

SOLVENT EXTRACTION STUDIES ON THORIUM SULPHATE AND HALIDES

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The effect of water-miscible alcohols, acetone and haloacids in the aqueous phase of sulphuric acid solutions has been studied on the extraction of thorium sulphate and halides by bis(2-ethylhexyl) phosphoric acid (HDEHP) and tri-n-butyl phosphate (TBP). The partition coefficient (E) is greatly affected by these additives, and this gives useful separations from many other elements. Besides, the log-log relationship between the E values and solvent concentration leads to some suggestions on the extraction mechanisms of this mixed system.

Introduction

The need for the recovery of thorium from certain raw materials in sulphuric acid process liquors had led to the development of solvent extraction processes utilizing both tri-n-butyl phosphate (TBP) and bis(2-ethylhexyl) phosphoric acid (HDEHP).

Liquid-liquid extraction by a cation exchanger solvent (HDEHP) from mixed solutions of sulphuric acid with halide acid or watermiscible alcohols has not yet been described in the literature. In the present paper a systematic study is reported on the extraction of thorium halides and sulphate from sulphuric acid, halo-acids and their binary mixtures with TBP and HDEHP. The addition of water-miscible alcohols and acetone to the aqueous phase was found to greatly increase the extraction power of the solvents. This increase has more advantages than the synergistic enhancement caused by the addition of the neutral organic solvent TBP to the organophosphorus acid.¹ The extraction mechanism is discussed in the light of the results obtained.

Experimental

Apparatus

Scintillation counter with a well-type NaI(Tl) crystal connected to an EKCO automatic scaler type No. N610B.

Reagents

Organic additives. The aliphatic alcohols used (methanol, ethanol and n-propanol) and acetone were reagents grade products of BDH, Fluka and Carlo Erba.

Acids. Analytical reagents BDH or Merck. Bidistilled water was used in the preparation of the aqueous solutions.

Tracers. ^{234}Th was separated from its parent-natural uranium by solvent extraction.^{2,3} Thorium solutions were evaporated redissolved in minimum amount of HCl, HBr or H_2SO_4 , then these salt solutions were diluted with distilled water.

Solvents. The solvents used were TBP (BDH) and HDEHP, a product of Fluka A. G. or Buchs S. G., was purified according to the procedure recommended by SCHMITT and BLAKE,⁴ benzene was used for dilution of both solvents to 50% v/v TBP, and to 0.6M HDEHP.

The determination of the distribution ratio (E) was done exactly as described before.⁵

Results and discussion

As a preliminary study the extraction of thorium from pure acids was investigated.

Extraction from pure halo-acids

The extraction of both thorium sulphate and its halides has been studied with TBP and HDEHP from pure halo-acid solutions. The results are given in Figs 1 and 2 for the extraction of thorium sulphate, chloride and bromide with HDEHP, on the other hand, the three complexes are not extracted with TBP even at the highest acidity. This implies that TBP competes with the halo-acids more than thorium complexes. The appearance of minima in Fig. 1 can be explained by the change of extraction mechanism from cation exchange⁶ to solvation. While in Fig. 2 curve a, the E value of thorium bromide increases to a maximum, which is similar to the first increase in Fig. 1, and its lack can be correlated to the difference in the electronegativity of Cl^- and Br^- ions. This difference is seen to be reflected on the interaction of these ions with thorium sulphate curve b Figs 1 and 2. It is clear from Fig. 4 curve d of slope 2 and the following discussion, that at the various two maxima the extracted species are ThX_2^{2+} , where X is Cl^- or Br^- ion.

Extraction from pure sulphuric acid solutions

The effect of sulphuric acid concentration on the E values of thorium sulphate and chloride for TBP and HDEHP is shown in Fig. 3. It can be noticed that in

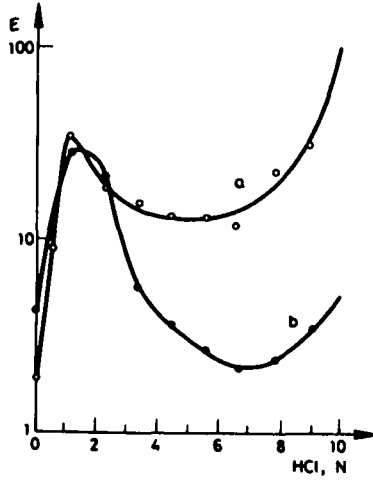


Fig. 1. Effect of HCl concentration on the extraction of thorium with HDEHP. Curves: a – thorium chloride, b – thorium sulphate

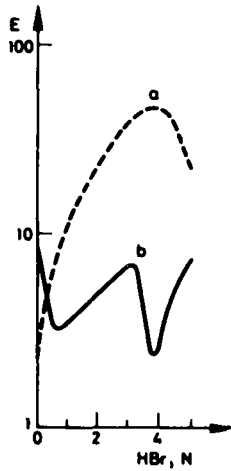


Fig. 2. Effect of HBr concentration on the extraction of thorium with HDEHP. Curves: a – thorium bromide, b – thorium sulphate

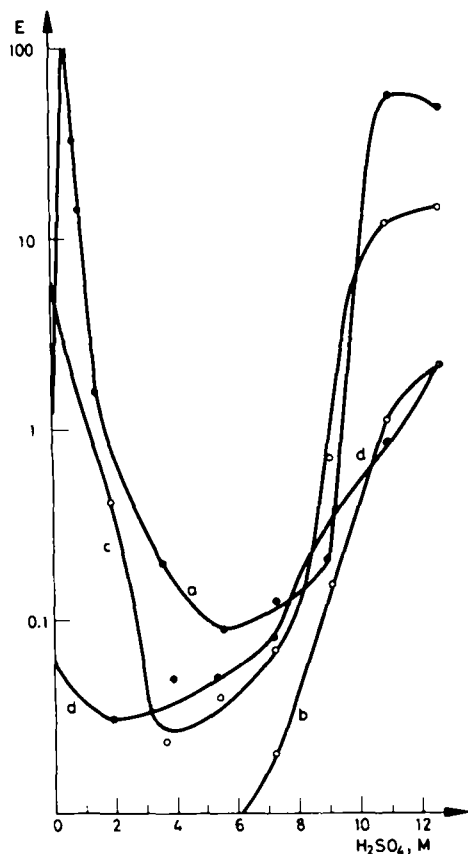


Fig. 3. Effect of sulphuric acid concentration on the distribution ratio (E) of thorium complexes. Curves: a - thorium chloride + 0.03N HCl - HDEHP, b - thorium chloride + 0.03N HCl - TBP, c - thorium sulphate - HDEHP, d - thorium sulphate - TBP

case of HDEHP the E values of thorium sulphate complexes at low sulphuric acid content (0.05M–1.5M) decrease monotonously with increasing acid concentration (curve c), while the E values of thorium chloride in the presence of 0.03N HCl (curve a) increases to a high maximum, then decreases with the same slope as that of sulphate, but to a relatively higher E values. This increase in the E values of chloride is in agreement with the fact that the predominant species extracted under these conditions are cationic thorium halides as expected from the stability order of thorium complexes with Cl⁻ ions and SO₄²⁻ ions.⁷ The effect of the HDEHP concentration on the E values (lg - lg plots) within these ranges of acidity can be de-

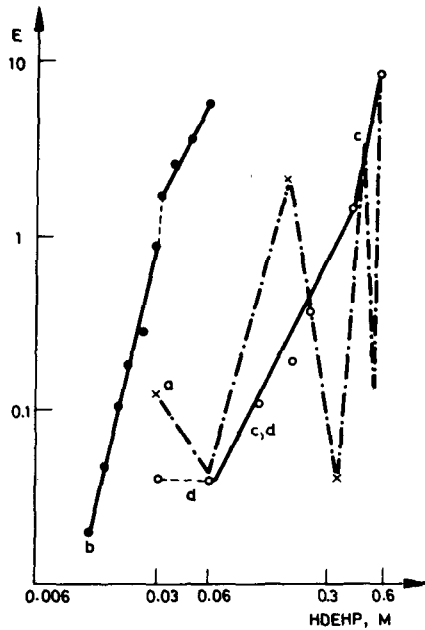
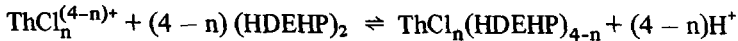


Fig. 4. Effect of HDEHP concentration on the E values of thorium complexes. Curves: a - 10.8M H₂SO₄ - thorium sulphate, b - 0.05M H₂SO₄ - thorium sulphate, c - 10.8M H₂SO₄ - 0.64N HBr - thorium bromide, d - 3.2N HBr - thorium bromide

scribed by slopes equal to 2 (Ref.⁷). Accordingly the mechanism for cationic thorium halides can be written as:

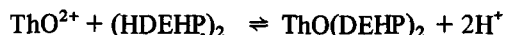
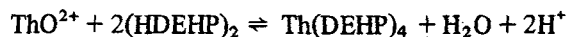
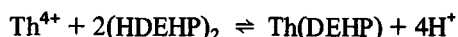


where n is the number of chloride ions, equal to 1, 2, 3 and 4 assuming ThCl₂²⁺ as the highly extractable species compared with ThSO₄²⁺.^{7,8}

On increasing the sulphuric acid concentration beyond the maxima to 6M H₂SO₄ the extraction decreases due to the formation of ThCl₃⁺ and ThCl₃⁺ that are formed from the dissociation of ThCl₂²⁺ in sulphuric acid.

Fig. 4, curve b, represent the effect of HDEHP concentration on the E values of thorium sulphate complex at constant 0.05M aqueous sulphuric acid concentration. It has been found that above 0.03M HDEHP the slope changed from 4 to 2 without any intermediate step. This can be related to the competition of the ionized acidic hydrogen of the hydroxyl group of HDEHP with water hydrated thorium

cations producing ThO^{2+} , and the following modes of extraction mechanisms operate in accordance with TEDESCO et al.⁹:



However, the hydrated ThO^{2+} cations are not present in the aqueous phase, they are formed in the extraction reactions of hydrated Th^{4+} with excess HDEHP through the engagement of the two phases.

On the other hand, the E values of both sulphate and chloride complexes were found to be negligible for TBP up to 8M H_2SO_4 beyond which the E values increase for both solvents up to the highest concentration. The extraction mechanism at this high sulphuric acid concentrations is completely different, for the acidic hydrogen of HDEHP cannot be ionized, and HDEHP acts as a solvating solvent. Fig. 4, dashed curve a, represent HDEHP concentration at constant 10.8M sulphuric acid, and it has an irregular slope that mainly depends only on the solvation of, $\text{H}_2\text{Th}(\text{SO}_4)_3$ while Fig. 8, curve b, has a slope equal to 2.6 under the same condition for TBP. Thus TBP extracts thorium sulphate complex as a $\text{H}_2\text{Th}(\text{SO}_4)_3 \cdot n\text{TBP}$ solvate where n varies between 2 and 3 and it is affected by the solvation of $\text{TBP} \cdot \text{H}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$ though the slope is not an integral number.

The addition of water miscible alcohols, acetone and halo-acids to the aqueous sulphuric acid solutions are found to influence the sensitivity of extraction. The effect of these additives were systematically studied.

Effect of water-miscible alcohols and acetone. In this part the effect of the addition of water-miscible alcohols (methanol, ethanol and n-propanol) and acetone to the aqueous phase has been investigated on the extraction of thorium chloride complex with HDEHP at 0.5M sulphuric acid concentration and thorium sulphate complex with HDEHP and TBP at 9M sulphuric acid concentration. Results of these investigations are given in Table 1 and Fig. 6.

The data in the above table show that the E values are greatly increased in the presence of these additives. This increase can be related to the decrease in the hydration of thorium cations, to the decrease in dielectric constant and proton - alcohol association in the aqueous phase, and to the formation of extractable alcohol-thorium-DEHP species in the organic phase. The decrease of E values with the further increase of the organic additive percentage is probably the result of an increasing

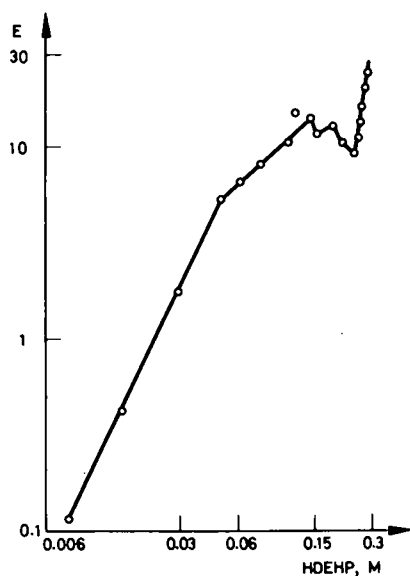


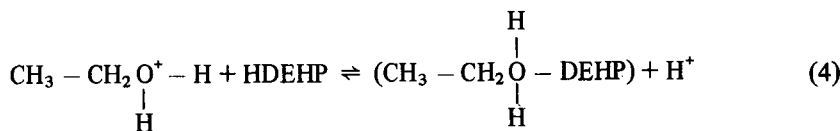
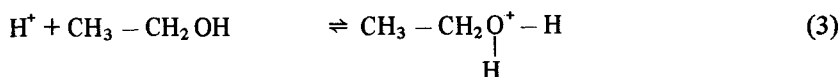
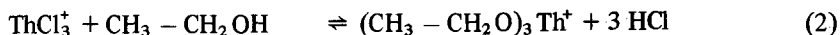
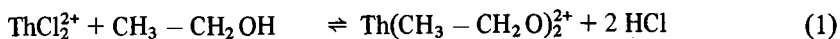
Fig. 5. Effect of HDEHP concentration on the E values of thorium chloride from 0.5M H_2SO_4 - 10% ethanol

interaction between HDEHP and alcohol through a protonated alcohol - DEHP bond Eqs (3) and (4), and the increase of the dielectric constant of the organic phase by the transfer of the additive which increases HDEHP polymerization. The increase of the volume of organic phase is 4%, 7.5%, 10%, 22.5% and 30% for the addition of 10%, 20%, 30%, 40% and 50% of ethanol or n-propanol to the aqueous phase, respectively, while in case of acetone and methanol the volume of the organic phase

Table 1
Effect of miscible organic additives on the extraction of thorium chloride from 0.5M H_2SO_4 with 0.6M HDEHP

Additive, %	E			
	Acetone	Methanol	Ethanol	n-Propanol
10	16.7	1338	1231	183
20	28.6	114.1	85	14.7
30	83.0	72.4	76.2	1.6
40	30.0	65	75.7	0.99
50	31.3	60	70.1	0.16

increases by not less than 4% for all the above percentages in aqueous phase. Thus in the extraction by HDEHP in the presence of alcohols at 0.5M sulphuric acid concentration there are other complicated reactions and the following competitive species may be proposed for all alcohols, represented here by ethanol:



It is clear that the slope of 2 in Fig. 5 corresponds to Eq. (1) up to 0.045M HDEHP, while between 0.045 and 0.14M Eq. (2) and (4) determine the slope of 1, then higher adducts are formed with alcohols as in Eq. (4). In general this effect of alcohols is similar to synergistic enhancement caused by the addition of TBP to HDEHP,¹ and more advantage due to its higher E values for very low concentrations of HDEHP.

The effect of water-miscible alcohols and acetone percentages on the E values of thorium sulphate and chloride complexes from 9M sulphuric acid for HDEHP and TBP are shown in Fig. 6. The figure shows that these additives have a much larger effect on the E values of chloride complexes than on those of sulphate. Thus the E values for HDEHP increase from 0.22 for pure 9M sulphuric acid to 70.2, 43.3, 39.5 and 29.9 and for TBP from 0.15, to 5, 4.3, 4.2 and 4 in the presence of 40% of acetone, methanol, ethanol and n-propanol, respectively. This proves the higher reactivity of species $\text{ThCl}_2^{2+} \cdot \text{SO}_4^{2-}$ with alcohols than that of thorium sulphate, and these species exist at higher sulphuric acid concentrations.

Fig. 7 represents the effect of HDEHP and TBP concentrations on the E values of thorium chloride at a constant aqueous sulphuric acid concentration of 9M in the presence of 30% ethanol. The slope equals to 2 for TBP and HDEHP. With TBP above 25% the slope changes to 3. This confirms the existence of the species $\text{ThCl}_2^{2+} \cdot \text{SO}_4$ and the reaction in Eq. (1). The higher slope with TBP can be related to the polymerization of TBP with alcohol - ThCl_2^{2+} or H_2SO_4 - alcohol solvates.¹⁰

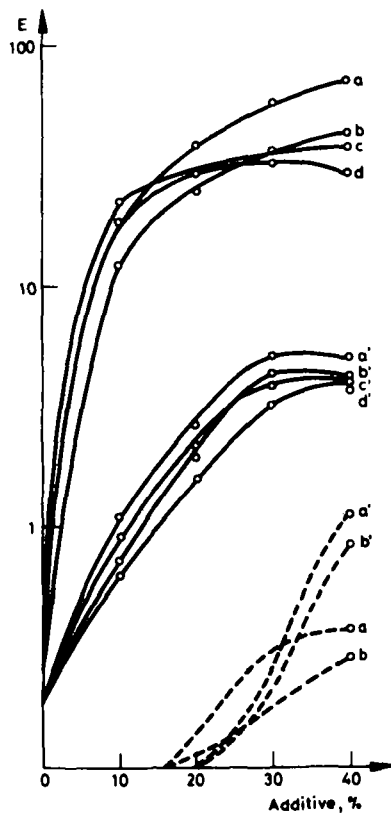


Fig. 6. Effect of water-miscible alcohols on the E values of thorium complexes from 9M sulphuric acid. Curves: a - acetone, b - methanol, c - ethanol, d - n-propanol. The two upper groups are thorium chloride for HDEHP and TBP, respectively, the two lower ones are thorium sulphate TBP and HDEHP

In general, since HDEHP is perhaps the most important reagent which is used for the separation of thorium and rare earths, the introduction of water-miscible alcohols and acetone would increase the number of factors influencing extraction and eventually the separation possibilities of thorium and rare earths, especially since these additives decrease the E values of rare earths at lower acidity.¹¹

Effect of halide acids. Recently the extraction behaviour of many elements, Co, Zn, Fe, Cd, Au, Ga, Hg, As, Se, Sn, Sb, Ge, Tl, U, Pd and In sulphates from sulphuric acid - halo-acid mixture by common extractants such as TBP, amines, and pure solvents (nitrobenzene, toluene, xylene, benzene, chloroform and carbon tetra-

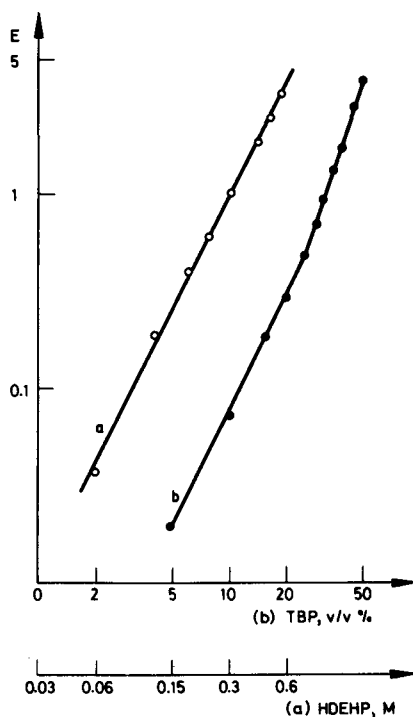


Fig. 7. Effect of HDEHP concentration (upper scale) and TBP (lower scale) concentrations on the E values of thorium chloride at 9M sulphuric acid – 30% ethanol

chloride) has been reported. Fortunately, the presence of quite low concentrations of hydrochloric or hydrobromic acid greatly increases the extraction of these elements and all elements that readily form anionic halide complexes in sulphuric acid solutions of medium concentration. For the separation of thorium from the elements mentioned above, a systematic work has been done on the extraction of thorium with TBP and HDEHP from 9M sulphuric in various halo-acid concentrations. As a preliminary step in this study the extraction of thorium sulphate by both solvents from different concentrations of sulphuric acid at constant concentration of hydrochloric (2.4N) or hydrobromic (1.8N) acids has been investigated. The results are illustrated in Table 2.

The analysis of the data in Table 2 shows that anionic thorium halide (H_2ThX_6) solvates are extracted between 9–12.6M H_2SO_4 by the two solvents, while at lower acid concentration Th^{4+} and ThX^{4-n} , formed stepwise, are the species extracted by

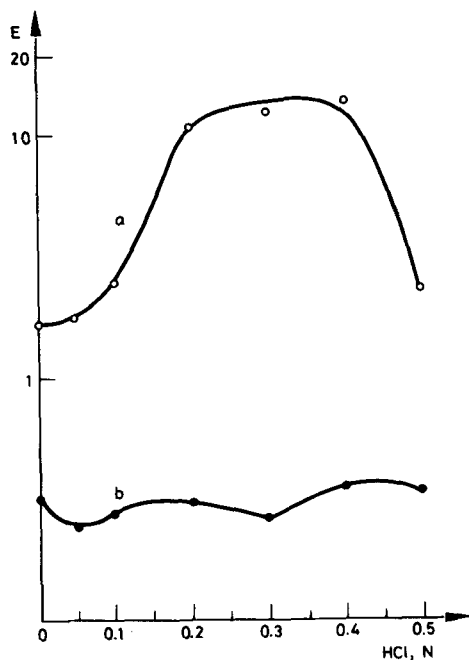


Fig. 8. Effect of hydrochloric acid concentration on the extraction of thorium chloride from 9M sulphuric acid. Curves: a – HDEHP, b – TBP

Table 2
The partition coefficient (E) of thorium sulphate from different sulphuric acid concentrations in the presence of 2.4N hydrochloric or 1.8N hydrobromic acid

H_2SO_4 M	TBP		HDEHP	
	2.4N HCl	1.8N HBr	2.4N HCl	1.8N HBr
0	0.02	0.001	16.6	4.47
1.8	0.03	0.001	0.36	3.88
3.6	0.02	0.001	0.07	0.05
4.4	0.01	0.03	0.06	0.001
7.2	0.16	0.14	0.18	0.163
9.0	0.39	0.42	1.46	2.76
10.8	0.98	1.28	3.42	6.38
12.6	2.13	1.76	6.62	2.29
14.4	0.76	0.49	0.88	0.54

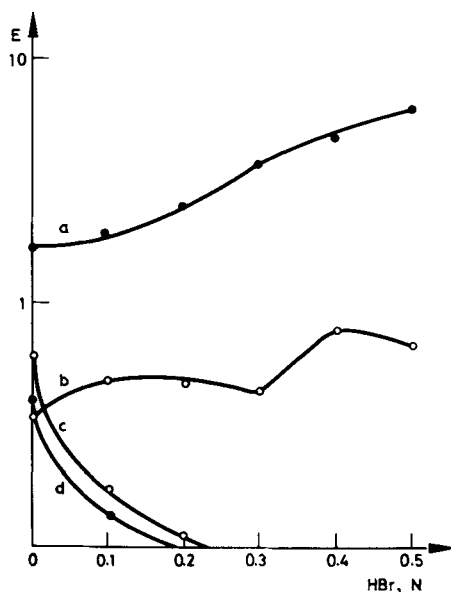


Fig. 9. Effect of hydrobromic acid concentration on the extraction of thorium complexes from 9M H_2SO_4 . Curves: a – thorium bromide-HDEHP, b – thorium bromide-TBP, c – thorium sulphate-HDEHP, d – thorium sulphate-TBP

HDEHP. The decrease of extraction beyond 12.6M H_2SO_4 can be related to the competition of H_2SO_4 and the halo-acid with the previous solvate and/or higher n-solvates are formed.

We studied the extraction behaviour of thorium sulphate and halide from 9M sulphuric acid at an increasing concentration of hydrochloric or hydrobromic acids within suitable acidity ranges. The results are shown in Figs 8 and 9. The extraction of thorium halides by HDEHP from 9M sulphuric acid is seen to increase in the presence of the two acids, while a slight effect has been found for TBP. The extraction of thorium sulphate by the two solvents, however, was not affected by the two halo-acids at the given concentrations, and this indicates that at these concentrations the formation of cations like ThX_2^{2+} predominates.

The dependence of E for thorium halides upon the concentration of HDEHP (Fig. 4) and TBP (Fig. 10), is seen to be of great interest for sulphuric acid – halo-acid mixtures. From Figs 4 and 10 curves c with slopes equal to 2 for 10.8M sulphuric acid – 0.64N HBr and from Fig. 4 a, one can deduce the presence of $ThBr_2^{2+} \cdot SO_4^{2-}$ species that are very stable at such high sulphuric concentration. The change of the slope to 4 in Fig. 4 c above 0.45M HDEHP may be due to the re-

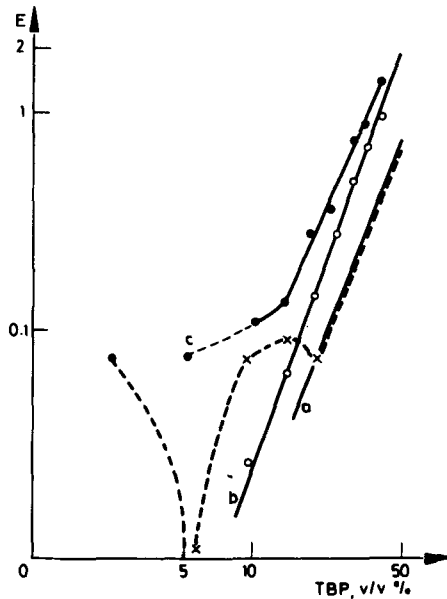


Fig. 10. Effect of TBP concentration on the E values of thorium complexes. Curves: a - 10.8M H_2SO_4 - thorium sulphate, b - 10.8M H_2SO_4 - 1.12N HCl-thorium chloride, c - 10.8M H_2SO_4 - 0.64N HBr-thorium bromide

placement of Br^- ions of ThBr_2^{2+} with DEHP anions and to the release of HBr which is also clear from the slope of 2 of curve d, using an aqueous 3.2N HBr only with HDEHP, the two lines are coincident with a slope of 2, supporting the presence of ThBr_2^{2+} species. By using 1.12N HCl instead of 0.6N HBr the slope of Fig. 10 b or TBP is equal to 2.6, and the curve lays under the HBr curve c, this concerning the properties of Cl^- and Br^- stability complexes.

Purification of thorium and its separation from other elements

Previous studies show that all elements that form stable neutral or anionic complexes are easily extracted by TBP from 9M H_2SO_4 in the presence of traces of halo-acids, while the thorium sulphate complex was not extracted to any significant extent, though TBP can be used for the separation or purification of thorium from these elements. On the other hand, thorium is completely extracted by HDEHP at low sulphuric acid content in the presence of alcohols, while rare earths are not, and complete separation can be achieved as mentioned before.

References

1. C. A. BLAKE, D. E. HORNER, J. M. SCHMITT, Report ORNL 2259, 1959.
2. F. L. MOORE, *Anal. Chem.*, 30 (1958) 908.
3. F. L. MOORE, NAS. NS 3101, Dec. 15, 1960.
4. J. M. SCHMITT, C. A. BLAKE Jr., Report ORNL, Feb., 1964, p. 3548.
5. A. ALIAN, A. HAGGAG, W. SANAD, *J. Radioanal. Chem.*, 20 (1974) 559.
6. D. F. PEPPARD, G. W. MASON, S. MCCARTHY, *J. Inorg. Nucl. Chem.*, 13 (1960) 138.
7. C. A. BLAKE Jr., C. F. BAES, K. B. BROWN, J. C. WHITE, Proc. 2nd Intern. Conf. Peaceful Uses Atomic Energy, Geneva, Vol. 28, 1958, p. 289.
8. A. J. ZIELEN, *J. Am. Chem. Soc.*, 81 (1959) 5022.
9. P. H. TEDESCO, V. B. DE RUMI, J. A. GONZALEZ QUINTANA, *J. Inorg. Nucl. Chem.*, 28 (1966) 3027.
10. E. BRAUER, E. HØGFELDT, *J. Inorg. Nucl. Chem.*, 67. (1961) 209.
11. A. ALIAN, H. J. BORN, *Radiochim. Acta*, 17 (1972) 168.