

## Solvent Extraction of $^{152, 154}\text{Eu}$ and $^{241}\text{Am}$ by Di-*n*-butyl Phosphate (DBP) in Different Organic Solvents

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The distribution of  $^{241}\text{Am}$  and  $^{152, 154}\text{Eu}$  between aqueous nitric acid and solutions of di-*n*-butyl phosphate (= HA) has been studied in seven organic solvents. The data indicated that in five systems, M is extracted into the organic phase predominately as  $\text{MA}_3(\text{HA})_3$ . The following values were found for  $\log K$  for the reaction  $\text{M}^{3+}(\text{aq}) + 3 \text{A}^-(\text{aq}) + 3 \text{HA}(\text{aq}) \rightleftharpoons \text{MA}_3(\text{HA})_3(\text{org})$ : in *n*-hexane 13.66 (Eu), 12.38 (Am); in  $\text{CCl}_4$  16.80 (Eu), 15.33 (Am); in  $\text{CHCl}_3$  19.33 (Eu), 17.98 (Am); in *iso*-propyl ether 14.94 (Eu), 13.72 (Am); in hexone 15.22 (Eu), 14.25 (Am); in hexol 14.15 (Eu), 14.02 (Am). In *n*-hexane, deviations at  $[\text{HA}] > 10^{-1.8}$  M indicate the formation of other complexes, perhaps  $\text{MA}_3(\text{HA})_6(\text{org})$ . — In hexol, complexes with less HA appear for  $[\text{HA}] < 10^{-3}$  M. The data may be accounted for by the additional reaction  $\text{M}^{3+} + 3 \text{A}^- \rightleftharpoons \text{MA}_3(\text{org})$ ,  $\log K = 5.76$  (Eu), 5.36 (Am). In tri-*n*-butyl phosphate (TBP), the reaction  $\text{M}^{3+} + 3\text{NO}_3^- + 3\text{TBP}(\text{org}) \rightleftharpoons \text{M}(\text{NO}_3)_3(\text{TBP})_3(\text{org})$  predominates for  $[\text{HA}] < 10^{-3}$  M; for  $[\text{HA}] > 10^{-4}$  M, the data indicate  $\text{M}^{3+} + 3 \text{A}^- \rightleftharpoons \text{MA}_3(\text{org})$ ,  $\log K = 7.49$  (Eu), 6.98 (Am).

Parallels are drawn between the effect of the solvent on metal extraction equilibria and on the dimerization and distribution of HA (DBP) itself.

For practical separation of Eu and Am, *n*-hexane,  $\text{CCl}_4$  and  $\text{CHCl}_3$  are the best of the solvents studied; for given concentrations of HA and  $\text{H}^+$ , *n*-hexane and  $\text{CCl}_4$  give the highest distribution ratio.

The use of dialkyl phosphates  $(\text{RO})_2\text{P}_2\text{OH}$  in solvent extraction for trivalent lanthanide and actinide ions has been reported by Peppard *et al.*<sup>1-4</sup>, Dyrssen<sup>5</sup>, Scadden and Ballou<sup>6</sup>.

The aim of the present investigation was to study the influence of various organic solvents on the extraction of  $\text{Am}^{3+}$  and  $\text{Eu}^{3+}$  ions from a 0.1 M  $\text{HNO}_3$  solution with DBP as complexing agent. The following organic solvents have been used: *n*-hexane,  $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$ , carbon tetrachloride,  $\text{CCl}_4$ , chloroform,  $\text{CHCl}_3$ , *isopropyl* ether,  $(\text{CH}_3)_2\text{CHOCH}(\text{CH}_3)_2$ ; methyl *isobutyl* ketone (hexone),  $(\text{CH}_3)_2\text{CHCH}_2\text{COCH}_3$ , tri-*n*-butyl phosphate,  $(n\text{-C}_4\text{H}_9\text{O})_3\text{PO}$ , and methyl *isobutyl* carbinol (hexol),  $(\text{CH}_3)_4\text{CHCH}_2\text{CH}(\text{OH})\text{CH}_3$ .

To explain the results one must take into account the extent of dimerization of DBP in the organic solvents. A separate investigation was carried out to study the distribution behaviour of DBP between the above mentioned organic solvents and an aqueous 0.1 M HNO<sub>3</sub> solution, the results of which are reported in the previous article <sup>7</sup>.

### EXPERIMENTAL

*Reagents:* The DBP, (n-C<sub>4</sub>H<sub>9</sub>O)<sub>2</sub>PO<sub>2</sub>H, kindly supplied by Albright and Wilson Ltd., London, was purified as described in the previous paper <sup>7</sup>.

The β-active nuclide (13 and 16 years) <sup>152, 154</sup>Eu and the α-active 458 years <sup>241</sup>Am were obtained from Harwell, England. No carrier was added to the solutions; but the initial concentration of Eu in the 0.1 M HNO<sub>3</sub> solution was about 2 × 10<sup>-6</sup> M; the initial concentration of <sup>241</sup>Am was calculated as 8 × 10<sup>-7</sup> M.

The 0.1 M HNO<sub>3</sub> solution was prepared from analytical grade reagent. The NH<sub>3</sub> solution, used for increasing the pH of the solution in the experiments with hexol, was also of analytical grade.

*Distribution measurements:* Equal volumes (5 ml) of a solution of DBP in an organic solvent and a 0.1 M HNO<sub>3</sub> solution containing Am and Eu were shaken for 24 h. The two liquid phases were separated by means of centrifugation. All experiments were carried out in a thermostated room at 25.0 ± 0.3°C. From each phase a 0.1 ml volume was pipetted, evaporated to dryness and then heated at 250°C to decompose the remaining organic substances. The activity measurements were carried out in a Tracerlab SC-16 windowless proportional counter. The α-activity was measured at 1 450 V and 10 mV sensitivity and the β-activity at 1 700 V, 1 mV sensitivity and using an Al absorber of 6.2 mg/cm<sup>2</sup> thickness. Corrections were made for background; in β-activity measurements correction was also made for γ-activity background from Am.

Measurements of the hydrogen ion concentration, when NH<sub>3</sub> was added, were carried out with a Radiometer pHM3i valve potentiometer, equipped with a Radiometer glass electrode G 100 and a calomel electrode K 100. The electrodes were standardized against 0.01 M HClO<sub>4</sub> + 0.09 M NaClO<sub>4</sub> (-log [H<sup>+</sup>] = 2.00). The constants used for the calculations of [H<sub>2</sub>A<sub>2</sub>]<sub>org</sub>, [HA]<sub>org</sub>, [HA] and [A<sup>-</sup>] (ionic medium = 0.1 M HNO<sub>3</sub>) are given in the previous article <sup>7</sup>.

### Symbols and formulas

[ ]	concentrations in the aqueous phase
[ ] <sub>org</sub>	concentrations in the organic phase
C <sub>A</sub>	initial total concentration of DBP in the organic phase
C <sub>org</sub> ; C <sub>aq</sub>	equilibrium total concentrations of DBP in each phase
HA	di-n-butylphosphate (DBP), (n-C <sub>4</sub> H <sub>9</sub> O) <sub>2</sub> PO <sub>2</sub> H
K <sub>a</sub> (eqn. 3)	stoichiometric acid dissociation constant
K <sub>d</sub> (eqn. 1)	distribution constant for HA
K <sub>2</sub> (eqn. 2)	dimerization constant in the organic phase
M	Am or Eu
q <sub>M</sub>	net distribution ratio of M (org/aq)

### RESULTS AND DISCUSSION

#### Conclusions about the extractable species

The experimental data obtained with our seven solvents are listed in Tables 1 and 2. The primary data are C<sub>A</sub>, the total (analytical) concentration

Table 1. The distribution of Eu and Am between solutions of DBP in different organic diluents and 0.1 M HNO<sub>3</sub> at 25°C.

	log $C_A$	log [HA]	log $q_{Eu}$	log $q_{Am}$	
<i>n</i> -Hexane	-0.283	-1.67	> +2.4	+2.351	
	-0.313	-1.74	> +2.4	+2.921	
	-0.494	-1.76	> +2.4	+2.442	
	-0.505	-1.70	> +2.4	+1.901	
	-0.711	-1.79	> +2.4	+2.178	
	-1.012	-1.88	+2.327	+1.373	
	-1.313	-2.01	+1.425	+0.394	
	-1.535	-2.16	+0.677	-0.590	
	-1.710	-2.27	+0.058	-1.301	
	-2.013	-2.49	-1.173	-2.499	
	-2.284	-2.62	< -2.5	-3.316	
	Carbon tetra- chloride	-0.301	-2.10	> +2.5	+2.108
		-0.699	-2.31	> +2.5	+1.341
		-1.000	-2.48	+1.806	+0.462
-1.301		-2.64	+0.818	-0.619	
-1.523		-2.76	+0.188	-1.178	
-1.724		-2.87	-0.421	-1.851	
-2.000		-3.02	-1.205	-2.292	
-2.301		-3.18	-2.203	-3.367	
-2.523		-3.31	< -3.2	< -3.5	
-3.000		-3.61	< -3.5	< -3.5	
Chloroform	-0.317	-2.86	+2.075	+0.745	
	-0.714	-3.06	+0.902	-0.372	
	-1.016	-3.22	+0.044	-1.369	
	-1.317	-3.37	-0.866	-2.254	
	-1.547	-3.49	-1.508	-2.771	
	-1.724	-3.57	-2.080	-3.264	
<i>Isopropyl</i> ether	-0.307	-2.00	+2.541	+1.598	
	-0.705	-2.19	+1.616	+0.548	
	-1.006	-2.35	+0.661	-0.441	
	-1.307	-2.54	-0.250	-1.449	
	-1.705	-2.79	-1.589	-2.819	
	-2.006	-2.99	-2.577	-3.485	
Hexone (methyl <i>isobutyl</i> ketone)	-0.304	-2.30	+1.267	+0.284	
	-0.401	-2.35	+0.989	+0.097	
	-0.577	-2.46	+0.481	-0.470	
	-0.702	-2.53	+0.047	-1.054	
	-0.799	-2.59	-0.143	-1.102	
	-0.906	-2.67	-0.991	-1.988	
	-1.100	-2.79	-1.000	-2.000	
	Tri- <i>n</i> -butyl phosphate (TBP)	-0.301	-2.45	+0.143	-0.338
-0.321		-2.47	+0.125	-0.481	
-0.418		-2.54	-0.158	-0.562	
-0.542		-2.64	-0.554	-1.068	
-0.719		-2.78	-0.782	-1.059	
-1.301		-3.30	-2.025	-2.079	
-1.398		-3.39	-2.353	-2.230	
-1.699		-3.68	-2.312	-2.473	
-2.000		-3.98	-2.299	-2.486	

Table 2. The distribution of Eu and Am between solutions of DBP in hexol (methyl isobutyl carbinol) and 0.1 M (H,NH<sub>4</sub>)NO<sub>3</sub> at 25°C.

log C <sub>A</sub>	-log [H <sup>+</sup> ]	log [HA]	log q <sub>Eu</sub>	log q <sub>Am</sub>
-0.306	1.895	-2.530	+1.630	+1.093
-0.481	1.000	-2.686	-1.700	-1.891
-0.514	1.000	-2.719	-1.636	-2.076
-0.560	1.376	-2.769	-1.110	-1.436
-0.657	1.000	-2.862	-2.636	-2.698
-0.704	2.107	-2.940	+0.473	-0.096
-0.958	1.376	-3.167	-2.575	-2.744
-1.007	2.206	-3.246	-0.378	-0.866
-1.306	2.262	-3.556	-1.058	-1.554
-1.536	2.359	-3.799	-1.616	-2.043
-1.703	2.362	-3.964	-2.042	-2.392

of HA in the organic phase at the start, and  $q_M$ , the distribution ratio of the metal between organic and aqueous phase. From previous work <sup>7</sup>, the following equilibrium constants are known:

$$K_d = [\text{HA}]_{\text{org}}[\text{HA}]^{-1}; K_2 = [\text{H}_2\text{A}_2]_{\text{org}}[\text{HA}]_{\text{org}}^{-2}; K_a = [\text{H}^+][\text{A}^-][\text{HA}]^{-1} \quad (1-3)$$

The total concentration of M is so low that the amount of A bound by M can always be neglected and since the volumes of the aqueous and organic phases are equal, we have

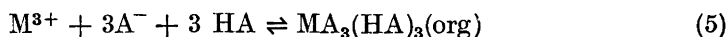
$$C_A = 2[\text{H}_2\text{A}_2]_{\text{org}} + [\text{HA}]_{\text{org}} + [\text{HA}] + [\text{A}^-] \quad (4)$$

Inserting [H<sup>+</sup>] and the equilibrium constants from the previous paper <sup>7</sup>, we may then find the concentrations of the various species for each C<sub>A</sub>. At C<sub>A</sub> > 0.06 M for hexane eqn (4) cannot be used since HA is further polymerized; [HA] and [A<sup>-</sup>] can, however, be determined from the distribution curve of DBP <sup>7</sup>.

We can now proceed to discuss the formulas of the M-containing species. For the five solvents, *hexane*, *carbon tetrachloride*, *chloroform*, *isopropyl ether* and *hexone*, practically rectilinear plots are obtained if log q<sub>M</sub> [A<sup>-</sup>]<sup>-3</sup> is plotted as a function of log [HA] (Figs 1—5). In all cases, the slope is practically equal to 3 (straight lines in Figs 1—5). It thus seems likely that the same reaction predominates in all these solvents. At these low concentrations it seems practically certain that the metal atoms exist as a mononuclear species; it should be noticed that the metal concentration in each phase has been varied by a factor of at least 100 which would be expected to cause deviations from linearity if polynuclear complexes had been important.

Moreover, we may assume that the species in aqueous solution is M<sup>3+</sup>, *i.e.* Eu<sup>3+</sup> or Am<sup>3+</sup>. In the various equilibrium mixtures, the concentration [HA] in the aqueous phase has varied from 10<sup>-2.0</sup> to 10<sup>-3.6</sup>, and one would have expected bent curves, if several species had been present in the aqueous phase.

Granted that the metals exist as M<sup>3+</sup> in the aqueous phase, and that q<sub>M</sub> is proportional to [A<sup>-</sup>]<sup>3</sup> and [HA]<sup>3</sup>, the following reaction is indicated:



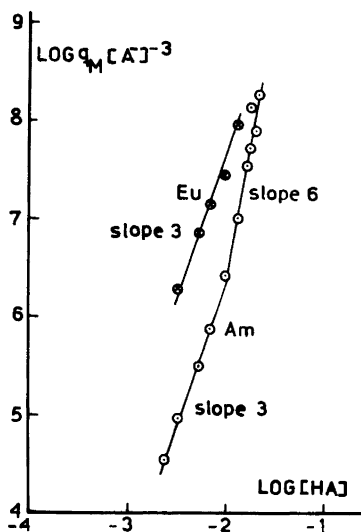


Fig. 1. DBP-hexane: Variation of  $q_M [A^-]^{-3}$  with  $[HA]$  for the extraction of Eu and Am from 0.1 M  $HNO_3$ . The distribution data are given in Table 1. The slope of the straight lines is 3.

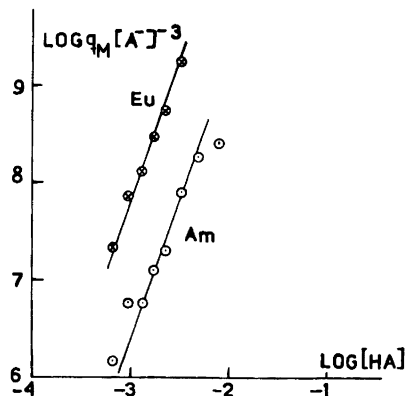


Fig. 2. DBP- $CCl_4$ : Variation of  $q_M [A^-]^{-3}$  with  $[HA]$  for the extraction of Eu and Am from 0.1 M  $HNO_3$ . The distribution data are given in Table 1. The slope of the straight lines is 3.

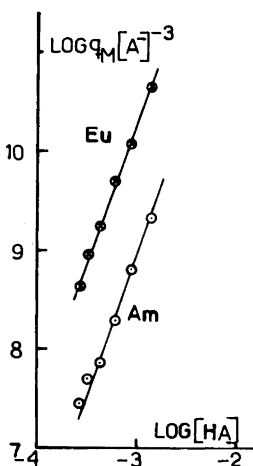


Fig. 3. DBP- $CHCl_3$ : Variation of  $q_M [A^-]^{-3}$  with  $[HA]$  for the extraction of Eu and Am from 0.1 M  $HNO_3$ . The distribution data are given in Table 1. The slope of the straight lines is 3.

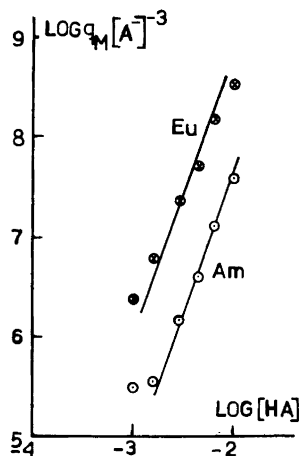
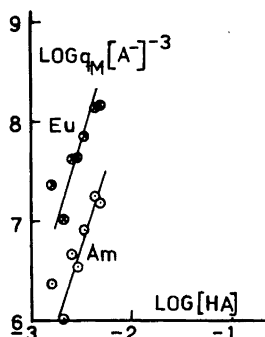


Fig. 4. DBP-isopropyl ether: Variation of  $q_M [A^-]^{-3}$  with  $[HA]$  for the extraction of Eu and Am from 0.1 M  $HNO_3$ . The distribution data are given in Table 1. The slope of the straight lines is 3.

Fig. 5. DBP-hexone: Variation of  $q_M [A^-]^{-3}$  with  $[HA]$  for the extraction of Eu and Am from 0.1 M  $HNO_3$ . The distribution data are given in Table 1. The slope of the straight lines is 3.



Since the concentration of  $HNO_3$  is kept constant it is not possible to preclude the possibility that  $M^{3+}$  is extracted as a complex also containing  $HNO_3$ , e.g.  $M(NO_3)_3(H_2A_2)_3$ . However, since the concentration of  $HNO_3$  is fairly low (0.1 M) it seems probable that nitrate complexes of M may be neglected in the organic phase except when TBP is used as a diluent (see below).

The equilibrium constant for this reaction is easily obtained from the plots:

$$\begin{aligned} \log K &= \log [MA_3(HA)_3]_{org} - \log [M^{3+}] - 3 \log [A^-] - 3 \log [HA] = \\ &= \log q_M - 3 \log [A^-] - 3 \log [HA] \end{aligned} \quad (6)$$

The following values for  $\log K$  were found from Figs 1—5:

In hexane: 13.66 (Eu), 12.38 (Am); in  $CCl_4$ : 16.80 (Eu), 15.33 (Am); in  $CHCl_3$ : 19.33 (Eu), 17.98 (Am); in *isopropyl ether*: 14.94 (Eu), 13.72 (Am); in hexone: 15.22 (Eu), 14.25 (Am).

The large values of  $K$  for chloroform suggest that this solvent is more active than the other solvents which might possibly be due to hydrogen bond formation between the H atom in  $CHCl_3$  and the PO groups in DBP (*cf.* Ref.7).

For *hexane*, the distribution experiments<sup>7</sup> with pure DBP indicated polymers higher than dimers at  $C_A > 0.06$  M. It seems as if this polymerization

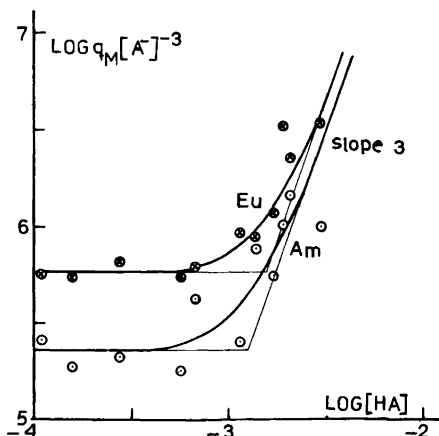
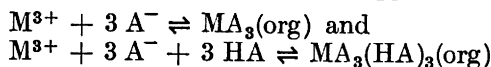


Fig. 6. DBP-hexol: Variation of  $q_M [A^-]^{-3}$  with  $[HA]$  for the extraction of Eu and Am from 0.1 M  $HNO_3$ . The distribution data are given in Table 2. The curves are drawn assuming the complexes  $MA_3$  and  $MA_3(HA)_3$  in the organic phase (normalized curve:  $\log (1 + x^3)$  versus  $\log x$ ).

affects the distribution of Am; a complex  $\text{MA}_3(\text{HA})_{\sim 6}$  is indicated in Fig. 1. For Eu,  $\log q$  is too high to be measured in the region where the corresponding complex could be formed.

For *hexol*, DBP is practically not dimerized in the organic phase. The value of  $K_d$  is also fairly large ( $= 162$ ) and thus  $C_A \simeq [\text{HA}]_{\text{org}}$ . The extraction from  $[\text{H}^+] = 0.1$  was rather low, so experiments were also performed with lower  $[\text{H}^+]$ , see Table 2. Assuming that  $\text{MA}_3$  reacts with a certain number of HA's in the organic phase to form an uncharged complex  $\text{MA}_3(\text{HA})_n$  it is reasonable to plot  $\log q_M[\text{A}^-]^{-3}$  as a function of  $\log [\text{HA}]$  (or  $\log [\text{HA}]_{\text{org}}$ ) as before. The experimental points in Fig. 6 are seen to fall roughly on single curves; there is no indication of a dependence on  $[\text{H}^+]$  as would be the case if there were complexes other than  $\text{MA}_3(\text{HA})_n$ , e.g.  $\text{M}(\text{NO}_3)_3(\text{HA})_3$ . The approximate constancy at low  $C_M$  indicates that the complex  $\text{MA}_3(\text{org})$  is formed at low  $[\text{HA}]$ ; one might expect HA to be added stepwise, but the accuracy certainly is insufficient for a detail treatment. Since the slopes tend towards 3, and the species  $\text{MA}_3(\text{HA})_3$  are indicated by work in other solvents, an attempt was made to describe the data as an approximation, neglecting all reactions except



By the usual technique of curve-fitting<sup>8</sup> the equilibrium constants ( $\log K$ ) were found from Fig. 6 to be: for the first reaction  $+ 5.76$  (Eu) and  $+ 5.36$  (Am); for the second reaction  $+ 14.15$  (Eu),  $+ 14.02$  (Am).

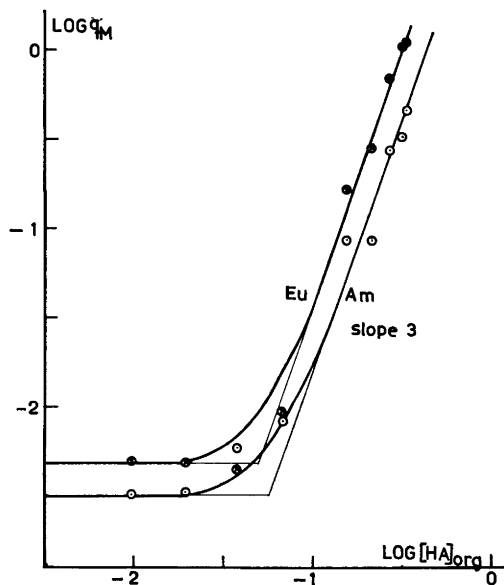
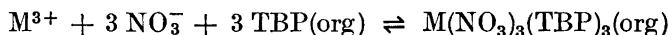


Fig. 7. DBP—TBP: Variation of the net distribution ratio with  $[\text{HA}]_{\text{org}}$  for the extraction of Eu and Am from 0.1 M  $\text{HNO}_3$ . The distribution data are given in Table 1. The curves are drawn assuming the presence of  $\text{M}(\text{NO}_3)_3$  and  $\text{MA}_3$  in the TBP phase (normalized curve:  $\log(1+x^3)$  versus  $\log x$ ).

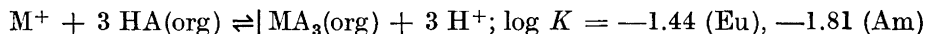
Whereas the first values seem to be reliable within  $\pm 0.1$ , the second constant is only intended as a very crude approximation, which may be used for approximate calculations but does not satisfactorily describe the real process, which is probably stepwise. A similar curve was previously obtained for the  $\text{UO}_2^{2+}$ -DBP-hexone system<sup>12</sup>.

In *tributyl phosphate* (TBP) also, HA mostly exists as single molecules, HA(org), which are, however, associated with TBP<sup>7</sup>. A plot of  $\log q_M$  versus  $\log [\text{HA}]_{\text{org}}$  indicated that  $q_M$  approaches a limiting value as  $[\text{HA}]_{\text{org}}$  decreases (Fig. 7). This should correspond to the reaction already studied by McKay *et al.*<sup>9-11</sup>

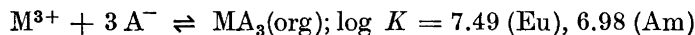


The present experiments, where  $[\text{TBP}]_{\text{org}}$  and  $[\text{NO}_3^-]$  were kept constant, do not give the composition of the complex.

For  $[\text{HA}]_{\text{org}} > 10^{-1.7}$  M,  $q_M$  increases with  $[\text{HA}]_{\text{org}}$ , which indicates that complexes with A are formed. The limiting slope would correspond to  $\text{MA}_3(\text{org})$ . The process is probably stepwise but the data suffice only to get approximate values for the total reaction. These were also found by curve-fitting:



or



These values are those obtained from the plot of  $\log q_M$  versus  $\log [\text{HA}]_{\text{org}}$ . The normalized curves are of the type  $\log(1 + x^3)$  versus  $\log x$ . The extracted complex may be  $\text{MA}_3(\text{TBP})_3$ , but this can only be proved by variation of the TBP concentration.

### Conclusions about the effect of the solvent on the net distribution of Eu and Am

It may be seen from Table 3 and Fig. 8 that for a given total concentration, of DBP ( $C_A = 0.1$  M) and acidity ( $[\text{H}^+] = 0.1$  M) the highest value of  $q_{\text{Eu}}$  is obtained with *n*-hexane and carbon tetrachloride. The extraction is very poor

Table 3. Summary of the results derived from Tables 1 and 2 for  $C_A = 0.1$  M and  $[\text{H}^+] = 0.1$  M. The net distribution ratio of DBP is derived from data reported in the previous paper<sup>7</sup>.

Solvent	$\log q_{\text{Eu}}$	$\log q_{\text{Am}}$	$\Delta \log q_{\text{Eu}-\text{Am}}$	$\log q_A$
<i>n</i> -Hexane	+2.60	+1.40	1.23	+0.48
$\text{CCl}_4$	+1.81	+0.46	1.30	+1.11
$\text{CHCl}_3$	+0.09	-1.27	1.36	+1.87
Isopropyl ether	+0.66	-0.44	1.10	+1.02
Hexone	-0.75	-1.81	1.05	+1.42
TBP	-1.78	-2.08	0.46	+1.73
Hexol	-3.34	-3.64	0.33	+1.91



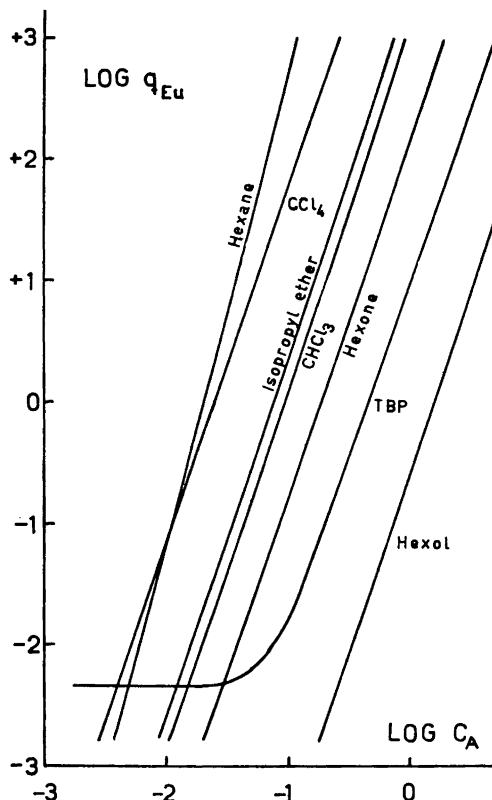


Fig. 3. The distribution of Eu for various organic solvents as a function of the initial concentration of DBP in the organic phase. The aqueous phase was 0.1 M  $\text{HNO}_3$  and the volumes of the two phases were equal. Data are given in Tables 1 and 2.

with TBP and hexol. Similar experience has been made with the  $\text{UO}_2^{2+}$ -dioctyl phosphate and  $\text{Ca}^{2+}$ -dibutyl phosphate systems (*cf.* Table 4).

In general the order of increasing capacity to extract  $\text{Eu}^{3+}$  (and  $\text{Am}^{3+}$ ) is that of decreasing value of  $K_d$  (*cf.* Table 2 in the previous paper <sup>7</sup>), the distribution constant of DBP monomer, or decreasing solubility of water in the organic solvent (*cf.* Table 4, Ref. <sup>7</sup>). It was pointed out in the previous paper <sup>7</sup> that an increase in  $K_d$  was probably due to the formation of a 1 : 1 complex between the DBP monomer, HA, and the solvent molecule. Such a reaction therefore seems to repress the metal extraction. In the case where the metal ion has been extracted from an aqueous phase with DBP in an inert solvent, *e.g.*  $\text{CCl}_4$ , back extraction into an aqueous layer should then be considerably facilitated by addition of *e.g.*, hexol to the organic layer. This has in fact been utilized by Dyrssen and Ekberg <sup>13</sup> for the preparation of carrier-free  $^{90}\text{Y}$ . With the uranyl ion, however, neutral phosphorylated reagents might enter into the coordination sphere, and thus enhance the extraction in spite of any complex formation with the dialkyl phosphate.<sup>17</sup>

Table 4. Influence of the diluent for the  $\text{UO}_2^{2+}$ -dioctyl phosphate system<sup>14</sup> (initial aq.phase: 0.004 M U(VI) in 0.5 M  $\text{SO}_4^{2-}$ , pH 1.1) and the  $\text{Ca}^{2+}$ -dibutyl phosphate system<sup>15</sup> (initial aq.phase: trace quantities of  $\text{CaCl}_2$  labelled with  $^{45}\text{Ca}$ ).

Diluent	Distribution ratio	
	$\text{UO}_2^{2+}$ - DOP	$\text{Ca}^{2+}$ - DBP
Kerosene	135	0.49
Hexane	110	1.13
Cyclohexane	—	1.16
Carbon tetrachloride	20	0.28
Isopropyl ether	17	0.121
Benzene	13	0.074
Chloroform	3	0.071
Hexone	—	0.037
Cyclohexanone	—	0.015
Isoamyl acetate	—	0.030
2-Ethyl hexanol	0.1	—
Octanol-2	0.08	—
Hexol	—	0.0039

Another factor to consider in choosing a suitable solvent is the distribution of DBP itself. As pointed out in the previous paper<sup>7</sup>,  $q_A$  varies considerably with the total concentration of DBP (*cf.* Fig. 1 in Ref.<sup>7</sup>); the values in Table 3 show, however, that for hexane,  $\text{CCl}_4$  and isopropyl ether considerable amounts of DBP are "lost" in aqueous phase. This could be reduced by using a compound with more carbon atoms, *e.g.* dioctyl phosphate.

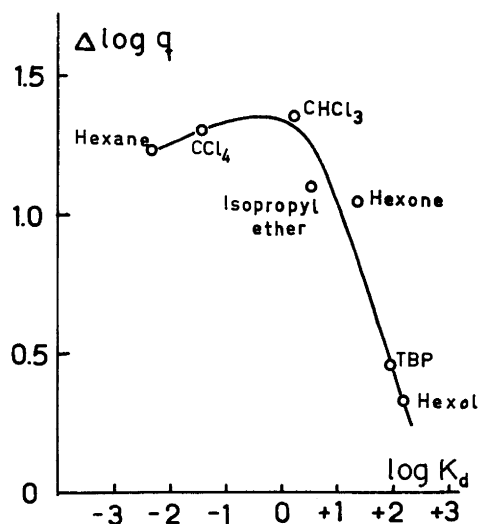


Fig. 9. The difference in distribution ratio  $q$  between Eu and Am at  $C_A = 0.1$  M for various organic solvents as a function of the distribution constant  $K_d$  for the DBP monomer. Aq. phase: 0.1 M  $\text{HNO}_3$ .

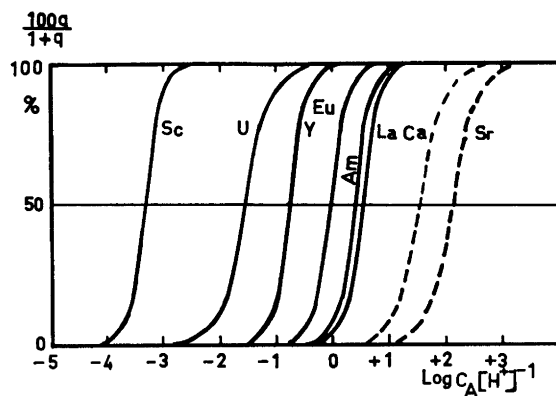


Fig. 10. Curves showing the percentage extraction with DBP- $\text{CHCl}_3$  of Sc(III), U(VI), Y(III), Eu(III), Am(III), La(III), Ca(II), and Sr(II) as a function of  $\log C_A [\text{H}^+]^{-1}$ . The curves for Ca and Sr are based on very few data.

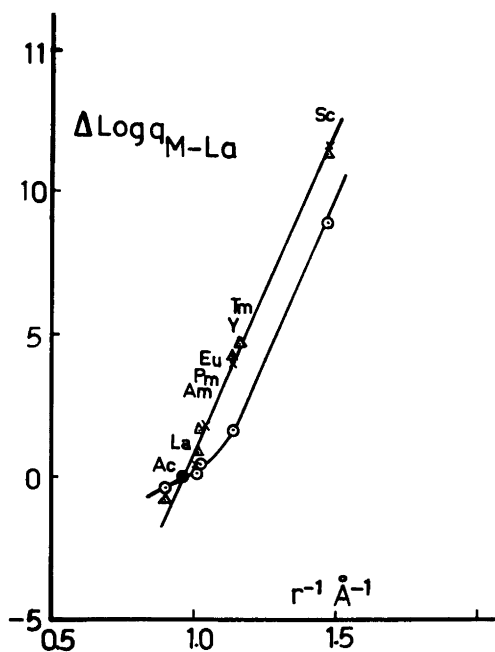


Fig. 11. The difference in distribution ratio,  $q$ , between trivalent metal ions and La(III) as a function of the inverted value of the ionic crystal ratio  $r$ , according to Zachriassen. Solvent extraction systems:  $\times$  DBP- $\text{CHCl}_3$  reported here,  $\Delta$  Diocetyl phosphate-toluene and  $\circ$  diocetylphenyl phosphate-toluene by Peppard *et al.*<sup>4</sup>

The separation of  $\text{Eu}^{3+}$  and  $\text{Am}^{3+}$  may be expressed as  $\Delta \log q$ . In Table 3 values of  $-\log q$  at  $C_A = 0.1 \text{ M}$  are given for the various solvents. These data are plotted in Fig. 9 against  $\log K_d$ . It may be seen that the inert solvents, hexane,  $\text{CCl}_4$  and  $\text{CHCl}_3$  give the best separation.

Throughout our experiments with DBP  $\text{Eu}^{3+}$  is better extracted than  $\text{Am}^{3+}$ . This is the order that could be expected from the values of the crystal ionic radii,  $r = 0.96 \text{ \AA}$  ( $\text{Eu}^{3+}$ ) and  $r = 0.99 \text{ \AA}$  ( $\text{Am}^{3+}$ ). Fig. 10 summarizes data for other metal ions taken from a FOA-report (not available) by Carlsson, Dyrssen, and Johansson. The order of extraction is generally the same as the order of ionic potential,  $Nr^{-1}$ . For three-valent ions there seems to be a straight line relationship between  $\Delta \log q_{M-La}$  and  $1/r$  (Fig. 11). Similar values of  $\Delta \log q$  were found by Peppard *et al.*<sup>4</sup> for dioctyl phosphate in toluene. However, with a dioctylphenyl derivative a different relationship is obtained; it seems as if this rather large complexing agent cannot differentiate very well between the larger tri-valent ions; this might be due to micelle formation. It has been shown by Dyrssen<sup>16</sup> that such a straight line relationship as with DBP and DOP is not obtained with the chelating agent  $\beta$ -isopropyl tropolone. Furthermore, with this compound  $\text{Eu}^{3+}$  is not better extracted than  $\text{Am}^{3+}$  into chloroform.

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