1. The ratio of the actual to the minimum E/R were 1.7 and 1.8, respectively. The calculated recoveries of DMAC for the extraction step were 99.6 and 99.8, respectively.

Equilibrium relationships, $(y/x)^*$, (Table 2) were evaluated at 25°C and 15°C. Using linear regression by least squares, $(y/x)^*$ was equal to 1.66-0.0224x and 1.19-0.0117x for runs A and B, respectively. The standard deviations were 17.9 and 8.8, respectively.

TABLE 1
OVERALL RUN DATA

	gph	ρ	lb/hr	R or E	x or y	X or Y	D
Run A (25-28°C)							
1. LF	33	1.026	282	155.1	45.0	81.8	126.9
2. HP	(67)	1.20	(669)	(543)	(18.9)	(23.3)	(126.4
3. LP	(17.1)	1.09	(155.6)	(155.2)	0.35	0.35	0.5
4. HF	49.4	1.32	543	543	0		0
5. E/R							

a) min+(o.45/0.55-0.0035)/(0.395① -0)=2.1
b) act/min=3.5/2.1=1.7

TABLE 1 (CONT.)

Run B (12-16°C)

1. LF	24	1.06	212	149.5	29.5	41.8	62.4
2. HP	36	1.27	382	320	16.2	41.8	62.2
3. LP	(16.4)	1.09	(149.5)	(149.3)	0.12	0.12	0.24
4. HF	29	1.32	320	320			
5. E/R							

a) min=(0.295/0.705-0.0012)/(0.336① -0)=1.2

b) act/min=2.16/1.2=1.8

① Y^*_{LF} See Table 3 and 5.

TABLE 2
EQUILIBRIUM DATA

x	$(y/x)^*_{xp}$	$(y/x)^*_{calc}$ ②	Dev	x	$(y/x)^*_{xp}$	$(y/x)^*_{calc}$ ②	Dev
←	25°C		→	←	15°C		→
0.23	(3.2)	1.66	(92)	1.4	1.28	1.17	-3.3
0.34	2.0	1.66	20.8	6.4	1.08	1.12	-10.7
0.51	1.8	1.65	9.0	7.1	0.99	1.11	5.2
3.5	1.1	1.58	-30.6	18.2	1.03	0.98	8.9
18.8	1.25	1.24	0.6			sd =	8.8
20.1	1.13	1.21	-6.9				
25.0	1.0	1.10	-9.4				
32.8	1.1	0.93	18.4				
		sd =	17.9				

② Linear regression by least squares:

a) 25°C $(y/x)^* = 1.66-0.0224x$

b) 15°C $(y/x)^* = 1.19-0.0117x$

RESULTS AND DISCUSSION

The number of theoretical stages were determined to be 3.1 (Table 3) and 5.8 (Table 5) for runs A and B, respectively. Run B gave HETS varying from 6.6 ft (n_1) to 2.1 ft (n_5). Breuer (1) reported that this equipment gave 1.2 to 2.4 stages per contactor, the experimental conditions not being specified.

The number of transfer units were 6.4 (Table 4) and 9.7 (Table 6) for runs A and B, respectively. The more complete data for run B shows that the number of transfer units per contactor increases with the driving force. Contactor n_1 with ΔX_{lm} of 0.16 has 1.06 N and contactor n_5 with ΔX_{lm} of 12 has 2.77N. There is no obvious explanation for the difference in transfer units for runs A and B.

The optimum E/R ratio was not determined. The actual to minimum E/R of 1.7 and 1.8 giving recoveries of 99.6 and 99.8 for runs A and B, respectively indicate that appreciably lower heavy feed rates could be employed. The minimum heavy feed rate is limited not only by equilibrium relationships, but also the density decrease which in turn affects the separation velocity of the phases.

The flooding point, where phase separation limits the throughput, was not determined. However, tests on a similar system indicate that rates of 75 and 150 gph for light and heavy feed can be achieved in this unit.

TABLE 3
THEORETICAL STAGES
(Run A, 25-28^{0}C)

n	③ x_n	$(y/x)^*_n$	y^*_n	Y^*_n	X^{op}_{n+1}	x^{op}_{n+1}	TS
1	0.35	1.66	0.58	0.58	2.38	2.32	1
2	2.32	1.62	3.76	3.91	14.0	12.3	2
3	12.3	1.40	17.2	20.8	73.2	42.3	3
4	42.3	0.76	32.1	47.3	165.9	62.4	3.1
5	45.0	0.63	28.3	39.5			

③ x_n for n = 1 + 5 are experimental and n = 2, 3 and 4 are obtained by stage to stage calculations.

TABLE 4
OVERALL RAFFINATE TRANSFER UNITS
(Run A, 25-28^{0}C)

n	④ x_n	y_{n-1}	$(y/x)^*_{n-1}$	x^*_{n-1}	X_n	X^*_{n-1}	ΔX
1	0.35	0		0	0.35	0	0.35
2'	(1.40)	(0.30)	(1.66)	(0.18)	1.42	0.18	1.24
3'	(5.60)	(1.56)	(1.64)	(0.96)	5.93	0.97	4.96
4'	(22.4)	(7.54)	(1.55)	(4.86)	28.9	(5.11)	23.8
6	45.0	18.9	1.35	14.0	81.8	16.3	65.5

n/n-1	dX	$(\Delta X)_{lm}$	$\int$
1/2'	1.07	0.70	1.5
2'/3'	4.51	2.68	1.7
3'/4'	23.0	12.0	1.9
4'/6	52.9	41.2	1.3

Σ N = 6.4

④ Values with prime are arbitrarily chosen as 4x preceding. Integrating with smaller intervals (i.e. more steps) yields the same result.

TABLE 5
INDIVIDUAL STAGE EFFICIENCY
(Run B, 12-16^{o}C)

n	x_n	$(y/x)^*_n$	y^*_n	Y^*_n	X^{op}_{n+1}	x^{op}_{n+1}	Eff
1	0.12	1.19	0.14	0.14	0.42	0.42	61
2	0.29	1.19	0.35	0.35	0.86	0.85	93
3	0.81	1.18	0.96	0.97	2.20	2.15	100
	(2.15)	1.16	2.49	2.55	5.61	5.31	10
4	2.5	1.16	2.90	2.99	6.58	6.17	100
	(6.17	1.12	6.91	7.42	16.1	13.9	22
5	7.9	1.10	8.69	9.52	20.7	17.2	100
	(17.2)	0.99	17.0	20.5	44.4	30.7	91
6	29.5	0.85	25.1	33.6			
						Σ =	580

TABLE 6
OVERALL RAFFINATE TRANSFER UNITS
(Run B, 12-16^{o}C)

n	x_n	y_{n-1}	$(y/x)^*_{n-1}$	x^*_{n-1}	X_n	X^*_{n-1}	ΔX
1	0.12	0	1.19	0	0.12	0	0.12
2	0.29	0.10	1.19	0.08	0.29	0.08	0.21
3	0.81	0.50	1.19	0.42	0.82	0.42	0.40
4	2.5	1.20	1.18	1.02	2.6	1.03	1.57
5	7.9	3.6	1.15	3.13	8.6	3.23	5.37
6	29.5	16.2	1.00	16.2	41.8	19.3	22.5

n/n-1	dX	ΔX_{lm}	$\int$
1/2	0.17	0.16	1.06
2/3	0.53	0.29	1.83
3/4	1.78	0.86	2.07
4/5	6.0	3.09	1.94
5/6	33.2	12.0	2.77
		Σ	9.7

NOMENCLATURE

act	Actual.
A	Run at 25-28^{o}C.
B	Run at 12-16^{o}C.
calc	Values calculated from straight line equation, $(y/x)^*$ vs x.
D	Decantor.
Dev	Percent deviation, $100 \left[(y/x)^*_{xp}-(y/x)^*_{calc}\right] /(y/x)^*_{calc}$.
DMAC	Dimethyl Acetamide, lb/hr.
E	Extractant (heavy) phase, DMAC free basis, lb/hr.
Eff	Individual stage efficiency, $100(x_{n+1}-x_n)/(x^{op}_{n+1}-x_n)$.
E/R	Extractant/Raffinate weight ratio, DMAC free basis.

	a) $(E/R)_{min}=(X_{LF}-X_{LP})/(Y^{*}_{LF}-Y_{HF})$, 2.1 and 1.2 for run A and B, respectively.
	b) $(E/R)_{act}=(dX_{n+1})/(dY_n)$, 3.50 and 2.16 for runs A and B, respectively.
F	Feed.
gph	Gallons per hour.
HETS	Height equivalent to a theoretical stage.
HF,HP	Heavy feed and product, respectively.
LF,LP	Light idem.
lm	Log mean average.
min	Minimum.
n	Number designation of the contactor, n_1 being that where HF was introduced.
N	Number of overall raffinate transfer units.
	a) $N=N_{tOR}=\int_{X_{n-1}}^{X_n}\frac{dX}{X_n-X^{*}_{n-1}}+\frac{1}{2}\ln\frac{(100+rX_{n-1})}{(100+rX_n)}$ from Treybal (2). The ½ln term is negligible and will be neglected.
op	A change in composition calculated for 1 theoretical stage.
P	Product.
r	Molecular weight ratio of nonsolute to solute, ∽18/87 = ∽0.21.
R	Raffinate (light) phase, DMAC free basis, contains ∽17 weight percent potassium acetate, lb/hr.
sd	Standard deviation.
TS	Theoretical stage.
xp	By experimental measurement.
x,y	Weight percent DMAC in light and heavy phase, respectively.
	a) x^{op}_{n+1} is calculated composition for 1 theoretical stage past x_n.
X,Y	One hundred times the weight ratio of DMAC to R and E, respectively.
	a) X^{op}_{n+1} equals $0.35 + 3.50Y_n$ and $0.12 + 2.16Y_n$ for runs A and B, respectively.
	b) X^{op}_{n+1} is calculated composition for 1 theoretical stage past X_n.
$(y/x)^*$	Equilibrium weight ratio of y_n to x_n.
	a) $(y/x)^{*}_{n}$ equals $1.66-0.0224x_n$ and $1.19-0.0117x_n$ for runs A and B, respectively.
$\int$	First term of N, $\int dX/(X_n=X_{n-1})$, and considered equal to N.
( )	In Tables 1 and 4, quantities calculated by material balance; in Table 2, quantities not considered.
ρ	Density at 25°C, g/cc
Σ	Summation of quantities.

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INDUSTRIAL SLUDGES PROCESSED BY THE USE OF SOLVENTS [*]

J. BRACH, J. DEWEZ, L. ROUSSEAU

Laboratory CELAC

Chaineux, BELGIUM

ABSTRACT

The processing of liquid-liquid extraction is applied to the treatment of sludges coming from industrial purification installation.

The purpose is to decontaminate the effluents by enhancing the value of the extracted components. Two kinds of sludges have been studied : the sludge of a wool scouring plant containing grease and the sludge containing metals. It has been proved that selective extraction with solvents offers a possibility of recuperating by-products which can either be enhanced in value or be recycled.

1. INTRODUCTION

In response to the demand of the "Programmation Scientifique Belge", our laboratory has been entrusted with the task of trying to valorize the sludges caused by industries or resulting from the purification of effluents of certain industries.

This research work purposes to make use of extraction technics liquid to liquid for the treatment of this kind of sludge with a view to decontaminate it and at the same time valorize one or several of its components.

We have examined different types of sludges and more specially sludges emanating from woolscouring and sludges containing metals.

2. WOOLSCOURING SLUDGES TREATMENT

2.1 INTRODUCTION

Wool in the grease contains a considerable amount of impurities which have to be eliminated by scouring.

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[*] Research made for the "Programmation de la Politique Scientifique Belge", within the framework of the National R-D Program.

The impurities to be considered for our study are the following :

- soluble suint, consisting chiefly of potassic salts of fatty acids,
- wool grease, emanating from the secretion of sebaceous glands,
- sand and soil, carried by the fleece of the sheep.

All sorts of purification technics have been tried in order to clean the wool scouring effluents : evaporation, ultrafiltration, acid cracking, floculation, flotation. All methods produce sludge in large quantities. The average weight of the sludge, which by the way contains 50 % of water, is equal to 50 % of the washed wool. The composition of these sludges is variable but the amount of wool grease they contain is always relatively high (30-50 % (w/w) of wool grease in relation to dry weight). Its recuperation by solvent extraction allows a valorization of a valuable by-product and the collection of a residue, which may be used as a fertilizer.

2.2 INFLUENCE OF THE EXTRACTION PARAMETERS ON THE DECANTABILITY

We have studied the parameters which influence the extraction of the grease with hexane, starting with sludges prepared by different methods. It appeared quickly that the structure of the sludge and the presence of detergents caused an important retention of hexane. In order to obtain a rapid decantation, we had to use a ratio of 5 to 1 : hexane/sludge. (fig. 1)

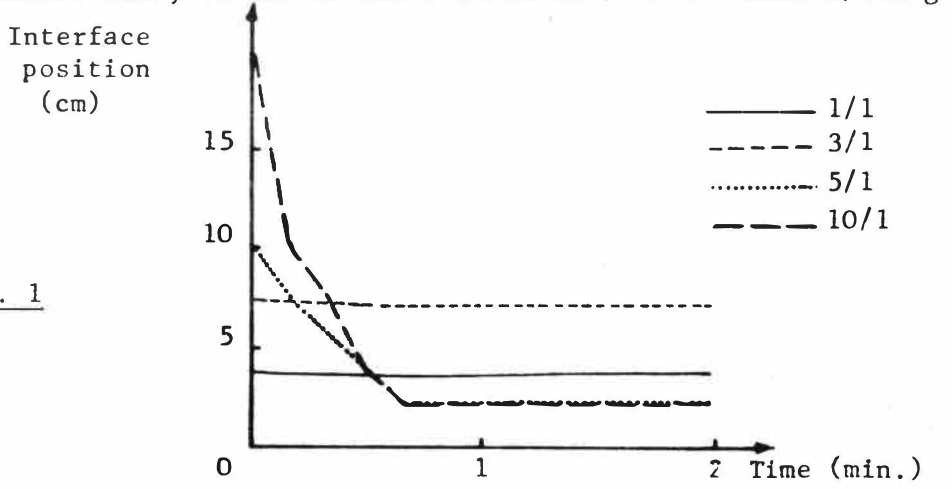


FIG. 1

The influence of the pH is equally preponderant, as may be seen by the decantation chart. (fig. 2)

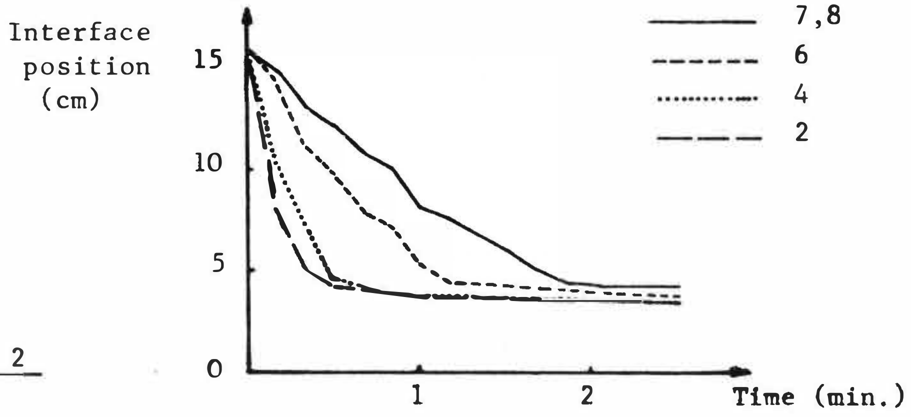


FIG. 2

2.3 INFLUENCE OF THE NUMBER OF EXTRACTION STAGES

Simulating in laboratory the industrial process, it is possible to draw extraction charts of the grease relating to the number of extractions as well as to the concentration of the "miscellas" at the different stages (fig. 3). The treatment based on the principle "mixer-settler" gives sometimes rise to certain inconveniences (the coming up again of the sludges through the effect of counter currents due to the pump, big quantities of hexan to be used, which entail a weak concentration of the "miscella".

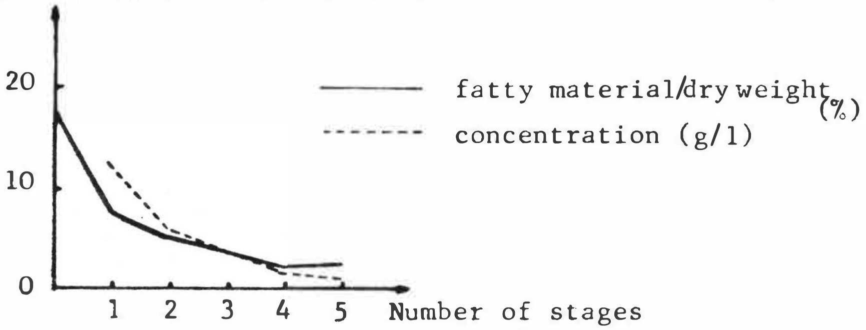
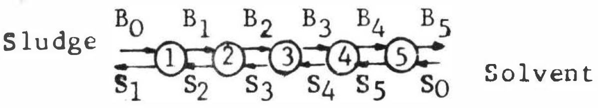


FIG. 3



2.4 SETTING UP OF A LIQUID-LIQUID EXTRACTOR FOR THE TREATMENT OF SLUDGES

We had therefore to construct an extractor in which a fine layer of sludge would be in contact with a large volume of hexane. This apparatus is constitued in the main by disks mounted on a shaft rotating slowly; the disks carry the sludge into the solvent phase. The extractor is divided in compartments to allow a systematic extraction with multiple actions and backflow of grease.

2.5 DRAWING UP OF THE EXTRACTION CHART RELATING TO THE NUMBER OF EFFECTS

The influence of various factors (rotation speed, number of effects, number of disks per effect) on the degreasing of the sludge has consequently been tested so that an appropriate extraction process regarding the various types of sludges, could be set up (fig. 4).

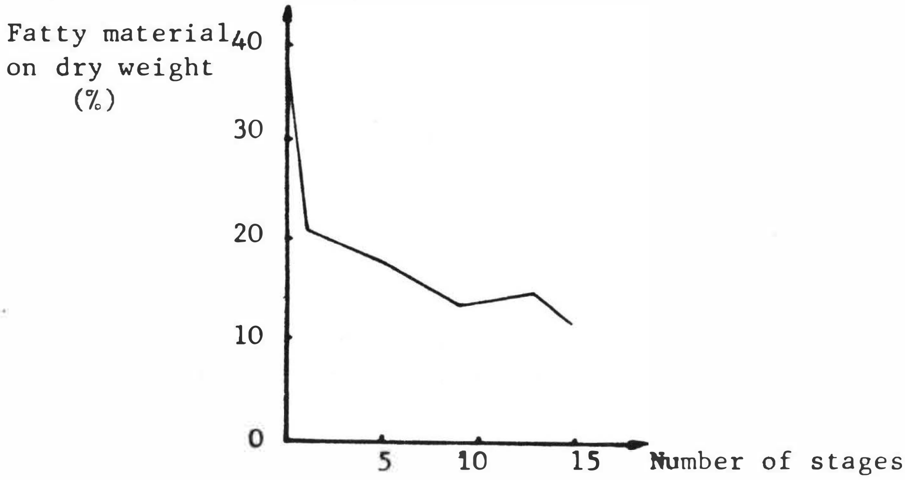


FIG. 4

2.6 VALORIZATION OF THE BY-PRODUCTS

The subsequent distillation of this solvent extract allows of course the recuperation of the crude grease, however it is advisable to proceed beforehand with the neutralization and bleaching of the grease if one desires to transform it into a valuable lanoline.
The sludge resulting from decantation has to be freed of solvent and dried either by atomising or by drying on heated drums. The resultant product may be used as a base for fertilizers as it contains : 2 to 4 % nitrogen, 4 to 6 % phosphate, 8 to 12 % potash. The flow-sheet of fig. 5 shows a complete installation. This procedure can consequently be considered as a complete valorizetion of the by-product.

2.7 FLOW SHEET OF AN EXTRACTION UNIT

After a preliminary concentration for the purpose of having a quantity of 25-30 % M.S., the sludges are prepared in a reactor. The preparatory work purposes to adjust the pH value to about 3 and to incorporate 5-10 % hexan. The so prepared sludges are degreased by a continuous back-flow in a liquid-liquid disk extractor. Coming out of the extractor the hexan is directed to a distillation plant or to a grease refining unit. The hexan is eliminated from the degreased sludges and the suint will eventually be dried. (fig.5)

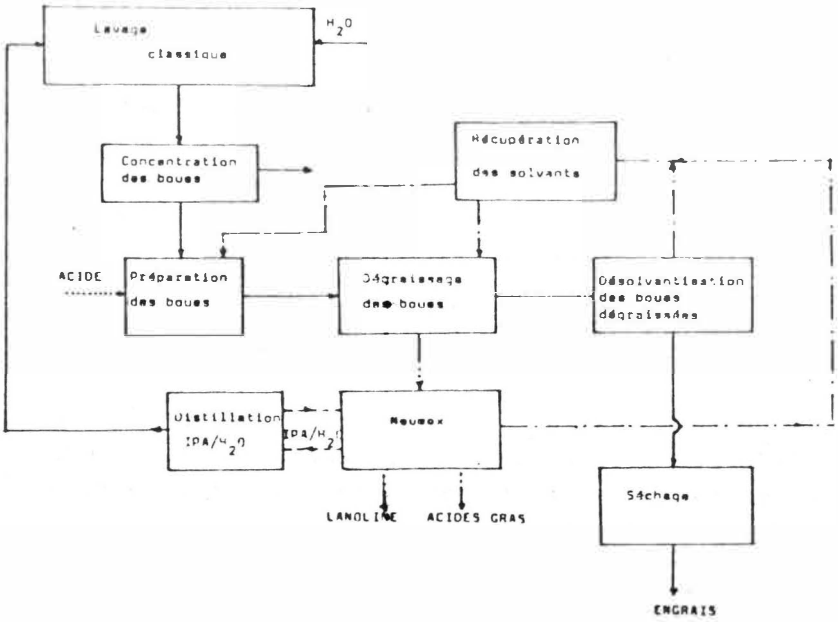


FIG. 5

2.8 STUDY OF THE ECONOMY OF THE PROCESS (fig. 6)

An economy calculation of the treatment which has been carried out is represented schematically for two sludges which originate from two different systems of purification.

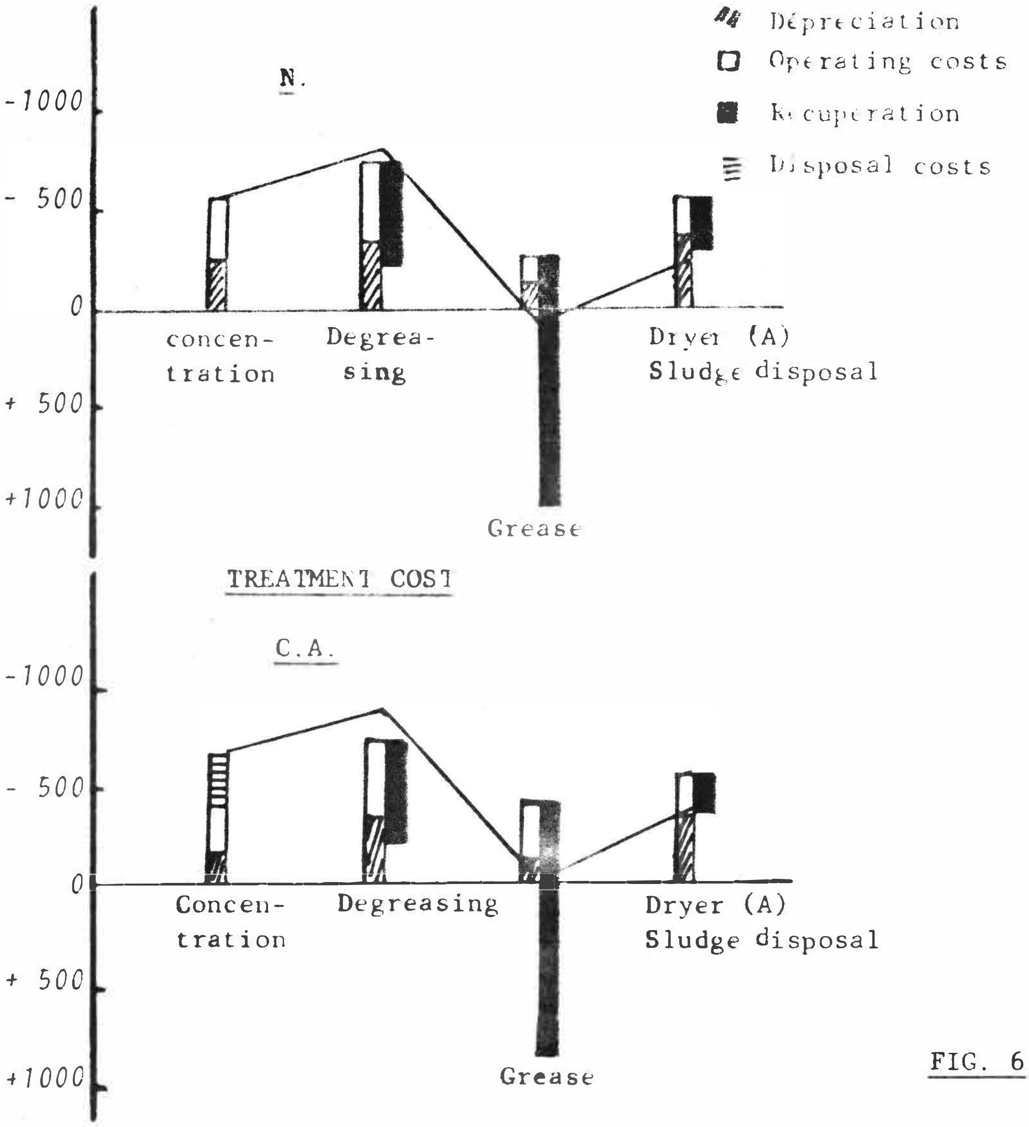


FIG. 6

The case of the wool scouring sludge is typical. It confirms the fact that it is advisable to treat industrial effluents separately (and not to mix them in a sewer) and to have in this way the possibility of valorizing its constitutive elements.

3. TREATMENT OF SLUDGES CONTAINING METALS

3.1 COMPOSITION OF THE SLUDGES

The first tests have been carried out on a sludge with a high degree of copper. The rinsing waters issuing from a continuous copperplating unit working on the principle of electrolisis are treated with a solution of caustic soda. After decantation the sludges are passed through a filterpress. The resultant cake has the following mean composition :

% M.S. (at 105°C)	22
% Ashes (at 600°C)	71,4
% Cu	34,6

% Ni (in relation to dry weight)	3,3
% Ca	11,7
% Fe	0,25
% Co	0,01
% Al	0,1
% Na	0,2

3.2

The leaching have been done by an acid attack (H_2SO_4). The resulting solutions have been treated with a specific extractant (LIX 64N) in order to recuperate copper by liquid-liquid extraction.

3.3 DETERMINATION OF THE ISOTHERMS OF EXTRACTION

Starting from the solution B (100 g of sludge + 1 litre H_2SO_4 22 g/l), The equilibrium curves have been determined experimentally : concentration in aqueous phase, concentration in organic phase for 2 percentages in LIX in 10-20 % kerosen. The aqueous solutions are put in contact with the organic solutions (10-20 %) varying the volumetric ratios of the phases. The results are to be found in fig. 7 and 8.

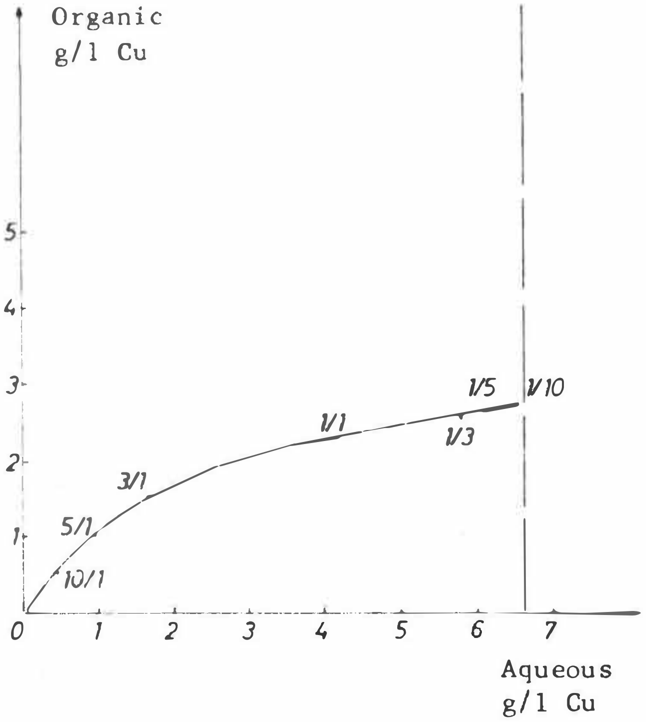


FIG. 7

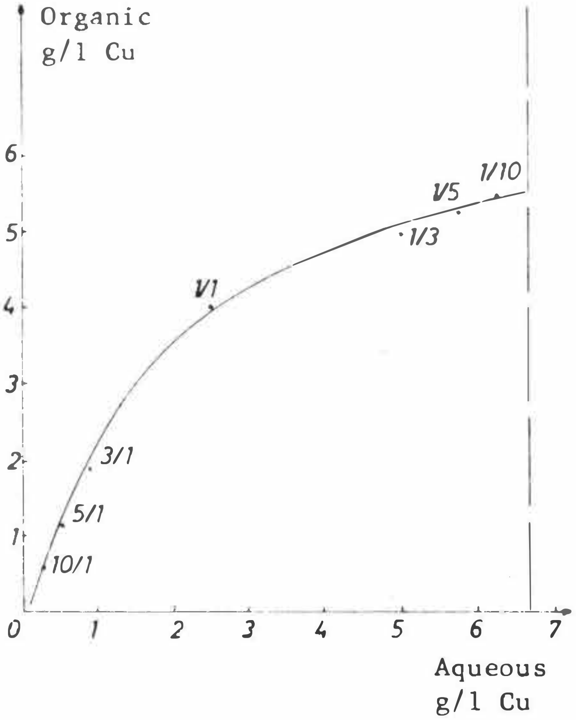


FIG. 8

On the basis of the equilibrium curves which have been obtained experimentally the theoretical number of stages has been calculated. Starting with a solution of a concentration of 6,6 g/l in copper and being admitted that the organic phase will be charged at 80-90 % of its maximum capacity and pushing the treatment in order to recuperate 95 %, it can be demonstrated that with a ratio of phase

$$\frac{FO}{FA} = \frac{3}{1} \text{ for LIX 10 \% and } \frac{FO}{FA} = \frac{1,25}{1} \text{ for LIX 20 \%}$$

the number of theoretical stages is 3 in the case of LIX 10 % and 4 in the case of LIX 20 % (See fig. 9 and 10).

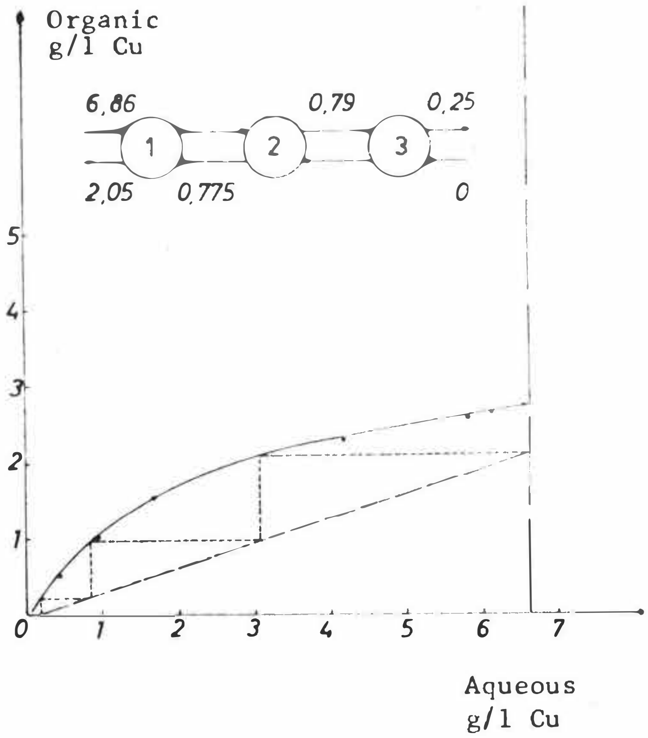


FIG. 9

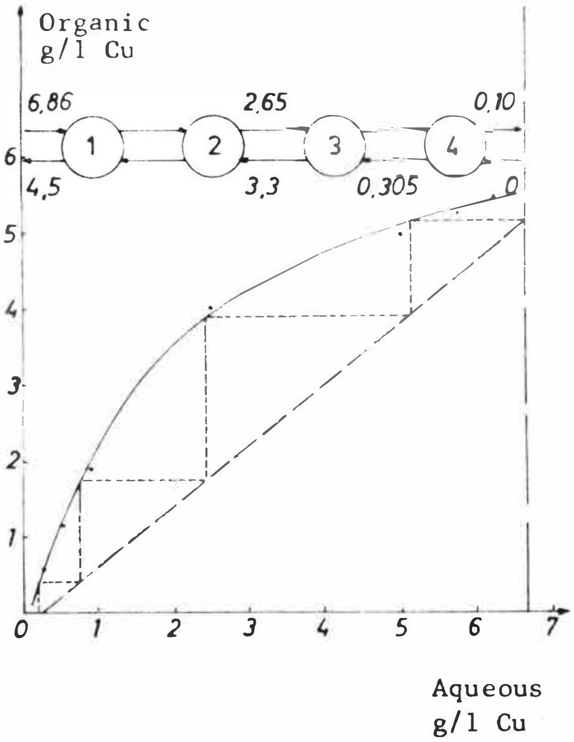


FIG. 10

Taking in account these results, continuous extractions with backflow have been simulated in separatory tunnels. These results which have been obtained confirm very well the theory.

3.4 STRIPPING

There has been a stripping with a solution of H_2SO_4 at 150 g/l (fig. 11 and 12).

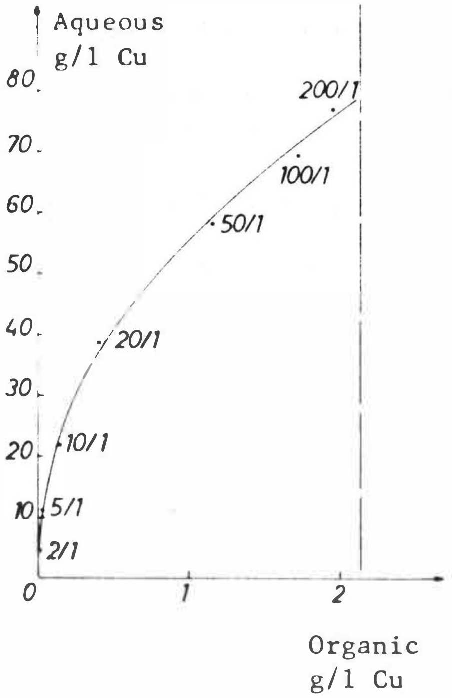


FIG. 11

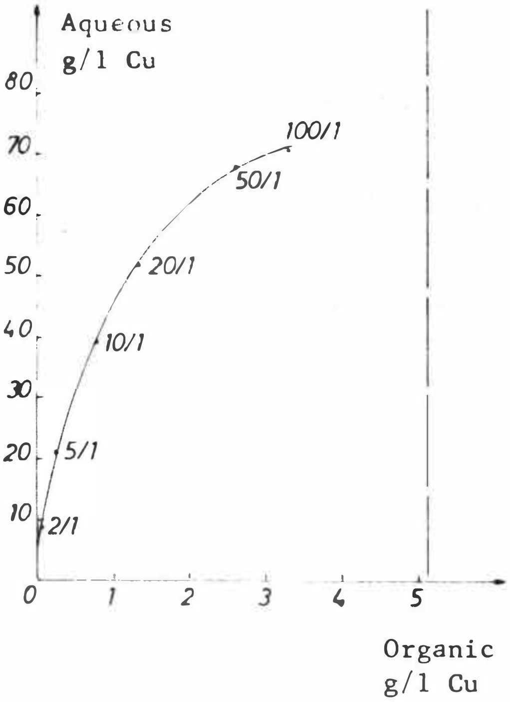


FIG. 12

4. CONCLUSIONS

The trials carried out on two types of different sludges have proved that the proceeding liquid-liquid extraction is likely to give a reliable solution for the valorisation of sludges.

The extraction of compounds enhanced in value by means of selective solvents gives the possibility of solving the problems : wastes free from contaminating residues and recycling one or more constitutive elements of the sludge.

The treatment of sludges containing fatty matter with hexan allows the spreading of the residue on the fields after having recuperated grease and oil. It is however necessary to use caution when it is desirable to avoid the retention of solvent in the sludge. The contact of the solvent with the sludge should be made progressively in order to facilitate the separation of the two phases.

The technic applied to the treatment of sludges coming from woolscouring plants has given very good results in laboratory. Extrapolating them, it has been demonstrated that the recuperation would yield a profit especially by valorizing the wool grease, that is to say the lanoline.

However these results should be confirmed by the setting up of a pilot plant, which could treat continuously the effluents of a Leviathan washer. Extrapolations as regards financial results are always risky and it appears indispensable to start with a pilot plant before committing oneself to definite conclusions.

Due to a lack of time it has not been possible to go as far with the problem of extraction of metals as with grease. Results obtained in the laboratory confirm the possibility of using this process in industry. The chief problem resides in the adaptation of a convenient technic for each type of sludge. The method appears to be satisfactory especially when the quantities are important and when the extractable products are easily valorizable.

It should be noted that the technic of liquid-liquid extraction can bring a solution for the treatment of industrial sludges, though its realization will necessitate important investments and probably entail fairly high running costs.

5. THANKS

The authors desire to express their thanks to the Belgic State and the "Service de la Programmation Scientifique" which has given them the opportunity to carry out this work. They also wish to thank the firms which have allowed them to visit their shops and which have given them the facilities of drawing adequate samples of the sludge indispensable for their analysis.

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SOLVENT EXTRACTION OF COPPER FROM SMELTER DUST TREATMENT LIQUORS WITH ACORGA P-5100

John F. Spisak
Federal-American Partners
Riverton, Wyoming USA

Richard J. McClincy
The Anaconda Copper Company
Denver, Colorado USA

ABSTRACT

The development of Imperial Chemicals' ACORGA P-5100 solvent extraction reagent, provides the capability to extract copper from hydrometallurgical process streams resulting from the treatment of smelter dusts accumulated from roasters, furnaces and converters through the use of equipment required by expanding environmental control.

Laboratory studies demonstrate the effective loading ability of the extractant to transfer copper from 10-15 gpl Cu liquors in the pH range of 1.5-2.0 while achieving 96-98% recoveries, high Cu/Fe selectivity ratios, excellent kinetics and phase disengagements.

Small commercial scale (0.90 tonnes/day) pilot plant studies indicate solvent stability, reliability and verifies results achieved in the laboratory.

INTRODUCTION

The contemporary copper reduction industry in the USA, attempting to function beneath an ever expanding plethora of regulatory and environmental constraints, confronts the escalating dilemma of evolving technically and economically efficacious methods for the processing of the continuous accumulations of dusts (emanating from oxidation roasters, furnaces and converters) rife with process expunged impurities (As, Bi, Cd, Pb, Sb) and concomitant metal values (Ag, Cu, Zn). Quantities of dust in the amount of 25-100 tonnes per day are commonplace at the average copper smelter (1).

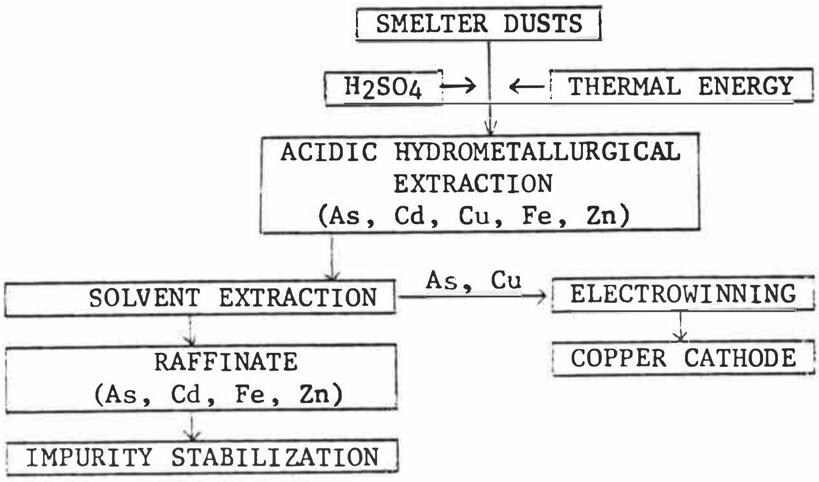
In general, these dusts are marginally amenable to direct pyrometallurgical process stream recycle and the greater segment must necessarily be bled from the process stream in order to minimize the circulating load of impurities (As, Bi, Cd, Pb, Sb) deleterious to copper anode quality (2-3).

This site-impounded proliferation of noxious dust has been exacerbated by ever expanding pollution control installations and these dusts must subsequently be reprocessed for innocuous disposal.

In order to effectively address the aforementioned requirements and problems, the hydrometallurgical approach was selected as it represents one of the cleanest and easily quantifiable methods available to the industry.

The basic procedure, illustrated in Fig. 1, consists of a sulphuric acid extraction of the various impurities and metal values from the dusts with the subsequent formation of a waste sludge, reduced in volume several times (dependent on process operational efficiency) over that of the original dust. The metal and impurity values contained in the acidic leach liquor report to solvent extraction where the critical separation of value from impurity must occur.

FIG. 1
HYDROMETALLURGICAL SMELTER DUST TREATMENT PROCESS



Resultant from the underlying chemistry of this process (acidic liquors in the range of pH 1.5-2.0 with copper concentrations of 10-15 gpl) evolved the requirement for an organic extractant of superior chelating strength at a lower pH (<1.5). Additionally, a second fundamental requirement promulgated by this type of hydrometallurgical dust treatment process was the necessity of reliable selectivity by the organic extractant for copper over soluble impurities (Fe, As and Cd in this case).

Historically, the complex interrelationships involving an extractant's chelating strength, a liquor's soluble iron, acid liberation during extraction and copper anode susceptibility to impurity degradation during electrowinning have burdened first generation solvent extraction circuits with a restricted pH range (as 1.5 grams of H_2SO_4 are liberated with each gram of copper extracted from sulfate liquors) and reduced copper concentration feed liquors (3-4 gpl Cu) (4). These limitations have necessitated the operation of commercial facilities with large solution volumes and flows in order to process any significantly economic quantity of copper. The capital investment, maintenance and labor disadvantages wrought by these conditions are self evident.

The introduction of Imperial Chemicals' ACORGA P-5100 copper solvent extraction reagent has provided a significant new capability in the treatment of smelter dusts for selective copper recovery. This reagent, which was derived from a parent salicylaldoxime compound and employed 4-nonylphenol in its synthesis (5), has overcome the constraints of high acid release extraction inhibition in high copper liquors without detriment to reaction kinetics or phase disengagement.

The following discussion will address the laboratory development of the solvent extraction aspect of the dust treatment process and its subsequent successful application in a full scale pilot plant designed and constructed to test the integrated process on a continuous operational level.

DISCUSSION - EXPERIMENTAL

The preliminary experimental work consisted of a test program designed to characterize a sample of ACORGA P-5100 acquired from Imperial Chemicals and to verify the technical data concomitantly supplied (6). A maximum loading profile was developed (See Table I) using a standard saturation capacity feedstock in order to determine an optimum extractant concentration. The diluent employed was Chevron Chemicals' "Ion Exchange Solvent", a (5-10%) low aromatic kerosene. All tests consisted of five minute separatory funnel shake tests at 20-22° C. Each contacted organic sample was contacted with an excess of fresh loading solution to insure a maximum load.

TABLE I
REAGENT CHARACTERIZATION

	Cu^{2+}(gpl)	Fe^{3+}(gpl)	gms Cu/% P-5100	pH
Max. Load Sol'n	4.02	4.10	-	1.75
Org. I - 10% $^{V}/o$ P-5100	4.13	0.001	0.413	-
Org. II - 20% $^{V}/o$ P-5100	8.91	0.27	0.446	-
Org. III - 25% $^{V}/o$ P-5100	10.78	0.28	0.431	-
Org. IV - 40% $^{V}/o$ P-5100	15.70	0.33	0.393	-

In addition to the results illustrated in Table I, qualitative physical observations recorded rapid phase separation (0.5-1.0 minute) of the 10, 20 and 25 volume percent P-5100 tests and no visual secondary haze in the water phase. The 40 volume percent P-5100 test suffered very slow phase separation (5-7 minutes) with the aqueous phase exhibiting a severe organic haze which was eliminated by a 5 minute immersion in a 50° C water bath.

Quantitatively, the loading profile illustrated in Table I indicates uniformity over a wide range of extractant strengths. Copper loaded per percent extractant averages 0.42 grams at the given pH of the feed liquor. Some iron was observed to load in the 20, 25 and 40 volume percent tests. However, even though the extractant's affinity for copper far surpasses its affinity for iron, the intermediate excess of extractant available during the loading steps in the higher strength tests would cause some amount of iron to load. This problem is easily eliminated in a continuous operational mode through the use of aqueous liquor recycles to maintain excess copper in the mixer.

The next phase of experimental extractant evaluation consisted of a series of continuous tests run in a clear PVC, counter-current, solvent extraction (mixer-settler) mini circuit (100 cc pumping mixers). The circuit included 3 extraction stages and 2 stripping stages. Flow rates were adjusted to obtain average mixer retention times of 3 minutes. A 25% $^{V}/o$ P-5100 was employed with an operating target of 90% of maximum load or 9.7 gpl Cu in the organic phase. All mini-plant runs were performed at 20° C for 5 continuous operational hours. Data samples were obtained during each run after the circuit had functioned at operational equilibrium for at least 3 hours (results of these mini plant runs are illustrated in Table III.)

Two basic feedstock liquors were utilized in the mini-plant tests, with each one derived by subjecting smelter dusts to the hydrometallurgical process described earlier. The composition of these solutions is shown in Table II. As illustrated, these feedstocks were synthesized at two different concentrations in order to properly evaluate the P-5100 extractant. Both feedstock solutions were adjusted to pH 2.0 with 10N NaOH before entering the mini-circuit.

TABLE II
FEEDSTOCKS

	Cu	Fe	As	Zn	H_2SO_4	pH
Smelter Dust Treatment Liquor I	13.70	11.40	5.4	2.68	4.0	1.65
Smelter Dust Treatment Liquor II	6.40	5.80	2.4	1.36	2.2	1.80

A synthetic electrolyte was obtained as a stripping agent by preparing a solution of 25 gpl Cu as $CuSO_4$ and 150 gpl H_2SO_4. The loaded organic solvent was only stripped to 4.5-5.0 gpl Cu resulting in a net transfer in the 5 gpl Cu range.

Throughout the duration of the mini-circuit testing program no problems with phase disengagement were encountered (specific flows of 60-80 l m^{-2} min^{-1}). No stable emulsion bands developed in the settlers and no significant quantities of organic solvent were observed in the aqueous reservoirs (raffinate and electrolyte settlers which were installed to signal entrainments of consequence).

TABLE III
ACORGA P-5100 SOLVENT EXTRACTION MINI-PLANT OPERATING DATA

Test No	O/A (Extractant/ Feed) Ratio	SX Feed GPL Copper	SX Feed GPL Iron	SX Raffinate GPL Copper	Net GPL* Iron To Electrolyte	Overall % Copper Extraction	Organic Net Transfer GPL Copper	Copper to Iron Selectivity Ratio*	Feed pH/ Final pH
I	2.73	12.30	11.40	0.40	0.008	96.75	5.10	1487	2.00/1.20
II	2.73	12.30	11.40	0.41	0.014	96.67	4.72	849	2.00/0.95
III	2.73	12.40	10.80	0.40	0.108	96.77	5.60	111	2.00/0.80
IV	2.40	12.20	11.00	0.38	0.090	96.89	4.46	131	2.00/0.75
V	1.26	5.76	4.86	0.16	0.058	96.88	4.40	97	2.00/0.85
VI	1.26	6.28	5.76	0.90	0.082	98.50	4.86	75	2.00/0.75
VII	1.31	6.00	4.88	0.10	0.084	98.33	4.98	70	2.00/1.15

*Note: These values were based on the assayed iron increase in the electrolyte. Undoubtedly, some quantity of iron was transferred through aqueous entrainment, although this value was not quantified.

The results of this testing program illustrated in Table III, indicated a successful application of this P-5100 extractant for the processing of smelter dust treatment liquors. The dual criteria of extracting high copper solutions in the presence of high acid and a selectivity for copper over iron were successfully achieved. The Cu/Fe selectivity ratio was of serious concern in later tests, (See Table III) as it rapidly declined. However, no correlation existed between net transfer, final pH raffinate strength or extraction. This appeared to lend legitimacy to the hypothesis that aqueous entrainment was occurring and subsequently transferring iron to the electrolyte.

DISCUSSION - PILOT PLANT

Based on the positive results obtained in the laboratory with the solvent extraction mini-circuit and the remainder of the hydrometallurgical dust processing data, the next logical step, of developing a commercial scale pilot plant, was executed.

The pilot facility was designed and constructed to process 0.90 tonnes of smelter dust per day and operate continuously in 10 day segments. The pilot facility was fully integrated as it consumed dry smelter dusts and produced wirebar grade copper cathode product. It concomitantly neutralized pernicious wastes while greatly reducing the volume of the original dust feed.

The solvent extraction segment of the process was diligently scrutinized in order to determine its ability to satisfy specific objectives. First, the solvent's capacity to maintain physical and chemical integrity under continuous operating conditions had to be established. Second, the solvent's selectivity for copper in a waste treatment process stream had to be reaffirmed conclusively. Finally, engineering and design data along with projected operational stability information had to be elucidated in order to provide an insight into process economics.

In order to satisfy these and the other objectives of the integrated pilot program, the site selected for the project was the Anaconda Copper Company's Reduction Works in Anaconda, Montana, USA. This propitious location provided the continuous availability of current process generated dusts and diverse stockpiles accumulated over years of changing copper smelter technology.

A typical solvent extraction circuit was designed and installed for the pilot testing (Refer to Fig. II) (7). The functional units consisted of modified radial turbine pumping-mixers and horizontal settler beds. All feed materials entering the circuit (spent electrolyte, feed and stripped organic) did so by gravity via elevated head tanks.

The extraction segment of the circuit consisted of two mixer-settlers equipped with aqueous recycles and pH and temperature probes in the aqueous overflow weir. A raffinate entrainment settler was installed to trap any residual solvent and return it to the first extraction stage.

The strip segment of the circuit also consisted of two aqueous recycle equipped mixer-settlers complete with temperature and pH probes. An electrolyte entrainment settler was installed for the same purpose as that in the extraction segment.

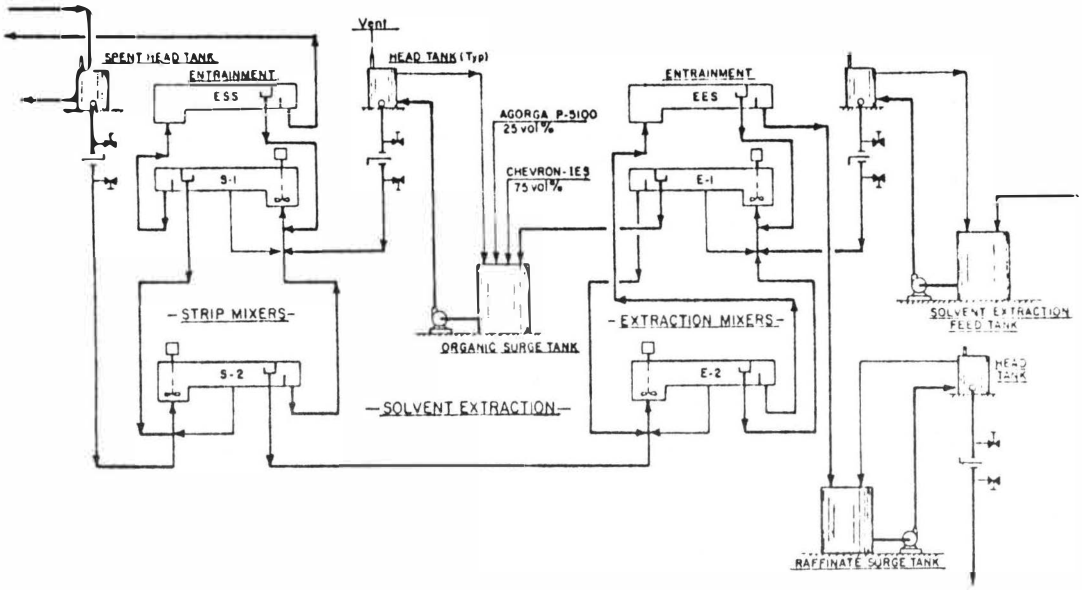
The solvent consisted of 25% ^{v}/o P-5100 and 75% ^{v}/o Chevron IES and was consistently maintained at this ratio through the use of maximum loading data obtained experimentally.

The acidic feed liquor was adjusted to pH 2.0 by slurrying with a particle size controlled and metered limestone slurry, filtered and the aqueous filtrate clarified by passing it through a 40μ bag filter. This procedure produced a stable feedstock with less than 100 ppm of suspended solids.

As shown in Table IV, the appropriate O/A feed ratios were developed based on the operating solvent net transfer and feed liquor copper. Mixer

O/A ratios were maintained at 1.0 O/A in E_1 and S_1 (the aqueous continuous mode mixer) and at 2.0 O/A in E_2 and S_2 (the organic continuous mode mixers) with the assistance of recycles. Mixer residence times averaged 3-5 minutes, with specific flows in the range of 60-80 l m^{-2} min^{-1}.

FIG. II
SMELTER FLUE DUST SOLVENT EXTRACTION PILOT CIRCUIT



The strip liquor feed to the circuit consisted of a 25 gpl copper, 150 gpl H_2SO_4 solution circulated through electrowinning cells for subsequent copper cathode production by copper removal.

The pilot scale extraction circuit functioned extremely well (Table IV) (7). Copper extractions ranged from 92 to 96 percent in two stages of extraction with a range of copper to iron selectivity ratios of 839 to 3475. No problems with stable emulsions or phase disengagement were encountered although the average operating temperature of the solvent extraction circuit hovered around 33° C. Phase disengagements in the aqueous continuous mixer-settlers (E_1 and S_1) were observed at less than one minute and were noted at 3-4 minutes in the organic continuous vessels (E_2 and S_2). Organic entrainments of less than 20 ppm were recorded for both the raffinate and the strip liquor (8).

Concerning entrainment and copper selectivity, an apparent paradox is discernable with careful scrutiny of the data of Table IV. Based on solvent analyses (a standard perchloric acid digestion method), iron extractions in Runs B and C appear to be 4.51% and 13.83% respectively while the Cu/Fe selectivity ratios are 458 and 3475 respectively. As noted, the selectivity ratios were determined by measuring the actual mass change in the iron content of the entire aqueous inventory of the solvent extraction-electrowinning circuit. This net change in soluble mass (Fe) provided an accurate representation of iron transferred in the aqueous mode via entrainment or other means. The obvious discrepancy is explained by the failure of a filtration

TABLE IV
PILOT PLANT RESULTS

Pilot Run A   O/A - 1.57

	Aqueous		Organic		
	Feed	Raffinate	Stripped	Loaded	Extraction %
LPM	8.12	8.12	12.76	12.76	-
Sp. Gr.	1.059	1.046	-	-	-
pH	2.36	0.99	-	-	-
°C	34.0	31.7	-	31.8	-
Cu	10.4	0.82	5.69	12.32	92.1
Fe	7.1	7.2	0.002	0.02	0.0
As	1.34	1.40	0.015	0.015	0.0

Pilot Run B   O/A - 2.37

	Aqueous		Organic		
	Feed	Raffinate	Stripped	Loaded	Extraction %
LPM	9.15	9.15	21.7	21.7	-
Sp. Gr.	1.063	1.046	-	-	-
pH	2.04	0.93	-	-	-
°C	29.0	31.0	-	31.0	-
Cu	11.58	0.59	5.96	11.10	94.9
Fe	7.76	7.40	0.01	0.01	4.51
As	1.60	1.51	0.006	0.007	5.63

Pilot Run C   O/A - 2.74

	Aqueous		Organic		
	Feed	Raffinate	Stripped	Loaded	Extraction %
LPM	9.14	9.14	25.0	25.0	-
Sp. Gr.	1.077	1.057	-	-	-
pH	1.92	1.01	-	-	-
°C	27.0	30.6	-	37.0	-
Cu	12.47	0.55	5.75	10.5	95.6
Fe	9.40	8.10	<0.01	0.02	13.83
As	2.02	2.07	<0.001	<0.001	0.0

Specific Flows (Runs A, B and C): 60-80 l m^{-2} min^{-1}

Pilot Runs

	A	B	C
Cu Net Transfer (gpl)	6.63	5.12	4.76
Cu/Fe Extraction Ratio*	839	458	3475

* Based on actual mass flow data for a 10 day pilot run.

system upstream from solvent extraction. This failure allowed a small but deleterious quantity of treated smelter dust particles to enter the solvent extraction circuit and become suspended in the mixers. This was verified by damage observed in the primary filtration system and the presence of interfacial "grungies" in E_1 and E_2. These solvent suspended iron bearing particulates were subsequently, unknowingly dissolved and assayed as part of the loaded solvent. The particulate material that reached the stripping vessels transferred to the aqueous fraction and subsequently migrated to the electrowinning circuit. This phenomenon was verified by the presence of an organic slime consisting of 75-85% (by weight) of treated smelter dusts coated with 15-25% organic (by weight) which had been floated to the cell surface through the action of anodic oxygen evolution during electrowinning. Evidently, the solid dust particles (even though coated with organic) were comprised of sufficient mass to fall from the organic fraction into the aqueous fraction during settling. This was further corroborated by the presence of some slime particles in the raffinate. Thus the actual contribution from entrainment, of iron transfer, can be considered to be negligible.

Although the circuit was contaminated by an operational accident, no deleterious effects were observed in the performance of the extractant. Since these situations are likely to occur in a commercial facility, this represents as asset favorable to the extractant.

During the course of this project several flocculants were tested in liquors upstream from solvent extraction with no deleterious effects on extraction or phase disengagement. Natural guar compound and polyacrylamide flocculants were tested.

SUMMARY AND CONCULSIONS

The ACROGA P-5100 extractant generally performed to expectations based on the technical data available from its manufacturer. It dependably and efficiently extracted copper from feed liquors concentrated in the 10-14 gpl Cu range in sulfuric acid media producing raffinates in the range of 0.5-0.8 gpl Cu, without exhibiting any effects of inhibition resultant from acid liberation. The solvent demonstrated excellent copper to iron selectivity and an ability to function following contamination with process activated solids. In addition, the extractant exhibited evidence of durability and stability. Following the 888 operational hours of the pilot facility, a composite sample of the in process solvent was obtained and subjected to a standard maximum load test. As the results in Table V indicate, there is no evidence to support a loss of extractive capability or solvent degradation.

TABLE V
POSTOPERATIONAL SOLVENT EVALUATION

	Cu^{2+}(gpl)	Fe^{3+}(gpl)	gms Cu/% P-5100	pH
Max. Load Sol'n	4.04	4.08	-	1.75
Org. - 25% v/o P-5100	11.06	0.18	0.464	-

The overall results of these two experimental programs illustrate the significant improvements and advantages of the ACORGA P-5100 extractant over the first generation of solvent extraction reagents. Its operating parameters confer on it a significant competitive advantage as it allows hydrometallurgical waste treatment process streams to be concentrated in copper, to levels varying in magnitude from 3 to 5 times greater than would be compatible with first generation extractants. This advantage allows for significant reductions in equipment and plant size concomitant with the reductions in energy consumption and total capital investment. Additional reductions in operating costs (and in some specialized cases the labor force) provide the technical and economic incentives necessary to develop metal recovery processes for the recovery of metal values from waste products.

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RECOVERY OF MERCURY FROM WASTES

J. Ortega and J. Gutiérrez
Junta de Energía Nuclear

Madrid. Spain

ABSTRACT

The solvent extraction properties of the dodecyl-thioglycolic acid, HDTG, has been studied. The extraction was carried out from aluminum nitrate-nitric acid and chloride solutions. Studies were made of the influence of TBP on the extraction of H_g (II) by HDTG and TLA. When HDTG is used as extractant the mercury stripping could be efficiently done whith HCl aqueous solutions without precipitate formation.

INTRODUCTION

Early in 1970 the public became aware of a newly discovered pollution problem from reports of high levels of mercury in freshwater fish at various locations. Experience in Japan showed that mercury could be dangerously toxic with large amaunts having been dispersed into the environment by industrial activity. As a consecuence the authorities established regulations concerning discharges of mercury to the environment. There were, in addition, economic reasons for developing separation processes to extract and recover mercury from dilute solutions.

The separation of mercury from aqueous industrial wastes can be performed by several procedures amongst which the most important are: electrolytic reduction, precipitation, ion exchance and liquid extraction.

In electrolytic reduction lead cathodes, porous cathodes and ion exchange membranes to separate the cathodic-anodic compartments, have been used (1,2,). Mercury precipitation in mainly carried out with Na_2S using hydroxides of iron (3.4), hydroxide of aluminum (5), diatoms (6) and filtration systems (7) as collectors. The Montedison (8) process replaces Na_2S by thiourea as the precipitating agent. The great affinity of mercury for the organic and inorganic sulphides is a property applied in separation of mercury ion by exchange resins. Anionic resins (Amberlite IRA-400 and Dowe X-1) are charged with metalic sulphides to separate mercury from aqueous solutions (9,10). Selective ion exchange resins, containing sulphur, have been developed(11,12, 13,14) and even vulcanized rubber containing 1% sulphur has been proposed (15).

It has been suggested that separation of mercury by liquid extraction with amines (16) is possible and a flowsheet has been proposed by Groenier (17) to separate mercury from brine effluents. Quaternary ammonium compounds have also been proposed by Moore (18). More recently organic compounds containing sulphur have been applied for mercury separation: primary and secondary mercaptans (19,20), diphenylthiourea (21), thiophosphorous compounds (22), alkylsulphides (23) and thioesters (24), are the most important ones. Taking advantage of the presence of sulphur in the lubricating base oil has led to these being suggested as organic extractants of mercury (25,26). The extraction of metal ion by carboxylic acids has been reviewed, by Flett and Jaycock (27), their data prove that the mercury (II) can not be extracted in an efficient way from strong acid media.

In the present work we are concerned with the separation of mercury by liquid extraction from wastes arising from the reprocessing of Material Testing Reactor (MTR) fuels. A carboxylic acid containing a sulphide group in beta position with respect to the carboxylic group has been used. The presence of sulphur enhances the mercuric ion extraction and allows their separation as well from strong acid media such as from high chloride concentration solutions. The good results obtained in separation of mercury from nitric acid-aluminum nitrate solutions led us to apply this extracting agent to separation of mercury from effluents of production plants of chlorine.

EXPERIMENTAL

REAGENTS

Dodecyl-thioglycolic acid, HDTG is a commercial product supplied by Phillips Petroleum Co., tributyl phosphate, TBP, and trilaurylamine, TLA, were Koch-Light products. Kerosene, Shell Sol T, was used as diluent in all experiments. Mercury tracer, ^{203}Hg, was obtained from Radiochemical Centre Amershan and its purity was cheked by gamma -spectrometry. All the other reagents used were high purity products of the chemical analysis type.

HDTG was purified by heating under reflux with activated carbon and ethylether. Shell Sol T was purified by treatment with concentrated sulfuric acid.

For our study we have used synthetic solutions of similar composition to that obtained in the reprocessing of MTR fuels and in chlorine-caustic soda production. Stock solution of mercury (II) were prepared weighing out appropriate inorganic salts and standardising the solution by complexometry.

PROCEDURE

All the aqueous solutions used in extraction had been marked with ^{203}Hg and all the organic solutions used in extraction equilibria had been previously pre-equilibrated with mercury free aqueous solutions. The equilibrium acidity was measured, after shaking, with a Metrohm pH meter (combination electrode).

For each extraction experiment 5 ml of the organic solution was added to a test-tube containing 5 ml aqueous phase. The tube was then sealed and agitated on a thermostated mechanical shaker, at 20° ± 0,5 °C for 30 min. For stripping experiments 2 ml aqueous solution and 2 ml organic solution only were used, the last having been obtained previously in a pre-extraction experiment. After shaking the tube was centrifuged for 2 min. Following centrifugation 1 ml samples of each phase were taken and transfered to plastic tubes and counted in a JEN, Mod. 17 scintilation counter with NaI (Tl) crystal.

The distribution coefficient, D, was defined as the ratio between the counts per unit time in 1.0 ml of organic phase and the counts for same unit time in the same volume of aqueous solution.

RESULTS AND DISCUSSION

EXTRACTION OF MERCURY FROM MTR WASTES

The dissolution of MTR fuels is carried out by means of nitric acid using mercuric nitrate as catalyzer. This mercuric nitrate appears in the radiactive wastes after reprocessing.

The extraction of mercury (II) from nitric acid aqueous solutions with HDTG presents the problem of emulsion formation with the corresponding bad phase separation. At concentrations of $(HDTG)_2$ lower than 5 10^{-3} M. emulsions are formed in each phase. From 10^{-2} M up to 6 10^{-2} M. of $(HDTG)_2$ the emulsion is only formed in the aqueous phase, O/A, and at higher concentrations effectively no emulsion phase is formed. For concentrations of $(HDTG)_2$ 10^{-2} M. in the organic phase, the presence of nitric acid and aluminum nitrate in the aqueous phase improves the separation of both phases. By using 20% ($^V/V$) HDTG as the organic phase and 1.5 M. $Al(NO_3)_3$ plus 1.0 M. HNO_3 as the aqueous phase the separation of phases takes place in less than 30 sec. without any type of emulsion.

In Figure 1 are the results obtained from the study as represented showing the variation of distribution coefficient with the concentration of $(HDTG)_2$. Cryoscopic and IR absortion spectra shown that HDTG is dissolved in kerosene as a dimer. The value of the slope in Figure 1 is approximately 2, which allows us to propose the following equilibrium equation.

$$H_g^{++} + 2\overline{(HDTG)_2} \rightleftharpoons \overline{H_g(DTG)_2.2HDTG} + 2H^+ \qquad (1)$$

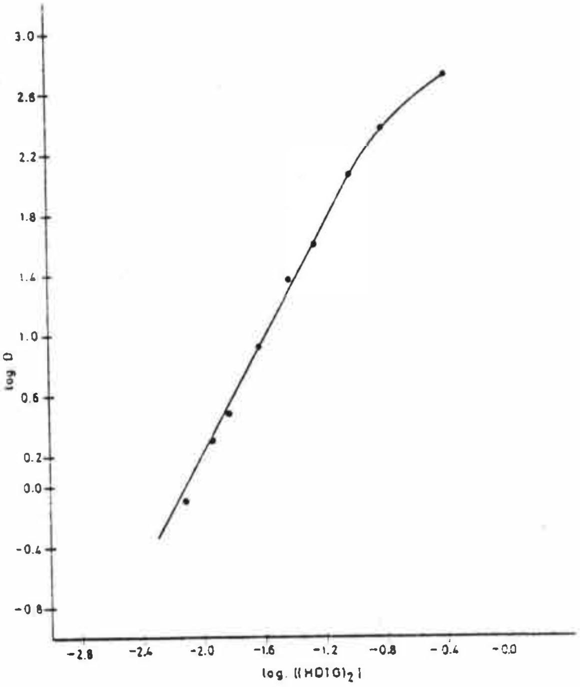

Fig. 1.- Mercury distribution coefficients in 1.5 M $Al(NO_3)_3$, 1 M HNO_3, 5 10^3 M $Hg(NO_3)_2$ as a funtion of organic phase $(HDTG)_2$ concentration at 20 °C.

For a 20% ($^V/V$) solutions of HDTG the distribution coefficient for mercury is higher than 3 10^2. With this high distribution coefficient only two o three stages would be required to recover more than 99.9% of mercury contained in wastes.

EXTRACTION OF MERCURY FROM SOLUTIONS OF SODIUM CHLORIDE

The effluents from the production plants of chlorine-caustic soda are 4.2-4.8 M. solutions of sodium chloride, which contain 10-30 ppm mercury and the pH between 2 and 3. The solutions used in our study were 4.8 M. sodium chloride at pH of 2.5. Figure 2 shows the distribution curve of mercury in 0.5 M. $(HDTG)_2$. The distribution coefficient increases when the mercury concentration decreases. For concentrations of 10-30 ppm the distribution coefficient is higher than 10^2 which allows a good separation of mercury in this type of solution.

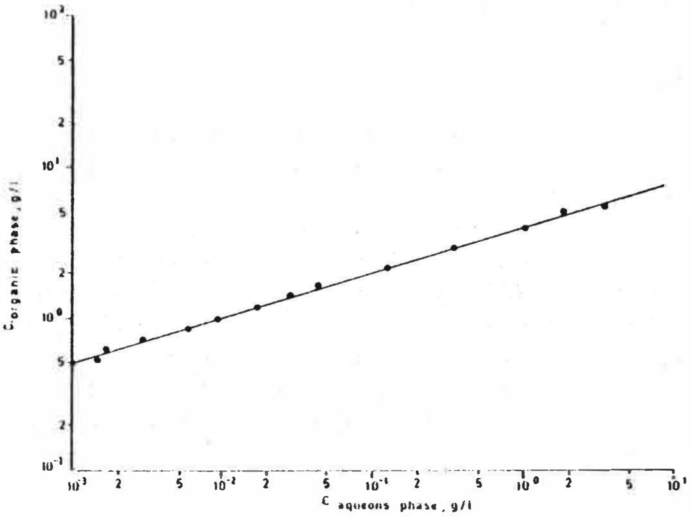

Fig.- 2 Mercury equilibrium distributium curve, between 0.5 M $(HDTG)_2$ in kerosene and 4.8 M NaCl at pH 2.5 and 20° C

Figure 3 shows the variation of D as a function of concentration of $(HDTG)_2$ in the organic phase. Initial concentration of mercury used were 1.32 g/l. At lower mercury concentration the distribution coefficient was very high and its determination rather imprecise because the ^{203}Hg activity in the aqueous phase was below background.

From Figure 3 we can deduce the intervention of two $(HDTG)_2$ molecules by mercuric ion for which the extraction equilibrium can be represented by

$$(H_gCl_4)^= + \overline{2(HDTG)_2} \rightleftharpoons \overline{H_g(HDTG)_2.2HDTG} + 4Cl^- + 2H^+ \tag{2}$$

In the chloride medium there is no formation of emulsion, which facilitates a rapid separation of phases.

The data obtained in the study on the influence of TBP on the mercuric ion extraction by HDTG or TLA are shown in Figure 4. The results obtained indicate that TBP has a synergistic effect stronger in the case of TLA in comparison with HDTG. For TLA the slope of the curve (slope 0,5) proves that one molecule of TBP for two ion mercuric participated in the extraction process.

The variation of the mercuric ion distribution coefficients for two types of organic solutions both containing a constant concentration of TBP and various concentrations of HDTG or TLA, is shown in Figure 5. The form of both curves are very similar always giving a greater extraction of mercury with HDTG than with TLA, with the extractant concentration being in percentage.

The effect on the distribution coefficient by the mercuric ion, when using a mixture of TBP with HDTG or TLA as organic phase, is shown in Table 1. At low mercuric ion concentration, the distribution coefficients for mixtures of TBP-HDTG are higher than for mixtures TBP-TLA. Nevertheless the increase of the mercuric ion concentration, from 8.7 g/l, in the aqueous phase reduces the distribution coefficient for HDTG more than for TLA, giving for concentrations of 25% values for TLA higher than HDTG. The cause of this may be the stronger synergistic effect of the TBP with TLA than with

ADTG.

This synergistic effect also influences the loading capacity of the organic phase for the mercuric ion. The mercuric ion loading capacity for 25% ($^V/V$) of HDTG does not change through the presence of TBP (18 g/l). In the case of 25% ($^V/V$) of TLA, the loading capacity increases from 15 g/l, when no TBP is present, to 27 g/l for 25% ($^V/V$) of TBP.

STRIPPING OF MERCURY FROM ORGANIC PHASE

From equation (2) it is evident that hydrogen ion facilitates the pasage of mercury from the organic phase to the aqueous phase. The hydrochloric acid combines the effect of both, the chloride ions and the hydrogen ions, and can be an appropriate agent for re-extraction of mercury.

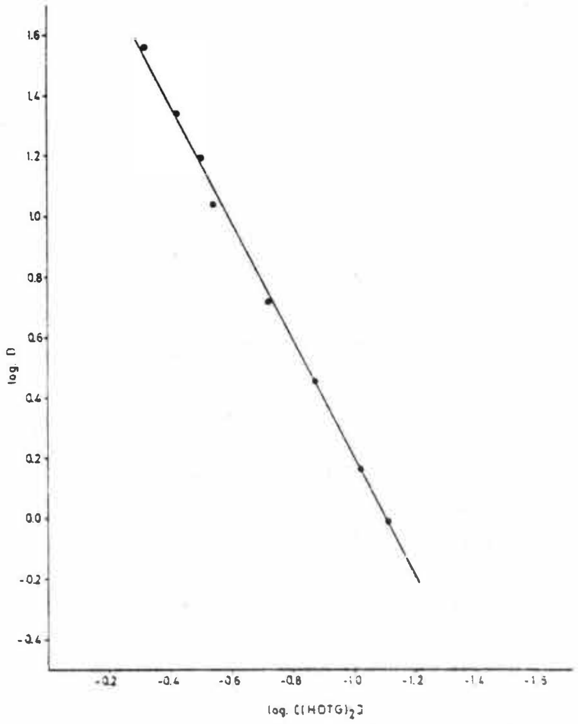

Fig. 3.- Mercury distribution coefficient as a function log [HDTG]. Aqueous solution. 4.8M NaCl and 6.25.10^{-3}M Hg at 20° C and p H 2.5

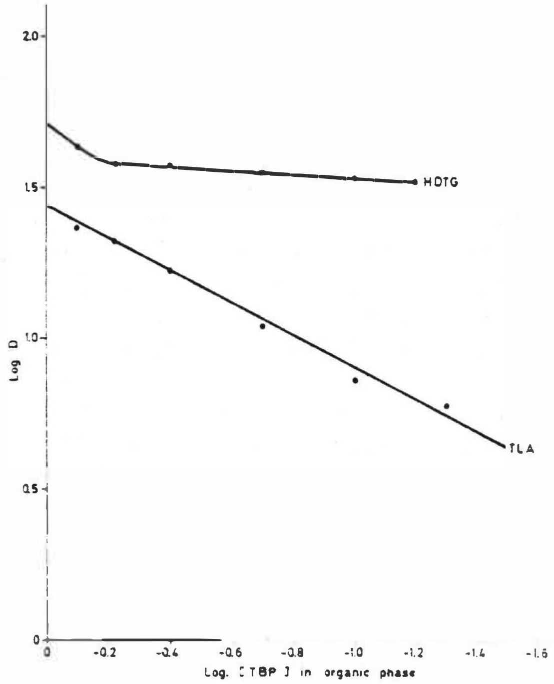

Fig. 4.- Mercury distribution coefficients between 25% (v/v) HDTG (or TLA) and 4.8 M Na Cl at pH. 2,5 as a function of organic phase TBP concentration at 20 °C.

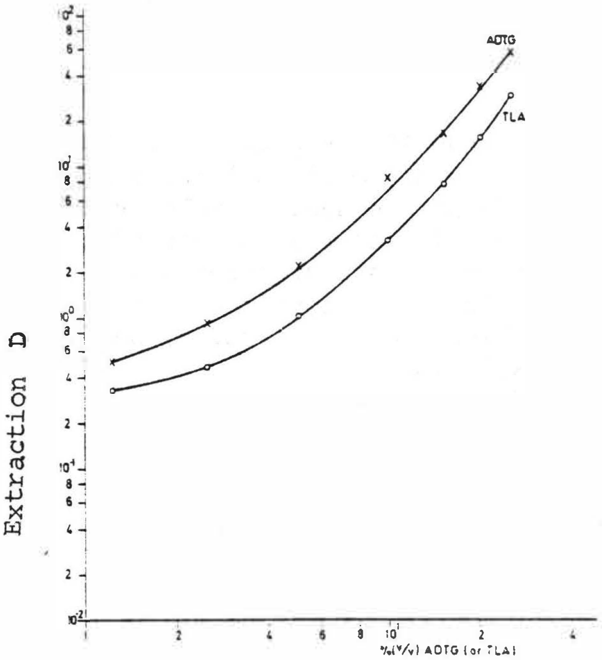

Fig. 5.- Mercury distribution coefficients between 25%(V/v) TBP and 4,8 M NaCl at pH 2,5 as a function of organic phase ADTG (or TLA) cocentration at 20 °C

If we represents by X the concentration of hydrochloric acid used in the stripping, according equation (2), the distribution coefficient for the mercury can be given in the form

$$D = K \frac{\left[(HDTG)_2\right]}{\left[Cl\right]^4 \left[H^+\right]^2} = K \frac{\left[(HDTG)_2\right]}{X^6} \qquad (3)$$

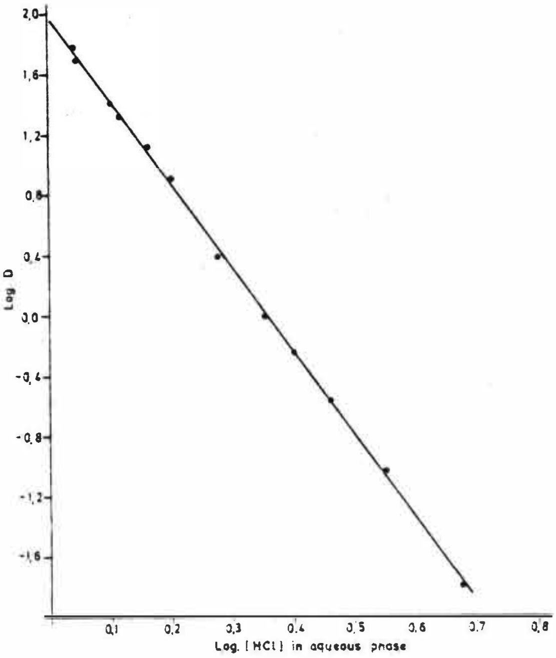

Fig. 6.- Mercury distribution coefficients between 0,5 M $(HDTG)_2$ in kerosene and hidrochloric acidat 20 °C asa function of log [HCl] in aqueou phase

In Figure 6 it can be seen that the variation of log. D with log(HCl) has a slope of 5,48 which corroborates the extraction equilibrium proposed in equation (2). At concentration above 3.5 M. HCl, D is less than 0.1 and at 4.4 M. reaches a value of 0.04. The concentrations of hydrochloric acid used for Figure 4 range from 1 M. to 4.4 M., extrapolations to higher concentrations of this acid gave values of D which did not agree with the experimental values.

CONCLUSION

The HDTG allows the efficient extraction of mercuric ion from liquid wastes arising from either MTR fuel reprocessing or from the brines of the production plants of chlorine-caustic soda.

The extraction of mercuric ion from medium nitrate presents the problem of organic, in aqueous, emulsion formation, O/A. This problem ca be almost completely resolved by using concentrations of HDTG in organic phase higher than 15% in presence of TBP.

The problem of emulsion does not exist in medium chloride and the solutions in percentage, of HDTG shows distribution coefficients for mercury rather superior to the correspondent ones with TLA. The addition of TBP to the organic phase produces a synergistic effect stronger for TLA than for HDTG. This synergistic effect is the reason that very similar distribution coefficients are obtained by adding the same amount of TBP to both extractant solutions.

The mercury ion stripping from TLA solutions can not be accomplished in homogeneous media. The mercury must be precipitated with aqueous solutions of alkylamines. When HDTG is used the mercury stripping could be efficiently done with 2.5-4.5 M. HCl aqueous solucions without precipitate formation, which is a great advantage because the precipitates could cause problems in the organic-aqueous interphase.

TABLE - I

Variation of mercury ion distribution coefficient as a function of TBP-ADTG (or TLA) concentration for different mercuric ion concentration in aqueous phase.

% ($^V/V$) ADTG or TLA	% ($^V/V$) TBP	MERCURY		DISTRIBUTION				COEFFICIENT			
		1.2 g/l Hg		Hg 3.1 g/l		Hg 4.9 g/l		Hg 8.4 g/l		Hg 13.6 g/l	
		HDTG	TLA	HDTG	TLA	HDTG	TLA	HDTG	TLA	HDTG	ATL
25	25	61	30	10	4.6	3.70	3.2	1.35	3.2	0.7	1.4
12.5	12.5	9.2	4.7	1.8	0.95	1.02	0.64	0.46	0.46	0.26	0.31
6.25	6.25	1.7	0.9	0.6	0.6	0.3	0.15	0.18	0.12	0.12	0.09
3.12	3.12	0.55	0.3	0.24	0.13	0.15	0.08	0.08	0.06	0.06	0.04

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EXTRACTION FROM BIOLOGICAL FLUIDS

Yagodin G.A., Lopukhin Yu.M.,
Yurtov E.V., Sergienko V.I.

Mendeleev Institute
of Chemical Technology,
The Second Medical Institute
Moscow, USSR

The modern development of medicine posed one of the most important problems - the problem of the body detoxifying and the homeostasis correction. At the time being the hemodialysis and ultrafiltration methods are under intensive development.

We have suggested to use for that purpose a different highly efficient method of chemical technology - the extraction by selective extractants, wich, to our minds, has a number of advantages.

We have studied in principle the possibility of extracting some most important biochemical components, such as cholesterol, urea, etc., from the biological fluids (blood, blood plasma). It turned out that under such conditions (t=37°C) non-specific extractants, such as oils, saturated hydrocarbons, chloroform, etc., almost would not extract the blood constituents. It has been shown that the extractants possessing the base properties could be used for extracting cholesterol, while the acid extractants - for extracting urea.

Table. Extraction by tri-n-octylamine

Component	Concentration		Unit of measurement
	before	after	
Cl^-	106±10	102	meq/liter
K^+	2.0±0.1	1.9	meq/liter
Na^+	140±5	138	meq/liter
Urea (BUN)	20±1	19	mg%
Glucose	360±10	340	mg%
Total Protein	6.1±0.2	5.9	gm%
Albumin	1.7±0.1	1.7	gm%
Ca^{++}	6.5±0.1	6.5	mg%
Inor. Phosphorus	1.5±0.1	1.4	mg%P
Cholesterol	100±10	60	mg%
Uric Asid	1.3±0.1	0.8	mg%
Total Bilirubin	0.3±0.1	0.2	mg%

The paper has given much consideration to the kinetics of the extraction from biological fluids, that extraction being practically always complicated by the formation of the films at the interface.

Studying the extraction from biological fluids is quite a new field and the sphere of its further utilization scarcely could be envisaged in all its spread.