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The Solvent Extraction of Metal Ions from Sulfuric Acid Solutions with a Mixed Extractant — Long-chain Primary Amine and Di-2-ethylhexylphosphoric Acid

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The distribution of metal ions between phases of dilute sulfuric acid and carbon tetrachloride containing long-chain primary amine (Primene JM) and di-2-ethylhexylphosphoric acid (D2EHPA) has been investigated. The degree of the extraction of bi- and tervalent metal ions, such as zinc, iron(III), indium, lanthanum, and cerium(III), is found to be the lowest when the organic phase contains 5 g/*l* of Primene JM and 7—8 g/*l* of D2EHPA, while a minimum extraction of thorium occurs at a different composition of the organic phase. Thus, thorium can be quantitatively separated from most other metals by extraction from a 0.1 N sulfuric acid medium with carbon tetrachloride containing 5 g/*l* of Primene JM and 7—8 g/*l* of D2EHPA. Under these extraction conditions, a single extraction is sufficient for the quantitative separation of thorium from high concentrations of lanthanide metals. Contrary to the usual method of extraction using long-chain amines, which involves a tedious multiple extraction, the mixed-extractant technique described is simple and will find many uses in the determinations of thorium in a variety of samples.

Solutions of long-chain amines in water-immiscible solvents have been found capable of extracting a wide variety of metal ions from acid solutions.[1] In particular, it has generally been accepted that ter- and quadrivalent metal ions can be readily extracted from a sulfuric acid solution by long-chain primary amines.[2-5] In this aspect, the present author has investigated the extraction of indium and iron(III) from dilute sulfuric acid solutions with Primene JM dissolved in carbon tetrachloride.[6] Such long-chain amines have frequently been called the "liquid anion exchangers." In contrast to the amines, there is another group of extractants that have been named the "liquid cation exchangers." Di-2-ethylhexylphosphoric acid, which is representative of the acidic organophosphorus compounds, has been used as a cationic extractant for a large number of aqueous cations.[7,8]

For both types of extractants, a synergistic effect has been demonstrated.[1,9-11] As in the case of uranium(VI) extraction, the addition of neutral organophosphorus compounds to D2EHPA enhances the distribution ratio of uranium(VI) by a factor of from ten to hundreds. The synergistic effect for the acidic organophosphorus compounds has been investigated extensively and used for the separation of metals. Although there have been a number of studies of the synergism in the extraction of metals, both with β-diketones, particularly thenoyl trifluoroacetone, and with bases,[12-16] little attention has been paid to the influence of certain acidic extractants on the metal extraction

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with high-molecular-weight amines. Deptula[9,17] has examined the extraction behavior of such compounds as H_2PtCl_6, $H_2Cr_2O_7$, and UO_2SO_4 from sulfuric acid solutions by a mixture of long-chain tertiary amines and dialkylphosphoric acids in benzene. He found that the extent of extraction was increased or decreased depending on the sulfuric acid concentrations, suggesting a synergistic or an antagonistic effect of the amine with the alkylphosphoric acid. However, no further attempt has been made at formulating a quantitative explanation of the extraction mechanism applicable to the mutual separation of metal ions.

A similar effect can be expected for the extraction of other metal ions. By a combination of long-chain amines and alkylphosphoric acids, it will be possible to change the selectivity of long-chain amines or alkylphosphoric acids to the metal ions. In this respect the present attempt was made to extract zinc, iron(III), indium, lanthanum, cerium(III), and thorium from sulfuric acid solutions with a mixture of Primene JM and D2EHPA in carbon tetrachloride. The results of the present experiment establish that thorium can be quantitatively separated from large amounts of bivalent and tervalent ions without multiple extraction or scrubbing.

Experimental

Apparatus. An Iwaki-V-S Shaking Unit was used for equilibration.

Reagents. The purification of D2EHPA[18] in carbon tetrachloride involves the scrubbing of the sodium monoalkylphosphate with an equal volume of a 10% sodium carbonate solution,[19] followed by acidification with an equal volume of a 1N sulfuric acid solution.

Primene JM,[20] trialkylmethylamine, a homologous mixture of C_{18-24} amines, was converted into the sulfate form by washing the amine solution in carbon tetrachloride with an equal volume of a 1N sodium hydroxide solution and by then equilibrating it twice with an equal volume of a 1N sulfuric acid solution. The concentration of the D2EHPA solution was determined by potentiometric titration with a standard sodium hydroxide solution in an ethanol medium.

Organic solutions of mixed extractants are prepared as follows. A constant portion of a purified amine solution and of various volumes of a purified D2EHPA solution are mixed together in a 100-m*l* volumetric flask, and the mixture is diluted to the mark with purified carbon tetrachloride. Then, these solutions are equilibrated with an equal volume of a 0.1N sulfuric acid solution. After the phases have separated, the organic phase was filtered through paper to remove the entrained aqueous phase.

The aqueous solutions used for the extraction of iron(III), zinc, lanthanum, indium, and thorium were prepared by the precipitation of the metal hydroxides and by the subsequent dissolution in a sulfuric acid solution of an appropriate concentration. The solution of cerium(III) was obtained by dissolving cerium(IV) sulfate into a sulfuric acid solution of an appropriate concentration and by subsequent reduction to cerium(III) with a suitable amount of hydrogen peroxide.

Procedure. For all the operations, 15-m*l* portions of the aqueous and the organic solutions were mixed together in a 100-m*l* glass separatory funnel and the mixture was equilibrated at room temperature. A fifteen-minutes shaking period at a rate of 200 strokes per minute was more than adequate. Then, the aqueous phase was filtered through paper to remove the entrained organic phase. The metal content in the aqueous phase was determined either spectrophotometrically or complexometrically.[21-23] The analytical procedures used are summarized in Table 1. The amount of metals in the organic phase was calculated by means of a material balance.

TABLE 1. THE ANALYTICAL METHODS USED

Metals	Spectrophotometric	Complexometric
Th	Xylenol Orange	EDTA, Xylenol Orange
Fe	*o*-Phenanthroline	EDTA, Variamine Blue B HCl
In	Xylenol Orange	EDTA, Xylenol Orange
La, Ce		EDTA, Xylenol Orange
Zn		EDTA, BT

Results

The effect of the D2EHPA concentration on the iron(III) extraction was examined at fixed concentrations of Primene JM and iron(III), and at various fixed concentrations of sulfuric acid. It follows from Fig. 1 that the degree of iron(III) extraction passes through a minimum and then increases with an increase in the D2EHPA concentrations. The composition of the organic phase at which an appreciable decrease in the iron(III) extraction occurs depends on the sulfuric acid concentration.

Similar behavior is observed with the extraction of indium and lanthanum from a 0.1N sulfuric acid solution as can be seen in Fig. 2. The degree of extraction decreases with the increase in the initial concentration of iron(III) because of the fixed amount of extractant in the organic phase, but the concentration ratio of Primene JM to D2EHPA at which minimum extraction is observed does not

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[18] The D2EHPA was kindly supplied by the Kao Soap Co., Ltd.

[19] C. A. Blake, K. B. Brown and C. F. Coleman, *USAEC ORNL*-1903 (1955).

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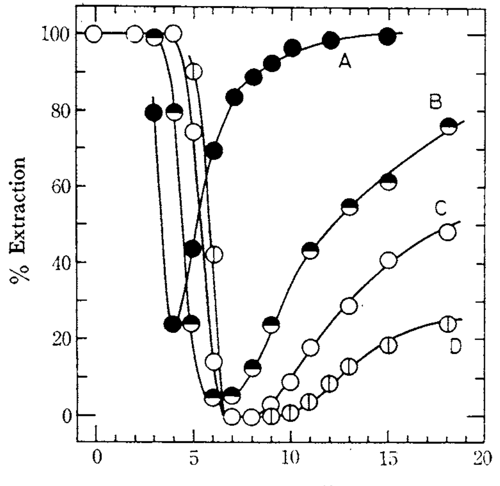

Fig. 1. The influence of D2EHPA on Fe^{3+} extraction with Primene JM (5 g/l) in CCl_4; 1.7×10^{-4}M total iron(III).
(A) 0.010N H_2SO_4 in aqueous phase, (B) 0.050N, (C) 0.10N, (D) 0.20N

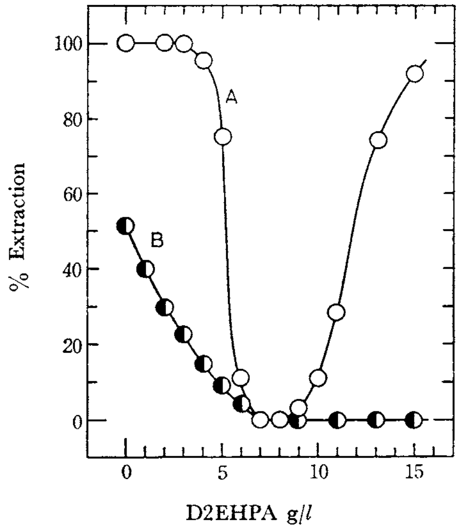

Fig. 2. The influence of D2EHPA on In^{3+} and La^{3+} extraction from 0.10N H_2SO_4 with Primene JM(5 g/l); (A) 3.48×10^{-5}M total indium, (B) 2.29×10^{-3}M total lanthanum.

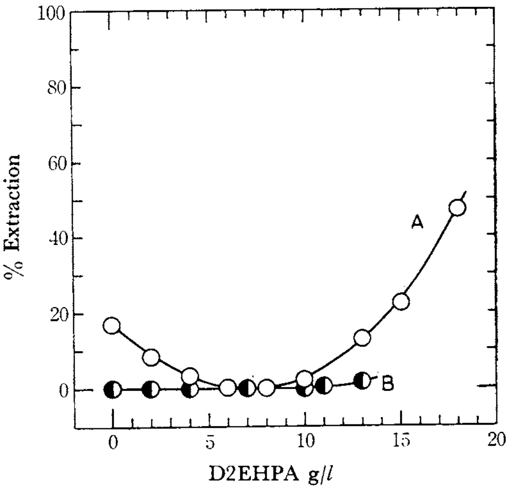

Fig. 3. The influence of D2EHPA on Fe^{3+} and Zn^{2+} extraction from 0.10N H_2SO_4 with Primene JM(5 g/l); (A) 8.40×10^{-3}M total iron(III), (B) 2.15×10^{-3}M total zinc.

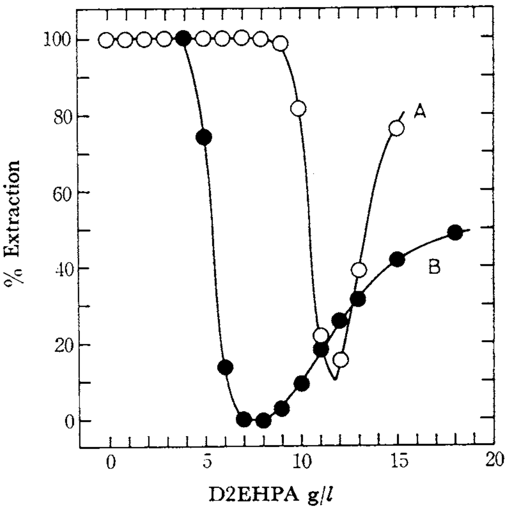

Fig. 4. The influence of D2EHPA on Th^{4+} and Fe^{3+} extraction from 0.10N H_2SO_4 with Primene JM(5 g/l); (A) 1.08×10^{-5}M total thorium, (B) 1.70×10^{-4}M total iron(III).

change appreciably with the initial concentration of iron(III), as is shown in Fig. 3. In order to examine the extraction behavior of bivalent cations, zinc was extracted from a 0.1N sulfuric acid solution. As is shown in Fig. 3, no extraction of zinc was obtained when iron is not extracted. On the contrary, thorium was found to be extractable when bi- and tervalent ions are not extracted, the minimum extraction occurring in the higher D2EHPA-concentration range. This is demonstrated in Fig. 4 for the case where the initial concentration of thorium is 1.08×10^{-5}M. In this figure, the extraction curve of iron(III) from the 0.1N sulfuric acid solution is shown for the sake of comparison with that of thorium. When the initial concentration of thorium is higher, the extractant concentration should be increased to achieve the complete recovery of thorium in the aqueous phase. For a high concentration of Primene JM, say 50 g/l,[24] thorium was completely extracted throughout the D2EHPA-concentration range studied. This

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[24] Tributyl phosphate was used to avoid any third-phase formation; the TBP concentration was 100 g/l.

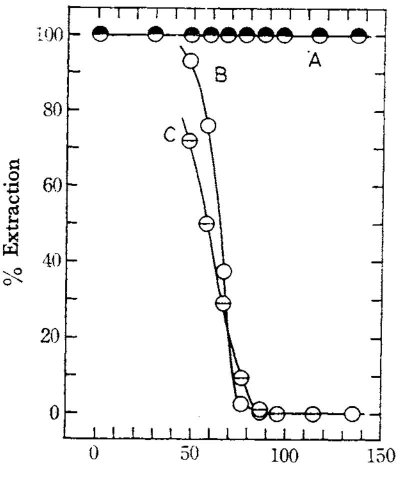

Fig. 5. The influence of D2EHPA on Th^{4+}, La^{3+} and Ce^{3+} extraction with Primene JM(50 g/l).

(A) $(0.212-1.09)\times10^{-2}$M total thorium, 0.01–0.5N H_2SO_4 in aqueous phase

(B) 5.32×10^{-3}M total lanthanum in 0.1N H_2SO_4

(C) 8.25×10^{-3}M total cerium(III) in 0.1N H_2SO_4

extraction behavior of thorium is quite different from that of lanthanum and cerium(III), as can be seen in Fig. 5.

Discussion

As is shown in Fig. 1, the extraction curve for iron(III) shows a minimum at a certain D2EHPA concentration. This can be explained, as has been done by Deptula,[9] on the basis of the interaction between amine sulfate and dialkylphosphoric acid in the organic phase. It is well known that iron(III) is extractable by either Primene JM or D2EHPA from dilute sulfuric acid solutions.[4,5] The appearance of a minimum in Fig. 1 may be due to the formation of an extremely stable complex by means of Eq. (1), which reduces the free concentration of both extractants participating in the extraction reactions and, hence, the degree of extraction.

$$(RNH_3)_2SO_4 + (HR)_2 = ((RNH_3)_2SO_4)(HR)_2 \qquad (1)$$

Note that HR, $(RNH_3)_2SO_4$, and R are D2EHPA, amine sulfate, and an alkyl chain respectively. Equations (2) and (3) are the simplest generalized expressions for the iron(III) extraction.[25,26]

$$Fe^{3+} + 3(HR)_2 = Fe(HR_2)_3 + 3H^+ \qquad (2)$$

$$Fe^{3+} + OH^- + SO_4^{2-} + (RNH_3)_2SO_4 = (RNH_3)_2FeOH(SO_4)_2 \qquad (3)$$

In Fig. 1, the descending portion of the extraction curve corresponds to the decrease in the free concentration of amine sulfate, and the increase in the extent of extraction beyond the minimum is due to the increase in the free concentration of D2EHPA.

As can be seen in Fig. 1, the extraction curves depend on the sulfuric acid concentration. This is attributable to the strong affinity of the protonated amine for D2EHPA in the organic phase. The formation reaction of protonated amine is shown by Eq. (4):

$$2RNH_2 + 2H^+ + SO_4^{2-} = (RNH_3)_2SO_4 \qquad (4)$$

For a decrease in the sulfuric acid concentration in the aqueous phase and, hence, for a small concentration of amine sulfate in the organic phase, a small amount of D2EHPA may be sufficient to complete the formation of $((RNH_3)_2SO_4)(HR)_2$, thereby resulting in the shift of the minimum in the extraction curve to the left. The concentration range of D2EHPA depressing the iron(III) extraction is broadened by increasing the sulfuric acid concentration. This trend may be caused by the competitive reaction of the hydrogen ion and the iron(III) ion against D2EHPA, as is represented by Eq. (2). If the equilibrium constant for the formation of $Fe(HR_2)_3$ or $(RNH_3)_2FeOH(SO_4)_2$ is comparable to that for the formation of $((RNH_3)_2SO_4)(HR)_2$, the minimum of the extraction curve will be found in the higher D2EHPA-concentration range. This is the case for thorium, as can be seen in Fig. 4. Thorium can be quantitatively extracted in the region in which no iron(III) is extracted. For high concentrations of Primene JM, say 50 g/l, thorium is quantitatively extractable over the whole range of D2EHPA studied (Fig. 5). This different extraction behavior from that indicated in Fig. 4 may be due to the higher concentration of Primene JM. As the concentration of Primene JM increases, the shape of the extraction curve at the minimum point tends to become sharp and the minimum point moves towards higher concentration ranges of D2EHPA. This can be explained by the concept that the equilibrium constant for the formation of extractable thorium species is comparable to that for the formation of $((RNH_3)_2SO_4)(HR)_2$.

The above treatment is not very accurate, however, since no account is taken of the presence of bisulfate species. In other words, Eqs. (1), (3) and (4) should have contained the terms of the bisulfate species.[27] However, the explanation using simple Eqs. (1)—(4) appeared to be satisfactory enough since the object of this investigation was to find the conditions which would enhance the selectivity

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[27] K. A. Allen, *J. Phys. Chem.*, **60**, 239, 943 (1956).

of extraction with high-molecular-weight amines.

It was found that the separation of thorium by extraction from many other metals can be carried out very easily using the present mixed-extractant system. That is, thorium can be completely extracted in the region in which no iron(III) is extracted (Fig. 4); tervalent indium, lanthanum, cerium, and also bivalent zinc behave analogously to iron(III), as can be seen Figs. 3 and 5.[28] As Figs. 2, 3, and 5 show, the initial concentrations of bi- and tervalent ions seem to have no appreciable influence on the thorium extraction. Thus, for the extraction of thorium these results may provide an improved method, one with a number of advantages over the previous methods using Primene JM as a single extractant.[5] A dilute solution of sulfuric acid can be used as the aqueous phase, and the complete separation of thorium can be achieved from large amounts of bi- and tervalent metals without multiple extraction and scrubbing. Further, there is the additional advantage that the separation of the two phases is very rapid compared to the case when single extractant is used. It was ascertained that thirty seconds are more than adequate for the complete separation.

From these experiments it is apparent that the degree of the extraction of bi- and tervalent metals can be successfully controlled by the combination of Primene JM with D2EHPA. This suggests that, with a proper combination, the selectivity of metal extraction with the high-molecular-weight amines and, presumably, with other extractants such as D2EHPA will be enhanced to an appreciable extent. Thus, there is good a possibility of developing a highly selective method of extraction for a certain metal ion on the basis of these findings.

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[28] Lanthanide metals show a different extraction behavior from that of iron(III), indium and zinc; above a certain D2EHPA concentration, the extraction remains completely depressed.