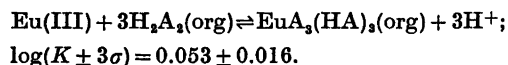


Studies on the Solvent Extraction of Europium(III) by Di-(2-ethylhexyl)phosphoric Acid (HDEHP) in Toluene

MANUEL AGUILAR and DJIET HAY LIEM

Department of Inorganic Chemistry, Royal Institute of Technology (KTH),
S-100 44 Stockholm 70, Sweden

The extraction of Eu(III) from 0.10 M (Na,H)-ClO₄ aqueous solution by di-(2-ethylhexyl)-phosphoric acid, HDEHP (=HA), in toluene has been studied. The distribution of Eu(III) between the two phases was measured by a radiometric method using Eu(III) labelled with the radioactive isotopes Eu-152(154). The distribution data has been analyzed by a graphical method as well as by the computer program LETAGROP-DISTR. The results may be explained by the formation of the following Eu(III)-di-(2-ethylhexyl)phosphoric acid species:



The possibility of the formation of Eu(III)-HDEHP species in the aqueous phase is indicated. The formation of EuClO₄²⁺ is indicated, tentative values for the equilibrium constants being $\log K_1 = -0.35$ in 1.0 M (Na,H)ClO₄ and $\log K_1 = -0.23$ in 0.1 M (Na,H)ClO₄ solution. A general expression for calculating the equilibrium constant K for the extraction of Eu(III) by HDEHP into toluene from a given aqueous ionic medium is described.

Dialkylphosphoric acids are effective complexing agents for the extraction of lanthanides and actinides.¹⁻³ One which has been used extensively is di(2-ethylhexyl)phosphoric acid, HDEHP (=HA), primarily due to its excellent complexing properties over a wide pH range, its low solubility in aqueous solution and its commercial availability. HDEHP is used in the Dapex process for the recovery of uranium from leach liquors⁴ and is being studied as a potential extractant for the reprocessing of spent nuclear fuel as an alternative to the established Purex process.^{5,6} Recently, the

potential use of HDEHP for the extraction of metals in non-nuclear industries, *e.g.* Zn,⁷ Co, Ni,¹⁶ V,^{8,16} Mo^{18,24} was also reported. By infrared spectroscopy and molecular weight determinations^{9,10} distribution studies^{11-13,20} and NMR studies,¹⁴ dialkylphosphoric acids were shown to form strong dimeric species in nonpolar organic solvents. Previous studies^{15,16} have shown that the metal extraction equilibria, when a dialkylphosphoric acid is used as extractant, are strongly influenced by the distribution and dimerization equilibria of HA. The use of HDEHP for the extraction of lanthanides and actinides has been previously reported.^{17,18} In general there is agreement as to which metal species were formed. However, the reported values of the formation constants of the metal HDEHP species vary¹⁷ (*cf.* Table 4). These deviations may in part be explained, because most authors have based their conclusions on the assumption that HDEHP is completely dimerized in all organic solvents over the whole range of concentration studied. However, these assumptions do not apply strictly for HDEHP and other dialkylphosphoric acids.¹³ In this work we report the extraction of Eu(III) by HDEHP from 0.10 M (Na,H)ClO₄ in toluene. In the analysis of the data we used the equilibrium constants for the distribution, dimerization and dissociation of HDEHP in the two-phases system.¹³

Symbols and equilibrium constants

- [] = equilibrium concentration in the aqueous phase
 []_{org} = equilibrium concentration in the organic phase
 C_A = initial total concentration of di-(2-ethylhexyl)-phosphoric acid
 HDEHP = di-(2-ethylhexyl)phosphoric acid
 K_{pqr}^{org} = formation constant of the complex $(H^+)_p(Eu^{3+})_q(HA)_r$ in the organic phase, cf. eqn. (1)
 K_{lmn}^{aq} = formation constant of the complex $(H^+)_l(Eu^{3+})_m(HA)_n$ in the aqueous phase, cf. eqn. (2)
 I_{aq}, I_{org} = γ -activity of $^{152},^{154}\text{Eu(III)}$ in the aqueous and organic phases, given in cpm for equal volumes of samples.
 D = $\sum[\text{Eu}]_{org}/\sum[\text{Eu}]_{aq} = I_{org}/I_{aq}$, net distribution of Eu(III)
 $\sigma(y)$ = standard deviation in y (cf. Ref. 27, eqn. 17)
 $K(X, I)$ = equilibrium constant for the extraction of Eu(III) by HDEHP from the ionic medium $(\text{Na}, \text{H})\text{X}$ with the ionic strength I into the organic phase, cf. eqn. (8)
 $K(\text{corr}, 0)$ = equilibrium constant for the extraction of Eu(III) by HDEHP into toluene from infinite diluted aqueous solution.

EXPERIMENTAL

HDEHP, di(2-ethylhexyl)phosphoric acid, $(\text{C}_8\text{H}_{17}\text{O})_2\text{P}(\text{OH})\text{O}$, was purified as described previously.^{12,13} NaClO_4 stock solution was prepared from Na_2CO_3 and HClO_4 as in Ref. 19. HClO_4 , Merck, *p.a.*, free of Fe(III) was used without further purification. The stock solution was standardized against NaOH solution. Four 0.1 M $(\text{Na}, \text{H})\text{ClO}_4$ solutions, where $2.5 > -\log [\text{H}^+] > 1.0$, were prepared. *Toluene*, Merck *p.a.*, was purified by washing with dilute solutions of NaOH and HCl and finally with distilled water.

Distribution experiments. The distribution of Eu(III) between two solutions S1 = H mM H^+ , $(100 - H)$ mM Na^+ , 100 mM ClO_4^- and S2 = C_A mM HDEHP in toluene was measured as a function of the total concentration of HDEHP in toluene, at different constant H levels. The experiments were performed by equilibrating in a rotating rack equal volumes of solutions S1 and S2 in glass-stoppered centrifuge tubes in a thermostated room at 25 ± 0.5 °C. After

equilibrium was attained, the tubes were centrifuged and aliquot samples were drawn from both phases for radiometric analysis of the metal distribution. The activity of the Eu-152(154) isotope was determined in a Tracerlab SC-57 low background Scintillation Counter with a Tl-activated NaI crystal, connected with a Tracerlab SC-70 COMPU/MATIC V scaler. As a rule a minimum of 10^4 counts of activity was measured giving a statistical error less than 1%. Toluene was found not to extract Eu(III) under the experimental conditions. In order to estimate the time necessary for attaining equilibrium, D was measured as a function of time for constant values of $C_A = 18.2$ mM and $-\log [\text{H}^+] = 2.3$ (cf. Fig. 1). No appreciable changes in the value of D can be observed after equilibration over a period of 4 h. In all the experiments the two phases were consequently equilibrated by shaking for at least 4 h. The $[\text{H}^+]$ in the aqueous phase was measured potentiometrically as described previously.¹³

Basic assumptions on the chemical model. In the analysis of the distribution data for Eu(III) we assume the formation of the species $(\text{H}^+)_p(\text{Eu}^{3+})_q(\text{HA})_r$ in the organic phase and $(\text{H}^+)_l(\text{Eu}^{3+})_m(\text{HA})_n$ in the aqueous phase. We denote these species by $(p, q, r)(\text{org})$ and $(l, m, n)(\text{aq})$; e.g. $(-3, 1, 6)(\text{org})$ represents $\text{EuA}_3(\text{HA})_6(\text{org})$ and $(-1, 0, 1)(\text{aq}) = \text{A}^-(\text{aq})$. The formation constant of these species is expressed by:

$$K_{pqr}^{org} = \frac{[(\text{H}^+)_p(\text{Eu}^{3+})_q(\text{HA})_r]_{org}}{[\text{H}^+]^p [\text{Eu}^{3+}]^q [\text{HA}]^r} \quad (1)$$

$$K_{lmn}^{aq} = \frac{[(\text{H}^+)_l(\text{Eu}^{3+})_m(\text{HA})_n]}{[\text{H}^+]^l [\text{Eu}^{3+}]^m [\text{HA}]^n} \quad (2)$$

Using (1) and (2) we derive the expression for the distribution ratio:

$$D = \frac{\sum[\text{Eu}]_{org}}{\sum[\text{Eu}]_{aq}} = \frac{\sum q K_{pqr}^{org} [\text{H}^+]^p [\text{Eu}^{3+}]^q [\text{HA}]^r}{\sum m K_{lmn}^{aq} [\text{H}^+]^l [\text{Eu}^{3+}]^m [\text{HA}]^n} \quad (3)$$

We make the assumptions that the extracted species are uncharged and that the activity factors for the different species are kept constant by the constant ionic strength of the aqueous solution. We now describe the two-phase system by a model containing the species denoted by sets of (p, q, r) and (l, m, n) .

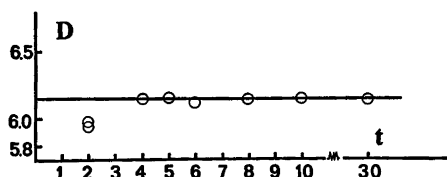


Fig. 1. The distribution of Eu(III) in the two-phase system Eu(III)-0.1 M (Na,H)ClO₄/HDEHP-toluene as a function of shaking time *t* (in h). -log [H⁺]=2.30 and C_A=18.2 mM. The speed of the rotating rack is approximately 20 rpm.

DATA ANALYSIS

Graphical analysis. The distribution data for Eu(III) are given in Table 1 and represented in Fig. 2 as log *D* versus -log (½C_A) for different constant values of log [H⁺]. The experimental points fall practically on straight lines with the slope approximately equal to -3. This indicates the predominant extraction of Eu-HDEHP species with the composition (H⁺)_p(Eu³⁺)_q(H₂A₂)_r. This conclusion follows from the following relationship and the pre-

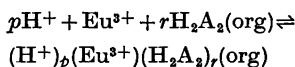
dominant formation of HDEHP dimers in the organic phase:¹³

$$C_A = 2[H_2A_2]_{org} + [HA]_{org} + 2[H_2A_2] + [HA] + [A^-] \approx 2[H_2A_2]_{org} \quad (4)$$

Assuming that Eu(III) exists as mononuclear species in both phases which is reasonable for the tracer concentration range used (C_{Eu} < 10⁻⁶ M), we derive the following expression for the distribution ratio *D*:

$$D = \frac{[(H^+)_p(Eu^{3+})(H_2A_2)_r]_{org}}{[Eu^{3+}]} = K^*_{p1r}[H^+]^p[H_2A_2]_{org}^r \quad (5)$$

where K*_{p1r} represents the equilibrium constant for the following reaction:



Introducing (4) into (5) the following relationship can be written:

$$\log D = \log K^*_{p1r} + p \log [H^+] + r \log [\frac{1}{2}C_A] \quad (6)$$

Table 1. The distribution of ^{152,154}Eu(III) between solutions of HDEHP-toluene and 0.10 M (Na,H)ClO₄ at 25 °C. Data given as C_A M and log *D*_{exp}. The initial concentration of Eu(III) in the aqueous phase C_{Eu} < 10⁻⁶ M. The volume ratio V_{org}V_{aq}⁻¹ = 1.

log [H ⁺] = -2.417							
0.0605,	2.6102;	0.0567,	2.5095;	0.0529,	2.4476;	0.0506,	2.4492;
0.0416,	2.1517;	0.0371,	2.0294;	0.0361,	2.0135;	0.0302,	1.7499;
0.0289,	1.6837;	0.0227,	1.3112;	0.0151,	0.7806;	0.0144,	0.7949;
0.0130,	0.6593;	0.0116,	0.4864;	0.0101,	0.2995;	0.0094,	0.2000;
0.0087,	0.1133;	0.0080,	-0.0353;	0.0072,	-0.1077;	0.0058,	-0.3868;
0.0043,	-0.7915;	0.0029,	-1.2711;	0.0015,	-2.1307.		
log [H ⁺] = -2.097							
0.0756,	2.0450;	0.0681,	1.9471;	0.0605,	1.7659;	0.0529,	1.5884;
0.0454,	1.3870;	0.0378,	1.1232;	0.0302,	0.8196;	0.0265,	0.6310;
0.0227,	0.4370;	0.0189,	0.2203;	0.0151,	-0.0613;	0.0144,	-0.1006;
0.0136,	-0.1493;	0.0129,	-0.2184;	0.0121,	-0.3193;	0.0106,	-0.4893;
0.0091,	-0.7032;	0.0076,	-0.9401.				
log [H ⁺] = -1.500							
0.1690,	1.3082;	0.1521,	1.1615;	0.1352,	1.0216;	0.1143,	0.7959;
0.1029,	0.6520;	0.0914,	0.5174;	0.0800,	0.3327;	0.0686,	0.1345;
0.0572,	-0.1001;	0.0457,	-0.3791;	0.0343,	-0.7572;	0.0229,	-1.2528.
log [H ⁺] = -1.000							
0.1690,	-0.2338;	0.1521,	-0.3713;	0.1352,	-0.5183;	0.1183,	-0.6915;
0.1143,	-0.7421;	0.1029,	-0.8693;	0.1014,	-0.9219;	0.0914,	-1.229;
0.0883,	-1.0811;	0.0800,	-1.1801;	0.0756,	-1.2263;	0.0686,	-1.386;
0.0605,	-1.5172;	0.0572,	-1.5976.				

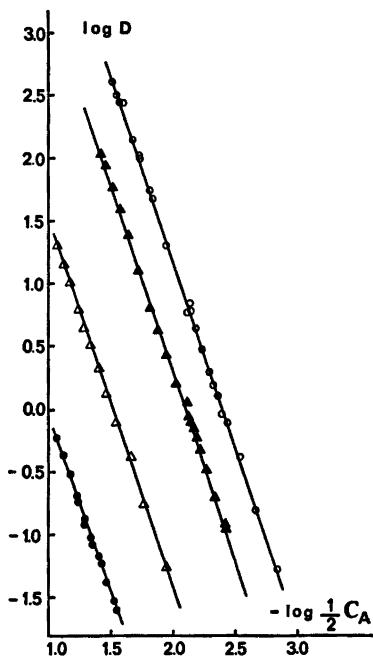


Fig. 2. The distribution of Eu(III) in the two-phase system 0.1 M $(\text{Na},\text{H})\text{ClO}_4/\text{HDEHP-toluene}$ as a function of the initial total concentration of HDEHP in the organic phase, C_A M, for different constant values of $-\log h = 1.000$ (\bullet), 1.500 (Δ), 2.097 (\blacktriangle), and 2.417 (\circ). The curves have been calculated (cf. Ref. 29), assuming the HDEHP species in Ref. 13 and Eu(III)-HDEHP species with the equilibrium constants given in Table 2, model 1.

A plot of $\log D$ versus $-\log (\frac{1}{2}C_A)$ will, according to (6) for a given constant $[\text{H}^+]$ give a straight line with a slope $-r$, which agrees with $r=3$ found in Fig. 2. In Fig. 3 the plot $\log D=f(-\log [\text{H}^+])$ for a set of constant values of C_A give straight lines with a slope of $+3$, which agrees with (6) for $p=-3$. In Fig. 4 we plot $\log D[\text{H}^+]^2$ versus $\log [\text{HA}]$, and find that all points practically fall on a straight line with a slope equal to 6, which indicates the predominant extraction of the species $\text{EuA}_3(\text{HA})_3(\text{org})$. Our results thus agree with those obtained previously for similar systems (cf. Table 3).

Computer analysis of the data. The distribution data ($Np=69$ points) has been analyzed with the LETAGROP-DISTR program.^{27,28} Using this program the computer calculates the set of constants K_1, K_2, \dots, K_n for the

formation of the $(\text{H}^+)_i(\text{Eu}^{3+})_m(\text{HA})_n(\text{aq})$ and $(\text{H}^+)_p(\text{Eu}^{3+})_q(\text{HA})_r(\text{org})$ species which will minimize the error-square sum $U = \sum_1^{Np} (\log D_{\text{calc}} - \log D_{\text{exp}})^2$ for the Np experimental points available. The results of the computer analysis is given in Table 2. The assumption of the formation of $\text{EuA}_3(\text{HA})_3(\text{org})$ (model 1) gives a better description of the data than when $\text{EuA}_3(\text{HA})_2(\text{org})$ is assumed (model 2). No significant improvement in both U_{min} and $\sigma(\log D)$ is found when the additional formation of $\text{EuA}_3(\text{HA})_2(\text{org})$ is assumed (model 3). For model 5 we assumed the additional formation of $\text{EuA}_3^+(\text{aq})$ and found a significant decrease in U_{min} and $\sigma(\log D)$. A similar effect was found in model 4 in which the additional formation of $\text{EuA}^{3+}(\text{aq})$ was assumed. Assuming the additional formation of both EuA^{3+} and EuA_3^+ in the aqueous phase (model 6) the calculations resulted in the rejection of the

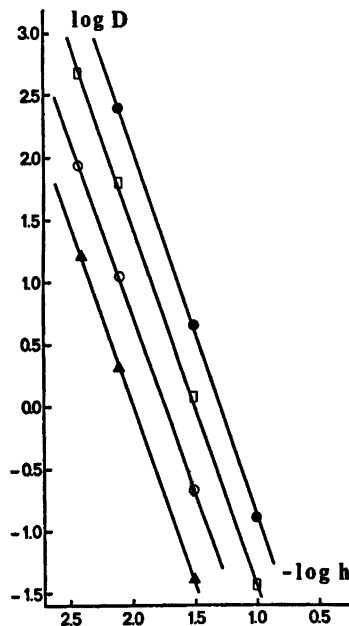


Fig. 3. The distribution of Eu(III) between HDEHP-toluene and 0.1 M $(\text{Na},\text{H})\text{ClO}_4$ as a function of $-\log h$ for various constant values of $C_A = 0.020$ M (\blacktriangle), 3.55×10^{-2} M (\circ), 6.32×10^{-2} M (\square) and 0.100 M (\bullet). The points were taken from the curves in Fig. 2 for the given values of C_A . The straight lines in the figure have a slope of -3 .

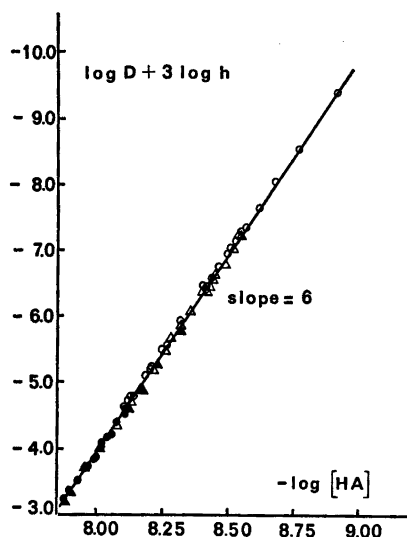


Fig. 4. The distribution of Eu(III) in the two-phase system 0.10 M (Na,H)ClO₄/HDEHP-toluene given as $\log Dh^{-3}$ versus $\log [\text{HA}]$ for various constant values of $-\log h = 1.000$ (●), 1.500 (▲), 2.097 (△) and 2.417 (○). The $[\text{HA}]$ was calculated assuming the formation of HDEHP species with the equilibrium constants given by Liem.¹³ The drawn line has been calculated (cf. Ref. 29), by assuming the formation of Eu(III)-HDEHP species and equilibrium constants given in Table 2, model 1.

EuA³⁺(aq) species as seen from the reduction of its formation constant to zero. No improvement of U_{\min} and $\sigma(\log D)$ is found in model 7,

Table 2. Equilibrium constants $\log \beta_{pqr}$ for the formation of $(\text{H}^+)_p(\text{Eu}^{3+})_q(\text{HA})_r$ species in the system Eu(III)–0.10 M (Na, H)ClO₄/HDEHP-toluene for various assumptions of chemical models which minimize the error-square sum $U = \sum_1^{69} (\log D_{\text{calc}} - \log D_{\text{exp}})^2$.

Model No.	$(\text{H}^+)_p(\text{Eu}^{3+})_q(\text{HA})_r(\text{aq})$	$(\text{H}^+)_p(\text{Eu}^{3+})_q(\text{HA})_r(\text{org})$	U_{\min}	$\sigma(\log D)$
1		(-3,1,6) 44.08 ± 0.02	0.125	0.048
2		(-3,1,5) 35.84 ± 0.09	3.883	0.239
3		(-3,1,5) 34.00, max. 34.64	0.123	0.043
4	(-1,1,1) 5.04, max. 5.25	(-3,1,6) 44.07 ± 0.03		
5 ^b	(-2,1,2) 10.78 ± 0.25	(-3,1,6) 44.11 ± 0.02	0.088	0.035
6	(-1,1,1) $\beta = 0$; (-2,1,2) 10.71, max. 11.00	(-3,1,6) 44.10 ± 0.02	0.085	0.035
7	(-1,1,1) 4.12, max. 5.43	(-3,1,6) 44.10 ± 0.02	0.085	0.036
	(-2,1,2) 10.73, max. 11.26	(-3,1,5) 33.81, max. 34.61	0.085	0.036
		(-3,1,6) 44.10 ± 0.04		

^a The equilibrium constant $\beta_{pqr} = [(\text{H}^+)_p(\text{Eu}^{3+})_q(\text{HA})_r]_i [(\text{H}^+)]^{-p} [\text{Eu}^{3+}]^{-q} [\text{HA}]^{-r}$, where the lower index i indicates the phase referred to in the reaction. The limits given correspond to approximately $\log [\beta \pm 3\sigma(\beta)]$ and if $\sigma(\beta) > 0.2 \beta$, the maximum value $\log [\beta + 3\sigma(\beta)]$ is given.

^b The "best" model assumed.

in which the formation of the species (-3,1,5)-(org) and (-1,1,1)(aq) are assumed as well as those of model 5. Assuming model 5 and minimizing the following different error-square sums, gives practically the same values for $\log K_{pqr}$

$$\sum (\log D_{\text{calc}} D_{\text{exp}}^{-1})^2: (-2,1,2)(\text{aq}) 10.78; (-3,1,6)(\text{org}) 44.10$$

$$\sum (D_{\text{exp}} D_{\text{calc}}^{-1} - 1)^2: (-2,1,2)(\text{aq}) 10.78; (-3,1,6)(\text{org}) 44.10$$

$$\sum (D_{\text{calc}} D_{\text{exp}}^{-1} - 1)^2: (-2,1,2)(\text{aq}) 10.79; (-3,1,6)(\text{org}) 44.09$$

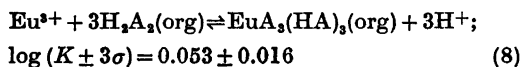
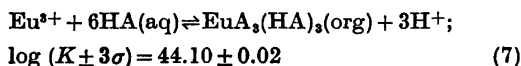
This means that the assignment of the same weight factor to the distribution data is reasonable. In the present work the weight factor has been given the value $w = 1$. In Fig. 5 the error-function, $\log (D_{\text{calc}} D_{\text{exp}}^{-1})$ is given as a function of C_A for model 5. The data are seen to show no systematic deviations.

Conclusions. The results thus show that Eu(III) is extracted by HDEHP in toluene predominantly as EuA₃(HA)₃. They also give indications for the formation of the species EuA₃⁺ or EuA₂²⁺ in the aqueous phase. However, this should be considered as not confirmed, since within the experimental error, the data may satisfactorily be explained by the formation of EuA₃(HA)₃(org) alone with the equilibrium constant

Table 3. Equilibrium constant $\log K$ for the reaction: $\text{Eu(III)} + 3\text{H}_2\text{A}_2(\text{org}) \rightleftharpoons \text{EuA}_3(\text{HA})_3(\text{org}) + 3\text{H}^+$, in the two-phase system aqueous solution/dialkylphosphoric acid-toluene. Temperature 25 °C if not otherwise stated:

Two-phase system	$\log K$	Ref.
1.0 M (H ⁺ ,Na ⁺)ClO ₄ /HDBP-toluene	1.73	31
1.0 M (H ⁺ ,Na ⁺)NO ₃ /HDBP-toluene	1.25	31
1.0 M (H,Na)ClO ₄ /HDAP-toluene	1.79	21
1.0 M (H,Na)NO ₃ /HDAP-toluene	1.31	21
1.0 M (H,Na)ClO ₄ /HDIAP-toluene	1.50	21
1.0 M (H,Na)NO ₃ /HDIAP-toluene	1.02	21
1.0 M (H,Na)ClO ₄ /HDOP-toluene	1.68	21
1.0 M (N,Na)NO ₃ /HDOP-toluene	1.20	21
1.0 M (H,Na)ClO ₄ /HDEHP-toluene	-0.35	21
1.0 M (H,Na)NO ₃ /HDEHP-toluene	-0.83	21
0.5 M HCl/HDEHP-toluene ^a	-0.44 ^b	24, 1
0.1 M (H,Na)ClO ₄ /HDEHP-toluene	0.053	This work
0.01 M HClO ₄ /HDEHP-toluene	1.57	33
1.0 M (Li,H)ClO ₄ /HDEHP-toluene	-0.92	35

^a Temperature 22 °C. ^b Calculated from the single experimental point available.



DISCUSSION

The formation of $\text{EuA}_3(\text{HA})_3(\text{org})$ found in this work thus agrees with the results found by other authors for comparable extraction systems (*cf.* Table 3). The formation of Eu(III)-HA species in the aqueous phase may be expected to increase with increasing pH and C_A . An indication of the formation of Hf(IV)-HDBP aqueous species in sulfate and perchlorate medium for $C_A > 10^{-3}$ M has been reported previously.²⁰ The value $\log K = -0.83$ for the formation of $\text{EuA}_3(\text{HA})_3(\text{org})$ in the system $\text{Eu(III)}-1.0$ M (Na,H)NO₃/HDEHP-toluene, given by Kolarik and Pankova²¹ was calculated by neglecting the formation of $\text{Eu(NO}_3)_3^{2+}(\text{aq})$. As has been shown,^{22,23} Eu(III)-nitrate species are formed in significant concentrations at 1 M NO₃⁻ solutions, and this may explain the lower value of $K = 10^{-0.83}$ for 1.0 M NO₃⁻ medium compared with $K = 10^{-0.35}$ for 1.0 M ClO₄⁻ medium for the reaction (8), (*cf.* Table 3). Using the value given by Choppin and Strazik²² for the formation of EuNO_3^{2+} at the ionic strength $I = 1.0$ M, $K_1 = 10^{0.31}$ M⁻¹,

we calculate for (8) the equilibrium constant for the extraction of Eu(III) from an ionic medium of $I = 1.0$ M:

$$K(\text{corr}, 1) = K(\text{NO}_3, 1)(1 + K_1[\text{NO}_3^-]) \quad (9)$$

Substituting $K(\text{NO}_3, 1) = 10^{-0.83}$ and $K_1 = 10^{0.31}$ in (9), we obtain $K(\text{corr}, 1) = 10^{-0.35}$, in excellent agreement with the value $10^{-0.35}$ found experimentally for the extraction from 1.0 M HClO₄ medium,²¹ where only weak complex formation between Eu(III) and ClO₄⁻ is expected. In Table 3 the value of $K(\text{Cl}, 0.5) = 10^{-0.44}$ from Peppard's data^{24,1} (*cf.* remark in Table 3), applied for 0.5 M ionic chloride medium, was calculated by neglecting the

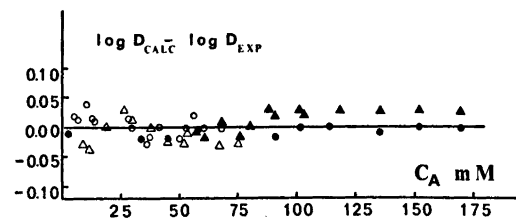


Fig. 5. The error $\log(D_{\text{calc}}D_{\text{exp}}^{-1})$ as a function of C_A for the distribution of Eu(III) in the two-phase system $\text{Eu(III)}-0.10$ M (Na,H)ClO₄/HDEHP-toluene, assuming the formation of $(\text{H}^+)_6(\text{Eu}^{3+})_4(\text{HA})_7$ species and equilibrium constants given in Ref. 13 and Table 2, model 1. $-\log h = 1.000$ (●), 1.500 (▲), 2.097 (△) and 2.417 (○).

formation of Eu(III)–Cl[−] species in the aqueous phase. Since Eu(III) is in tracer concentration, we assume that the ratios of the activity factors $f(\text{EuCl}_2^{2+})f^{-1}(\text{Eu}^{3+})$ and $f(\text{EuCl}_2^+) \times f^{-1}(\text{Eu}^{3+})$ do not vary significantly with the ionic strength for $I = 0.5$ to 1.0 M. This assumption is supported by the value found for the ratio of $f(\text{EuNO}_3^{2+})/f(\text{Eu}^{3+})$ at $I = 1.0$ and 0.2 M. Using the values $K_1 = 10^{0.31}$ at $I = 1.0$ and $K_1 = 10^{0.43}$ M^{−1} at $I = 0.2$ M for the formation of EuNO_3^{2+} in Ref. 22 and $f(\text{NO}_3, 1) = 0.615$, $f(\text{NO}_3, 0.2) = 0.698$ (cf. Ref. 26), we may calculate the following value:

$$\begin{aligned} & [f(\text{EuNO}_3^{2+}, 1)/f(\text{Eu}^{3+}, 1)][f(\text{EuNO}_3^{2+}, 0.2)/ \\ & f(\text{Eu}^{3+}, 0.2)]^{-1} = K(\text{NO}_3, 0.2). \\ & K^{-1}(\text{NO}_3, 1.0)f(\text{NO}_3, 1.0)f^{-1}(\text{NO}_3, 0.2) = 1.1 \approx 1. \end{aligned}$$

Using the values $K_1(\text{Cl}, 1) = 10^{-0.1}$ M^{−1} and $K_2(\text{Cl}, 1) = 10^{-0.6}$ M^{−2} for the formation of EuCl^{2+} and EuCl_2^+ for 1.0 M $\text{H}(\text{Cl}, \text{ClO}_4)$ given by Choppin and Unrein²⁵ and $f(\text{Cl}, 1) = 0.556$ and $f(\text{Cl}, 0.5) = 0.615$ (cf. Kielland²⁶), we calculate the values of the formation constants of these species at $I = 0.5$ M:

$$\begin{aligned} K_1(\text{Cl}, 0.5) &= f(\text{Cl}, 0.5)f^{-1}(\text{Cl}, 1)K_1(\text{Cl}, 1) = \\ & 10^{-0.056} \text{ M}^{-1}, \text{ and} \\ K_2(\text{Cl}, 0.5) &= f^2(\text{Cl}, 0.5)f^{-2}(\text{Cl}, 1)K_2(\text{Cl}, 1) = \\ & 10^{-0.512} \text{ M}^{-2} \end{aligned}$$

Using these values we calculate from Pappard's data:

$$\begin{aligned} K(\text{corr}, 0.5) &= K(\text{Cl}, 0.5)(1 + K_1(\text{Cl}, 0.5)[\text{Cl}^-] + \\ & K_2(\text{Cl}, 0.5)[\text{Cl}^-]^2) = 10^{-0.44}[1 + 10^{-0.056} \times 0.5 + \\ & 10^{-0.512} \times (0.5)^2] = 10^{-0.26}, \text{ for the extraction of} \\ & \text{Eu(III) by HDEHP into toluene as given by} \\ & (8) \text{ from a medium of ionic strength } I = 0.5 \text{ M.} \end{aligned}$$

Test for the formation of europium(III) perchlorate complex. The significant difference between the values of K for the extraction of Eu(III) in toluene from 1.0 , 0.1 , and 0.01 M ClO_4^- medium (cf. Table 3) may be due to the formation of Eu(III)-perchlorate complexes. Assuming that for $C_{\text{ClO}_4} < 1$ M the predominant species formed is EuClO_4^{2+} , the following relationship applies:

$$\begin{aligned} f(\text{Eu}^{3+})f^{-3}(\text{H}^+)K^{-1}(\text{ClO}_4, I) &= \\ K^{-1}(\text{corr}, 0)K^*(K^{*-1} + a_{\text{ClO}_4}) & \quad (10) \end{aligned}$$

where $K(\text{ClO}_4, I)$ is the experimentally found extraction constant for Eu(III) for a ClO_4^-

medium of ionic strength I , $K(\text{corr}, 0)$ the extraction constant for infinite diluted aqueous solution, $K^* = K_1(\text{ClO}_4, 0)f(\text{Eu}^{3+}) \times f^{-1}(\text{EuClO}_4^{2+})(K_1(\text{ClO}_4, 0))$ is the formation constant of EuClO_4^{2+} at infinite dilution, and $a_{\text{ClO}_4} = f(\text{ClO}_4^-)[\text{ClO}_4^-]$. In (10) $K(\text{corr}, 0)$ and K^* may be assumed constant since as discussed previously the ratio of the activity factors $f(\text{Eu}^{3+})/f(\text{EuClO}_4^{2+})$ is expected to be constant in the range of ionic strength studied. In Fig. 6 we plot $\log Y = F(\log a_{\text{ClO}_4})$, where $Y = f(\text{Eu}^{3+}) \times f^{-3}(\text{H}^+)K^{-1}(\text{ClO}_4, I)$, and find that the points fall on a line of slope approximately +1 which agrees with (10). The constant for the formation of the EuClO_4^{2+} may be calculated from:

$$\begin{aligned} K(\text{corr}, 0) &= K(\text{ClO}_4, 1)f^3(\text{H}^+, 1)f^{-1}(\text{Eu}^{3+}, 1) \times \\ (1 + K_1(\text{ClO}_4, 1) \times 1) &= K(\text{ClO}_4, 0.1)f^3(\text{H}^+, 0.1) \times \\ f^{-1}(\text{Eu}^{3+}, 0.1)(1 + K_1(\text{ClO}_4, 0.1) \times 0.1) & \quad (11) \end{aligned}$$

where $K(\text{ClO}_4, 1) = 10^{-0.35}$ and $K(\text{ClO}_4, 0.1) = 10^{0.053}$ are the extraction constants and $K_1(\text{ClO}_4, 1)$, $K_1(\text{ClO}_4, 0.1)$ the constants for the formation of $\text{EuClO}_4^{2+}(\text{aq})$ for 1.0 M and 0.1 M perchlorate medium, respectively. As discussed previously the ratio of the activity factors $f(\text{EuClO}_4^{2+})/f(\text{Eu}^{3+})$ is assumed to be constant for $I = 0.1 - 1$ M. One may then express the relationship:

$$K_1(\text{ClO}_4, 1)/K_1(\text{ClO}_4, 0.1) = f(\text{ClO}_4, 1)/f(\text{ClO}_4, 0.1),$$

where $f(\text{ClO}_4, 1) = 0.582$ and $f(\text{ClO}_4, 0.1) = 0.763$

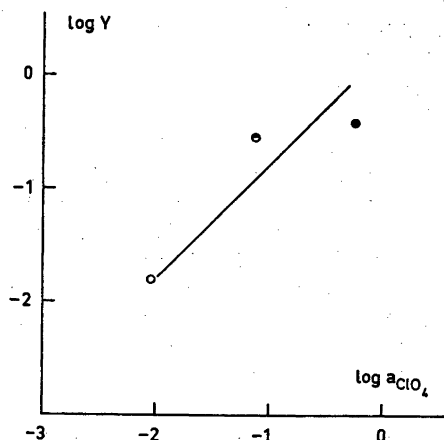


Fig. 6. The extraction of Eu(III) by HDEHP into toluene from 0.01 M ClO_4^- (○, Chiarizia *et al.*²³), 0.1 M ClO_4^- (●, this work) and 1.0 M ClO_4^- medium (●, Kolarik and Pankova²¹) (cf. text).

are the activity factors for ClO_4^- at $I=1.0$ and 0.1 M (cf. Ref. 26). Substituting $K_1(\text{ClO}_4, 1)/K_1(\text{ClO}_4, 0.1)=0.763$ and $f(\text{Eu}^{3+}, 1)=0.071$, $f(\text{H}^+, 1)=0.745$, $f(\text{Eu}^{3+}, 0.1)=0.180$ and $f(\text{H}^+, 0.1)=0.827$ (cf. Kielland²⁶) into (11) we obtain:

$$\text{Eu}^{3+} + \text{ClO}_4^- \rightleftharpoons \text{EuClO}_4^{2+}; K_1 = 10^{-9.35} \text{ M}^{-1} \\ (I = 1.0 \text{ M}); K_1 = 10^{-9.23} \text{ M}^{-1} (I = 0.1 \text{ M}).$$

From (11) we may calculate $K(\text{corr}, 0) = 10^{0.56}$ for the extraction of Eu^{3+} by HDEHP into toluene from infinite diluted aqueous solution. The extraction constant from a medium with non-complexing ligands and an ionic strength I can thus be expressed by:

$$K(\text{corr}, I) = f(\text{Eu}^{3+}, I) f^{-3}(\text{H}^+, I) \times 10^{0.56} \quad (12)$$

Given the activity factors for Eu^{3+} and H^+ , e.g. from Kielland's relationship²⁶ and the constant $K_n = [\text{EuX}_n^{3-n}][\text{Eu}^{3+}]^{-1}[\text{X}^-]^n$ for the formation of complexes between Eu^{3+} and the ionic ligand X^- (e.g. NO_3^- , Cl^-) in the aqueous phase, we may express the equilibrium constant $K(\text{X}, I)$ for the extraction of $\text{Eu}(\text{III})$ by HDEHP into toluene from the ionic medium, e.g. $(\text{Na}, \text{H})\text{X}$, with a given ionic strength I and containing the $\text{EuX}_n^{3-n}(\text{aq})$ species:

$$K(\text{X}, I) = f(\text{Eu}^{3+}, I) f^{-3}(\text{H}^+, I) \times \\ (1 + \sum K_n [\text{X}^-]^n)^{-1} \times 10^{0.56} \quad (13)$$

Using $f(\text{Eu}^{3+}, 1) = 0.071$, $f(\text{H}^+, 1) = 0.745$ and $K_1 = 10^{0.31} \text{ M}^{-1}$ for the formation of EuNO_3^{2+} (cf. Ref. 22), we calculate, from (13), the equilibrium constant for the extraction of $\text{Eu}(\text{III})$ by HDEHP from 1.0 M $(\text{Na}, \text{H})\text{NO}_3$ into toluene, $K(\text{NO}_3, 1) = 10^{-0.67}$. This value is in fair agreement with the value $10^{-0.83}$ found experimentally by Kolarik and Pankova²¹ for the same extraction system. Using $f(\text{Eu}^{3+}, 0.5) = 0.091$, $f(\text{H}^+, 0.5) = 0.766$, and $K_1 = 10^{-0.956}$, $K_2 = 10^{-0.513}$ for the formation of EuCl^{2+} and EuCl_2^+ at 0.5 M $(\text{Na}, \text{H})\text{Cl}$ calculated previously, we calculate using (13) the equilibrium constant for the extraction of $\text{Eu}(\text{III})$ from 0.5 M Cl^- medium $K(\text{Cl}^-, 0.5) = 10^{-0.30}$, in agreement with the value $10^{-0.44}$ found experimentally for the same system (cf. Peppard *et al.*²⁴ and Baes¹).

Acknowledgements. The work has been financially supported by the Swedish National Science Research Council and the Swedish

Board for Technical Development. We are much obliged for the criticism given by Prof. Ingmar Grenthe. Dr. Derek Lewis and Mr. Ian Duncan, B.Sc. have revised the English text.

REFERENCES

1. Baes, Jr. C. F., *J. Inorg. Nucl. Chem.* **24** (1962) 707.
2. Liem, D. H. *Inaugural Dissertation, Royal Institute of Technology, Stockholm* 1971 (available on request).
3. Peppard, D. F. *Annu. Rev. Nucl. Sci.* **21** (1971).
4. Blake, Jr., C. A., Baes, Jr., C. F., Brown, K. B., Coleman, C. F. and White, J. C. *2nd Int. Conf. Peaceful Uses Atomic Energy*, Paper 1550, Geneva 1958; *ORNL-2171, Oak Ridge* 1956.
5. Flanary, J. R. *Progr. Nucl. Energy Ser. 3, Process Chemistry I* (1956) 195.
6. Goldschmidt, B., Regnaut, P. and Prevot, I. *Int. Conf. Peaceful Uses Atomic Energy*, Geneva 1955, Paper No. P/349.
7. Riele, W. A. M., Cloete, F. I. D., Haines, A. K., Sampson, T. D. and Tunley, T. F. *TMS Paper No. A74-17, Metallurgical Society of AIME*, 1974.
8. Fletcher, A. W. *U.S. Patent* 3,055,754 (1962).
9. Peppard, D. F., Ferraro, J. R. and Mason, G. W. *J. Inorg. Nucl. Chem.* **4** (1957) 334.
10. Peppard, D. F., Ferraro, J. R. and Mason, G. W. *J. Inorg. Nucl. Chem.* **7** (1958) 231.
11. Dyrssen, D. *Acta Chem. Scand.* **11** (1957) 1771.
12. Dyrssen, D. and Liem, D. H. *Acta Chem. Scand.* **14** (1960) 1091.
13. Liem, D. H. *Acta Chem. Scand.* **26** (1972) 191.
14. Ferraro, J. R. and Peppard, D. F. *J. Phys. Chem.* **67** (1963) 2639.
15. Dyrssen, D. and Liem, D. H. *Acta Chem. Scand.* **14** (1960) 1100.
16. *Solvent Extraction Chemistry, Proc. Int. Conf. Solvent Extraction Chem. (ISEC) Gothenburg*, Dyrssen, D., Liljenzin, J. O. and Rydberg, J., Eds., North-Holland, Amsterdam 1967.
17. Marcus, Y., Kertes, A. S. and Yanir, E. *Equilibrium Constants of Liquid-Liquid Distribution Reactions, International Union of Pure and Applied Chemistry*, Butterworths, London 1974.
18. Marcus, Y. and Kertes, A. S. *Ion Exchange and Solvent Extraction of Metal Complexes*, Wiley-Interscience, New York 1969.
19. *Some Laboratory Methods in Current Use at the Department of Inorganic Chemistry, Royal Institute of Technology, Stockholm, Mimeograph* 1959.
20. Liem, D. H. and Sinegribova, O. *Acta Chem. Scand.* **25** (1971) 277.

21. Kolarik, Z. and Pankova, H. *J. Inorg. Nucl. Chem.* 28 (1966) 2325.
22. Choppin, G. R. and Strazik, W. F. *Inorg. Chem.* 4 (1965) 1250.
23. Bansal, B. M. L., Patil, S. K. and Sharma, H. D. *J. Inorg. Nucl. Chem.* 26 (1964) 993.
24. Peppard, D. F., Mason, G. W., Maier, J. L. and Driscoll, W. J. *J. Inorg. Nucl. Chem.* 4 (1957) 334.
25. Choppin, G. R. and Unrein, P. J. *J. Inorg. Nucl. Chem.* 25 (1963) 387.
26. Kielland, J. *J. Am. Chem. Soc.* 2 (1937) 1675.
27. Ingri, N. and Sillén, L. G. *Ark. Kemi* 23 (1964) 97; Sillén, L. G. and Warnqvist, B. *Ark. Kemi* 31 (1969) 315; Sillén, L. G. and Warnqvist, B. *Ark. Kemi* 31 (1969) 341; Arnek, R., Sillén, L. G. and Wahlberg, O. *Ark. Kemi* 31 (1969) 353.
28. Liem, D. H. *Acta Chem. Scand.* 25 (1971) 1521.
29. Ingri, N., Kakolowicz, W., Sillén, L. G. and Warnqvist, B. *Talanta* 14 (1967) 1261.
30. Duyckaerts, G., Dreze, Ph. and Simon, A. *J. Inorg. Nucl. Chem.* 13 (1960) 332.
31. Kuča, L. *Collect. Czech. Chem. Commun.* 32 (1967) 288.
32. Brown, K. B., Coleman, C. F., Crouse, D. J. and Ryon, A. D. *Oak Ridge National Laboratory Progress Report* 1957, ORNL-2268.
33. Chiarizia, R., Danesi, P. R., Raieš, M. A. and Scibona, G. *J. Inorg. Nucl. Chem.* 37 (1975) 1495.
34. Liem, D. H. *Unpublished work.*
35. Moulin, N., Hussonnois, M., Brillard, L. and Guillaumont, R. *J. Inorg. Nucl. Chem.* 37 (1975) 2521.

Received October 3, 1975.