Acta Chemica Scandinavica A 37 (1983) 743–753

Hydrophilic Complexes of the Actinides. II. Comparison of TBP, HTTA and HDEHP Liquid–Liquid Distribution Systems

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The liquid–liquid distribution equilibria of the Am(III), Eu(III), U(IV), Th(IV) and UO_2^{2+} ions with tributyl phosphate (TBP), di-(2-ethylhexyl) phosporic acid (HDEHP) and 2-thenoyltrifluoroaceton (HTTA) have been studied at 25 °C by tracer technique, pH-measurements and optical methods. The ionic strength was maintained constant by adding $NaClO_4$, NaCl or $NaNO_3$, while heptane and toluene were employed as diluents. The distribution equilibrium (extraction) constants are summarized in Tables 1 and 2.

The acidity, the ionic strength and the ligand concentration were in each case varied systematically to ascertain the stoichiometry and kinetics of the extraction reactions. The application and usefulness of the three extraction reagents for their use in actinide complex chemistry studies are discussed in some details.

We have recently focused our interest on actinide complexation with hydrophilic ligands because of its importance for predicting the fate of nuclear waste stored in groundwater environment. Most of our work has been carried out with radioactive tracers using a liquid–liquid distribution system, with the organic phase containing an organophilic extraction reagent and the aqueous phase containing a hydrophilic ligand.

The versatility of the liquid–liquid distribution method for the investigation of metal complexation has led to a vast number of successful studies in the last two or three decades. Some illustrative examples for such applications, reported in the literature, have been examined and compared by Marcus and Kertes, and Beck.[1,2] In order to obtain optimal usefulness of the distribution system, one may have to use different extraction reagents, depending on the metal and hydrophilic ligand, since they will extract with different mechanisms. HTTA (2-thenoyltrifluoroacetone) has been one of the most commonly used extraction reagents for determining stability constants (the "TTA-method"), but HTTA has some drawbacks, particularly at high pH.

The aim of this work is to compare HTTA with two other common extractants TBP (tributyl phosphate) and HDEHP (di-2-ethylhexyl-phosphoric acid). The results will serve as a basis for continued studies of the hydrophilic actinide complexes, and we have chosen to study first some representative metal ions: Eu(III), Th(IV), U(IV), U(VI) and Am(III).

EXPERIMENTAL

Chemicals. All experiments were carried out with *p.a.* quality chemicals when possible. TBP was supplied by Fluka (*puriss p.a.*), HTTA (Merck) was purified by recrystallization. HDEHP was supplied from Farbenfabriken Bayer AG, purified by washings with strong acid, and analyzed by acidic titration. Heptane and toluene served as organic diluent. $NaClO_4$ solutions were prepared from $NaClO_4 \cdot H_2O$ (Fluka) and filtrated through a millipore (pore size 400 nm) disc. The carbonate content was found to be negligible for our purposes.[3]

Radionuclides. ^{22}Na, ^{152}Eu, ^{233}U, and ^{241}Am were purchased from Radiochemical Centre, Amersham, while ^{235}U originated from AB

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0302-4377/83 $2.50

Atomenergi, Studsvik. ^{234}Th was prepared from natural uranium by extractive separation using the TBP–HCl system. Stock solutions containing about 10^5 Bq/ml of the radionuclides in 0.1 M $HClO_4$ were prepared.

Analysis. The activities of the radionuclides were measured by γ spectrometry or by liquid scintillation. Natural uranium was detected by X-ray fluorescence spectrometry or absorption spectrophotometry (240 and 260 nm for U(VI), 648 nm for U(IV) and 520 nm and 615 nm for U(III)).

Reduction of U(VI). Electrolytic reduction of U(VI) to U(IV) and U(III) was carried out with the use of either a platinum wire or a mercury pool cathode. The anode compartment was separated from the bulk with a dense fritted glass diaphragm as described previously.[4] The current and time necessary for complete reduction were determined by on-line spectrophotometric surveillance of the oxidation state.

Determination of distribution ratios. The distribution experiments were carried out in a closed glass vessel at 25±0.1 °C. 15 ml organic phase, 15 ml aqueous phase and the radioisotope were introduced into the vessel. The system was stirred until equilibrium was attained, which usually took 5–20 min depending on the conditions (extracting agent, pH and reagent concentrations). The HDEHP system is rather slow at high pH and high HDEHP concentration. We found the equilibrium in this type of extraction device to be attained rapidly (*ca.* 5 min) when $[HDEHP]/[H^+] \lesssim 0.5$. Samples of 1 ml volume were withdrawn for radioactivity counting. Due to the extraction of $NaClO_4$ and $HClO_4$ by TBP it was necessary to pre-equilibrate TBP twice with $NaClO_4$ in order to maintain a constant ionic strength of the extraction system. The hydrogen ion concentration was determined (±0.01 pH units) by EMF measurements using a glass–silver–chloride combination electrode (Radiometer, Copenhagen), modified as described earlier.[4] A solution of known acidity served as standard.

RESULTS

TBP. Tributylphosphate belongs to the class of solvating extractants which extract a metal salt into the organic phase by forming an organophilic compound. The extraction equilibria can be written as in eqn. (1),

$$M(H_2O)_p^{m+} + mClO_4^- + n\overline{TBP} \rightleftarrows \overline{M(H_2O)_q(ClO_4)_m(TBP)_n} + (p-q)H_2O \qquad (1)$$

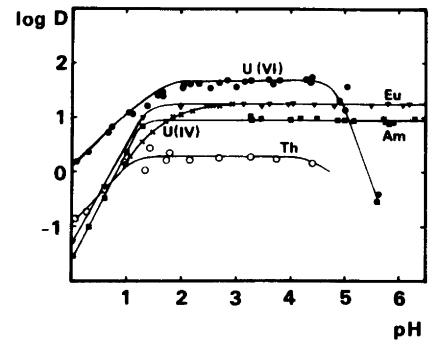

Fig. 1. Extraction of U(VI), U(IV), Th(IV), Am(III) and Eu(III) by tributylphosphate TBP (100 %) from 1 M (Na,H)ClO_4; log D as a function of pH. (●) denotes U(VI), (×) U(IV), (○) Th(IV), (■) Am(III) and (▼) Eu(III). 25 °C.

where m is the charge of the metal cation M^{m+}, p and q stand for the number of solvating water molecules and the bar above the formula indicates the organic phase. Despite the enormous use of TBP in industrial applications, it seems that this reagent has not been used for complex chemistry studies until recently.[3]

The distribution $D=[M(org)]/[M]$ of U(VI), U(IV), Am(III), Eu(III) and Th(IV) between 100 % TBP and 1 M (Na,H)ClO_4 is shown in Fig. 1 as a function of pH. Typically, a plateau is reached at high pH. At lower pH the distribution decreases. The decrease in D starts at about pH 1.5 for Am, Eu and Th while the decrease for U(IV) begins already at pH 3. However, from eqn. (1) one would expect a pH independent

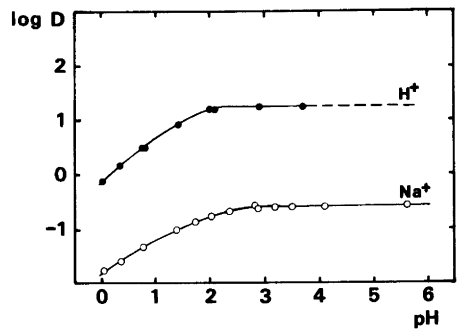

Fig. 2. Distribution, log D, of $HClO_4$ and $NaClO_4$ between 100 % TBP and 1 M (Na,H)ClO_4 at 25 °C as a function of pH. (●) denotes $HClO_4$ and (○) $^{22}NaClO_4$.

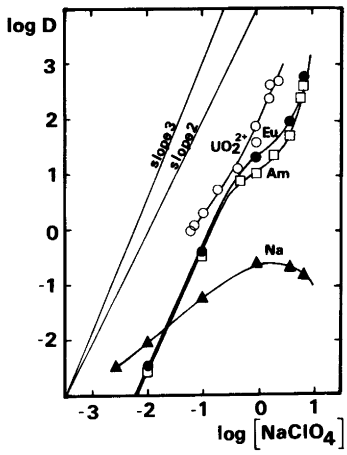

Fig. 3. Influence of the sodium perchlorate concentration on the distribution. Log D, of UO_2^{2+}, Am^{3+}, Eu^{3+} and Na^+ between 100 % TBP and aqueous perchlorate solutions of constant acidity. (○) UO_2^{2+}, pH 2.5, for $NaClO_4$ >1 M pH 3; (□) Am(III), pH 2; (●) Eu(III), pH 2; (▲) Na^+, pH 2.

distribution over the entire acidity range. The observed decrease at lower pH seems mainly (ignoring the influence of the change in the composition of the ionic media) to be due to the competition for "free" TBP caused by the simultaneous extraction of $HClO_4$. $HClO_4$ and

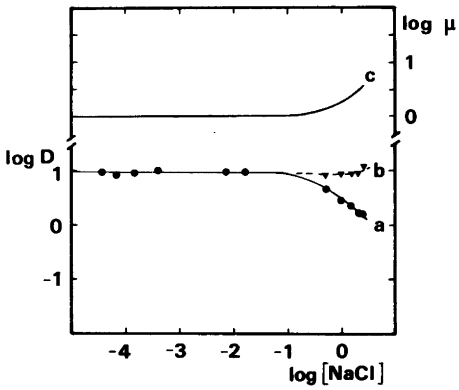

Fig. 4. The effect of ionic strength μ on the distribution, log D, of Am between 100 % TBP and aqueous NaCl. (a) At constant (=1 M) sodium perchlorate concentration, pH 3, 25 °C. (b) The distribution curve corrected for chloride complexation. (c) The ionic strength, μ, of the aqueous phase.

$NaClO_4$ are readily extracted by TBP, see Fig. 2. The distribution constant k_d=[$MClO_4$(org)]/[$MClO_4$] in 1M $NaClO_4$ was derived to 18±2 for $HClO_4$ and 0.3±0.05 for $NaClO_4$. Despite the decrease in the distribution of $HClO_4$ at lower pH, the $HClO_4$ concentration increases in the organic phase since the total $HClO_4$ concentration increases.

At high pH the metal distribution also deviates from the plateau (Fig. 1). This decrease is caused by the onset of hydrolysis of the metal cations [pH≳4.5 for U(VI), pH≳4 for Th(IV), pH≳6.7 for Am(III) and Eu(III)]. Since U(IV) is an acid of considerable strength, it will never reach the plateau corresponding to pH independent distribution coefficients before hydrolysing. Therefore U(IV) will not follow eqn. (1).

Eqn. (1) shows that the influence of the perchlorate ion concentration on the D-value would be proportional to the m:th-power of the perchlorate concentration provided other reactions do not take place, as for example extraction of $NaClO_4$ or $HClO_4$ mentioned above. Fig. 3 shows the influence of the perchlorate concentration on the distribution of Am(III), Eu(III), Na(I) and U(VI). Roughly the slopes of log D *versus* log $NaClO_4$ correspond to the ionic charge m in accordance with eqn. (1).

A more detailed description of the extraction equilibria is difficult, because of *e.g.* the mutual solubility of TBP and the aqueous phase.[5] Hence various values of n have been suggested in the literature (*e.g.* n=5 to 7 for the lanthanides).[6,7] Since precise knowledge of the extraction mechanisms is not needed for our purpose, we have made no attempt to elaborate it. TBP and related metal and acid extraction systems have been extensively treated in several monographies.[1,8–13] Further information on the TBP extraction of U(VI) and U(IV) can be found in Refs. 14–18.

In the use of the TBP distribution system for complexation studies the perchlorate concentration should preferably be held constant in order to simplify the interpretation of the distribution data. However, when studying a weak complexant which requires large additions of ligand, this leads to a noticeable increase in ionic strength. In order to enable us to make corrections for such increases we have made a preliminary study of the influence of the ionic strength on the distribution of Am by adding NaCl at constant 1 M

$NaClO_4$, Fig. 4. The formation of americium chlorides leads to a decrease in the distribution values because the chloride complexes are inextractible as was found from a separate TBP-NaCl experiment in which log $D_{Am} \lesssim -3$ for 0.1–3.5 M NaCl. However, one may compensate for the decrease by correcting for the chloride complexation, the remaining change in the distribution was relatively small; log D_{Am} increases $\lesssim 0.1$ units by an increase in ionic strength from 1 to 3.5 M. The extent of chloride complexation was calculated using stability constants reported in the literature, $\beta_1 = 1.04$, $\beta_2 = 0.43$ (Ref. 21) and we estimate β_3 to 0.1.[19–21]

HTTA. 2-Thenoyltrifluoroacetone belongs to the class of chelate forming agents which form organophilic compounds with metal ions. The distribution coefficient λ_m of the neutral metal chelate is very high for many metals and solvent combinations so λ_m has not always been possible to observe.[1,9–11,22] Straight lines of log D *versus* pH plots are often obtained corresponding to the overall extraction equilibrium shown in eqn. (2) with the extraction constant K_{ex}.

$$M^{m+} + m\,\overline{HTTA} \rightleftarrows \overline{M(TTA)_m} + mH^+ \qquad (2)$$

Fig. 5 shows log D as a function of pH for the distribution of Am^{3+} and Eu^{3+} between an organic phase with heptane or toluene as diluent and a 1 M sodium perchlorate aqueous phase. Fig. 6 shows the log D values of Am^{3+} *versus* the reagent concentration log [HTTA]. The slopes of +3 in both figures are in accordance with eqn. (2), $m=3$. These distribution systems are therefore suitable for studies of hydrophilic complexation of the metal in the aqueous phase. However, a low HTTA concentration will be required for work at high pH to avoid too high log D values.

Furthermore, log D must be appreciably less than log λ_3 if the simple extraction equilibria of eqn. (2) is to be employed. At low HTTA concentration the extraction system seems to be very sensitive to impurities and at pH>4 we also noticed loss of activity to the interface and the walls (poor mass balance). Stirring periods of about 30 min were used in order to establish equilibrium at pH<4. The extraction constants, K_{ex}, obtained are collected in Table 1.

HDEHP. The versatility of di-2-ethylhexylphosphoric acid is due to its capability of forming very extractable selfadduct complexes with metals, of which many have very high distribution values. The extraction will greatly depend upon the choice of organic diluent, because of its influence on the HDEHP activity and aggregation state, and upon the ionic composition of the aqueous phase. Furthermore HDEHP may even extract metal salts at high metal or salt concentra-

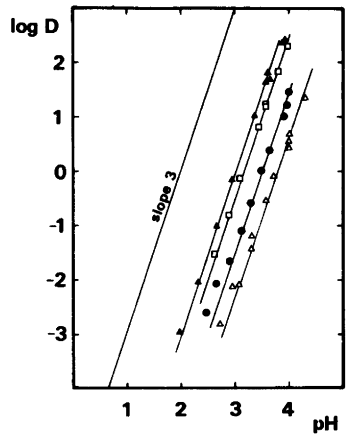

Fig. 5. The pH dependency of the distribution log D of Am and Eu between organic HTTA solutions and 1 M $NaClO_4$ at 25 °C. (●) Am^{3+}; 0.2 M HTTA in n-heptane, (△) Am^{3+}; 0.1M HTTA in n-heptane, (□) Am^{3+}; 0.5 M HTTA in toluene, (▲) Eu^{3+}; 0.5 M HTTA in toluene. (Initial HTTA concentrations).

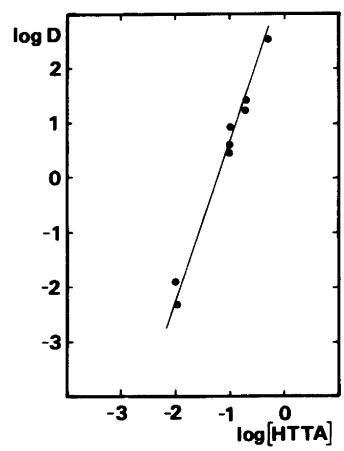

Fig. 6. The relation between the distribution, log D, of Am^{3+} and the initial HTTA concentration in n-heptane. Aqueous phase; 1 M $NaClO_4$, pH 4. 25 °C.

Table 1. Extraction constants K_{ex} for the distribution of Am^{3+} and Eu^{3+} between aqueous $NaClO_4$ and HTTA in various diluents at 25 °C. $K_{ex}[M^{3+}+3HTTA(org) \rightleftarrows M(TTA)_3(org)+3H^+]$. Initial concentration of HTTA was used in the calculations of K_{ex}.

Diluent	log K_{ex} Am	Eu	Conditions M HTTA	M(Na,H)ClO_4	pH	log D range	Ref.
Heptane	−8.40±0.10		0.01−0.5	1	2.5−5	−3−2.5	This work
Toluene	−8.66±0.15		0.5	1	2.3−4	−2−2.4	This work
Toluene		−8.16±0.10	0.5	1	2−4	−3−2.5	This work
Toluene		−8.2[a]	0.2	0.1M(NH_4^+,H^+)CH_2ClCOO^-			13
Benzene		−7.80[b,c]	0.1	0.1	2.5−3.8	−1−1	41
Toluene	−8.6[a]		0.2	0.1M(NH_4^+,H^+)CH_2ClCOO^-			13

[a] Calculated from distribution data, Ref. 40, [b] 25 °C?, [c] ΔH=15.7 kcal/mol, ΔS=16.8 cal/deg mol.

tion by solvation in analogy with neutral organophosphorus compounds like TBP.[1,23] In order to use HDEHP for complex studies it is essential to establish the predominant extraction mechanism of the actual system.

The trivalent metal ions Am^{3+} and Eu^{3+} were found, Fig. 7, to be extracted with a linear relationship to the pH over the entire acidity range investigated. The slope of log *D versus* pH equals +3. The same behaviour was found not only in 1 M $NaClO_4$ but also in 3 and 6 M $NaClO_4$.

Using heptane as diluent it was found that the dependence of log D on the logarithm of HDEHP total concentration was linear with a slope of +2.5, Fig. 8. Fig. 8 also shows that the influence of the HDEHP concentration is independent of the acidity. Assuming that HDEHP predominantly exists as a dimer in heptane under the present conditions (literature data on the dimerization and distribution constants are insufficient but it may be estimated that log $[HDEHP_2]/[HDEHP]^2 \approx 4.5$,[12,13]) one obtains the apparent extraction mechanism, eqn. (3), for Am^{3+} and Eu^{3+}.

$$M^{3+}+2.5\ \overline{(HDEHP)_2} \rightleftarrows \overline{M(DEHP)_3(HDEHP)_2}+3H^+ \quad (3)$$

This behaviour has also been found previously by other investigators from work with heptane and other aliphatic solvents using trace concentrations of trivalent metals.[24–27] The suggested composition of the extracted metal species is derived from the stoichiometry of eqn. (3) only and does not prove the actual structure. The composition could have equally well been written in an alternative way, *i.e.* $MY(HY_2)_2$, where Y=DEHP.

Using aromatic solvents it has been found that the reagent concentration dependency is +3, eqn. (4).[24,27–30] Even in aliphatic solvents a third power reagent concentration dependency has been observed at low HDEHP concentrations ($10^{-4.7}$ to $10^{-3.5}$ M).[29]

$$M^{3+}+3\ \overline{(HDEHP)_2} \rightleftarrows \overline{M(DEHP)_3(HDEHP)_3}+3H^+ \quad (4)$$

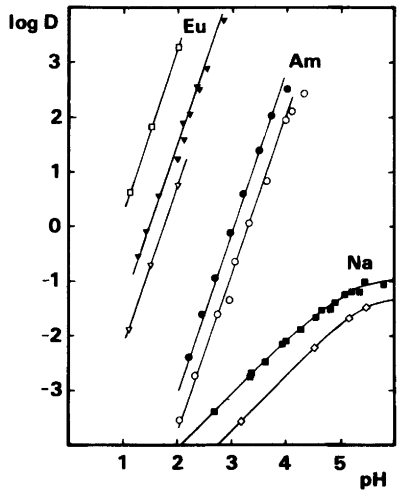

Fig. 7. The distribution, log D, of Am^{3+}, Eu^{3+} and Na^+ between HDEHP in n-heptane and 1 M $NaClO_4$ as a function of pH. 25 °C. (●) Am^{3+} 0.001 M HDEHP; (○) Am^{3+} 0.0005 M HDEPH; (□) Eu^{3+} 0.05 M HDEHP; (▽) Eu^{3+} 0.005 M HDEHP; (▼) Eu^{3+} 0.01 M HDEHP and 6 M $NaClO_4$; (■) Na^+ 0.1 M HDEHP; (◇) Na^+ 0.05 HDEHP.

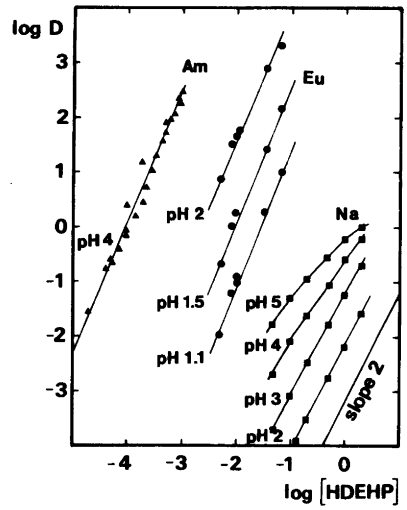

Fig. 8. The HDEHP dependency on the distribution, log D, of Am^{3+}, Eu^{3+} and Na^+. (Initial and total HDEHP concentrations). The aqueous phase is 1 M $NaClO_4$. 25 °C. The slopes of Am^{3+} and Eu^{3+} are 2.5.

The distribution data can be interpreted either in terms of concentration dependencies following eqn. (3) or in terms of activity coefficients of the HDEHP assuming that eqn. (4) represents the ideal behaviour. Authors who prefer to express the extraction mechanism according to eqn. (4) explain the observed slope with a decrease in the activity coefficient of HDEHP. It is believed to be a consequence of the interactions between the HDEHP dimers.[31–33]

The apparent extraction constant K_{ex} for the studied systems of Am and Eu were calculated according to eqn. (3) and these have been collected in Table 2. It should be noted that the initial concentration of the HDEHP dimer has been used in these calculations, although the actual concentration might be somewhat lower due to loss of the reagent to the aqueous phase, and conversion of the reagent into its sodium salt, the latter not only reduces the HDEHP dimer concentration but it also changes the extraction mechanism. However, our choice of HDEHP concentrations and pH were such that the concentration of NaDEHP in the organic phase and of HDEHP in the aqueous phase were negligible.

The extraction of Na^+ was investigated using ^{22}Na, Figs. 7 and 8. We deduced an extraction mechanism according to eqn. (5)

$$Na^+ + 2\,\overline{(HDEHP)_2} \rightleftarrows \overline{NaDEHP(HDEHP)_3} + H^+ \qquad (5)$$

Although this mechanism was previously established, no extraction constants K_{ex} of eqn. (5) were derived for sodium perchlorate solutions.[24,34,35] From the linear relationships of the distribution functions we calculated log $K_{ex} = -3.56 \pm 0.08$ (1 M $NaClO_4$, heptane, Table 2). The extraction mechanism of sodium is, however, changed at high pH because of a gradual, and finally complete, transformation of the extraction reagent in the organic phase into NaDEHP. This was concluded from the stoichiometry of the pH titration and from the existence of plateaues in the relation log $D_{Na} = f(pH)$ at pH≥6 (one plateau for each initial HDEHP concentration). The distribution constant k_d=[NaDEHP(heptane)]/[NaDEHP(1 M $NaClO_4$)]=3.5±0.3 was derived for 25 °C.

Table 2. Apparent extraction constants K_{ex} for the distribution of Am^{3+}, Eu^{3+} and Na^+ between aqueous $NaClO_4$ and HDEHP in various diluents at 25 °C. $K_{ex}(M^{3+}+2.5(HDEHP)_2(org) \rightleftarrows M(DEHP)_3(HDEHP)_2(org)+3H^+)$ and $K_{ex}(Na^++2(HDEHP)_2(org) \rightleftarrows Na(DEHP)(HDEHP)_3(org)+H^+)$. The initial dimer concentration of HDEHP in the organic phase was used in the calculation of K_{ex}.

Diluent	log K_{ex} Am	Eu	Na	M HDEHP (formal conc.)	M(Na,H)ClO_4)	pH	log D range	Ref.
Heptane	−0.85±0.10			$10^{-3.3}-10^{-3}$	1	2−4	−3.5−2.5	This work
Heptane	−0.63[a]			0.02−0.3	1M (Na,H)Cl	0.4−1.7	−1.5−2.2	25
Heptane	0.2[a]			0.02−0.3	0.1M HCl	1	−2.3−1.3	25
Heptane		1.15±0.10		$10^{-3.6}-10^{-1.3}$	1	1.1−3.6	−2−3.3	This work
Heptane		1.08±0.10		10^{-2}	3	1−2.5	−1.5−2.6	This work
Heptane		1.18±0.10		10^{-2}	6	1.3−2.8	−0.6−3.8	This work
Heptane		0.65±0.10		10^{-2}	1M NaCl	1.3−2	−0.8−1.3	This work
Heptane		1.0±0.1		10^{-2}	1M $NaNO_3$	2	1.3	This work
Heptane		1.03[a]		0.02−0.3	1M (Na,H)Cl	0−1	−1−2.5	25
Dodecane		1.4[a]		10^{-3}−0.5	1M (Na,H)Cl	1.28	−3.5−3.4	32
Heptane		1.75[a]		0.02−0.3	0.1M HCl	1	−0.5−2.6	25
Hexane		1.58[a]		0.01−0.1[b]	0.1M HCl	1	−1−1.3	24
Heptane			−3.56±0.08	0.05−1	1	2−3	−4.5− −1.2	This work

[a] Calculated from distribution data. [b] Deviation at higher conc.

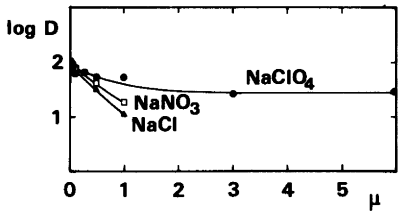

Fig. 9. The influence of the ionic strength μ on the distribution, log D, of Eu^{3+} between 0.01 M HDEHP in n-heptane and an aqueous solution of $NaClO_4$, $NaNO_3$ or NaCl at pH 2 and 25 °C. (●) $NaClO_4$, (▲) NaCl, (□) $NaNO_3$.

Furthermore it was noted that a second organic phase consisting of almost pure heptane forms at pH≳5.8 (if the initial HDEHP concentration was less than 2 M). The volume ratio between the reagent deficient and the reagent rich organic phases increases with diminishing initial HDEHP concentration. This phenomenon leads to the assumption that all NaDEHP is contained in an interfacial film (*i.e.* skin formation) at reagent concentrations below ≈0.1 M.

The influence of the aqueous phase composition was investigated by varying the ionic strength by means of sodium salt additions. Fig. 9 shows the distribution log D of Eu as a function of the NaCl, $NaNO_3$ and $NaClO_4$ salt concentration at pH 2. The $NaClO_4$ was tested up to 6 M, the effect of the increased ionic strength was fairly small, a slow decrease in the distribution values was observed. $NaNO_3$ and NaCl were tested up to 1 M ionic strength and it was found that the decrease in log D was more pronounced. The rate of the decrease followed the order $Cl^- > NO_3^- > ClO_4^-$ which also is the order of complex formation strength between Eu and the anions. Further support for that chloride complexation is stronger than perchlorate complexation was obtained by substituting ClO_4^- with Cl^- at a constant ionic strength of 1 M at pH 2. The D value diminished with increasing chloride concentration.

DISCUSSION

We have made a comparison of the usefulness of the three extractants HTTA, TBP and HDEHP for studying hydrophilic complexation. The conclusions are based on the experience in this study and the results are summarized in Table 3.

Generally, we conclude that TBP is very useful because of its pH independence and its stability, especially when using 100 % reagent. However, it might not be the best choice for studying weak complexes as perchlorate is extracted together with the metal species. Furthermore, the use of TBP at acid conditions is somewhat complicated by the extraction of $HClO_4$. This extraction is not known in great detail although it is believed that perchloric acid is extracted as $HClO_4(TBP)_y$ where $y=3-4$.[6,34]

HDEHP is a very reliable reagent and offers a great freedom in adjusting the distribution level. Very high or low D values can be obtained which makes HDEHP indispensable in studying extremely strong complexants. Its drawbacks are mainly related to slow kinetics under certain conditions and to the strong pH dependency of HDEHP which necessitates careful determination of the influence of the acidity on the complex system. Other disadvantages are the change in extraction mechanism which may occur, depending on the diluent, when increasing the reagent concentration and the conversion of HDEHP into its salt form at high pH which may result in a third phase or skin formation.

HTTA should offer the same advantages as HDEHP but somewhat surprisingly we have not found HTTA to be very easy to work with in contrast to its homologue acetylacetone (HAA) which behaves very regularly. Conflicting observations about the time needed to obtain equilibrium have been made; Edroth, *e.g.*, found no indication of true equilibrium in the HTTA(benzene)–Th(IV),$NaClO_4$ distribution system even after a month, and Kassierer and Kertes found no equilibrium with HTTA-lanthanides even after 6 h if pH<4, whereas the equilibrium was attained rapidly at higher pH.[37,38] In this work we found that at least pseudo-equilibrium is obtained within 30 min if pH<4, but that the reproducibility is poor at pH>4. Despite these contradictory observations about the equilibrium kinetics it seems that our distribution data for HTTA are compatible both with Kassierer and Kertes' results and other values reported in the literature (Table 1).

Unless the kinetics is carefully elucidated, we feel reluctant to recommend the use of HTTA for metal complexation studies, except for analytical

Table 3. Comparison of the usefulness of HTTA, TBP and HDEHP as extraction agents for metal complexation studies.

Reagent class	Reproducibility	Mechanism, complication	Kinetics	Stability of reagent	Suitability for complex studies Weak complexes	Strong complexes	Hydrolysis
HTTA β-diketone	poor mass balance at pH>4	Unpredictable mechanism for some metals.[a]	Sometimes very slow.[e]	light sensitive, decomposition at pH>9.	good	good	poor because nonreproducibility at high pH;[b]
TBP neutral organophosphorous compound	good	Extraction of H^+, Na^+ and NH_4^+ salt.	rapid	stable	poor	good	very good because pH independent extraction mechanism
HDEHP acid organophosphorous compound	good at low pH	Mechanism depends on diluent. Extraction of Na^+ and NH_4^+.	Usually rapid[c]	stable	good	good	poor because nonreproducibility at high pH;[b,d]

[a] *E.g.* UO_2^{2+}, PaO^{2+} and HfO^{2+}, Ref. 39. [b] Very high *D*-values implies use of extremely low reagent concentrations which leads to sensitivity towards impurities *etc.* [c] A detailed kinetic study is given in Ref. 33.[d] Third phase and formation of interface layer (skin). [e] Depending on pH, Refs. 37, 38 and this work.

or separation purposes. Other properties of HTTA which must be considered are its decomposition at pH>9 and its, in comparison with other β-diketones, very stable ketohydrate. In addition β-diketones give unexpected extraction mechanisms with oxycations (*e.g.* UO_2^{2+}, PaO^{2+}, HfO^{2+}).[36]

Acknowledgements. Eng. Theresia Rodinson and Eng. Eva Jomar are thanked for careful experimental assistance. Valuable suggestions and criticism have been given by Prof. Jan Rydberg. Dr. Lu expresses his gratitude for the financial support of the Royal Swedish Academy of Engineering Sciences and Academia Sinica during his two year visit to Sweden. This work was supported by the Swedish Natural Science Research Council which is gratefully acknowledged.

REFERENCES

1. Marcus, Y. and Kertes, A. S. *Ion Exchange and Solvent Extraction of Metal Complexes,* Wiley, London 1969.
2. Beck, M. T. *Chemistry of Complex Equilibria,* Van Nostrand-Reinhold, London 1970.
3. Lundqvist, R. *Acta Chem. Scand. A 36* (1982) 741.
4. Lundqvist, R. *Acta Chem. Scand. A 28* (1974) 243.
5. Leroy, P. *CEA-R 3207, Commissariat a L'Energie Atomique-France,* 1967.
6. Kolarik, Z. *J. Inorg. Nucl. Chem. 36* (1974) 409.
7. Yoshida, H. *J. Inorg. Nucl. Chem. 26* (1964) 619.
8. Ahrland, S., Liljenzin, J. O. and Rydberg, J. *Comprehensive Inorganic Chemistry,* Pergamon, Oxford and New York 1973, Vol. 5, p. 542.
9. Liljenzin, J. O. and Lundqvist, R. *Gmelin Handbuch der Anorganischen Chemie,* 8th Ed., Protactinium, Ergänzungsband 2, Systemnummer 51, Springer, Berlin, 1977, p. 187.
10. Markl, P. *Extraktion und Extraktions-Chromatographie in der Anorganischen Analytik, Metoden der Analyse in der Chemie,* Band 13, Akad.-Verlag., Frankfurt am Main 1972.
11. Sekine, T. and Hasegawa, Y. *Solvent Extraction Chemistry, Fundamentals and Applications,* Dekker, New York 1977.
12. Marcus, Y., Kertes, A. S. and Yanir, E., *Equilibrium Constants of Liquid–Liquid Distribution Reactions. Part 1: Organophosphorous Extractants,* IUPAC Chem. Data Series, No. 3, Butterworth, London 1974.
13. Marcus, Y. *Critical Evaluation of some Equilibrium Constants Involving Organophosphorous Extractants,* IUPAC Chem. Data Series, No. 1, Butterworth, London 1974.
14. Nikolotova, E. I. and Kartachova, N. A. *Handbook of Extraction, Vol. 1., Extraction of Neutral Organic Compounds,* Atomizdat, Moscow 1976.
15. Hesford, E. and McKay, H. A. C. *J. Inorg. Nucl. Chem. 13* (1969) 165.
16. Woodhead, J. L. and McKay, H. A. C. *J. Inorg. Nucl. Chem. 27* (1965) 2747.
17. Marcus, Y. *J. Inorg. Nucl. Chem. 37* (1975) 493.
18. Marcus, Y. and Kolaric, Z. *J. Chem. Eng. Data 18* (1973) 155.
19. Högfeldt, E., Ed., *Stability Constants of Metal-Ion Complexes. Part A: Inorganic Ligands,* IUPAC Chem. Data Series, No. 21, Pergamon, Oxford 1982.
20. Sillén, L. G. and Martell, A. E., Eds., *Stability Constants of Metal Ion Complexes,* Special publications Nos. 17 and 25, The Chemical Society, Burlington House, London 1964 and 1971.
21. Khopkar, P. K. and Narayanankutty, P. *J. Inorg. Nucl. Chem. 33* (1971) 495.
22. Stary, I. and Freiser, H. *Equilibrium Constants of Liquid–Liquid Distribution Reactions. Part IV: Chelating Extractants,* IUPAC Chem. Data Series No 18, Pergamon, Oxford 1978.
23. Lenz, T. G. and Smutz, M. *J. Inorg. Nucl. Chem. 30* (1968) 621.
24. Dubuquoy, C., Guillaumont, R. and Bouissières, G. *Radiochim. Acta 8* (1967) 49.
25. Mason, G. W., Metta, D. N. and Peppard, D. F. *J. Inorg. Nucl. Chem. 38* (1976) 2077.
26. Weaver, B. and Shoun, R. R. *J. Inorg. Nucl. Chem. 33* (1971) 1917.
27. Mason, G. W., Schofer, N. L. and Peppard, D. F. *J. Inorg. Nucl. Chem. 32* (1970) 3911.
28. Peppard, D. F., Mason, G. W., Driscoll, W. J. and Sironen, R. J. *J. Inorg. Nucl. Chem. 7* (1958) 276.
29. Kandil, A. T. and Farah, K. *J. Inorg. Nucl. Chem. 42* (1980) 277.
30. Zikovský, L. *J. Inorg. Nucl. Chem. 35* (1973) 2917.
31. Alstad, J., Augustson, J. H., Danielssen, T. and Farbu, L. *Proc. Int. Solvent Extraction Conf.,* ISEC-77, Lyon 1974, Society of Chemical Industry, London 1974, Vol. 2, p. 1083.

32. Danesi, P. R. and Vandergrift, G. F. *Inorg. Nucl. Chem. Lett. 17* (1981) 109.
33. Danesi, P. R. and Vandergrift, G. F. *J. Phys. Chem. 85* (1981) 3646.
34. McDowell, W. J. and Coleman, C. F. *J. Inorg. Nucl. Chem. 27* (1965) 1117.
35. Lanin, V. P., Smelov, V. S. and Smyk, Z. A. *Sov. Radiochem. 14* (1972) 694.
36. Tebelev, L. G. and Melkaya, R. F. *Sov. Radiochem. 18* (1976) 733.
37. Edroth, B. *Unpublished work.*
38. Kassierer. E. F. and Kertes, A. S. *J. Inorg. Nucl. Chem. 34* (1972) 3221.
39. Lundqvist, R. *Proc. Int. Solvent Extraction Conf. ISEC-80,* Liège, Belgium, Sept. 6–12. Vol. 1, Session 16, Paper 80–51.
40. Magnusson, L. B. and Andersson, M. L. *J. Am. Chem. Soc. 76* (1954) 6207.
41. Kandil, A. T., Aly, H. F., Raieh, M. and Choppin, G. R. *J. Inorg. Nucl. Chem. 37* (1975) 229.

Received February 14, 1983.