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

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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:

$$Eu(III) + 3H_2A_4(org) = EuA_4(HA)_4(org) + 3H^+;$$

$$\log(K + 3r) = 0.053 \pm 0.016.$$  

The possibility of the formation of Eu(III)-HDEHP species in the aqueous phase is indicated. The formation of EuClO₄ is indicated, tentative values for the equilibrium constants being $log K_2 = -0.38$ in 1.0 M (Na,H)ClO₄ and $log K_2 = -0.23$ 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. 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 liquors and is being studied as a potential extractant for the reprocessing of spent nuclear fuel as an alternative to the established Purex process. Recently, the potential use of HDEHP for the extraction of metals in non-nuclear industries, e.g. Zn, Co, Ni, V, Mo was also reported. By infrared spectroscopy and molecular weight determinations, distribution studies and NMR studies, dialkylphosphoric acids were shown to form strong dimeric species in nonpolar organic solvents. Previous studies 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. 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 vary (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. 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.
Symbols and equilibrium constants

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

\[ C_A \] = initial total concentration of di-(2-ethylhexyl)-phosphoric acid

\[ \text{HDEHP} \] = di-(2-ethylhexyl)-phosphoric acid

\[ K_{pq}^{\text{org}} \] = formation constant of the complex \((H^+)_p(Eu^{3+})_q(\text{HA})_r\) in the organic phase, cf. eqn. (1)

\[ K_{lmn}^{\text{aq}} \] = formation constant of the complex \((H^+)_l(Eu^{3+})_m(\text{HA})_n\) in the aqueous phase, cf. eqn. (2)

\[ I_{\text{aq}}, I_{\text{org}} \] = \(\gamma\)-activity of \(^{151,153}\text{Eu}^{\text{III}}\) in the aqueous and organic phases, given in cpm for equal volumes of samples.

\[ D = \sum [\text{Eu}]_{\text{org}}/\sum [\text{Eu}]_{\text{aq}} = I_{\text{org}}/I_{\text{aq}} \] = net distribution of \(\text{Eu}^{\text{III}}\)  

\[ \sigma(y) \] = standard deviation in \(y\) (cf. Ref. 27, eqn. 17)

\[ K(X,I) \] = equilibrium constant for the extraction of \(\text{Eu}^{\text{III}}\) by HDEHP from the ionic medium \((\text{Na,H})X\) with the ionic strength \(I\) into the organic phase, cf. eqn. (8)

\[ K(\text{corr},0) \] = equilibrium constant for the extraction of \(\text{Eu}^{\text{III}}\) by HDEHP into toluene from infinite diluted aqueous solution.

Experimental

\(\text{HDEHP}\), di-(2-ethylhexyl)phosphoric acid, \((C_9H_{17}O)P(OH)J\), was purified as described previously. \(\text{NaClO}_4\) stock solution was prepared from \(\text{Na}_2\text{CO}_3\) and \(\text{HClO}_4\) as in Ref. 18. \(\text{HClO}_4\), Merck, p.a., free of \(\text{Fe(II)}\) was used without further purification. The stock solution was standardized against \(\text{NaOH}\) solution. Four 0.1 M \((\text{Na,H})\text{ClO}_4\) solutions, where \(2.5 > -\log [H^+] > 1.0\), were prepared. Toluene, Merck p.a., was purified by washing with dilute solutions of \(\text{NaOH}\) and \(\text{HCl}\) and finally with distilled water.

Distribution experiments. The distribution of \(\text{Eu}^{\text{III}}\) between two solutions \(S_1 = H\) mM \(H^+\), \((100 - H)\) mM \(\text{Na}^+\), 100 mM \(\text{ClO}_4^-\) and \(S_2 = C_A\) 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 \(S_1\) and \(S_2\) in glass-stoppered centrifuge tubes in a thermostated room at \(25 \pm 0.5^\circ\text{C}\). 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 \(\text{Eu}-152(154)\) isotope was determined in a Tracelec SC-57 low background Scintillation Counter with a Tl-activated NaI crystal, connected with a Tracelec 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 \(\text{Eu}^{\text{III}}\) 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 \(-\log [H^+] = 2.3\) (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 \([H^+]\) 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 \(\text{Eu}^{\text{III}}\) we assume the formation of the species \((H^+)_p(Eu^{3+})_q(\text{HA})_r\) in the organic phase and \((H^+)_l(Eu^{3+})_m(\text{HA})_n\) 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 \(\text{Eu}_3\text{A}_6(\text{HA})_6(\text{org})\) and \((-1,0,1)(\text{aq}) = \text{A}^- (\text{aq})\). The formation constant of these species is expressed by:

\[ K_{pq}^{\text{org}} = \frac{[H^+]^p[Eu^{3+}]_q[\text{HA}]_r}{[\text{Eu}^{3+}]_r[\text{HA}]_r} \] (1)

\[ K_{lmn}^{\text{aq}} = [H^+]_l[Eu^{3+}]_m[\text{HA}]_n[H^+]_n \] (2)

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

\[ D = \frac{\sum [\text{Eu}]_{\text{org}}}{\sum [\text{Eu}]_{\text{aq}}} = \frac{\sum qK_{pq}^{\text{org}}[H^+]^p[Eu^{3+}]^q[\text{HA}]_r}{\sum mK_{lmn}^{\text{aq}}[H^+]_l[Eu^{3+}]_m[\text{HA}]_n} \] (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 ([C_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⁺)ₜ(Eu⁺)ₜ(H₂A₃)ₜ. This conclusion follows from the following relationship and the predominant formation of HDEHP dimers in the organic phase:¹

\[
C_A = 2[H_2A_3]_{org} + [HA]_{org} + 2[H_4A_2] + [HA] + [A^-] \approx 2[H_4A_2]_{org}
\]

(4)

Assuming that Eu(III) exists as mononuclear species in both phases which is reasonable for the tracer concentration range used (C_Eu < 10⁻⁴ M), we derive the following expression for the distribution ratio D:

\[
D = \frac{[(H^+)_p(Eu^{3+})(H_4A_2)_r]_{org}}{[Eu^{3+}]} K^*_{p/r}[H^+] [H_4A_2]_{org}
\]

(5)

where \( K^*_{p/r} \) represents the equilibrium constant for the following reaction:

\[
pH^+ + Eu^{3+} + rH_4A_2(\text{org}) \rightleftharpoons (H^+)_p(Eu^{3+})(H_4A_2)_r(\text{org})
\]

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

\[
\log D = \log K^*_{p/r} + p \log [H^+] + r \log [C_A]
\]

(6)

Table 1. The distribution of ¹⁵⁵,¹⁵⁴Eu(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 \( C_{Eu} < 10^{-4} \) M. The volume ratio \( V_{org}/V_{aq} = 1 \).

<table>
<thead>
<tr>
<th>log [H⁺] = −2.417</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0605, 2.6102; 0.0567, 2.5095; 0.0529, 2.4476; 0.0506, 2.4492;</td>
</tr>
<tr>
<td>0.0416, 2.1517; 0.0371, 2.0294; 0.0361, 2.0135; 0.0302, 1.7499;</td>
</tr>
<tr>
<td>0.0289, 1.6837; 0.0227, 1.3112; 0.0151, 0.7806; 0.0144, 0.7949;</td>
</tr>
<tr>
<td>0.0130, 0.6583; 0.0116, 0.4864; 0.0101, 0.2995; 0.0094, 0.2000;</td>
</tr>
<tr>
<td>0.0087, 0.1133; 0.0030, −0.0353; 0.0072, −0.1077; 0.0058, −0.3868;</td>
</tr>
<tr>
<td>0.0043, −0.7915; 0.0029, −1.2711; 0.0015, −2.1007;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>log [H⁺] = −2.097</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0756, 2.0450; 0.0681, 1.9471; 0.0605, 1.7659; 0.0529, 1.5884;</td>
</tr>
<tr>
<td>0.0454, 1.3870; 0.0378, 1.1232; 0.0302, 0.8196; 0.0265, 0.6310;</td>
</tr>
<tr>
<td>0.0227, 0.4370; 0.0189, 0.2203; 0.0151, −0.0613; 0.0144, −1.006;</td>
</tr>
<tr>
<td>0.0136, −0.1493; 0.0129, −0.2184; 0.0121, −0.3193; 0.0106, −0.4683;</td>
</tr>
<tr>
<td>0.0091, −0.7032; 0.0076, −0.9401;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>log [H⁺] = −1.500</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1690, 1.3082; 0.1521, 1.1615; 0.1352, 1.0216; 0.1143, 0.7959;</td>
</tr>
<tr>
<td>0.1029, 0.6520; 0.0914, 0.5174; 0.0800, 0.3327; 0.0686, 0.1345;</td>
</tr>
<tr>
<td>0.0572, −0.1001; 0.0457, −0.3791; 0.0343, −0.7572; 0.0229, −1.2528;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>log [H⁺] = −1.000</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1690, −0.2338; 0.1521, −0.3713; 0.1352, −0.5183; 0.1183, −0.6915;</td>
</tr>
<tr>
<td>0.1143, −0.7421; 0.1029, −0.9093; 0.1014, −0.9219; 0.0914, −1.229;</td>
</tr>
<tr>
<td>0.0833, −1.0811; 0.0800, −1.1801; 0.0756, −1.2263; 0.0686, −1.386;</td>
</tr>
<tr>
<td>0.0605, −1.5172; 0.0572, −1.5976;</td>
</tr>
</tbody>
</table>

The formation of the \((H^+)_n\text{(Eu}^{3+})_m\text{(HA)}_p\text{(aq)}\) and \((H^+)_p\text{(Eu}^{3+})_q\text{(HA)}_r\text{(org)}\) species which will minimize the error-square sum \(U = \sum \frac{1}{N} (D_{\text{calc}} - D_{\text{exp}})^2\) for the \(N\) experimental points available. The results of the computer analysis is given in Table 2. The assumption of the formation of EuA\(_4\text{(HA)}_4\text{(org)}\) (model 1) gives a better description of the data than when EuA\(_4\text{(HA)}_4\text{(org)}\) is assumed (model 2). No significant improvement in both \(U_{\text{min}}\) and \(\sigma(\log D)\) is found when the additional formation of EuA\(_4\text{(HA)}_4\text{(org)}\) is assumed (model 3).

For model 5 we assumed the additional formation of EuA\(_4\)\text{(aq)} and found a significant decrease in \(U_{\text{min}}\) and \(\sigma(\log D)\). A similar effect was found in model 4 in which the additional formation of EuA\(_4\)\text{(aq)} was assumed. Assuming the additional formation of both EuA\(_4\) and EuA\(_4\)\text{(aq)} in the aqueous phase (model 6) the calculations resulted in the rejection of the model.

**Fig. 2.** The distribution of Eu(III) in the two-phase system 0.1 M (Na, H)ClO\(_4\)/HDEHP-toluene as a function of the initial total concentration of HDEHP in the organic phase, \(C_A\) M, for different constant values of \(-\log h = 1.000 (\bullet), 1.500 (\triangle), 2.097 (\Delta),\) and 2.417 (○). 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 \([H^+]\) give a straight line with a slope \(-\tau\), which agrees with \(\tau = 3\) found in Fig. 2. In Fig. 3 the plot \(\log D = f(\log [H^+])\) 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 \(\log D[H^+]^p\) versus \(\log [HA]\), 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 EuA\(_4\)\text{(HA)}\(_4\)\text{(org)}\). Our results thus agree with those obtained previously for similar systems (cf. Table 3).

**Computer analysis of the data.** The distribution data (\(N = 69\) points) has been analyzed with the LETAGROP-DISTR program.\(^{25,28}\) Using this program the computer calculates the set of constants \(K_1, K_2, \ldots, K_n\) for the

**Fig. 3.** The distribution of Eu(III) between HDEHP-toluene and 0.1 M (Na, H)ClO\(_4\) as a function of \(-\log h\) for various constant values of \(C_A = 0.020\) M (△), 3.55 \times 10\(^{-5}\) M (○), 6.32 \times 10\(^{-5}\) (□) and 0.100 M (●). 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 \(-3\).

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 \(\log K_{\text{for}}\)

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

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

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

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 EuA₄(HA)₅. They also give indications for the formation of the species EuA₊ or EuA₊ in the aqeous phase. However, this should be considered as not confirmed, since within the experimental error, the data may satisfactorily be explained by the formation of EuA₄(HA)₅(aq) alone with the equilibrium constant

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**Table 2.** Equilibrium constants \(^a\) \(\log \beta_{\text{for}}\) for the formation of \((H^+)_p(Eu^{3+})_q(HA)_r\) 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 \(U = \sum (\log D_{\text{calc}}-\log D_{\text{exp}})^2\).

<table>
<thead>
<tr>
<th>Model (H⁺)ₚ(Eu³⁺)ₗ(HA)ᵣ(aq)</th>
<th>(H⁺)ₚ(Eu⁺)ₗ(HA)ᵣ(org)</th>
<th>(U_{\text{min}})</th>
<th>(\sigma(\log D))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>((-3,1,6)) 44.08 ± 0.02</td>
<td>0.125</td>
<td>0.048</td>
</tr>
<tr>
<td>2</td>
<td>((-3,1,5)) 35.84 ± 0.09</td>
<td>3.883</td>
<td>0.239</td>
</tr>
<tr>
<td>3</td>
<td>((-3,1,5)) 34.00, max. 34.64</td>
<td>0.123</td>
<td>0.043</td>
</tr>
<tr>
<td>4</td>
<td>((-3,1,6)) 44.07 ± 0.03</td>
<td>0.088</td>
<td>0.035</td>
</tr>
<tr>
<td>5b</td>
<td>((-3,1,6)) 44.11 ± 0.02</td>
<td>0.085</td>
<td>0.035</td>
</tr>
<tr>
<td>6</td>
<td>((-3,1,6)) 44.11 ± 0.02</td>
<td>0.085</td>
<td>0.036</td>
</tr>
<tr>
<td>7</td>
<td>((-3,1,5)) 33.81, max. 34.61</td>
<td>0.085</td>
<td>0.036</td>
</tr>
<tr>
<td>8</td>
<td>((-3,1,6)) 44.10 ± 0.04</td>
<td>0.085</td>
<td>0.036</td>
</tr>
</tbody>
</table>

\(^a\) The equilibrium constant \(\beta_{\text{for}} = ([H⁺]_p(Eu⁺)ₗ(HA)ᵣ)[(H⁺)⁻¹][Eu⁺]⁴(HA)ᵣ]^{⁻¹},\) where the lower index \(t\) indicates the phase referred to in the reaction. The limit given correspond to approximately \(\log [β \pm 3σ(β)]\) and if \(σ(β)>0.2\ β,\) the maximum value \(\log [β \pm 3σ(β)]\) is given.

\(^b\) The "best" model assumed.

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Table 3. Equilibrium constant log $K$ for the reaction:

$$\text{Eu(III)} + 3 \text{H}_2\text{A}_4\text{(org)} \rightleftharpoons \text{EuA}_4\text{(HA)}_3\text{(org)} + 3\text{H}^+,$$

in the two-phase system aqueous solution/dialkylphosphoric acid-toluene. Temperature 25 °C if not otherwise stated:

<table>
<thead>
<tr>
<th>Two-phase system</th>
<th>log $K$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 M (H$^+$,Na$^+$)ClO$_4$/HDBP-toluene</td>
<td>1.73</td>
<td>31</td>
</tr>
<tr>
<td>1.0 M (H$^+$,Na$^+$)NO$_3$/HDBP-toluene</td>
<td>1.25</td>
<td>31</td>
</tr>
<tr>
<td>1.0 M (H,Na)ClO$_4$/HDAP-toluene</td>
<td>1.79</td>
<td>21</td>
</tr>
<tr>
<td>1.0 M (H,Na)NO$_3$/HDAP-toluene</td>
<td>1.31</td>
<td>21</td>
</tr>
<tr>
<td>1.0 M (H,Na)ClO$_4$/HDIAP-toluene</td>
<td>1.50</td>
<td>21</td>
</tr>
<tr>
<td>1.0 M (H,Na)NO$_3$/HDIAP-toluene</td>
<td>1.02</td>
<td></td>
</tr>
<tr>
<td>1.0 M (H,Na)ClO$_4$/HDOP-toluene</td>
<td>1.68</td>
<td>21</td>
</tr>
<tr>
<td>1.0 M (H,Na)NO$_3$/HDOP-toluene</td>
<td>1.20</td>
<td>21</td>
</tr>
<tr>
<td>1.0 M (H,Na)ClO$_4$/HDEHP-toluene</td>
<td>-0.35</td>
<td>21</td>
</tr>
<tr>
<td>1.0 M (H,Na)NO$_3$/HDEHP-toluene</td>
<td>-0.83</td>
<td>21</td>
</tr>
<tr>
<td>0.5 M HCl/HDEHP-toluene</td>
<td>-0.44</td>
<td>24, 1</td>
</tr>
<tr>
<td>0.1 M (H,Na)ClO$_4$/HDEHP-toluene</td>
<td>0.053</td>
<td></td>
</tr>
<tr>
<td>0.01 M HClO$_4$/HDEHP-toluene</td>
<td>1.57</td>
<td>33</td>
</tr>
<tr>
<td>1.0 M (Li,H)ClO$_4$/HDEHP-toluene</td>
<td>-0.92</td>
<td>35</td>
</tr>
</tbody>
</table>

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

Eu$^{2+}$ + 6HA(aq) $\rightleftharpoons$ EuA$_4$(HA)$_3$(org) + 3H$^+$;

$$\log (K \pm 3\sigma) = 44.10 \pm 0.02$$  (7)

Eu$^{2+}$ + 3H$_2$A$_4$(org) $\rightleftharpoons$ EuA$_4$(HA)$_3$(org) + 3H$^+$;

$$\log (K \pm 3\sigma) = 0.053 \pm 0.016$$  (8)

**DISCUSSION**

The formation of EuA$_4$(HA)$_3$(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.$^{29}$ The value log $K = -0.83$ for the formation of EuA$_4$(HA)$_3$(org) in the system Eu(III) – 1.0 M (Na,H)NO$_3$/HDEHP-toluene, given by Kolarik and Pankova,$^{31}$ was calculated by neglecting the formation of Eu(NO$_3$)$_3^{2+}$(aq). As has been shown,$^{35,36}$ Eu(III)-nitrate species are formed in significant concentrations at 1 M NO$_3^-$ solutions, and this may explain the lower value of $K = 10^{-6.38}$ for 1.0 M NO$_3^-$ medium compared with $K = 10^{-6.83}$ for 1.0 M ClO$_4^-$ medium for the reaction (8), (cf. Table 3). Using the value given by Choppin and Strazik,$^{22}$ for the formation of EuNO$_3^{2+}$ at the ionic strength $I = 1.0$ M, $K_1 = 10^{9.31}$ M$^{-1}$, we calculate for (8) the equilibrium constant for the extraction of Eu(III) from an ionic medium of $I = 1.0$ M:

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

Substituting $K(\text{NO}_3, 1) = 10^{-5.83}$ and $K_1 = 10^{9.31}$ in (9), we obtain $K_{\text{corr}, 1} = 10^{-4.84}$, in excellent agreement with the value $10^{-4.84}$ found experimentally for the extraction from 1.0 M HClO$_4$ medium,$^{21}$ where only weak complex formation between Eu(III) and ClO$_4^-$ is expected. In Table 3 the value of $K(\text{Cl}, 0.5) = 10^{-4.44}$ from Peppard’s data$^{24}$ (cf. remark in Table 3), applied for 0.5 M ionic chloride medium, was calculated by neglecting the

![](image.png)

**Fig. 5.** The error log ($D_{\text{calc}}/D_{\text{exp}}$) as a function of $C_A$ for the distribution of Eu(III) in the two-phase system Eu(III) – 0.10 M (Na,H)ClO$_4$/HDEHP-toluene, assuming the formation of (H$^+$)$_b$(Eu$^{3+}$)$_k$(HA)$_l$ species and equilibrium constants given in Ref. 13 and Table 2, model 1. $-\log h = 1.000$ (.), 1.500 (△), 2.097 (△) and 2.417 (O).
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 \( f(\text{EuCl}^{2+})/f(\text{Eu}^{3+}) \) and \( f(\text{EuCl}^{2+})/f(\text{Eu}^{3+}) \) 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 \( K_1 = 10^{0.21} \) at \( I = 1.0 \) and \( K_1 = 10^{0.48} \) M⁻¹ at \( I = 0.2 \) M for the formation of EuNO₃⁺ 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:

\[
[f(\text{EuNO}_3^{2+}, 1)]/[f(\text{Eu}^{3+}, 1)] [f(\text{EuNO}_3^{2+}, 0.2)]/[f(\text{Eu}^{3+}, 0.2)]^{-1} = K(\text{NO}_3^{-}, 0.2).
\]

\( K^{-1}(\text{NO}_3^{-}, 1) f(\text{NO}_3^{-}, 1) f(\text{NO}_3^{-}, 0.2) = 1.11 \pm 1. \)

Using the values \( K_1(\text{Cl}, 1) = 10^{-0.51} \) M⁻¹ and \( K_4(\text{Cl}, 1) = 10^{-0.24} \) M⁻² for the formation of EuCl²⁺ and EuCl³⁺ for 1.0 M HCl(ClO₄) given by Choppin and Unrein 35 and \( f(\text{Cl}, 0.5) = 0.556 \) and \( f(\text{Cl}, 0.5) = 0.615 \) (cf. Kielland 36), we calculate the values of the formation constants of these species at \( I = 0.5 \) M:

\[
K_1(\text{Cl}, 0.5) = f(\text{Cl}, 0.5) f^{-1}(\text{Cl}, 1) K_1(\text{Cl}, 1) = 10^{-0.058} \text{ M}^{-1}, \text{and}
\]

\[
K_4(\text{Cl}, 0.5) = f(\text{Cl}, 0.5) f^{-4}(\text{Cl}, 1) K_4(\text{Cl}, 1) = 10^{-0.512} \text{ M}^{-1}.
\]

Using these values we calculate from Peppard's data:

\[
K(\text{corr}, 0.5) = K(\text{Cl}, 0.5)(1 + K_1(\text{Cl}, 0.5)[\text{Cl}^{-}]) + K_4(\text{Cl}, 0.5)[\text{Cl}^{-}]) = 10^{-0.168}(1 + 10^{-0.058} \times 0.5 + 10^{-0.512} \times 0.5] = 10^{-0.38}, \text{ for the extraction of Eu(III) by HDEHP into toluene as given by (8) from a medium of ionic strength } I = 0.5 \text{ M.}
\]

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 ClO₄⁻ medium (cf. Table 3) may be due to the formation of Eu(III)-perchlorate complexes. Assuming that for ClO₄⁻ < 1 M the predominant species formed is EuClO₄²⁺, the following relationship applies:

\[
f(\text{Eu}^{3+}) f^{-3}(\text{H}^{+}) K^{-1}(\text{ClO}_4^{-}, I) = K^{-1}(\text{corr}, 0) K^{*}(K^{*-1} + a_{\text{ClO}_4^{-}}) \quad (10)
\]

where \( K(\text{ClO}_4^{-}, I) \) is the experimentally found extraction constant for Eu(III) for a ClO₄⁻ medium of ionic strength \( I \), \( K(\text{corr}, 0) \) the extraction constant for infinite diluted aqueous solution, \( K^{*} = K_1(\text{ClO}_4^{-}, 0)/f(\text{Eu}^{3+}) f^{-3}(\text{EuClO}_4^{2+})(K_1(\text{ClO}_4^{-}, 0)) \) is the formation constant of EuClO₄²⁺ 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 \( Y = f(\text{Eu}^{3+}) f^{-3}(\text{H}^{+}) K^{-1}(\text{ClO}_4^{-}, I) \), and find that the points fall on a line of slope \( \text{approximately } +1 \) which agrees with (10). The constant for the formation of the EuClO₄²⁺ may be calculated from:

\[
K(\text{corr}, 0) = K(\text{ClO}_4^{-}, 1) f(\text{H}^{+}, 1) f^{-3}(\text{Eu}^{3+}, 1) \times \left(1 + K_1(\text{ClO}_4^{-}, 1) \times 1\right) = K(\text{ClO}_4^{-}, 0.1) f(\text{H}^{+}, 0.1) \times f^{-3}(\text{Eu}^{3+}, 0.1) \left(1 + K_4(\text{ClO}_4^{-}, 0.1) \times 0.1\right) \quad (11)
\]

where \( K(\text{ClO}_4^{-}, 1) = 10^{-0.38} \) and \( K(\text{ClO}_4^{-}, 0.1) = 10^{-0.033} \) are the extraction constants and \( K_4(\text{ClO}_4^{-}, 1) \), \( K_4(\text{ClO}_4^{-}, 0.1) \) the constants for the formation of EuClO₄²⁺(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 \( I = 0.1 \) to 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 ClO₄⁻ (O, Chiarizia et al.23), 0.1 M ClO₄⁻ (●, this work) and 1.0 M ClO₄⁻ medium (●, Kolarik and Pankova21) (cf. text).
are the activity factors for ClO$_4^-$ at $I = 1.0$ and 0.1 M (cf. Ref. 28). Substituting $K_1$ (ClO$_4$, 1)/$K_1$ (ClO$_4$, 0.1) = 0.763 and $f$(Eu$^{3+}$, 1) = 0.071, $f$(H$^+$, 1) = 0.745, $f$(Eu$^{3+}$, 0.1) = 0.180 and $f$(H$^+$, 0.1) = 0.827 (cf. Kielland 22) into (11) we obtain:

$$\text{Eu}^{3+} + \text{ClO}_4^- \leftrightarrow \text{EuClO}_4^{3+}; \quad K_1 = 10^{-4.4} \text{ M}^{-1} \quad (I = 1.0 \text{ M}); \quad K_1 = 10^{-4.25} \text{ M}^{-1} \quad (I = 0.1 \text{ M}).$$

From (11) we may calculate $K$ (corr, 0) = 10$^{-9.14}$ 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 ion strength $I$ can thus be expressed by:

$$K \text{(corr, I)} = f(\text{Eu}^{3+}, I)f^{-2}(\text{H}^+, I) \times 10^{q,14} \quad (12)$$

Given the activity factors for Eu$^{3+}$ and H$^+$, e.g. from Kielland’s relationship 22 and the constant $K_a = [\text{EuX}_a^{-}\text{aq}][\text{Eu}^{3+}]^{-1}[\text{X}^-]^2$ for the formation of complexes between Eu$^{3+}$ and the ionoid ligand X$^-$ (e.g. NO$_3^-$, Cl$^-$) in the aqueous phase, we may express the equilibrium constant $K(X, I)$ for the extraction of Eu(III) by HDEHP into toluene from the ion medium, e.g. (Na, H)X, with a given ion strength I and containing the EuX$_a^{-\text{aq}}$ (aq) species:

$$K(X, I) = f(\text{Eu}^{3+}, I)f^{-2}(\text{H}^+, I) \times (1 + \sum K_a [\text{X}^-]^2) \times 10^{q,14} \quad (13)$$

Using $f(\text{Eu}^{3+}, 1) = 0.071$, $f(\text{H}^+, 1) = 0.745$ and $K_1 = 10^{-4.25}$ for the formation of EuNO$_3$$^{3+}$ (cf. Ref. 22), we calculate, from (13), the equilibrium constant for the extraction of Eu(III) by HDEHP from 1.0 M (Na, H)NO$_3$ into toluene, $K(\text{NO}_3, I) = 10^{-4.47}$. This value is in fair agreement with the value $10^{-4.85}$ found experimentally by Kolarik and Pankova 21 for the same extraction system. Using $f(\text{Eu}^{3+}, 0.5) = 0.091$, $f(\text{H}^+, 0.5) = 0.766$, and $K_1 = 10^{-4.24}$ for the formation of EuCl$_3$$^{3+}$ and EuCl$_4$$^{3+}$ at 0.5 M (Na, H)Cl calculated previously, we calculate using (13) the equilibrium constant for the extraction of Eu(III) from 0.5 M Cl$^-$ medium $K(\text{Cl}^-, 0.5) = 10^{-6.09}$, in agreement with the value $10^{-6.04}$ found experimentally for the same system (cf. Peppard et al. 24 and Baes 1).

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