COMPLEX FORMATION OF LANTHANIDE(III) WITH ACETYLACETONE
STUDIED BY THE AKUFVE-LISOL TECHNIQUE

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Introduction. The formation of lanthanide(Ln(III)) complexes with the organic reagent acetylacetone (HAA) has been studied with a liquid-liquid extraction technique using trace amounts of radioactive lanthanides and the AKUFVE-LISOL technique. The extraction is poor with a maximum distribution ratio (D) between the organic and aqueous phase of 0.05(Nd) - 1.3(Lu) at 1 M HAA. The cause of this low extraction, which also holds for trivalent actinides, is surprising in comparison to how well the tetra- and hexavalent actinides are extracted, and therefore worth investigating, considering its importance in nuclear fuel reprocessing. Also a better understanding of the coordination chemistry of the lanthanides can be achieved.

Experimental equipment. The AKUFVE is a continuous solvent extraction apparatus developed a long time ago [1], while the LISOL is a recent detector-system [2], now coupled to the AKUFVE. LISOL stands for Liquid Scintillation On-Line. The new system has made it possible to investigate complexation more thoroughly and with much higher precision than before. Thus the AKUFVE-LISOL is able to measure distribution values between $10^{-5}$ and $10^{5}$, and at as high pH as 9. The principle of the technique is a continuous withdrawal of a small fraction of the streaming liquid, aqueous or organic, to which a strong acid to suppress sorption and a scintillation cocktail is added. After mixing of the liquids, they are fed to a scintillation detector arrangement.

The most prominent features of the LISOL is that when most other measuring systems fail because of problems with memory effects at high sorption levels, the LISOL can be used for measurements at very high sorption levels with no significant effect on the measured D-value. Moreover, the technique is almost independent of the radioactive decay scheme of the used nuclide. The limitation is the quenching problem, which can be severe for certain systems [3]; this can, however, be corrected for in most chemical systems.

Chemical conditions. The complex formation of acetylacetone with the lanthanides has been studied in a two-phase system with 0.1 - 4 M HAA in benzene/ 1 M Na(H)ClO$_4$ in water at pH 3-9.

The organic phase consisted of distilled HAA dissolved in washed benzene and the aqueous phase was prepared using NaClO$_4$ of analytical grade. The radioactive lanthanides were prepared by neutron activation of the pure oxides (>99.999%) and the radiochemical purity was checked by gamma spectrometry.
No radiochemical impurity could be detected. In all experiments the concentra-
tion of lanthanides was between $10^{-4}$ and $10^{-6}$ M, and the temperature was
kept at 25°C. The experiments were made in an inert nitrogen atmosphere.

For each lanthanide three different sets of experiments were done. (i) The
first set consisted of extraction with 1.0 M and 3.0 M original concentration
of HAa in the organic phase. The pH was varied between 3 and 9. Each extrac-
tion curve contained about 40 points. (ii) For better understanding of the
complexes formed in the organic phase, a second set of experiments were per-
formed, where the $[Aa^-]$ was kept constant but the HAa-concentration in the
organic phase was varied. This is easily done by on-line addition of small
amounts of $H^+$ or $OH^-$ to keep pH constant in the continuous AKUFVE system.
(iii) To account for the quenching, a third set of experiments were done
under the same conditions, but this time no radioactivity was added to the
AKUFVE. The activity was instead added to the strong acid used for the LISOL
sorption suppression, the same amount for each phase, and the ratio of measured
counts in the two phases was recorded and used for correcting the measured D-values.

At the high pH required (pH ≤ 9) for the extraction, hydrolysis and mixed
complexes can not be excluded. By using available literature data [4,5] and
the extrapolation technique described in ref. [6], the contribution of each
of these other complexes to the total complexation was estimated. It was
found that these other species could be neglected compared to the simple
LnAAg-species (y=1 to 4). In the organic phase an adduct formation of HAa to
the LnAAg-complex is indicated. Taking the above mentioned into considera-
tion, the model equation for the Ln(III)-extraction will be:

$$D = \frac{P_3\beta_3[Aa^-]^3(1+ka_1[HAa]+ka_2[HAa]^2)}{1+\beta_1[Aa^-]+\beta_2[Aa^-]^2+\beta_3[Aa^-]^3+\beta_4[Aa^-]^4}$$  (1)

where $\beta_n$ is the equilibrium constant for formation of $LnAA_n^{3-n}$ ($\beta_n=[LnAA_n^{3-n}]/$
$[Ln^{3+}][Aa^-]^n$), $P_3$ is the distribution constant for LnAAg between the organic
and the aqueous phase and $ka_n$ is the adduct formation constant for the
LnAAg(HAa)_n complex in the organic phase. Upper bars refer to the organic
phase.

At equal phase volumes, the free ligand concentration, $[Aa^-]$, is

$$[Aa^-]=\frac{Ka[HAa]_0}{[H^+]+P_{HAa}[H^+]+Ka}$$  (2)

where $P_{HAa}$=4.5 and $Ka=10^{-9.0}$ at 25°C and 1 M NaClO$_4$, and $[HAa]_0$ is the original
concentration of HAa in the organic phase.
Results and discussion. The experimental data were fitted to eqn. 1 with a least squares program (simplex method), where the weighted error square sum was minimized. From the fitting it was concluded that the first formation constant $P_1$ could not be evaluated with any high accuracy. Since our $P_1$-values agreed with those of Grenthe et al. [7], and since their technique for obtaining $P_1$ is more accurate than ours, we have used their $P_1$-values in our evaluation of the other constants. The literature value for $P_1$ adjusted to 1 M Na(H)C104 and the values of $P_2$, $P_3$, $P_4$, $P_3$ and $ka_1$ are listed in Table 1.

Table 1. Equilibrium constants of lanthanide acetylacetonates

<table>
<thead>
<tr>
<th>Atomic number</th>
<th>$P_1$</th>
<th>$P_2$</th>
<th>$P_3$</th>
<th>$P_4$</th>
<th>$P_3$</th>
<th>$ka_1$</th>
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<tbody>
<tr>
<td>$^{60}$Nd</td>
<td>5.21</td>
<td>8.87</td>
<td>11.86</td>
<td>13.57</td>
<td>-3.5</td>
<td>2.6</td>
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<tr>
<td>$^{61}$Pm</td>
<td>5.30</td>
<td>9.20</td>
<td>12.23</td>
<td>14.07</td>
<td>-2.8</td>
<td>1.9</td>
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<tr>
<td>$^{62}$Sm</td>
<td>5.50</td>
<td>9.30</td>
<td>12.59</td>
<td>14.31</td>
<td>-2.2</td>
<td>1.3</td>
</tr>
<tr>
<td>$^{63}$Eu</td>
<td>5.78</td>
<td>9.79</td>
<td>13.12</td>
<td>14.97</td>
<td>-1.7</td>
<td>0.71</td>
</tr>
<tr>
<td>$^{65}$Tb</td>
<td>5.93</td>
<td>10.00</td>
<td>13.34</td>
<td>15.26</td>
<td>-1.4</td>
<td>0.62</td>
</tr>
<tr>
<td>$^{67}$Ho</td>
<td>5.96</td>
<td>9.93</td>
<td>13.31</td>
<td>15.24</td>
<td>-1.0</td>
<td>0.54</td>
</tr>
<tr>
<td>$^{69}$Tm</td>
<td>6.00</td>
<td>10.43</td>
<td>13.82</td>
<td>15.66</td>
<td>-0.35</td>
<td>0.25</td>
</tr>
<tr>
<td>$^{71}$Lu</td>
<td>6.14</td>
<td>10.58</td>
<td>13.91</td>
<td>15.70</td>
<td>-0.05</td>
<td>0.12</td>
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Figure 1. The distribution constant $P_3$ for LnAa$_3$ and the adduct formation constant $ka_1$ for LnAa$_3$*HAA versus atomic number.
The $\beta_n$-values show an increase with increasing atomic number (Tab. 1), as expected due to the lanthanide contraction which increases the metal charge density and thus also the strength of the electrostatic bond to the acetylacetonate oxygen atoms. The fourth complex ($\text{LnAa}_4^-$), though not earlier reported except for $^{63}\text{Eu}$ [6], is clearly indicated in our investigation.

That the value $P_3$ for the distribution constant of the $\text{Ln(Aa)}_3$-complex is low is probably because the extracted species contain 2 or 3 water molecules which makes them rather hydrophilic. It can be compared with the coordinatively saturated $\text{PuAa}_4^-$, which has a $P_4$ of about 400 [8]. This supports that an adduct complex can be formed in the organic phase, one HAA replacing two $\text{H}_2\text{O}$.

From the distribution of the uncharged complex ($P_3$) in Fig. 1, it can be seen that there is a break around atomic number 63 (europium). This is also shown in the adduct formation constant $k_{a1}$. It may be explained by the fact that the coordination number of 8 is reached around atomic number 63, and from then on the organic phase equilibrium is dominated by the reaction

$$\text{LnAa}_3(\text{H}_2\text{O})_2^+\text{HAA} \rightleftharpoons \text{LnAa}_3\text{HAA}+2\text{H}_2\text{O}.$$ 

Acknowledgement. This work has been supported by grants from the Swedish Natural Science Research Council. The experimental assistance by Asa Lindh and Arshad Mahmood is gratefully acknowledged.

References