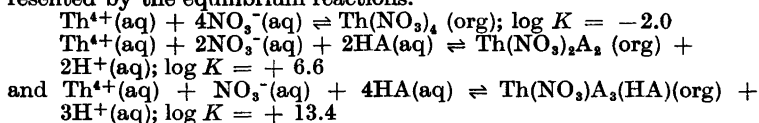


Solvent Extraction Studies of Thorium(IV) by Dibutylphosphate (DBP) in Chloroform, Hexol (Methylisobutylcarbinol) and Hexane

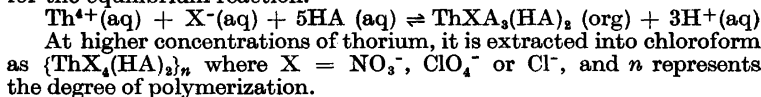
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The distribution of ^{232}Th between aqueous perchloric, nitric and hydrochloric acid and solutions of dibutylphosphate (= HA) in chloroform, hexol and hexane has been studied. From nitric acid and perchloric acid media Th is extracted into chloroform predominantly as $\text{Th}(\text{NO}_3)_4\text{A}_3(\text{HA})_2$ and $\text{Th}(\text{ClO}_4)_4\text{A}_3(\text{HA})_2$ and the extraction can be represented by the equilibrium reactions $\text{Th}^{4+}(\text{aq}) + \text{X}^-(\text{aq}) + 5\text{HA}(\text{aq}) \rightleftharpoons \text{ThXA}_3(\text{HA})_2(\text{org}) + 3\text{H}^+(\text{aq})$ where $\text{X}^- = \text{NO}_3^-$ or ClO_4^- ; the value of $\log K$ was found to be 19.6 in both cases. From hydrochloric acid medium the Th^{4+} is extracted in chloroform as $\text{ThA}_4(\text{HA})_2$ and the value of $\log K$ for the reaction $\text{Th}^{4+}(\text{aq}) + 6\text{HA}(\text{aq}) \rightleftharpoons \text{ThA}_4(\text{HA})_2(\text{org}) + 4\text{H}^+(\text{aq})$ was found to be $\log K = 22.5$. With hexol and aqueous nitric acid solution Th^{4+} is extracted mainly as $\text{Th}(\text{NO}_3)_4$ for $[\text{HA}] < 10^{-6}$ M, $\text{Th}(\text{NO}_3)_2\text{A}_2$ for $10^{-4.6}$ M $< [\text{HA}] < 10^{-3.5}$ M, and $\text{Th}(\text{NO}_3)_4\text{A}_3(\text{HA})$ for $[\text{HA}] > 10^{-3.4}$ M. The extraction can thus be represented by the equilibrium reactions:



With hexane and aqueous nitric acid or hydrochloric acid Th^{4+} is probably extracted as $\text{ThXA}_3(\text{HA})_2$, where $\text{X}^- = \text{NO}_3^-$ or Cl^- , with the following approximate $\log K$ values: 14.4 (NO_3^-) and 15.5 (Cl^-), for the equilibrium reaction:



The addition of TBP causes a decrease of the distribution coefficient of the extraction. This antagonistic effect of TBP (= B) is explained by the formation of HAB complex, thus reducing $[\text{HA}]$ and $[\text{A}^-]$ for a given total concentration of DBP. The solvent interaction of HA and H_2A_2 for different organic diluents is discussed.

A summary of the results is given in Table 21.

The use of dialkylphosphate for the extraction of Th(IV) was first reported by Peppard *et al.*,¹ who concluded that the extracted complexes were $\text{ThA}_4(\text{HA})_2$ and $\text{ThXA}_3(\text{HA})_2$, where X was nitrate, chloride or perchlorate and HA symbolized di-2-ethylhexyl, and di-*para*-(1,1,3,3-tetramethylbutyl)-phenyl phosphoric acid.

The aim of the present investigation is to carry out a systematic study of the extraction of thorium by dibutylphosphate in some organic solvents. The results of our previous studies^{2,3} with radioactive DBP enabled us to calculate the equilibrium concentrations of the different DBP species, which are necessary for an understanding of the extraction mechanism and for determination of the composition of the extracted thorium complexes. The calculated [HA] will be used as a convenient parameter in the treatment of the distribution data.

EXPERIMENTAL

Reagents. The DBP, $(n\text{-C}_4\text{H}_9\text{O})_2\text{PO}_2\text{H}$, kindly supplied by Albright and Wilson Ltd, London, with a purity of approximately 95 %, was further purified by the procedure described previously.³

The tracer isotope ^{234}Th was prepared in the following way: nuclear reactor quality UO_2 , kindly supplied by the Swedish Atomic Energy Company, was dissolved in 8–9 M HCl solution containing approximately 1 % conc. HNO_3 and was boiled for a few minutes to oxidize any small amounts of U(IV) to U(VI). The acid uranyl chloride solution was run through a column of the anion-exchange resin Dowex 1-8X (Kebo), whereby U(VI), but not Th(IV) is adsorbed. The ion-exchange resin Dowex 1-8X of 100–200 mesh had been previously washed several times with distilled water and treated with 8–9 M HCl solution.

The hydrochloric acid solution containing carrier free ^{234}Th , which was obtained from the ion-exchange column was neutralized with concentrated ammonia solution (*p.a.* Merck Darmstadt) to pH about 3, and then shaken with 0.1 M β -isopropyltropolone (IPT) in CHCl_3 , which extracts the ^{234}Th completely into the CHCl_3 phase. The CHCl_3 was shaken three times with distilled water to wash away any HCl, and the carrier-free ^{234}Th was now back-extracted with 1 M HClO_4 , HNO_3 or HCl solution. The acid solution of ^{234}Th was washed 2–3 times with CHCl_3 and was then used for the experiments.

The radiometric purity of the carrier-free ^{234}Th was checked by following the decay over 11 days and the half-life thus found agreed with the value of 24.1 days reported for this nuclide. $\text{Th}(\text{NO}_3)_4$ solutions were prepared from $\text{Th}(\text{NO}_3)_4$ (*p.a.*) and used without further purification. Thorium was determined as ThO_2 by igniting $\text{Th}(\text{NO}_3)_4$ at 700–800°C in an electric furnace.

CHCl_3 (*p.a.*, Merck-Darmstadt) was washed three times with distilled water to remove the alcohol, which had been added as stabilizer. HClO_4 , HNO_3 and HCl (Merck-Darmstadt) were all of analytical grade and were used without further purification. NaClO_4 was prepared from Na_2CO_3 (*p.a.*, Merck-Darmstadt) and HClO_4 (*p.a.*) as described in Ref.⁴

NaN_3 and NaCl (*p.a.*, Merck-Darmstadt) were dried at 120°C and used without further purification.

Tributylphosphate $(\text{C}_4\text{H}_9\text{O})_3\text{P}=\text{O}$ (Kebo) was purified by washing it with an equal volume of 1 M NaOH solution, then with 0.1 M HNO_3 and finally with water. The purified product was dried for half an hour at about 120°C with an infrared lamp under reduced pressure in N_2 atmosphere.

Hexol (methylisobutylcarbinol), purity min. 99 % and boiling range 130–133°C (Kebo), was further purified by washing it with dilute NaHCO_3 , dilute HNO_3 and finally several times with distilled water.

Distribution experiments. Equal volumes of aqueous and organic phases (usually 7 ml each) in a glass stoppered centrifuge tube were equilibrated by tilting the tubes slowly for 2–15 h. The results of a few special experiments indicated that under these conditions equilibrium was reached within one hour. The equilibrated solutions were then centrifuged to obtain good phase separation.

Samples of the solutions (5 ml) were pipetted out into polyethylene tubes and the γ -radioactivity counted in a Tracerlab SC-57 low back ground well scintillation counter connected with a Tracerlab SC-18A Compu/Matic V or SC-73 Versa/Matic II scaler. The tubes were allowed to stand for at least 10 min in order to let the 1.175 min ^{234}Pa and ^{234}Th come into steady state before they were counted.

The hydrogen ion concentration was calculated from the amount of the acid added. The ionic strength of the aqueous solution was kept constant by adding the appropriate salt solution.

In the distribution experiments with thorium nitrate as carrier, the experimental distribution ratios were corrected for the activity in the original thorium nitrate solution by duplicate experiments without ^{234}Th .

All experiments were carried out at 25°C in thermostated rooms.

DATA

Table 1. The distribution of ^{234}Th between solutions of DBP in CHCl_3 and 1 M $(\text{Na,H})\text{ClO}_4$ at 25°C. Data given as $\log q$, $\log C_A$, $\log[\text{HA}]$.

$[\text{H}^+] = 0.10 \text{ M}$
 + 2.698, -2.035, -3.77; + 2.684, -2.213, -3.86; + 2.734, -2.336, -3.93; + 2.455, -2.513, -4.02; + 1.735, -2.809, -4.17; + 1.178, -3.035, -4.29; + 1.001, -3.114, -4.34; + 0.737, -3.213, -4.40; + 0.248, -3.338, -4.47; -0.196, -3.513, -4.57; -1.102, -3.769, -4.74; -1.924, -4.114, -4.98.

$[\text{H}^+] = 0.20 \text{ M}$
 + 3.8, -1.007, -3.24; + 3.3, -1.313, -3.40; + 3.2, -1.354, -3.42; + 3.121, -1.834, -3.66; + 2.893, -1.674, -3.58; + 2.859, -1.959, -3.73; + 2.502, -2.073, -3.79; + 2.320, -2.136, -3.82; + 1.868, -2.377, -3.95; + 1.753, -2.437, -3.98; + 1.131, -2.685, -4.11; + 0.860, -2.771, -4.15; + 0.493, -2.907, -4.23; + 0.368, -3.075, -4.32; + 0.184, -3.083, -4.32; -0.490, -3.373, -4.47; -0.630, -3.384, -4.50; -2.038, -3.738, -4.71; -2.824, -3.959, -4.86; -3.634, -4.136, -4.98, -3.879, -4.355, -5.13; -3.923, -4.437, -5.19.

$[\text{H}^+] = 0.50 \text{ M}$
 + 2.864, -1.309, -3.40; + 3.064, -1.437, -3.46; + 2.550, -1.500, -3.49; + 2.271, -1.738, -3.61; + 1.815, -1.959, -3.72; + 1.389, -2.136, -3.82; + 1.290, -2.198, -3.85; + 0.609, -2.437, -3.98; -0.114, -2.685, -4.11; -0.638, -3.073, -4.32; -1.174, -3.083, -4.32; -1.637, -3.211, -4.40; -2.907, -3.738, -4.70; -3.331, -3.959, -4.84; -3.9, -4.437, -5.23.

$[\text{H}^+] = 1.00 \text{ M}$
 + 3.135, -1.075, -3.28; + 2.895, -1.136, -3.31; + 2.737, -1.260, -3.37; + 2.494, -1.427, -3.46; + 1.639, -1.738, -3.61; + 0.568, -2.136, -3.82; + 0.351, -2.208, -3.86; + 0.074, -2.305, -3.90; -0.107, -2.384, -3.95; -0.380, -2.481, -4.00; -0.825, -2.685, -4.12; -1.943, -3.083, -4.34.

Table 2. The distribution of ^{234}Th between 1 M $(\text{Na,H})\text{ClO}_4$ and 2.059×10^{-3} M DBP solution in CHCl_3 at 25°C. Data given as $\log q$, $-\log[\text{H}^+]$.

-0.940, 0.000; -0.823, 0.032; -0.743, 0.067; -0.661, 0.105; -0.558, 0.146; -0.412, 0.196; -0.266, 0.243; -0.146, 0.301; + 0.049, 0.368; + 0.311, 0.448; + 0.719, 0.544; + 1.463, 0.845.

Table 3. The distribution of ^{234}Th between solutions of DBP-TBP in chloroform and 1 M HClO_4 , for different constant TBP concentrations at 25°C. Data given as $\log q$, $\log C_A$, $\log[\text{HA}]$.

$C_B = 0.08 \text{ M}$
 + 2.957, -1.317, -3.41; + 1.994, -1.618, -3.57; + 0.700, -2.016, -3.78; -0.285, -2.317, -3.95; -1.176, -2.715, -4.18.

$C_B = 0.1 \text{ M}$

+ 3.477, -0.636, -3.06; + 3.107, -0.937, -3.21; + 2.758, -1.238, -3.37; + 1.937, -1.539, -3.53; + 1.227, -1.761, -3.65; -0.151, -2.238, -3.91.

$C_B = 0.2 \text{ M}$

+ 3.910, -0.761, -3.13; + 3.307, -1.062, -3.29; + 2.193, -1.413, -3.48; + 2.111, -1.335, -3.44; + 1.648, -1.617, -3.59; + 1.530, -1.636, -3.60; + 0.549, -1.937, -3.78; + 0.478, -2.015, -3.82; -0.280, -2.238, -3.96; -0.454, -2.316, -4.01; -1.635, -2.714, -4.272, -3.083, ($C_A = 0$).

$C_B = 0.5 \text{ M}$

+ 2.140, -1.481, -3.57; + 0.970, -1.782, -3.77; -0.092, -2.083, -3.98; -1.122, -2.402, -4.21; -2.320, -2.763, -4.51; -3.105, -4.481, -6.15; -3.121, -4.782, -6.45.

$C_B = 1 \text{ M}$

+ 0.988, -1.685, -3.82; + 0.580, -1.782, -3.90; -0.594, -2.083, -4.13; -1.618, -2.384, -4.39; -2.257, -3.782, -5.72; -2.664, -4.481, -6.40; -3.001, -3.481, -5.44; -3.079, -4.083, -6.02; -3.196, -3.159, -5.12.

$C_B = 2 \text{ M}$

+ 1.774, -1.208, -3.66; + 1.220, -1.384, -3.74; + 0.175, -1.685, -4.00; -0.566, -1.907, -4.20; -0.579, -1.907, -4.20; -0.927, -2.083, -4.36; -1.043, -2.083, -4.36; -1.564, -2.384, -4.65; -1.873, -2.384, -4.65; -2.033, -2.606, -4.87; -2.147, -2.782, -5.04; -2.729, -3.083, -5.35.

Table 4. The distribution of ^{234}Th between solution of DBP in CHCl_3 and 1 M HNO_3 at 25°C . Data given as $\log q$, $\log C_A$, $\log [\text{HA}]$.

+ 2.873, -1.260, -3.38; + 2.543, -1.437, -3.47; + 1.780, -1.738, -3.62; + 0.738, -2.136, -3.82; + 0.337, -2.260, -3.89; + 0.000, -2.357, -3.94; -0.078, -2.437, -3.98; -0.168, -2.437, -3.98; -0.437, -2.533, -4.03; -1.033, -2.738, -4.14; -2.107, -3.136, -4.06.

Table 5. The distribution of ^{234}Th between solution of DBP in CHCl_3 and 1 M HCl at 25°C . Data given as $\log q$, $\log C_A$, $\log [\text{HA}]$.

+ 2.299, -1.225, -3.36; + 1.525, -1.526, -3.51; + 0.219, -1.925, -3.72; + 0.218, -1.919, -3.71; -1.040, -2.317, -3.92; -1.834, -2.618, -4.08; -2.333, -2.919, -4.24; -2.838, -3.308, -4.46.

Table 6. The distribution of ^{234}Th between 1 M $\text{H}(\text{NO}_3, \text{ClO}_4)$ and solution of DBP in CHCl_3 at 25°C . $C_A = 3.843 \times 10^{-3} \text{ M}$. Data given as $\log q$, $\log [\text{NO}_3^-]$.

-0.306, $[\text{NO}_3^-] = 0$; -0.301, -0.845; -0.171, -0.544; -0.156, -0.368; -0.123, -0.243; -0.151, -0.146; -0.176, -0.067; -0.169, 0.0.

Table 7. The distribution of ^{234}Th between $6.195 \times 10^{-3} \text{ M}$ DBP in CHCl_3 and 1 M $(\text{Na}, \text{H})\text{Cl}$ at 25°C . Data given as $\log q$, $-\log [\text{H}^+]$.

-0.420, 0.000; -0.640, 0.000; -0.553, 0.047; -0.215, 0.138; + 0.099, 0.233; + 0.474, 0.315; + 0.826, 0.415; + [1.174, 0.504; + 1.442, 0.591; + 1.857, 0.700; + 2.069, 0.767; + 2.033, 0.846.

Table 8. The distribution of Th between DBP-TBP- CHCl_3 solution and 1 M $(\text{Na}, \text{H})\text{ClO}_4$ aqueous solution at 25°C . $C_A = 6.20 \times 10^{-3} \text{ M}$ and $C_B = 0.50 \text{ M}$ kept constant and $[\text{HA}] = 8.61 \times 10^{-5} \text{ M}$ practically constant. Data given as $\log q$, $-\log [\text{H}^+]$.

-0.642, 0.000; -0.502, 0.032; -0.507, 0.067; -0.363, 0.105; -0.318, 0.146; -0.144, 0.192; -0.116, 0.243; + 0.239, 0.301; + 0.273, 0.368; + 0.781, 0.443; + 0.990, 0.554; + 1.564, 0.845.

Table 9. The distribution of Th between DBP-hexol solution and 1 M HNO₃ at 25°C. Data given as log *q*, log *C_A*, log[HA]. *q_{corr}* is the net distribution ratio corrected for the contribution due to the extraction of Th(NO₃)₄, *q_{corr}* = *q* - 1.028 × 10⁻².

+ 3.178, -0.295, -2.61; + 2.725, -0.198, -2.51; + 2.506, -0.390, -2.70; + 2.210, -0.487, -2.80; + 1.806, -0.580, -2.89; + 1.423, -0.681, -2.99; + 1.010, -0.788, -3.10; + 0.725, -0.867, -3.18; 0.000, -1.089, -3.40; -0.383, -1.198, -3.51; -0.575, -1.265, -3.58; -0.724, -1.330, -3.64; -1.045, -1.499, -3.81; -1.441, -1.788, -4.10; -1.736, -2.043, -4.36; -1.877, -2.344, -4.66; -2.023, -2.645, -4.96; -1.985, -3.043, -5.36; -1.988, *C_A* = 0, [HA] = 0.

Table 10. The distribution of Th between DBP-hexol solution and 1 M (Na,H)NO₃ aqueous solution at 25°C. Data given as log *q*, -log[H⁺]. *q_{corr}* is the net distribution ratio corrected for the contribution due to the extraction of Th(NO₃)₄, *q_{corr}* = *q* - 1.028 × 10⁻².

C_A = 9.06 × 10⁻² M
+ 0.220, 0.000; + 0.192, 0.046; + 0.672, 0.232; + 0.854, 0.314; + 1.436, 0.503; + 2.281, 0.699; + 2.521, 0.845.
C_A = 1.631 × 10⁻³ M
-1.441, 0.000; -1.416, 0.046; -1.139, 0.232; -1.031, 0.314; -0.696, 0.503; -0.305, 0.699; + 0.043, 0.845.

Table 11. The distribution of Th between DBP-hexane solution and 1 M HNO₃ at 25°C. Data given as log *q*, log *C_A* and log[HA].

+ 1.193, -2.009, -2.38; + 0.852, -2.106, -2.46; + 1.605, -2.185, -2.51; + 2.110, -2.282, -2.57; + 1.733, -2.340, -2.61; + 0.866, -2.437, -2.69; + 0.613, -2.532, -2.75; + 0.161, -2.629, -2.82; -0.686, -2.929, -3.07; -2.159, -3.185, -3.29.

Table 12. The distribution of Th between DBP-hexane solution and 1 M HCl at 25°C. Data given as log *q*, log *C_A* and log[HA].

+ 2.502, -2.009, -2.38; + 2.467, -2.106, -2.46; + 2.071, -2.185, -2.51; + 1.641, -2.282, -2.57; + 1.891, -2.437, -2.69; + 1.966, -2.532, -2.75; + 1.547, -2.629, -2.82; -0.315, -2.929, -3.07; -1.832, -3.185, -3.29.

Table 13. The distribution of Th between DBP-CHCl₃ solution and 1 M HNO₃ with increasing Th concentration at 25°C. The net distribution ratios were corrected for the activity in the original thorium nitrate solution by duplicate experiments without ²³⁴Th.

log <i>q</i>	<i>C_{Th}</i> M	[Th] _{aq} M	<i>C_A</i> /[Th] _{org}
<i>C_A</i> = 4.38 × 10 ⁻³ M			
-1.823	0.1560	0.1535	1.905
-1.747	0.1245	0.1222	1.905
-1.660	9.354 × 10 ⁻²	9.141 × 10 ⁻²	2.188
-1.232	3.119 × 10 ⁻²	2.951 × 10 ⁻²	2.576
-0.951	1.560 × 10 ⁻²	1.403 × 10 ⁻²	2.735
-1.031	1.245 × 10 ⁻²	1.138 × 10 ⁻²	3.981
-0.956	9.354 × 10 ⁻³	8.418 × 10 ⁻³	4.710
-0.846	6.223 × 10 ⁻³	5.458 × 10 ⁻³	5.610
-0.739	3.119 × 10 ⁻³	2.636 × 10 ⁻³	9.120
<i>C_A</i> = 8.68 × 10 ⁻³ M			
-1.396	0.1245	0.1197	1.807
-1.389	9.354 × 10 ⁻²	8.974 × 10 ⁻²	2.344
-0.891	3.119 × 10 ⁻²	2.767 × 10 ⁻²	2.483
-0.667	9.354 × 10 ⁻³	7.691 × 10 ⁻³	5.236
-0.082	3.119 × 10 ⁻²	1.710 × 10 ⁻³	6.152

Table 14. The distribution of Th between 6.19×10^{-3} M DBP- CHCl_3 solution and 1 M $(\text{Na,H})\text{NO}_3$ aqueous solution at 25°C . The original thorium concentration in the aqueous phase $C_{\text{Th}} = 0.160$ M was kept constant. The net distribution ratios were corrected for the activity in the original thorium nitrate solution by duplicate experiments without ^{234}Th . Data given as $\log q$, $-\log[\text{H}^+]$.

-1.667, -0.060; -1.633, -0.104; -1.723, -0.155; -1.660, -0.192; -1.699, -0.232;
-1.732, -0.327; -1.754, -0.367; -1.727, -0.413; -1.751, -0.465; -1.794, -0.523.

Table 15. The distribution of Th between DBP- CHCl_3 and 1 M HNO_3 aqueous solution at 25°C . The original thorium concentration in the aqueous phase $C_{\text{Th}} = 6.226 \times 10^{-2}$ M was kept constant. The net distribution ratios were corrected for the activity in the original thorium nitrate solution by duplicate experiments without ^{234}Th . Data given as $\log q$, $\log C_A$.

-2.449, $C_A = 0$; -2.301, -3.301; -2.166, -3.000; -1.219, -2.437; -1.293, -2.357;
-1.204, -2.260; -1.062, -2.136; -0.798, -1.738; -0.272, -1.260; +0.274, -0.925.

Table 16. The effect of replacing NO_3^- for Cl^- on the extraction of Th from 0.160 M $\text{Th}(\text{NO}_3)_4$ solution in 6.19×10^{-3} M DBP- CHCl_3 at 25°C . The hydrogen ion concentration $[\text{H}^+] = 1.0$ M was kept constant. The net distribution ratios were corrected for the activity in the original thorium nitrate solution by duplicate experiments without ^{234}Th . Data given as $\log q$, $\log [\text{NO}_3^-]$ and $\log [\text{Cl}^-]$.

-1.753, 0.132, -0.804; -1.760, 0.089, -0.544; -1.727, 0.040, -0.383; -1.750, -0.007,
-0.277; -1.699, -0.054, -0.201; -1.764, -0.100, -0.146; -1.850, -0.143, -0.101;
-1.818, -0.184, -0.367.

Table 17. The effect of replacing NO_3^- by ClO_4^- on the extraction of Th from 0.160 M $\text{Th}(\text{NO}_3)_4$ solution in 6.19×10^{-3} M DBP- CHCl_3 at 25°C . $[\text{H}^+] = 1.0$ M was kept constant. The net distribution ratios were corrected for the activity in the original thorium nitrate solution by duplicate experiments without ^{234}Th . Data given as $\log q$, $\log [\text{NO}_3^-]$ and $\log [\text{ClO}_4^-]$.

-1.627, -0.018, -0.277; -1.676, -0.054, -0.197; -1.604, -0.098, -0.146; -1.756,
-0.148, -0.097; -1.639, -0.185, -0.067.

SYMBOLS AND EQUILIBRIUM CONSTANTS

HA = dibutylphosphoric acid $(n\text{-C}_4\text{H}_9\text{O})_2\text{PO}_2\text{H}$, (DBP) (or other dialkylphosphate)

[] = equilibrium concentration in the aqueous phase

[]_{org} = equilibrium concentration in the organic phase

[*]_{org} = equilibrium concentration in the organic phase of the free molecular species

C_A = initial total concentration of HA in the organic phase

K_a = $[\text{H}^+][\text{A}^-]/[\text{HA}]$ stoichiometric acid dissociation constant

K_d = $[\text{HA}]_{\text{org}}/[\text{HA}]$ distribution constant

K_{d}^* = $[\text{HA}^*]_{\text{org}}/[\text{HA}]$

K_2 = $[\text{H}_2\text{A}_2]_{\text{org}}/[\text{HA}]_{\text{org}}^2$ dimerization constant in the organic phase

K_{2d} = $[\text{H}_2\text{A}_2]_{\text{org}}/[\text{HA}]^2$

K_{2d}^* = $[\text{H}_2\text{A}_2^*]_{\text{org}}/[\text{HA}]^2$

- q = $[\text{Th}]_{\text{org}}/[\text{Th}]$ net distribution ratio of Th
 B = tributylphosphate (TBP, $(n\text{-C}_4\text{H}_9\text{O})_3\text{PO}$), or trioctylphosphineoxide (TOPO, $(n\text{-C}_8\text{H}_{17})_3\text{PO}$)
 S = organic solvent
 K_{B1} = $[\text{HAB}]_{\text{org}}/[\text{HA}]_{\text{org}}[\text{B}]_{\text{org}}$
 K_{B1}^* = $[\text{HAB}]_{\text{org}}/[\text{HA}^*]_{\text{org}}[\text{B}]_{\text{org}}$
 K_{B2} = $[\text{H}_2\text{A}_2\text{B}]_{\text{org}}/[\text{H}_2\text{A}_2]_{\text{org}}[\text{B}]_{\text{org}}$
 K_{B2}^* = $[\text{H}_2\text{A}_2\text{B}]_{\text{org}}/[\text{H}_2\text{A}_2^*]_{\text{org}}[\text{B}]_{\text{org}}$
 K_{S1} = $[\text{HAS}]_{\text{org}}/[\text{HA}^*]_{\text{org}}[\text{S}]_{\text{org}}$
 K_{S2} = $[\text{H}_2\text{A}_2\text{S}]_{\text{org}}/[\text{H}_2\text{A}_2^*]_{\text{org}}[\text{S}]_{\text{org}}$
 C_{Th} = initial total concentration of Th(IV) in the aqueous phase.

CALCULATIONS OF DBP AND TBP SPECIES

The primary data in Tables 1–17 are given as $\log q$, $\log C_A$ or C_A , $-\log[\text{H}^+]$ or $[\text{H}^+]$ and C_B . If no B was present, the equilibrium concentrations in the aqueous phase $[\text{HA}]$ were calculated from the following relationships:

$$\begin{aligned}
 C_A &= [\text{A}^-] + [\text{HA}] + [\text{HA}]_{\text{org}} + 2[\text{H}_2\text{A}_2]_{\text{org}} = \\
 &= K_a[\text{H}^+]^{-1}[\text{HA}] + [\text{HA}] + K_d[\text{HA}] + 2K_2K_d^2[\text{HA}]^2 = \\
 &= (K_a[\text{H}^+]^{-1} + 1 + K_d)[\text{HA}] + 2K_2K_d^2[\text{HA}]^2
 \end{aligned}$$

The equilibrium constants have been determined previously^{2,3} $K_a = 0.1$, $\log K_d = +0.34$ (chloroform), -2.34 (hexane), $+2.21$ (hexol), and $\log K_2 = 4.48$ (chloroform), 6.87 (hexane), $K_2 = 0$ (no dimerization, in hexol).

Fig. 1 shows the mole percentage of the different species of DBP in the

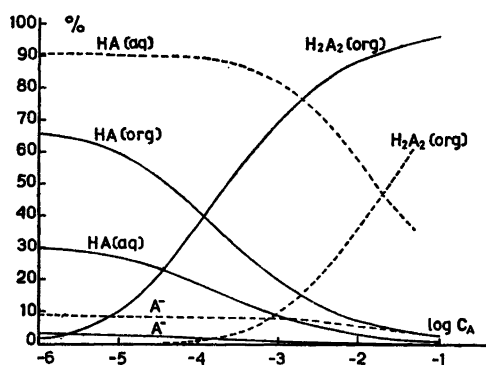


Fig. 1. The mole percentage of different DBP species in the two-phase systems chloroform/1 M H^+ (full lines) and hexane/1 M H^+ (dashed lines) as a function of C_A . At $[\text{H}^+] = 1 \text{ M}$, $[\text{A}^-] = 0.1 [\text{HA}]$.

chloroform or hexane, and aqueous phases. In experiments where we have a mixture of DBP and TBP in chloroform, $[\text{HA}]$ was calculated from the equation:

$$\begin{aligned}
 C_A &= [\text{A}^-] + [\text{HA}] + [\text{HA}]_{\text{org}} + 2[\text{H}_2\text{A}_2]_{\text{org}} + [\text{HAB}]_{\text{org}} = \\
 &= (K_a[\text{H}^+]^{-1} + 1 + K_d + 2K_2K_d^2[\text{HA}] + K_{B1}K_d[\text{B}]_{\text{org}})[\text{HA}]
 \end{aligned}$$

where $[B]_{\text{org}} \simeq C_B$, the initial total concentration of TBP in the organic phase. For reasons to be given in the appendix, H_2A_2B has been neglected in these calculations.

Figs. 2 and 3 show the mole percentage of the different species in both

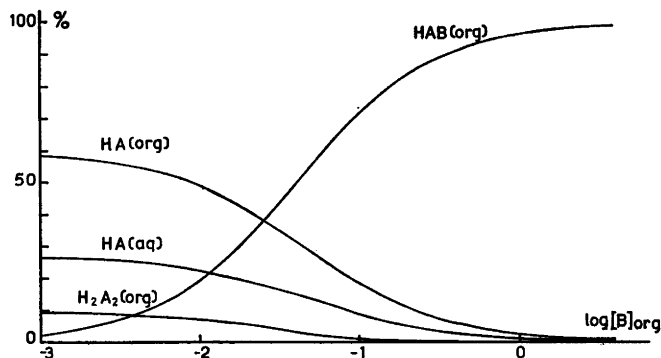


Fig. 2. The mole percentage of different DBP species and HAB in the two-phase systems chloroform/1 M H^+ as a function of $[B]_{\text{org}}$, at $C_A = 10^{-5} \text{ M}$.

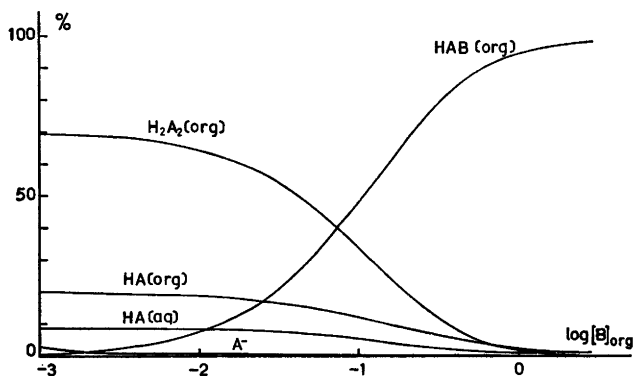


Fig. 3. The mole percentage of different DBP species and HAB in the two-phase systems chloroform/1 M H^+ as a function of $[B]_{\text{org}}$, at $C_A = 10^{-3} \text{ M}$.

phases as a function of the TBP concentration for two different C_A (10^{-5} M and 10^{-3} M).

THE INFLUENCE OF THE AQUEOUS IONIC MEDIUM

Extraction from chloride medium. Fig. 4 shows that in chloride medium, where $[H^+] = 1.0 \text{ M}$, a straight line with slope of 6 can be fitted to the data $\log q$ versus $\log[HA]$. Fig. 5 shows that at constant C_A (and practically constant $[HA]$) the data $\log q$ versus $-\log[H^+]$ fall on the straight line with a slope of

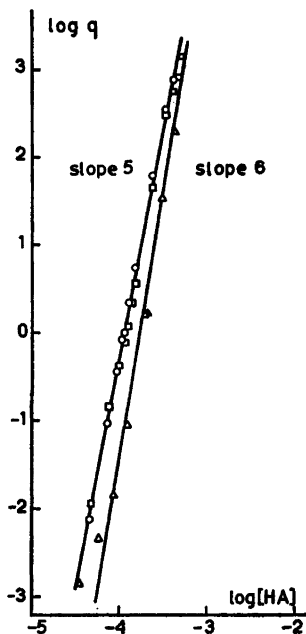


Fig. 4. The distribution ratio of Th(IV) between DBP—CHCl₃ and 1 M HClO₄ (□), 1 M HNO₃ (O), 1 M HCl (Δ), as a function of [HA]. The distribution data are given in Tables 1, 4, and 5.

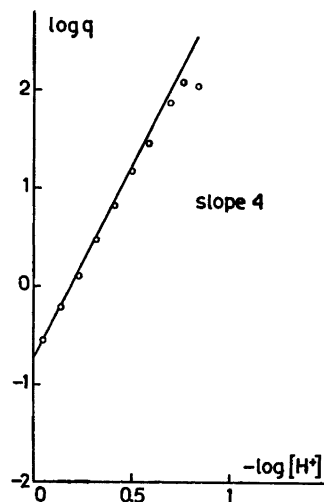
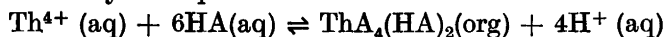


Fig. 5. The distribution ratio of Th(IV) between DBP, CHCl₃ and 1 M (Na₂H)Cl solution as a function of $-\log[H^+]$ at constant $C_A = 6.195 \times 10^{-3}$ M (and practically constant $[HA] = 1.38 \times 10^{-2}$ M). The distribution data are given in Table 7.

4. In chloride medium the extraction of Th by DBP in CHCl₃ can thus be described by the equilibrium reaction:



From the straight lines $\log q = 6 \log[HA] + 22.5$, at $[H^+] = 1$ M, in Fig 4 or $\log q = -4 \log[H^+] - 0.72$ at $C_A = 6.195 \times 10^{-3}$ M, in Fig. 5, we find the equilibrium constant

$$K = [\text{ThA}_3(\text{HA})_2]_{\text{org}}[\text{H}^+]^4[\text{Th}^{4+}]^{-1}[\text{HA}]^{-6} = 10^{22.5}$$

As $[\text{Cl}^-] = 1$ M was constant in these experiments it was not possible to decide to which extent the Th^{4+} is complexed by Cl^- .

Extraction from perchlorate medium. Fig. 4 shows that at constant $[H^+] = 1.0$ M a straight line with a slope of 5 can be fitted to the perchlorate data $\log q$ versus $\log[HA]$. Fig. 6 gives data at constant $C_A = 2.06 \times 10^{-3}$ M (hence practically constant $[HA]$) and varying $[H^+]$; the data $\log q$ versus $-\log[H^+]$ practically fall on a straight line with slope of 3. These observations indicate that the main extracted complex is of the form $\text{Th}(\text{ClO}_4)_3(\text{HA})_2$.

The extraction can thus be described by the equilibrium reaction:

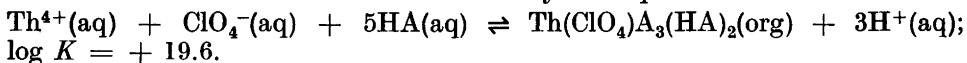


Fig. 6. The distribution of Th between DBP-CHCl₃ and 1 M (Na,H)ClO₄ solution as a function of $-\log [H^+]$ at constant $C_A = 2.059 \times 10^{-3}$ M (and practically constant $[HA] = 9.54 \times 10^{-6}$ M). ● = points obtained from Fig. 7 for $\log [HA] = -4.02$, ○ = data given in Table 2.

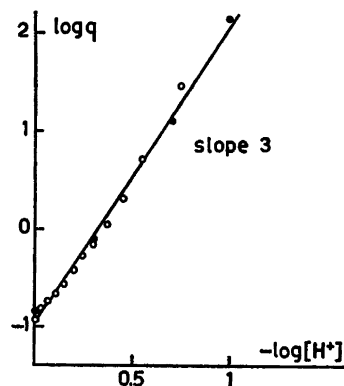


Fig. 7 shows the extraction of Th⁴⁺ from 1 M (Na,H)ClO₄ and different constant $[H^+] = 0.1, 0.2, 0.5,$ and 1.0 M. The data $\log q$ versus $\log [HA]$ are seen to fit straight lines with slope of 5. To normalize the hydrogen ion dependency, $\log q[H^+]^5$ is plotted against $\log [HA]$ in Fig. 8, where one can see that all

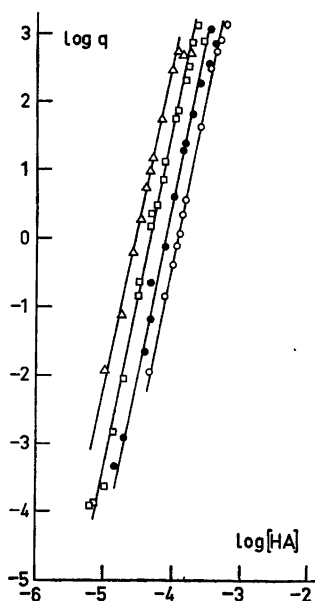


Fig. 7. The distribution of Th between DBP-CHCl₃ and 1 M (Na,H)ClO₄ solution as a function of $[HA]$ at different constant $[H^+] = 0.1$ (Δ), 0.2 (\square), 0.5 (\bullet) and 1 M (\circ). The slope of the straight lines is 5. The distribution data are given in Table 1.

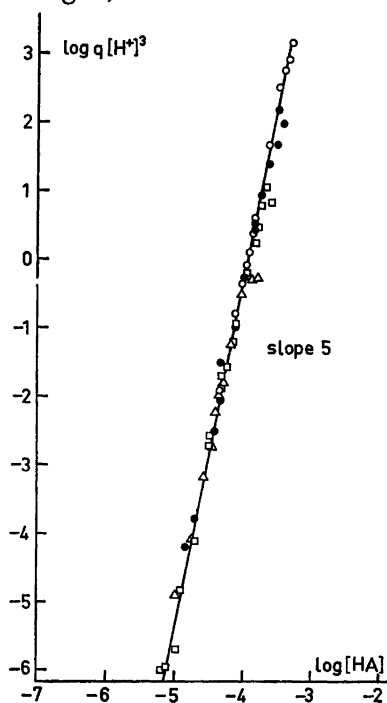


Fig. 8. Variation of $q[H^+]^5$ with $[HA]$ for the extraction of Th from 1 M (Na,H)ClO₄ in CHCl₃. The distribution data are given in Table 1. The experimental data correspond to different constant $[H^+] = 0.1$ (Δ), 0.2 (\square), 0.5 (\bullet), and 1 M (\circ).

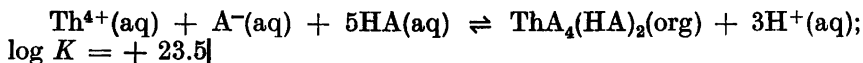
the experimental points now fall on a single straight line with a slope of 5. This indicates that the extracted complex is predominantly $\text{Th}(\text{ClO}_4)_3(\text{HA})_2$ in the range of C_A and $[\text{H}^+]$ studied.

Extraction from nitrate medium. Peppard *et al.*¹ have reported that for the extraction of Th from 1 M aqueous acid solution with *para*-(1,1,3,3-tetramethylbutyl)phenylphosphoric acid in toluene the extraction increases in the order of $\text{HClO}_4 > \text{HCl} > \text{HNO}_3$, and with di-2-ethylhexylphosphoric acid the order is: $\text{HNO}_3 > \text{HClO}_4 > \text{HCl}$.

However, as shown in Fig. 4, the data, $\log q$ versus $\log[\text{HA}]$, for 1 M HNO_3 falls practically on the same line as the values for 1 M HClO_4 . This fact is surprising, since one might have expected a different extraction behavior in nitrate and perchlorate medium.

At constant $C_A = 3.843 \times 10^{-3}$ M and $[\text{H}^+] = 1.0$ M the distribution ratio q is practically constant when the ClO_4^- ions are replaced by NO_3^- ions in the range of $[\text{ClO}_4^-] = 1.0 - 0$ M (Table 6). From these facts the extraction reaction of Th from the nitrate medium can be assumed to be similar to that from perchlorate medium and can thus be described by the equilibrium reaction:
 $\text{Th}^{4+}(\text{aq}) + \text{NO}_3^-(\text{aq}) + 5\text{HA}(\text{aq}) \rightleftharpoons \text{Th}(\text{NO}_3)_3\text{A}_3(\text{HA})_2(\text{org}) + 3\text{H}^+(\text{aq});$
 $\log K = +19.6$

In the concentration range of DBP studied ($C_A = 1 - 630$ mM) the distribution ratio for Th extraction from chloride medium is lower than that from perchlorate and nitrate medium. Our data have indicated that from chloride solution Th is extracted as $\text{ThA}_4(\text{HA})_2$, while from nitrate and perchlorate solution the extracted complexes are of the mixed complex type $\text{ThXA}_3(\text{HA})_2$. This can be partly understood if one considers that NO_3^- and ClO_4^- form extractable complexes with ions like Th^{4+} more readily than does Cl^- . To compare the extraction constant of A^- with that of NO_3^- and ClO_4^- above ($\log K = 19.6$), the equilibrium from the chloride medium can be written as follows:



THE "ANTAGONISTIC" EFFECT * OF TBP

It has been reported that for the extraction of some metal ions,⁵⁻⁸ *e.g.* UO_2^{2+} , the combination of dialkylphosphate and neutral alkylphosphate can cause an enhancement of the distribution ratio compared with the sum of the distribution ratios contributed by the dialkylphosphate and neutral alkylphosphate separately. This phenomenon is known as the "synergistic effect" and has been attributed to the formation of mixed complexes MA_pB_q . Our experiments aim to study the effect of the addition of TBP on the extraction of Th with DBP in CHCl_3 from aqueous perchlorate solution.

* In the following, just as in Classical Greek, the word "antagonism" will be used for the opposite to synergism. This is common usage, *e.g.* in pharmacy and plant physiology. The word "anti-synergism" which has been occasionally used, does not seem to be acceptable to linguists.

The interaction between DBP and TBP in CHCl_3 and CCl_4 has been reported in our previous work.^{2,3} The general problem of the solvent interaction of HA and H_2A_2 is treated in the appendix, where we show that DBP and TBP seem to form practically only the 1:1 complex HAB, in CHCl_3 solution.

In Fig. 9 $\log q$ is plotted *versus* $\log C_A$ for different constant concentrations of TBP: 0, 0.1, 0.2, 0.5, 1.0, 2.0 M. The extraction is seen to decrease with

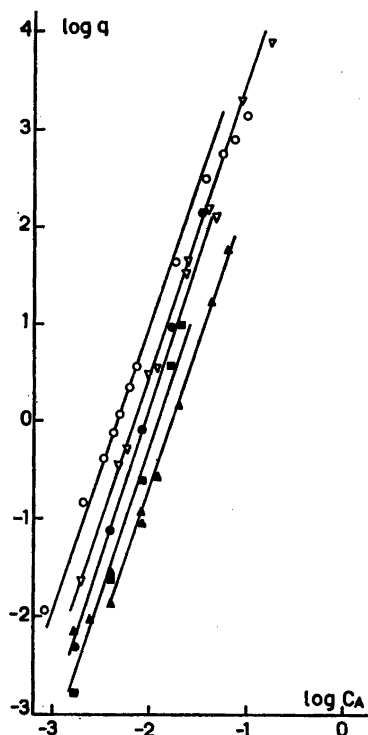


Fig. 9. The distribution of Th between DBP-TBP- CHCl_3 and 1 M HClO_4 solution as a function of C_A at different constant C_B : 2 (▲), 1 (■), 0.5 (●), 0.2 (▽), and 0 M (○). The distribution data are given in Table 3.

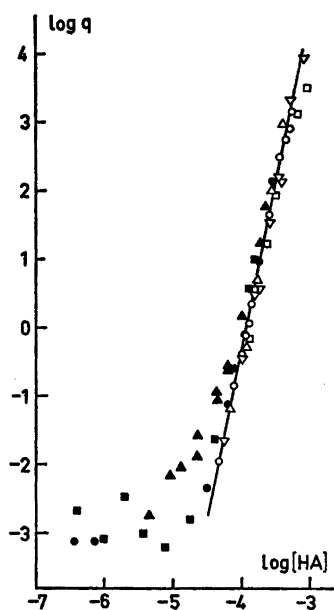


Fig. 10. The distribution of Th between DBP-TBP- CHCl_3 solution and 1 M HClO_4 as a function of $[\text{HA}]$ at different constant C_B : 2 (▲), 1 (■), 0.5 (●), 0.2 (▽), 8.1×10^{-2} (△), 0.1 (□), and 0 M (○). The slope of the straight line is 5. The distribution data are given in Table 3.

increasing TBP concentration over the range of C_A^* studied. However when $\log q$ is plotted *versus* $\log[\text{HA}]$, as shown in Fig. 10, the data fit a single straight line which has a limiting slope of 5 and is independent of the $[\text{TBP}]$ in the concentration range of $[\text{TBP}]$ studied (0 to 2 M), except for deviations at very low concentrations of DBP and high concentrations of TBP. In Fig. 11 $\log q$ is plotted *versus* $-\log[\text{H}^+]$ at constant $[\text{TBP}] = 0.5$ M and constant $C_A = 6.177 \times 10^{-3}$ M, $[\text{HA}]$ practically constant. The data are seen to fit a straight

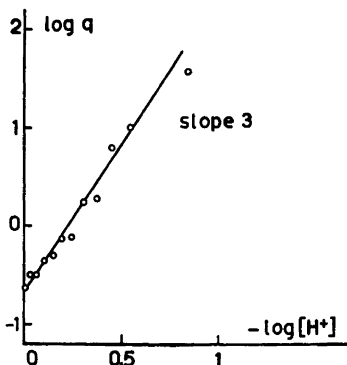


Fig. 11. The distribution of Th between DBP-TBP- CHCl_3 and 1 M $(\text{Na,H})\text{ClO}_4$ as a function of $[\text{H}^+]$ at constant $C_A = 6.20 \times 10^{-8}$ M, $C_B = 0.5$ M and practically constant $[\text{HA}] = 8.61 \times 10^{-5}$ M. The distribution data are given in Table 8.

line with a slope of 3. From the experimental data in Figs. 10 and 11 the conclusion can be drawn that the extracted complex is $\text{Th}(\text{ClO}_4)_3(\text{HA})_2$ and the effect of TBP on the extraction is limited to the effect of decreasing $[\text{HA}]$ for a constant C_A value, due to the formation of HAB complex. In other words the addition of TBP decreases the amount of free DBP available for the extraction. In this case TBP can be said to exert an antagonistic effect on Th extraction. Similar effects have been observed^{9,10} with the trivalent ions Y^{3+} , Eu^{3+} , and Am^{3+} .

At the highest TBP concentrations studied (0.5 to 2 M) and $[\text{HA}] < 10^{-4}$ M, however, the values of $\log q$ in Fig. 10 lie above the straight line with slope 5. This indicates that $\text{Th}(\text{ClO}_4)_3(\text{HA})_2$ is no more the predominant complex in the chloroform phase. The complex extracted under the above mentioned conditions can be represented by the general formula $\text{Th}(\text{ClO}_4)_{4-x}\text{A}_x(\text{HA})_y$, where x and y probably decrease as the $[\text{TBP}]/[\text{DBP}]$ ratio increases. At $[\text{HA}] < 10^{-5}$ M $\log q$ is practically constant (Table 3), indicating the extraction of complexes like $\text{Th}(\text{ClO}_4)_4(\text{TBP})_2$ (cf. Ref.¹¹).

EXTRACTION WITH HEXOL AND HEXANE

The extraction with hexol. In order to investigate the influence of the organic solvent on the distribution of Th we chose to study the extraction with hexol (methylisobutylcarbinol) and hexane in addition to chloroform.

Previous studies with $\text{Eu}(\text{III})$ and $\text{Am}(\text{III})$ ¹⁰ have shown that the nature of the organic solvent plays an important part in the metal extraction with DBP, and this was explained by the tendency of DBP to associate with the solvent molecules.^{3,10} This tendency can be characterized by the association constant $K_{S1} = [\text{HAS}]_{\text{org}}/[\text{HA}]_{\text{org}}[\text{S}]_{\text{org}}$. For hexol (methylisobutylcarbinol) we estimated³ $K_{S1} = 550 \text{ M}^{-1}$, while K_{S1} is approximately 0 for hexane. This solvent interaction is further discussed in the appendix in the light of recent work.^{12,13}

The extraction of Th from 1 M HNO_3 solution in hexol is, as shown in Fig. 12, independent of $[\text{HA}]$ for low concentrations of DBP, which means that at $[\text{HA}] < 10^{-5}$ M the complex extracted does not contain HA and is

practically $\text{Th}(\text{NO}_3)_4$. When the distribution ratio q is corrected for the contribution due to the extraction of $\text{Th}(\text{NO}_3)_4$, the data $\log q_{\text{corr}}$ versus $\log[\text{HA}]$ in Fig. 13 can be fitted to two straight lines of slope 2 at $[\text{HA}] < 10^{-3.5}$ M and

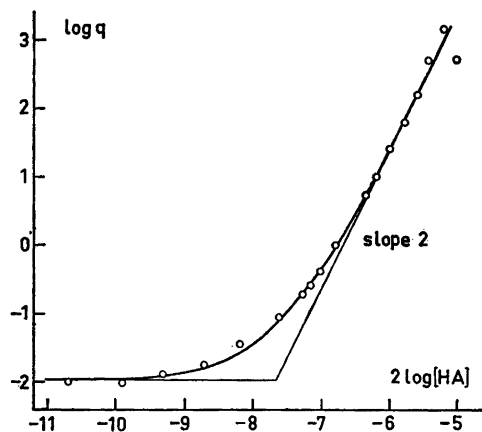


Fig. 12. DBP-hexol: Variation of the net distribution ratio with $[\text{HA}]^2$ for the extraction of Th from 1 M HNO_3 . The distribution data are given in Table 9. The curve is drawn assuming the presence of $\text{Th}(\text{NO}_3)_4$, $\text{Th}(\text{NO}_3)_2\text{A}_2$, and $\text{ThNO}_3\text{A}_3(\text{HA})$ in the hexol phase (normalized curve: $\log Y = \log(1 + pv + v^2)$, $\log X = \log v$, where $p = 5$ is found to give the best fit).

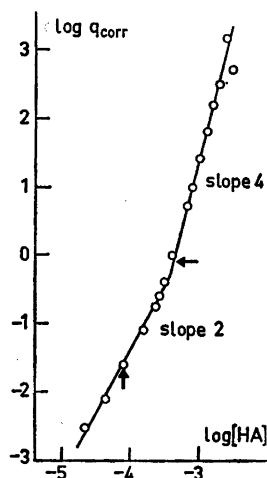


Fig. 13. DBP-hexol: Variation of the net distribution ratio corrected for the contribution by the extraction of $\text{Th}(\text{NO}_3)_4$, with $[\text{HA}]$ for the extraction of Th from 1 M HNO_3 . The distribution data are given in Table 9. The arrows indicate the values of $[\text{HA}]$, at which the $[\text{H}^+]$ dependency of the extraction of Th is investigated (Fig. 14).

slope 4 at $[\text{HA}] > 10^{-3.4}$ M. This indicates the presence of the two complexes $\text{Th}(\text{NO}_3)_{4-x}\text{A}_x(\text{HA})_{2-x}$ and $\text{Th}(\text{NO}_3)_{4-x}\text{A}_x(\text{HA})_{4-x}$. In Fig. 12 the experimental data $\log q$ versus $\log [\text{HA}]^2$ are fitted to the normalized curve $\log Y = \log(1 + 5v + v^2)$, $\log X = \log v$. This is in agreement with the conclusions drawn before, namely, that we are dealing with mainly three species in the hexol phase: $\text{Th}(\text{NO}_3)_4$, $\text{Th}(\text{NO}_3)_{4-x}\text{A}_x(\text{HA})_{2-x}$, and $\text{Th}(\text{NO}_3)_{4-x}\text{A}_x(\text{HA})_{4-x}$. To determine the value of x in these formulas we investigated the $[\text{H}^+]$ dependency of the extraction at constant $[\text{HA}]$. In Fig. 14 $\log q_{\text{corr}}$ is plotted as a function of $-\log[\text{H}^+]$ at constant $C_A = 0.061 \times 10^{-2}$ M and 1.631×10^{-3} M, corresponding to $[\text{HA}] = 7.96 \times 10^{-5}$ M ($\log [\text{HA}] = -4.10$) and 4.42×10^{-4} M ($\log [\text{HA}] = -3.36$). These values of $[\text{HA}]$, each fall in one of the two regions shown in Fig. 13, where they are marked by arrows, and they are practically constant in the pH range between 0 and 1 because $K_d \gg K_a[\text{H}^+]^{-1}$. It is seen from Fig. 14 that the $[\text{H}^+]$ dependency is different for the two $[\text{HA}]$ and that $x = 2$ in $\text{Th}(\text{NO}_3)_{4-x}\text{A}_x(\text{HA})_{2-x}$ and $x = 3$ in $\text{Th}(\text{NO}_3)_{4-x}\text{A}_x(\text{HA})_{4-x}$. With these experimental facts the conclusion can now be drawn that from 1 M HNO_3 solution the extraction of Th by DBP into hexol can be described by the following equilibrium reactions:

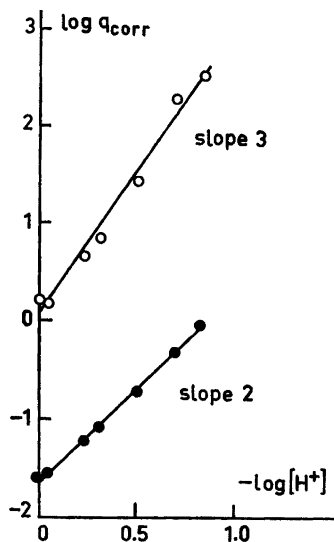
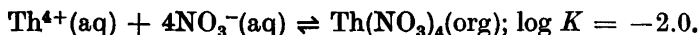
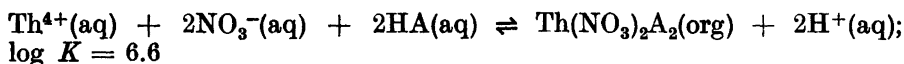
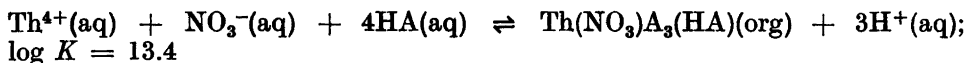


Fig. 14. The distribution of Th between DBP-hexol and 1 M (Na,H)NO₃ as a function of [H⁺] at constant C_A: 9.061 × 10⁻³ M (O) and 1.631 × 10⁻³ M (●). The distribution ratio is corrected for the contribution by the extraction of Th(NO₃)₄. The distribution data are given in Table 10.



Of all possible complexes with the general form Th(NO₃)_{4-x}A_x(HA)_y, the three complexes Th(NO₃)₄, Th(NO₃)₂A₂ and Th(NO₃)A₃(HA) have thus been found to predominate under the conditions, which were used here. In general it is not possible to obtain more than three parameters from a distribution curve (*e.g.* log *q* against log[HA]), due to limitations imposed by the accuracy of the data.

The extraction with hexane. The extraction of Th from 1 M HNO₃ and HCl solutions by DBP into hexane was complicated by the fact that a precipitate of thorium salt seemed to be formed, since the total radioactivity could not always be recovered satisfactorily (activity recovery ranging between 2 and 100 %).

This fact indicates that the Th complex extracted was not very soluble in the non-polar hexane, which is reasonable if mixed Th complexes are supposed to be formed. The results presented in Fig. 15 and Tables 11 and 12 should only be considered as an approximate picture of the extraction process. The plot of log *q* as a function of log[HA] for both nitrate and chloride media seems to fit with a slope of 5. This indicates that the complex extracted is of the form ThXA₃(HA)₂ where X = NO₃⁻ or Cl⁻ similar with the previous experiment where Th is extracted from nitrate or perchlorate media into chloroform. The Th extraction into hexane can thus be represented by the equilibrium reactions:

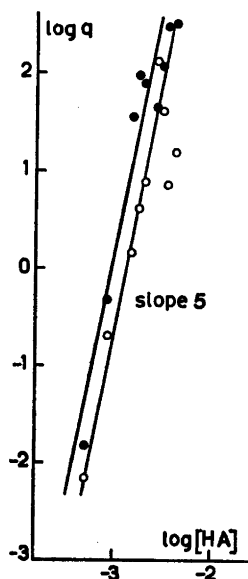


Fig. 15. DBP-hexane: Variation of the net distribution ratio with HA for the extraction of Th from 1 M HNO₃ (O) and 1 M HCl (●). The distribution data are given in Tables 11 and 12.

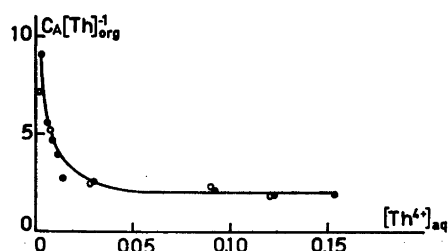
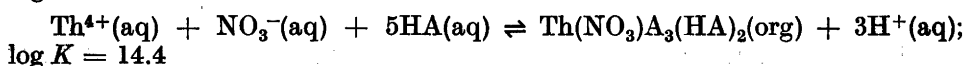
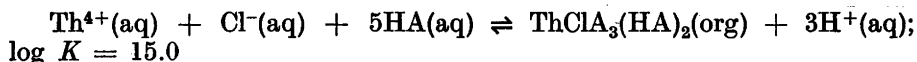


Fig. 16. The effect of increasing thorium concentration on the extraction of Th(IV) from 1 M HNO₃ solution by DBP in CHCl₃, at $C_A = 4.38 \times 10^{-3}$ M (O) and 8.68×10^{-3} M (□). The data are plotted as $C_A/[Th]_{org}$ versus $[Th]_{aq}$. The distribution data are given in Table 13. $C_A/[Th]_{org}$ approaches a limiting value of 2.



EXTRACTION AT MACRO LEVEL

It has been reported by Dyrssen and Kuča⁷ for the extraction of U(VI) by DBP in chloroform and by Peppard *et al.*¹⁵ for the extraction of Th(IV) by dialkylphosphonic acid, that the extraction process at higher metal concentrations differ from that at tracer level concentration.

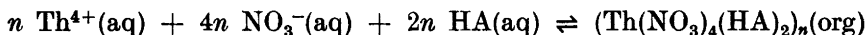
Peppard *et al.*¹⁵ reported that at macro level Th is extracted from aqueous acid solution into toluene by 2-ethylhexyl hydrogen 2-ethylhexyl phosphonate ((EHO)(EH)POOH = HA) as a mixture with the empirical composition $\text{Th}(\text{NO}_3)_{1.9}\text{A}_{2.2}$, $\text{Th}(\text{Cl})_{0.9}\text{A}_{2.9}$ and $\text{Th}(\text{ClO}_4)_{0.4}\text{A}_{3.7}$.

To study the effect of increasing thorium concentration, C_{Th} , on the extraction of Th from 1 M HNO₃ solution by DBP into chloroform, a series of experiments were carried out, where C_{Th} was varied from tracer level ($< 10^{-6}$ M) to 0.156 M, while $[\text{H}^{+}] = 1$ M and $C_A = 4.38 \times 10^{-3}$ M and 8.68×10^{-3} M were

kept constant. The result is shown in Fig. 16, where $C_A/[\text{Th}]_{\text{org}}$ is plotted as a function of $[\text{Th}]_{\text{aq}}$, and as can be seen from the curve, $C_A/[\text{Th}]_{\text{org}}$ seems to approach a limiting value of 2. This indicates that at macro level conditions, there would be two DBP bound per Th atom in the extracted Th complex. The extracted thorium complex could thus generally be represented as $(\text{Th}(\text{NO}_3)_{4-x}\text{A}_x(\text{HA})_{2-x})_n$, where n may represent the degree of polymerisation.

With decreasing $[\text{Th}]_{\text{aq}}$ the extracted Th complex must approach $\text{Th}(\text{NO}_3)_4(\text{HA})_2$, which has been found as the extracted complex at tracer level conditions. For intermediate $[\text{Th}]_{\text{aq}}$, complexes with more NO_3 are likely to be formed, however, with the experimental data available quantitative conclusions on the intermediate complexes are not possible.

The value of x can be determined by studying the hydrogen ion dependency of the extraction with $C_{\text{Th}} = 0.16 \text{ M}$, $C_A = 6.19 \times 10^{-3} \text{ M}$ and $[\text{NO}_3^-] = 1 \text{ M}$. The result is shown in Fig. 17, where $\log q$ versus $-\log[\text{H}^+]$ gives practically a straight horizontal line in the range $-\log[\text{H}^+] = 0$ to 0.5 studied. This means that $x = 0$ and the extraction can be represented by the equilibrium:



It must be mentioned here that under the conditions of extractions where $C_A = 5.38 \times 10^{-3} \text{ M}$ and $[\text{H}^+] = 1 \text{ M}$ were kept constant and C_{Th} varied, a white precipitate was formed at $C_{\text{Th}} = 0.6\text{--}12.5 \text{ mM}$, however, the precipitate disappeared when $C_{\text{Th}} > 16 \text{ mM}$. A possible explanation of this phenomenon could be that, on increasing the $\text{Th}(\text{NO}_3)_4$ concentration from tracer level to macro level one has a stepwise complex formation of the general form

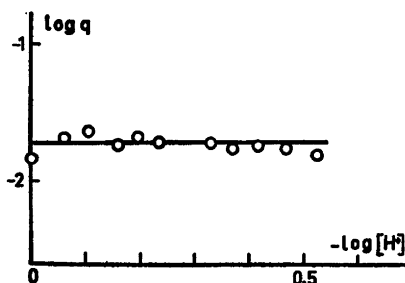


Fig. 17. The net distribution ratio as a function of $[\text{H}^+]$ for the extraction of Th from $(\text{Na},\text{H})\text{NO}_3$ solution with CHCl_3 at $C_A = 6.19 \times 10^{-3} \text{ M}$ and $C_{\text{Th}} = 0.16 \text{ M}$. The distribution data are given in Table 14.

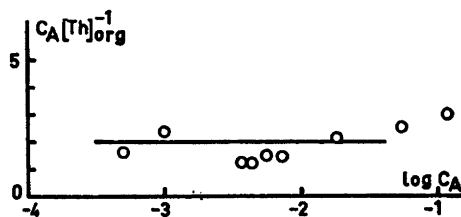


Fig. 18. The distribution of Th between DBP- CHCl_3 and 1 M HNO_3 solution with varying C_A at constant $C_{\text{Th}} = 6.226 \times 10^{-2} \text{ M}$. The distribution data are given in Table 15. The data are plotted as $C_A/[\text{Th}]_{\text{org}}$ versus $\log C_A$.

$(\text{Th}(\text{NO}_3)_x\text{A}_{4-x}(\text{HA})_2)_n$, where the value of x can be 1, 2, 3, and 4, and that one of the first three complexes has a low solubility in chloroform.

The distribution of thorium at $C_{\text{Th}} = 6.226 \times 10^{-2} \text{ M}$ between DBP-chloroform solution and 1 M HNO_3 was studied as a function of C_A . We may assume that under these extraction conditions practically all DBP is bound to the extracted thorium.

$$C_A = [\text{A}^-] + [\text{HA}] + [\text{HA}]_{\text{org}} + 2[\text{H}_2\text{A}_2]_{\text{org}} + m[\text{Th}]_{\text{org}} \approx m[\text{Th}]_{\text{org}}$$

where m represents the number of DBP bound per atom thorium extracted. From this and $q = [\text{Th}]_{\text{org}}/[\text{Th}]_{\text{aq}}$, $C_{\text{Th}} = [\text{Th}]_{\text{org}} + [\text{Th}]_{\text{aq}}$ we can derive the following relationship:

$$m = \frac{C_{\text{A}}}{[\text{Th}]_{\text{org}}} = \frac{C_{\text{A}}(1 + q)}{qC_{\text{Th}}}$$

In Fig. 18 the calculated values of $m = C_{\text{A}}/[\text{Th}]_{\text{org}}$ are plotted versus $\log C_{\text{A}}$, and as can be seen the points are found to scatter around $m \approx 2$ at low C_{A} . This would indicate that the extracted complex is predominantly of the form $\text{Th}(\text{NO}_3)_{4-x}\text{A}_x(\text{HA})_{2-x}$. Considering the result obtained from the preceding experiment if $C_{\text{Th}} \approx 0.10$ M, it is likely that the complex predominantly extracted is also $\text{Th}(\text{NO}_3)_4(\text{HA})_2$ corresponding to $x = 0$. The data indicate that on increasing C_{A} , thus increasing the ratio $C_{\text{A}}/C_{\text{Th}}$, the extracted complex seems to have m values higher than 2, which is not unexpected.

Distribution studies at $C_{\text{Th}} = 6.226 \times 10^{-3}$ M and $[\text{H}^+] = 1$ M were complicated by the formation of colloidal precipitate over the whole range of DBP concentration studied (1–100 mM). As mentioned this might be caused by the formation of less soluble $\text{Th}(\text{NO}_3)_x\text{A}_{4-x}(\text{HA})_2$ complex.

The Th/DBP ratio of the extracted thorium complex at macro level was supported by the amount of Th-salt present per ml of chloroform phase, which was determined simply by evaporating the solution at 120°C and weighing the residue.

$q = [\text{Th}]_{\text{org}}/[\text{Th}]_{\text{aq}} = [\text{Th}]_{\text{org}}/(C_{\text{Th}} - [\text{Th}]_{\text{org}})$, where C_{Th} is the original thorium concentration.

$$[\text{Th}]_{\text{org}} = \frac{q}{1 + q} C_{\text{Th}}$$

If the organic phase contains p mg Th-salt/ml, then the value $M = p(1 + q)/qC_{\text{Th}}$ was found to be 917 ± 57 , which agrees with the theoretical formula weight of 900.3 for the complex $\text{Th}(\text{NO}_3)_4(\text{HA})_2$.

To study the influence of the ionic medium on the extraction of thorium from 1 M HNO_3 solution by DBP in chloroform at macro level, extraction studies were carried out, where $C_{\text{Th}} = 0.16$ M, $C_{\text{A}} = 6.19 \times 10^{-3}$ M DBP and $[\text{H}^+] = 1$ M were constant, and NO_3^- replaced by Cl^- or ClO_4^- . The results given in Tables 16 and 17 show that the distribution ratio q was practically constant in both cases. This indicates that at macro level thorium will probably also be extracted from 1 M HCl or 1 M HClO_4 solution by DBP in chloroform as $\text{ThX}_4(\text{HA})_2$, where $\text{X} = \text{Cl}^-$ or ClO_4^- .

COMPARISON WITH OTHER ORGANOPHOSPHATE EXTRACTIONS

Fig. 19 shows the percentage thorium extracted from 1 M HNO_3 as a function of the total concentration of the organophosphate for three different systems: DBP-chloroform, di-2-ethylhexylphosphate-toluene¹ and 2-ethylhexylhydrogen-2-ethylhexyl-phosphonate-toluene.¹⁵

Possible explanations of the influence of the reagent structure and solvent on organophosphate extractions have recently been discussed by Baes¹⁴ and Krašovec.¹⁶

Table 21. Summary of results.

DATA Fig. Table No.	Predominating complex	Concentration range	org. phase	Equilibrium reaction and constant
4,6	$\text{Th}(\text{ClO}_4)_2\text{A}_3(\text{HA})_2$	1 M (Na, H)ClO ₄ [H ⁺] ≥ 0.1 M $C_{\text{Th}} < 10^{-6}$ M	DBP - CHCl ₃ $C_A = 0.1 - 100$ mM	$\text{Th}^{4+}(\text{aq}) + \text{ClO}_4^-(\text{aq}) + 5\text{HA}(\text{aq}) \rightleftharpoons \text{Th}(\text{ClO}_4)_2\text{A}_3(\text{HA})_2(\text{org}) + 3\text{H}^+(\text{aq})$ log K = + 19.6
7,8				
9,10	$\text{Th}(\text{ClO}_4)_2\text{A}_3(\text{HA})_2$ ^a	1 M (Na, H)ClO ₄ [H ⁺] ≥ 0.1 M $C_{\text{Th}} < 10^{-6}$ M	DBP - TBP - CHCl ₃ $C_A = 0.1 - 250$ mM $C_{\text{TBP}} = 0 - 2$ M	$\text{Th}^{4+}(\text{aq}) + \text{ClO}_4^-(\text{aq}) + 5\text{HA}(\text{aq}) \rightleftharpoons \text{Th}(\text{ClO}_4)_2\text{A}_3(\text{HA})_2(\text{org}) + 3\text{H}^+(\text{aq})$ log K = + 19.5
4	$\text{Th}(\text{NO}_3)_2\text{A}_3(\text{HA})_2$	1 M HNO ₃ $C_{\text{Th}} > 10^{-6}$ M	DBP - CHCl ₃ $C_A = 0.8 - 62$ mM	$\text{Th}^{4+}(\text{aq}) + \text{NO}_3^-(\text{aq}) + 5\text{HA}(\text{aq}) \rightleftharpoons \text{Th}(\text{NO}_3)_2\text{A}_3(\text{HA})_2(\text{org}) + 3\text{H}^+(\text{aq})$ log K = + 19.6
4	$\text{ThA}_4(\text{HA})_2$	1 M (Na, H)Cl [H ⁺] ≥ 0.1 M $C_{\text{Th}} < 10^{-6}$ M	DBP - CHCl ₃ $C_A = 0.5 - 60$ mM	$\text{Th}^{4+}(\text{aq}) + 6\text{HA}(\text{aq}) \rightleftharpoons \text{ThA}_4(\text{HA})_2(\text{org}) + 4\text{H}^+(\text{aq})$ log K = + 22.5 $\text{Th}^{4+}(\text{aq}) + \text{A}^-(\text{aq}) + 5\text{HA}(\text{aq}) \rightleftharpoons \text{ThA}_4(\text{HA})_2(\text{org}) + 3\text{H}^+(\text{aq})$ log K = + 23.5
12,13	$\text{Th}(\text{NO}_3)_2\text{A}_3(\text{HA})_2$ ^a	1 M (Na, H)NO ₃ [H ⁺] ≥ 0.1 M $C_{\text{Th}} < 10^{-6}$ M	DBP-hexol $C_A = 63 - 630$ mM	$\text{Th}^{4+}(\text{aq}) + \text{NO}_3^-(\text{aq}) + 4\text{HA}(\text{aq}) \rightleftharpoons \text{Th}(\text{NO}_3)_2\text{A}_3(\text{HA})_2(\text{org}) + 3\text{H}^+(\text{aq})$ log K = + 13.4
14				

DATA Fig Table No. No.	Complex	Concentration range aq. phase	org. phase	Equilibrium reaction and constant
12,13 9,10	$\text{Th}(\text{NO}_3)_2\text{A}_3$	1 M $(\text{Na}_2\text{H})\text{NO}_3$ [H^+] ≥ 0.1 M $C_{\text{Th}} < 10^{-3}$ M	DBP-hexol $C_A = 5-40$ mM	$\text{Th}^{4+}(\text{aq}) + 2\text{NO}_3^-(\text{aq}) + 2\text{HA}(\text{aq}) \rightleftharpoons \text{Th}(\text{NO}_3)_2\text{A}_3(\text{org}) + 2\text{H}^+(\text{aq})$ $\log K = +6.6$
12	$\text{Th}(\text{NO}_3)_4$	1 M HNO_3 $C_{\text{Th}} < 10^{-3}$ M	DBP-hexol $C_A < 2$ mM	$\text{Th}^{4+}(\text{aq}) + 4\text{NO}_3^-(\text{aq}) \rightleftharpoons \text{Th}(\text{NO}_3)_4(\text{org})$ $\log K = -2.0$
16 17	$\{\text{Th}(\text{NO}_3)_4(\text{HA})_{2n}\}_n$ ^b	1 M $(\text{H}_2\text{Na})\text{NO}_3$ $C_{\text{Th}} < 0.16$ M [H^+] ≥ 0.1	DBP- CHCl_3 $C_A = 4.38$ mM and 8.68 mM	$n \text{Th}^{4+}(\text{aq}) + 4n\text{NO}_3^-(\text{aq}) + 2n\text{HA}(\text{aq}) \rightleftharpoons \{\text{Th}(\text{NO}_3)_4(\text{HA})_{2n}\}_n(\text{org})$
18	$\{\text{Th}(\text{NO}_3)_4(\text{HA})_{2n}\}_n$	1 M HNO_3 $C_{\text{Th}} = 0.06226$ M	DBP- CHCl_3 $1 \text{ mM} < C_A < 100$ mM	$n \text{Th}^{4+}(\text{aq}) + 4n\text{NO}_3^-(\text{aq}) + 2n\text{HA}(\text{aq}) \rightleftharpoons \{\text{Th}(\text{NO}_3)_4(\text{HA})_{2n}\}_n(\text{org})$
16	$\{\text{ThCl}_4(\text{HA})_{2n}\}_n$	1 M $\text{H}(\text{NO}_3\text{Cl})$ $C_{\text{Th}} < 0.16$ M	DBP- CHCl_3 $C_A = 4.38$ mM	$n \text{Th}^{4+}(\text{aq}) + 4n\text{Cl}^-(\text{aq}) + 2n\text{HA}(\text{aq}) \rightleftharpoons \{\text{ThCl}_4(\text{HA})_{2n}\}_n(\text{org})$
16	$\{\text{Th}(\text{ClO}_4)_4(\text{HA})_{2n}\}_n$	1 M $\text{H}(\text{ClO}_4, \text{NO}_3)$ $C_{\text{Th}} < 0.16$ M	DBP- CHCl_3 $C_A = 4.38$ mM	$n \text{Th}^{4+}(\text{aq}) + 4n\text{ClO}_4^-(\text{aq}) + 2n\text{HA}(\text{aq}) \rightleftharpoons \{\text{Th}(\text{ClO}_4)_4(\text{HA})_{2n}\}_n(\text{org})$
15	$\text{Th}(\text{NO}_3)_2\text{A}_3(\text{HA})_2$ ^c	1 M HNO_3 $C_{\text{Th}} < 10^{-6}$ M	DBP-hexane $C_A = 1-10$ mM	$\text{Th}^{4+}(\text{aq}) + \text{NO}_3^-(\text{aq}) + 5\text{HA}(\text{aq}) \rightleftharpoons \text{Th}(\text{NO}_3)_2\text{A}_3(\text{HA})_2(\text{org}) + 3\text{H}^+(\text{aq})$ $\log K = 14.4$
15	$\text{ThCl}_3(\text{HA})_2$ ^c	1 M HCl $C_{\text{Th}} < 10^{-6}$ M	DBP-hexane $C_A = 1-10$ mM	$\text{Th}^{4+}(\text{aq}) + \text{Cl}^-(\text{aq}) + 5\text{HA}(\text{aq}) \rightleftharpoons \text{ThCl}_3(\text{HA})_2(\text{org}) + 3\text{H}^+(\text{aq})$ $\log K = 15.0$

^a $\text{Th}(\text{ClO}_4)_2\text{A}_3$ and $\text{Th}(\text{ClO}_4)_4(\text{TBP})_n$ at $C_{\text{TBP}} = 2$ M and $[\text{HA}] < 10^{-4}$ M. ^b white precipitate formed at $C_{\text{Th}} = 0.6-12.5$ mM. ^c loss of radioactivity.

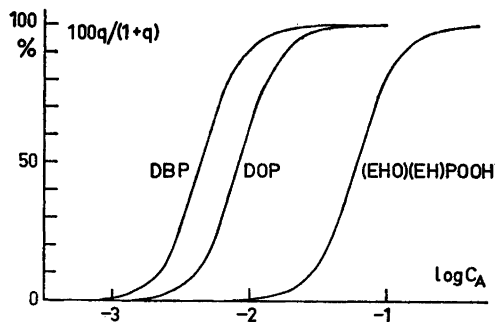


Fig. 19. The percentage thorium extracted from 1 M HNO₃ as a function of the total concentration of the organophosphate for three different systems: DBP-chloroform, reported in this work, di-2-ethylhexylphosphate-toluene (DOP) and 2-ethylhexylhydrogen-2-ethylhexylphosphonate-toluene ((EHO)(EH)POOH) by Peppard *et al.*^{1,15}

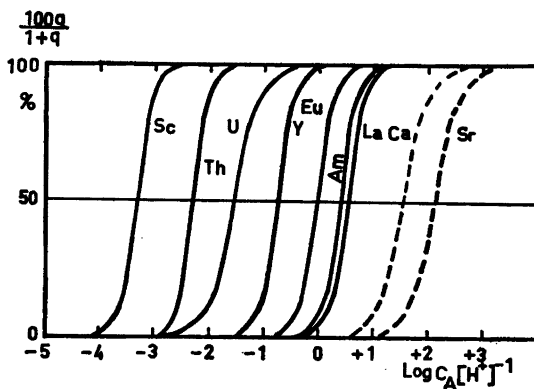


Fig. 20. The percentage extraction with DBP-CHCl₃ of Sc(III), Th(IV), U(VI), Y(III), Eu(III), Am(III), La(III), Ca(II), and Sr(II) as a function of $\log C_A/[H^+]^1$. (*cf.* Ref.¹⁰.)

In Fig. 20 we have compared the DBP-CHCl₃ extractions of Th⁴⁺ and several other ions. As seen from this figure the order of extractability between Sc(III), Th(IV), and U(VI) is Sc > Th > U. For TTA-C₆H₆ one finds¹⁷ Th > Sc > U, while the IPT-CHCl₃ system gives¹⁷ U > Th > Sc. This change in order may reflect the change of the covalency of the metal ion-reagent bond, the β -isopropyltropolonate ion (IPT) being a powerful chelating ligand.

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APPENDIX

THE INTERACTION BETWEEN HA, H₂A₂ AND THE ORGANIC SOLVENT

Earlier distribution studies^{2,3,18} of DBP (= HA) between different organic solvents and an acid aqueous phase have shown that the dimerization and distribution of HA is highly dependent on the organic solvent. These differences were explained by assuming that HA and H₂A₂ form HAS and H₂A₂S complexes with the organic solvent (= S). The existence of an HAB complex between DBP (= HA) and TBP (= B) in CCl₄ was confirmed experimentally³ in a distribution study using radioactive DBP where the concentration of TBP was varied by diluting with CCl₄; any complex formation between HA and the latter solvent was neglected. Infrared measurements¹³ have shown that the dimer of dioctylphosphate (= H₂A₂) and trioctylphosphine oxide (= B) form a H₂A₂B complex in octane. Also in this case formation of a complex between H₂A₂ and the diluent was neglected.

In the following we will try to give a more quantitative treatment on the interaction between HA, H₂A₂ and the organic solvent.

First we will recall the experimental background and the earlier description of the distribution data without assuming complexes between HA and S.

The equilibrium between HA and A⁻, described by the acid constant $K_a = [A^-][H^+]/[HA]$ (1) is assumed to be known, and [HA] can be calculated from [H⁺] and total conc. of A in the aqueous phase (= Σ[HA]).

1) *The extraction of HA, in case no B is present (or organic phase = B).* In the organic phase we assume the species HA and H₂A₂ are present. Then the following relationships apply:

$$\Sigma[HA]_{\text{org}} = [HA]_{\text{org}} + 2[H_2A_2]_{\text{org}} \quad (2)$$

$$[HA]_{\text{org}} = K_d[HA] \quad (3)$$

$$[H_2A_2]_{\text{org}} = K_2[HA]^2_{\text{org}} = K_2K_d^2[HA]^2 = K_{2d}[HA]^2 \quad (4)$$

The distribution ratio is:

$$q' = \frac{\Sigma[HA]_{\text{org}}}{\Sigma[HA]} \quad (5)$$

Introducing (2) in (5):

$$q' = \frac{[HA]_{\text{org}} + 2[H_2A_2]_{\text{org}}}{[HA] + [A^-]} = (K_d + 2K_{2d}[HA])\phi^{-1} \quad (5a)$$

Table 18. The distribution of DBP between 0.1 M HNO₃ and different organic solvents.³

	log K _d	log K _{2d}	[S] _{org} ^o ^a M
Hexane <i>n</i> -C ₆ H ₁₄	-2.34	+ 2.19	7.66
Carbontetrachloride CCl ₄	-1.44	+ 3.61	10.37
Chloroform CHCl ₃	+ 0.24	+ 4.13	12.53
TBP (<i>n</i> -C ₄ H ₉ O) ₃ PO	+ 1.97	-4.06	3.43

^a Calculated for the solvent saturated with water at 20°C.

where $\varphi = 1 + K_a/[H^+]$ is assumed to be known. Analysis gives K_d and K_{2d} for various organic solvents (Table 18).

2) *The extraction of HA in the presence of B.* Assuming that the complexes HAB and H_2A_2B are present in the organic phase, we have:

$$\Sigma[HA]_{org} = [HA]_{org} + [HAB]_{org} + 2[H_2A_2]_{org} + 2[H_2A_2B]_{org} \quad (6)$$

We now introduce the equilibrium constants K_{B1} and K_{B2} :

$$[HAB]_{org} = K_{B1}[HA]_{org}[B]_{org} = K_{B1}K_d[HA][B]_{org} \quad (7)$$

$$[H_2A_2B]_{org} = K_{B2}[H_2A_2]_{org}[B]_{org} = K_{B2}K_{2d}[HA]^2[B]_{org} \quad (8)$$

Introducing (6), (7), and (8) into (5) we find:

$$q' = \{K_d(1 + K_{B1}[B]_{org}) + 2K_{2d}[HA](1 + K_{B2}[B]_{org})\}\varphi^{-1} \quad (9)$$

In experiments with carbontetrachloride³ and chloroform² $[HA]$ was kept low, so that the second term in (9) may be neglected. The experimental values of K_{B1} for carbon tetrachloride and chloroform and that of K_{B2} reported by Baes and Baker¹³ for the system dioctylphosphate-trioctylphosphineoxide in octane are tabulated in Table 20 under the column "exptl".

3) *The complex formation of HA and the organic solvent.* Now we shall assume that in addition to free HA and H_2A_2 , which will be denoted by HA^* and $H_2A_2^*$, the complexes HAS and H_2A_2S are also formed ($S = \text{solvent}$).

Other conceivable complexes, such as HAS_2 , $HASB$, BS will not be considered. Then, in the above expressions $[HA]$ and $[H_2A_2]$ is each a sum of two terms:

$$[HA]_{org} = [HA^*]_{org} + [HAS]_{org} \quad (10)$$

$$[H_2A_2]_{org} = [H_2A_2^*]_{org} + [H_2A_2S]_{org} \quad (11)$$

We now assume that the law of mass action can be applied, using M as concentration unit. Denoting the equilibrium constants by K_{S1} and K_{S2} we then have:

$$[HAS]_{org} = K_{S1}[HA^*]_{org}[S]_{org} \quad (12)$$

$$\text{and } [H_2A_2S]_{org} = K_{S2}[H_2A_2^*]_{org}[S]_{org} \quad (13)$$

Moreover we now introduce the constants K_d^* and K_{2d}^* for the free species:

$$[HA^*]_{org} = K_d^*[HA] \quad (14)$$

$$[H_2A_2^*]_{org} = K_{2d}^*[HA]^2 \quad (15)$$

$$[HAB]_{org} = K_{B1}^*[HA^*]_{org}[B]_{org} \quad (16)$$

$$[H_2A_2B]_{org} = K_{B2}^*[H_2A_2^*]_{org}[B]_{org} \quad (17)$$

Combining (10), (11), (12), (13), (14), (15), (16), and (17) with (5) we find for the distribution ratio q' :

$$\text{without B: } q' = \{K_d^*(1 + K_{S1}[S]_{org}) + 2[HA]K_{2d}^*(1 + K_{S2}[S]_{org})\}\varphi^{-1} \quad (18)$$

with B:

$$q' = \{K_d^*(1 + K_{S1}[S]_{org} + K_{B1}^*[B]_{org}) + 2[HA]K_{2d}^*(1 + K_{S2}[S]_{org} + K_{B2}^*[B]_{org})\}\varphi^{-1} \quad (19)$$

Table 19. The interaction between HA, H₂A, and different organic solvents.

	K _{S1}	K _{S2}
Hexane	0	0
CCl ₄	0.67	2.44
CHCl ₃	30.26	63.2
TBP	5952	12.14

which may be compared with eqns. (5a) and (9). It goes without saying that [B]_{org} is the free concentration of B, thus corrected for formation of HAB and H₂A₂B.

Comparing eqns. (5a) and (18) we find:

$$K_d = K_d^*(1 + [S]_{org}^\circ K_{S1}) \quad (20)$$

and

$$K_{2d} = K_{2d}^*(1 + [S]_{org}^\circ K_{S2}) \quad (21)$$

Here [S]_{org}^o represents the concentration of the undiluted organic solvent (= 1000 × density/mol. wt.). We may use [S]_{org} = [S]_{org}^o for all equations without [B], since C_A is always < 0.2 M. However, when B is added, we must correct for the decrease in [S]_{org}, using the relationship:

$$[S]_{org} = [S]_{org}^\circ - [B]_{org} \frac{[S]_{org}^\circ}{[B]_{org}^\circ} = [S]_{org}^\circ - [B]_{org} \psi \quad (22)$$

where $\psi = [S]_{org}^\circ / [B]_{org}^\circ$

We shall now try the assumption that for hexane there is no complex formation with HA and H₂A₂, so that

$$K_d^* = K_d \text{ (hexane)} \text{ and } K_{2d}^* = K_{2d} \text{ (hexane)} \quad (23)$$

Introducing values for K_d, K_{2d}, [S]_{org}^o, we obtain K_{S1} and K_{S2} for different organic solvents given in Table 19.

The values of K_{S1} and K_{S2} may be taken as a relative measure of the interaction between HA, H₂A₂ and the organic solvent S. From the calculated values of K_{S1} and K_{S2} in Table 19, we may expect that the order of increasing interaction between HA and S is: hexane < CCl₄ < CHCl₃ < TBP and between H₂A₂ and S: hexane < CCl₄ < TBP < CHCl₃.

In experiments with B, we have to introduce the correction factor ψ in eqn. (19):

$$q' = \varphi^{-1} K_d^* [1 + K_{S1} [S]_{org}^\circ + [B]_{org} (K_{B1}^* - K_{S1} \psi)] + 2[HA] \varphi^{-1} K_{2d}^* [1 + K_{S2} [S]_{org}^\circ + [B]_{org} (K_{B2}^* - K_{S2} \psi)] \quad (24)$$

Comparing eqn. (24) with (9) and using eqns. (20) and (21) we find:

$$K_{B1} = \frac{(K_{B1}^* - K_{S1} \psi) K_d^*}{K_d} = \frac{K_{B1}^* - K_{S1} \psi}{1 + K_{S1} [S]_{org}^\circ}$$

$$K_{B2} = \frac{(K_{B2}^* - K_{S2} \psi) K_{2d}^*}{K_{2d}} = \frac{K_{B2}^* - K_{S2} \psi}{1 + K_{S2} [S]_{org}^\circ}$$

We may now calculate what K_{B1} and K_{B2} should be for different organic solvents if our assumption were exactly true by introducing the known values of

Table 20. The influence of the organic solvent on the formation of the complexes HAB and H_2A_2B .

	K_{B1}		K_{B2}	
	calc.	exptl. ^{3,2}	calc.	exptl. ¹³
DBP-TBP-hexane	5952		12.14	
DBP-TBP- CCl_4	749	692	0.18	
DBP-TBP- $CHCl_3$	15.4	40	-0.28	
DOP-TOPO-octane				100 ± 50

ψ and $[S]_{org}^\circ$, and the calculated values of K_{S1} and K_{S2} (Table 19). By definition $K_{B1}^* = K_{S1}(TBP)$ and $K_{B2}^* = K_{S2}(TBP)$.

The calculated K_{B1} and K_{B2} for different organic solvents are given in Table 20, in the column "calc".

Comparison of the calculated K_{B1} with the experimental values shows that the agreement for K_{B1} between them are surprisingly good. The small deviation found for $CHCl_3$ may partly be understood if one considers that $CHCl_3$ by means of hydrogen bonding can be expected to interact with DBP and TBP more extensively, and complexes as HAS_2 , BS might be formed.

The calculated values of K_{B2} indicate that there is little chance to find the H_2A_2B complex in CCl_4 and $CHCl_3$ even at high $[B]_{org}$. However, in hexane H_2A_2B might perhaps be found at high $[B]_{org}$ and C_A .

REFERENCES

1. Peppard, D. F., Mason, G. W. and McCarty, S. J. *Inorg. Nucl. Chem.* **13** (1960) 138.
2. Dyrssen, D. *Acta Chem. Scand.* **11** (1957) 1771.
3. Dyrssen, D. and Liem, D. H. *Acta Chem. Scand.* **14** (1960) 1091.
4. *Some laboratory methods in current use at the department of inorganic chemistry*, Royal Institute of Technology, Stockholm, Mimeograph 1959.
5. Blake, C. A., Baes, C. F., Brown, K. B., Coleman, C. F. and White, J. C. *2nd Intern. Conf. Peaceful Uses Atomic Energy*, Paper 1550, Geneva 1958; ORNL-2172, Oak Ridge 1956.
6. Kennedy, J. *AERE C/M 369*, Harwell 1958.
7. Dyrssen, D. and Kuča, L. *Acta Chem. Scand.* **14** (1960) 1945.
8. Baes, C. F. *Nucl. Sci. Eng.* **16** (1963) 405.
9. Dyrssen, D. and Ekberg, S. *Acta Chem. Scand.* **13** (1960) 1909.
10. Dyrssen, D. and Liem, D. H. *Acta Chem. Scand.* **14** (1960) 1100.
11. McKay, H. A. *Progress in Nuclear Energy, Series III, Process Chemistry Vol. I* (1956) 122.
12. Baes, Jr., C. F. *J. Phys. Chem.* **66** (1962) 1629.
13. Baker, H. T. and Baes, Jr., C. F. *J. Inorg. Nucl. Chem.* **24** (1962) 1277.
14. Baes, Jr., C. F. *J. Inorg. Nucl. Chem.* **24** (1962) 707.
15. Peppard, D. F., Namboodiri, M. H. and Mason, G. W. *J. Inorg. Nucl. Chem.* **24** (1962) 979.
16. Krašovec, F. *Croat. Chem. Acta.* **35** (1963) 183.
17. Dyrssen, D. *Acta Chem. Scand.* **15** (1961) 1614.
18. Hardy, C. J. and Scargill, D. J. *Inorg. Nucl. Chem.* **11** (1959) 128.

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