Solvent Extraction and Separation of Europium(III) and Terbium(III) from Uranium(VI) by Monooctyl anilinobenzylphosphonate

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The solvent extraction behaviour of Eu(III) and Tb(III) between aqueous solutions and a ligroin solution of monooctyl α-anilinobenzylphosphonate has been investigated. The distribution studies were carried out using the radionuclides ^{152}Eu and ^{160}Tb as tracers. Uranium was determined spectrophotometrically. The effect of varying the concentration of extractant in the organic phase and of varying the hydrogen ion concentration of the aqueous phase has been studied. Chloride, perchlorate, nitrate, and sulphate solutions were employed as aqueous phases. The metal-ligand ratios of the extractable Eu(III) and Tb(III) complexes have been determined from log-log plots of the partition coefficients *vs.* the concentrations of extractant in the organic phase and hydrogen ion concentration in the aqueous phase. Conditions for the separation of Eu(III) and Tb(III) from U(VI) are given together with the separation coefficients which were found to range from 10^3 to 10^4. The possibility of back-extracting the extracted uranium is discussed.

The application of phosphoric acid esters to the extraction of metal ions from aqueous solutions has led to results of interest both in the laboratory and in large scale industrial processes. During the past decade the rapid development in the synthetic chemistry of organophosphorus compounds has resulted in the preparation of a huge number of such organic derivatives, of which a number have found application as solvent extraction agents. It has been shown[1] that the substitution of an oxy-aryl (alkyl) ester bond in the phosphoric acid esters by a phosphorus-carbon bond leads to enhanced extraction properties due to the increased electron density on the phosphoryl oxygen atom. The increase in extracting power follows the sequence:

phosphoric acids, $(RO)_3PO$	phosphonic acids, $(RO)_2RPO$
phosphinic acids, $(RO)R_2PO$	phosphine oxides R_3PO

where R represents an alkyl or aryl radical. The extraction properties of a great number of such compounds have been investigated[2-9]. Recently, a considerable amount of interest has been directed towards the monoesters of phosphonic acids by means of which the alkaline earth elements[10], the lanthanides[11,12], thorium[13] and the curides[14,15] have been extracted. Up to

date, however, there does not appear to be any report in the literature of the use of either the neutral or acidic esters of α-amino-alkyl phosphonic acids as extraction agents. In an earlier paper[16], the extraction of certain metals using monoesters of α-anilinobenzylphosphonic acid was described. The present paper deals with the use of such a system for the extraction of Eu(III) and Tb(III) and their separation from U(VI). The variation of the distribution coefficient D as a function of the hydrogen ion concentration in aqueous chloride, perchlorate, and nitrate phases and as a function of the concentration of extractant in the organic phase has been studied. From log-log plots of the distribution ratio against the concentration of extractant in the organic phase, and against the hydrogen ion concentration in the aqueous phase, the metal-ligand ratios of species formed in the organic phase have been deduced.

<div align="center">EXPERIMENTAL</div>

Preparation of Solutions

Standard solutions of europium and terbium compounds were prepared by dissolving Eu_2O_3 and Tb_2O_3 (Johnson, Matthey and Co. Ltd., London) in suitable mineral acids. Solutions of radioactive nuclides (U.K.A.E.A., Harwell, Britain) were prepared analogously by adding negligible concentrations of the tracer to the standard solutions of europium and terbium. Solutions of uranium(VI) were obtained by dissolving uranyl acetate in doubly distilled water and then adding sulphuric acid until the desired acidity was achieved. All chemicals were of reagent grade purity.

Monooctyl α-anilinobenzylphosphonate (MOABP) was prepared as described in an earlier paper[17]. A solution of MOABP in ligroin (E. Merck, B.P. 150—180°C) was employed as the organic phase.

Measurement of Distribution Ratios

Distribution ratios for Eu(III) and Tb(III) were determined radiometrically, by measuring the activities of ^{152}Eu and ^{160}Tb in the two phases. The activity was measured using a well-type γ-scintillation counter. All counts were corrected for background. After the phases had been mixed for a period of two minutes, and then separated, 1 ml. of each phase was taken for assay. A contact time of 2 minutes sufficed in all cases for the attainment of equilibrium. The distribution ratios were determined from the corrected activities of the aqueous and organic phases. The values of D refer to one-step shaking. The ratio of the phase volumes was always 1 : 1 and the volume of each phase was usually 5 ml. Uranium was determined as the 8-hydroxyquinolate complex by measuring the absorption on a Hilger spectrophotometer at 425 mμ according to the method described by B. Hök[18].

Only aqueous phases were assayed for uranium since in the case of the organic phases difficulties arose due to the formation of insoluble uranium phosphate during the degradation of the extractant with a mixture of nitric and perchloric acids.

<div align="center">RESULTS</div>

I. The Extraction of Europium(III) and Terbium(III) with MOABP

(a) Variation of the distribution ratio as a function of acid concentration. — The variation of the distribution ratios of Eu(III) and Tb(III) with varying the hydrogen ion concentration in the aqueous phase is shown in Figures 1 and 2. The experiments were carried out using aqueous solutions of hydrochloric, perchloric and nitric acid. The ionic strength was kept constant by adding sodium chloride, perchlorate, and nitrate respectively. The hydrogen ion concentration values were obtained by measuring the pH

of the aqueous phases after the equilibrium was attained. The results show that for the aqueous perchlorate solutions the distribution ratio for europium and terbium is dependent on the third power of the hydrogen ion concentration. Similar properties are exhibited by hydrochloric acid solutions. Thus the slope —3 is obtained for europium and —2.6 for terbium. The deviation from the slope —3 is more significant for aqueous solutions of nitric acid. This discrepancy is probably due to complex forming properties of anions.
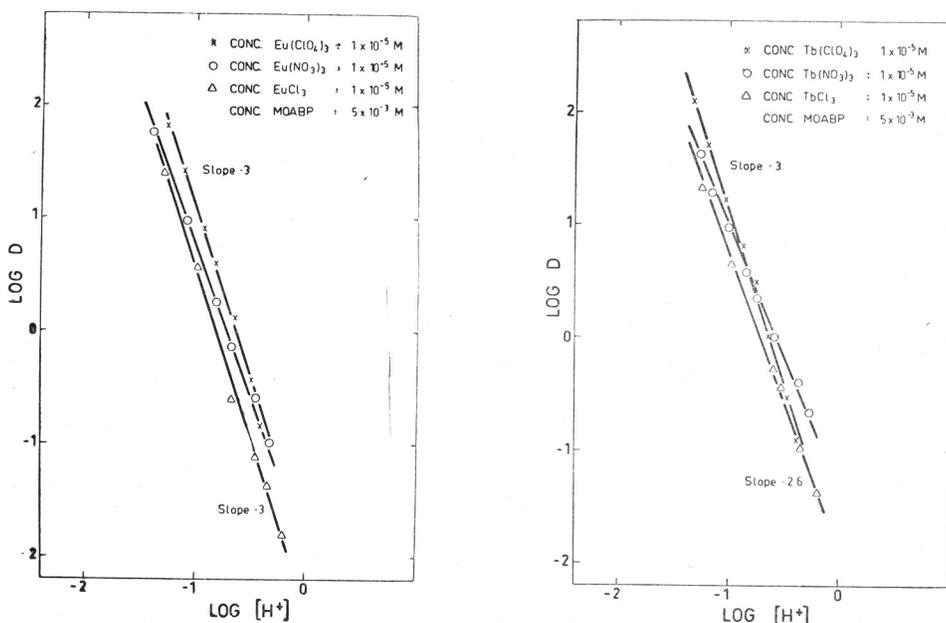
Fig. 1. Influence of the hydrogen ion concentration in the aqueous phase on the distribution ratios, D, of europium(III). Aqueous phase: $\times$ NaClO$_4$ + HClO$_4$, ClO$_4^-$ = 1M const.; O NaNO$_3$ + + HNO$_3$, NO$_3^-$ = 1M const; $\triangle$ NaCl + HCl, Cl$^-$ = 1M const. Ratio of phases 1 : 1. Shaking time 2 minutes.

Fig. 2. Influence of the hydrogen ion concentration in the aqueous phase on the distribution ratios, D, of terbium(III). Aqueous phase: $\times$ NaClO$_4$ + HClO$_4$, ClO$_4^-$ = 1M const.; O NaNO$_3$ + + HNO$_3$, NO$_3^-$ = 1M const.; $\triangle$ NaCl + HCl, Cl$^-$ = 1M const.

(b) *Variation of D with the concentration of extractant in the organic phase.* — The variation of the distribution ratios of Eu(III) and Tb(III) as a function of the concentration of MOABP in the organic phase is shown as a log-log plot in Figures 3 and 4. Extractions were carried out employing aqueous phases maintained at a constant concentration 0.2 M of HClO$_4$, HNO$_3$ and HCl. The total concentration of the MOABP was at least 50 times the metal ion concentrations. Thus it was possible to neglect the quantity of reagent bound to the metal and to plot the logarithm of the total concentration of the MOABP rather than of the free extracting agent. From Fig. 3 and 4 it may be seen that the distribution ratios for europium and terbium is dependent on the second power of the MOABP concentration in the organic phase. The possible compositions of extractable europium and terbium complexes can be deduced from these results and are discussed later in the paper.
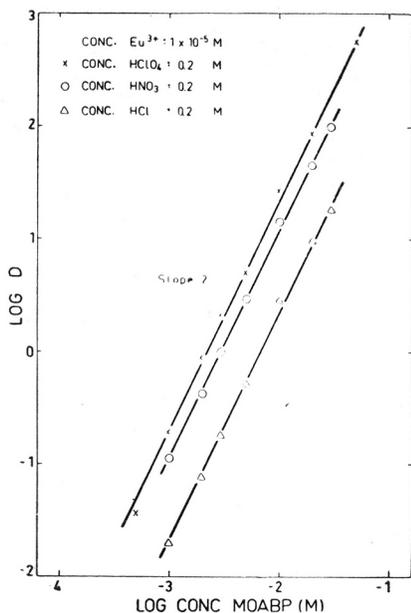
Fig. 3. Influence of the MOABP concentration in the organic phase on the distribution ratios, D, of Eu(III) in the presence of: ✕ perchloric, ○ nitric and △ hydrochloric acid. Initial concentration of acids 0.2M.
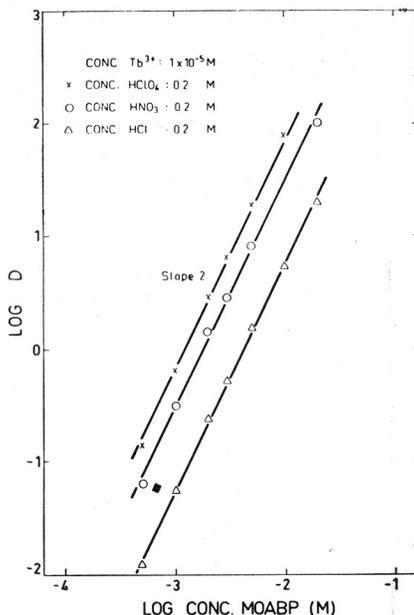
Fig. 4. Influence of the MOABP concentration in the organic phase on the distribution ratios, D, of Tb(III) in the presence of: ✕ perchloric, ○ nitric and △ hydrochloric acid. Initial concentration of acids 0.2M.

II. Separation of Europium(III) and Terbium(III) from Uranium(VI) with MOABP

The dependence of the extraction of Eu(III) and Tb(III) expressed in per cent of extracted metal, on the concentration of hydrochloric, nitric, and sulphuric acid in the aqueous phase is shown in Figs. 5 and 6. The extraction of both metals is very similar. The maximum value of the distribution ratio of Eu(III) and Tb(III) (D_{max}. ∼ 10^2 to 10^3) occurs at an acid concentration of 0.01 N. The distribution ratios decrease rapidly with increasing the acid concentration until they attain a value of practically zero at 1 M concentration of the acids.

Experimental studies have shown that the extraction of U(VI) by MOABP is almost quantitative provided the concentration of the extractant is five times the uranium concentration[16], and furthermore that the extraction of uranium remains quantitative at considerably higher hydrogen ion concentrations (i.e. from 0.01 M to 5 M H_2SO_4) whilst already with 0.5 M H_2SO_4, the per cent of extracted europium and terbium is very small (D ∼ 10^{-2} to 10^{-3}) as can be seen from Figures 5 and 6. The separation of uranium from Eu and Tb is based on this difference. Results of experiments on the separation of uranium and europium are shown in Table I. Various mutual concentrations of metal and MOABP were studied. The separation factors defined as the ratio D_{UO_2}/D_{Eu} were found to range from approximately 10^3 to 10^4 The results of the separation of terbium from uranium have not been given since they resemble the results for the UO_2 : Eu system so closely.
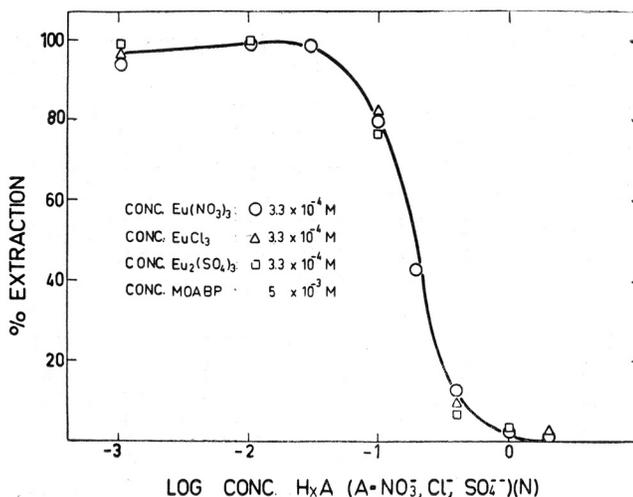
Fig. 5. Extraction of europium(III) ($3.3 \times 10^{-4} M$) with ligroin solution of MOABP ($5 \times 10^{-3} M$) from the aqueous solution of ○ nitric, △ hydrochloric and □ sulphuric acid. Acid concentration varied.

III. Back-extraction of U(VI) from the Organic Phase

Earlier investigations have shown that uranium(VI) combines with MOABP to form a complex that is very stable in acid solutions.* Attempts to back-extract uranium from the organic phase with aqueous solutions of hydrofluoric acid (5%), oxalic acid (0.5 M), alkaliphosphates, sodium carbonate and ammonia have not proved successful. However, when a solution of the uranyl complex in an organic solvent (ligroin, ether) was shaken with a 1M solution of aqueous NaOH or KOH, the complex decomposed quantitatively.
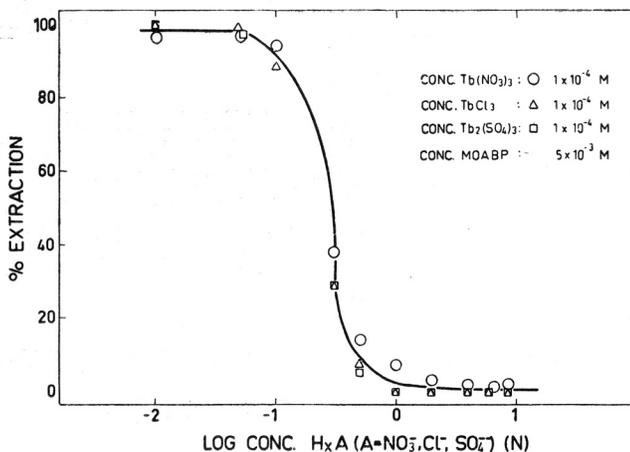

Fig. 6. Extraction of terbium(III) ($1 \times 10^{-4} M$) with ligroin solution of MOABP ($5 \times 10^{-3} M$) from the aqueous solution of ○ nitric, △ hydrochloric and □ sulphuric acid. Acid concentration varied.

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* In the uranyl—MOABP complex, two molecules of MOABP are bound to the uranyl ion.
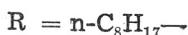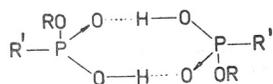
TABLE I

Separation of europium(III) from uranium(VI) by means of MOABP from the aqueous solutions with the constant concentration of sulphuric acid 1M

MOABP concentration, N	Eu^{3+} concentration, N	UO$_2^{2+}$ concentration, N	Distribution ratios, D		Per cent of extraction		Separation factor $\beta = D_{UO_2}/D_{Eu}$
			Eu^{3+}	UO$_2^{2+}$	Eu^{3+}	UO$_2^{2+}$	
5×10^{-2}	2×10^{-9}	4×10^{-3}	0.026	140	2.5	99.4	5.4×10^3
,,	,,	1×10^{-2}	0.0138	361.3	1.3	99.8	2.6×10^4
,,	,,	2×10^{-2}	0.0199	192	1.9	99.6	9.6×10^3
,,	,,	4×10^{-2}	0.0255	2.88	3.0	75,0	1.1×10^2
5×10^{-3}	1×10^{-4}	1×10^{-4}	0.0022	10.85	0.2	91.5	4.9×10^0
,,	,,	4×10^{-4}	0.0035	42.0	0.3	99.0	1.2×10^4
,,	,,	1×10^{-3}	0.0011	26.2	0.1	96.5	2.4×10^4
,,	,,	4×10^{-3}	0.0055	144.3	0.5	99.4	2.6×10^4
,,	2×10^{-9}	4×10^{-4}	0.0128	42.0	1.3	99.0	3.3×10^3
,,	,,	1×10^{-3}	0.0101	35.33	1.0	97.3	3.5×10^3
,,	,,	2×10^{-3}	0.0065	144	0.5	99.5	2.2×10^4
,,	,,	4×10^{-3}	0.0112	197	1.0	99.5	1.8×10^4

The uranium was precipitated as the diuranate and the extractant passed into the aqueous phase as the soluble sodium or potassium salt. After the precipitated uranium salt had been separated, the solution containing the alkali metal salt of MOABP was acidified with a mineral acid, whereby the acidic phosphonic ester passed back into the organic phase. Where very diluted solutions of MOABP had been employed for the extraction of uranium it was necessary to concentrate the organic phase by distillation *in vacuo* before carrying out the back-extraction. When ligroin was employed as the diluent, it was found possible to concentrate the organic phase up to a point where it contained 0.1M of MOABP saturated with uranium.

DISCUSSION

Molecular weight experiments on MOABP in chloroform indicate that the substance exists in the form of dimers. This is analogous to the results found in investigations on phosphonic acid[19] and the mono-basic esters of orthophosphoric acid.[20] The formation of the dimer probably takes place through the formation of hydrogen bridges between the acidic OH and the phosphoryl $P \rightarrow O$ groups of two neighbouring MOABP molecules, whereby an 8-membered cyclic system results.

$$R'-P\underset{O-H\cdots O}{\overset{RO}{\underset{}{\big\downarrow}}}\overset{O\cdots H-O}{\underset{OR}{P-R'}} \qquad R' = C_6H_5NHCH(C_6H_5)-$$
$$R = n\text{-}C_8H_{17}-$$

The existence of such a dimer indicates the low electronegativity of the nitrogen atom bound to the benzene ring since »betaine« formation might be expected to occur between an electronegative -NH group and the POOH group[17], *e.g.* $C_6H_5\overset{+}{N}H_2CH(C_6H_5)PO(OC_8H_{17})O^-$. Intramolecular proton migration

leading to such structures has not been observed but intermolecular condensation leading to the formation of the dimer occurs. Since the dimer is formed in solvents of low dielectric constant such as chloroform (dielectric constant 5.05), their occurrence in non-polar solvents of even lower dielectric constant (e.g. in ligroin, dielectric constant = approx. 2) is even more probable. If dimerisation of the reagent is taken into account together with the dependence of log D on the second power of the log concentration of the extractant in the organic phase and on the third power dependence of the log hydrogen ion concentration in the aqueous phase, and with the fact that europium and terbium exhibit a usual coordination number of 6, then it would appear that monoionisation of the dimeric molecules of extractant occurs. This may be represented by the following equation:
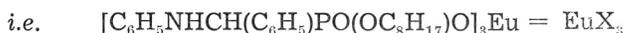
$$[C_6H_5NHCH(C_6H_5)PO(O.C_8H_{17})OH]_2 \rightleftarrows$$
$$\{[C_6H_5NHCH(C_6H_5)PO(OC_8H_{17})O^-]_2H^+\}^- + H^+ \qquad (1)$$
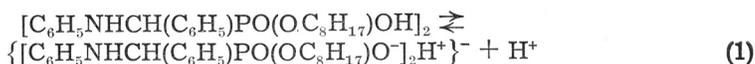
The monoionisation of dimeric molecules has also been shown to occur in the case of the diester of orthophosphoric acid[21], $(RO)_2PO(OH)$, as well as in the case of the monoesters of phosphonic acid[22], $(RO)RPO(OH)$. The overall reaction occurring between europium and terbium ions and the organic dimers may then be written:

$$M^{3+}_{aq.} + 2(HX)_{2_0} \rightleftarrows MX_2(HX_2)_0 + 3H^+ \qquad (2)$$
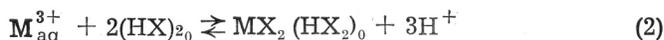
where M^{3+} represents the metal ion, $(HX)_2$ the dimerised MOABP; $MX_2(HX_2)$ is the neutral metal complex formed and the subscripts aq. and o refer to equilibrium species present in the aqueous and the organic phases respectively.

From equation 2 it can be assumed that one molecule of the dimer $(HX)_2$ is monoionised while the second one is completely dissociated. The function of monoionised molecules of the dimer $(HX_2)^-$ as ligands, as proposed in equation (2), has been illustrated by the following experiment. By the addition of an aqueous solution of sodium octyl anilinobenzylphosphonate to a solution of a europium salt, a solid was precipitated in which one atom of Eu(III) was bound to three anions of MOABP.

i.e. $[C_6H_5NHCH(C_6H_5)PO(OC_8H_{17})O]_3Eu = EuX_3$

The formation of EuX_3 in aqueous solution can be understood since the anion $C_6H_5NHCH(C_6H_5)PO(OC_8H_{17})O^-$ coexists together with undissociated molecules of the Na salt. Hence the formation of the above complex may be represented by the equation:

$$Eu^{3+}_{aq.} + 3X^-_{aq.} \rightarrow EuX_3 \downarrow \qquad (3)$$

EuX_3, unlike $EuX_2(HX_2)$, is insoluble in organic solvents. If, however, EuX_3 is suspended in an ether or ligroin solution of MOABP, it dissolves completely with the probable formation of the complex $EuX_2(HX_2)$. Since this may also be written as $EuX_3 \cdot HX$ it is plausible that this additional molecule of the extractant, bound as solvate molecule through a hydrogen bridge to the neutral metal complex EuX_3, causes the solubility of such a complex in organic solvents.

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IZVOD

Ekstrakcija europija(III) i terbija(III) i njihova separacija od urana(VI) pomoću monooktilnog estera anilinobenzilfosfonske kiseline

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Ispitana je ekstrakcija europija(III) i terbija(III) iz vodenih otopina pomoću petrolejske otopine monooktilnog estera α-anilinobenzilfosfonske kiseline. Koeficijenti ekstrakcije su određivani pomoću radionuklida 152-Eu i 160-Tb. koji su dodavani standardnim otopinama metala. Uran je određivan spektrofotometrijski. Studirana je ovisnost koeficijenata ekstrakcije o koncentraciji ekstraktanta u organskoj fazi i o promjeni pH u vodenoj fazi u prisutnosti iona perklorata, klorida i nitrata. Iz ovisnosti logaritama koeficijenta ekstrakcije od logaritma koncentracije ekstraktanta u organskoj fazi i logaritma koncentracije vodikovih iona u vodenoj fazi određeni su omjeri metal — ligand u kompleksima Eu(III) i Tb(III) koji nastaju kod ekstrakcije. Određeni su uvjeti pod kojima je moguća separacija Eu(III) i Tb(III) od U(VI). Nađeni koeficijenti separacije iznose 10^3 do 10^4. Opisana je mogućnost reekstrakcije urana uz regeneriranje ekstraktanta.