Solvent Extraction Study of Trivalent Actinide and Lanthanide Complexes in Aqueous Solutions

III. Oxalate Complexes of La(III), Eu(III), Lu(III), and Am(III) in 1 M Na(ClO$_4$)

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The complex formation of La(III), Eu(III), Lu(III) and Am(III) with oxalate ion in 1 M Na(ClO$_4$) at 25°C has been studied by a distribution method.

The metal distribution between an organic phase containing 2-thenoyltrifluoroacetone (TTA) and tributylphosphate (TBP) or methylisobutylketone (hexone), and aqueous phases of various oxalate concentrations was measured, and the stability constants were calculated from the decrease of the distribution ratio caused by the formation of oxalate complexes after making a correction for the formation of HC$_2$O$_4^-$ (the dissociation of acid oxalate was determined as pK_{a_2} = 3.54 ± 0.01 in 1 M Na(ClO$_4$) at 25°C by separate experiments). The constants were finally refined by a generalized least squares method using the LETAGROP VRID computer program.

The best-fit stability constants thus obtained are

$$\beta_n = [M(C_2O_4)_n^{3-2n}] / [M^{3+}] [C_2O_4^{2-}]^n:$$

	log β_1	log β_2	log β_3
La(III)	4.26 ± 0.11	7.85 ± 0.12	10.27 ± 0.21
Eu(III)	4.77 ± 0.10	8.72 ± 0.09	11.39 ± 0.12
Lu(III)	5.11 ± 0.08	9.18 ± 0.12	12.79 ± 0.08
Am(III)	4.63 ± 0.08	8.35 ± 0.09	11.15 ± 0.07

(The range of error gives three times the standard deviation, 3σ).

A s it is well known, lanthanide elements, yttrium and thorium can be separated quantitatively from most other ions as oxalate precipitates by the addition of excess oxalic acid to a weakly acidic aqueous solution.

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These oxalate precipitates are very insoluble but only when the solution is acidic. If the hydrogen ion concentration is lowered, they dissolve to some extent; thorium oxalate is more soluble than trivalent lanthanide oxalates, and the heavier lanthanide oxalates are more soluble than the lighter ones.

The anion exchange adsorption of trivalent lanthanides and thorium from oxalate solution also indicates formation of oxalate complexes.[3] A summary on the chemistry of oxalate complexes has been published by Krishnamurty and Harris.[4]

In the present study, the author has studied the formation of oxalate complexes of La(III), Eu(III), Lu(III), and Am(III) by a distribution method, using radioactive tracers. This technique is very suitable since the solubility of the metal oxalates is low and one must work at low metal concentration.

2-Thenoyltrifluoroacetone (TTA) in chloroform containing tributylphosphate (TBP) or in carbon tetrachloride containing methylisobutylketone (hexone) was used as the metal extracting chelating acid. TBP or hexone was added as adduct-forming ligand which increases the metal extraction at a given TTA concentration, and may decrease the amount of TTA complex formation in the aqueous phase.

As the experiments were carried out at $-\log [H^+] \approx 3$ to 4, it was necessary to correct for the formation of $HC_2O_4^-$. Determination of the dissociation of oxalic acid was made in separate experiments and the correction was made using the values, $pK_{a1} \approx 1.0$ $pK_{a2} = 3.54 \pm 0.01$.

The stability constants were finally refined by a generalized least squares method using LETAGROP VRID which is an improved version of the LETA-GROP computer program.[5]

APPLICATION OF THE LAW OF MASS ACTION

The equations used for the calculation of the stability constants were as follows (for details see Paper I [1]).

Notations

M^{3+}: trivalent metal ion
L^- : complex-forming ligand with negative charge l^-.
β_n : overall stability constant of the nth complex
D : net distribution ratio of metal
HA : organophilic chelating acid
N : organophilic adduct forming ligand
K_{ex} : extraction constant
β_{An} : overall formation constant for the nth adduct MA_3N_n
K_{ex}': extraction constant when adduct chelates are formed in the organic phase
D_0D^{-1}: the ratio of distribution ratios in two systems where $[H^+]$ and $[HA]_{org}$ are the same. D_0 denotes the distribution ratio when L^- is absent and D denotes that when the concentration of L^- is $[L^-]$.

Table 1. Metal distribution between the organic phase and 1 M NaClO$_4$ at 25°C.

The organic phase was for La(III): 0.2 M TTA in CHCl$_3$ containing 0.1 M TBP, for Eu(III), Lu(III), and Am(III): 0.1 M TTA in CCl$_4$ containing 10 % hexone (by volume). The data are given as $-\log[\text{H}^+]$, $\log D$, $(-\log D\ [\text{H}^+]^3\ [\text{HA}]_{\text{org}}^{-3})$; (*cf.* the extraction constant in eqn. (4). Here $[\text{HA}]_{\text{org}}$ or $[\text{N}]_{\text{org}}$ is constant.)

(a) La(III): 3.068, -0.173 (7.28); 3.263, 0.401 (7.29); 3.395, 0.834 (7.25); 3.410, 0.831 (7.30).

(b) Eu(III): 2.693, -1.220 (6.30); 2.715, -1.200 (6.35); 2.845, -0.779 (6.31); 3.155, 0.188 (6.28); 3.312, 0.625 (6.31); 3.447, 1.025 (6.32); 3.471, 1.149 (6.26); 3.496, 1.190 (6.30); 3.893, 2.324 (6.36).

(c) Lu(III): 2.887, -0.918 (6.58); 3.143, -0.173 (6.43); 3.403, 0.589 (6.62); 3.581, 1.127 (6.62); 3.655, 1.267 (6.70).

(d) Am(III): 2.742, -1.475 (6.70); 2.849, -1.149 (6.70); 2.984, -0.762 (6.71); 3.217, -0.081 (6.73); 3.358, 0.312 (6.76); 3.501, 0.773 (6.73); 3.658, 1.196 (6.78).
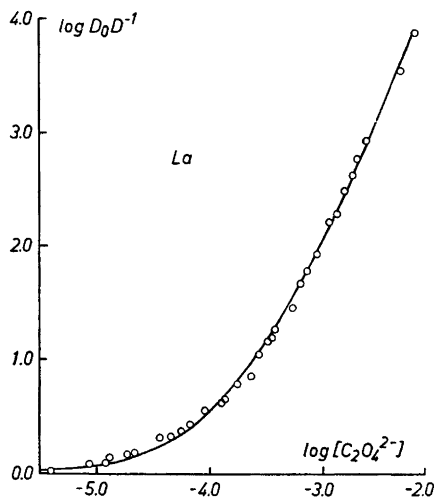

Fig. 1. The variation of the distribution ratio of lanthanum(III) as a function of the concentration of oxalate ion. D_0D^{-1} gives $1 + \beta_1[\text{C}_2\text{O}_4^{2-}] + \beta_2[\text{C}_2\text{O}_4^{2-}]^2 + \beta_3[\text{C}_2\text{O}_4^{2-}]^3$ (*cf.* eqn. (5)). The curve gives the calculated curve from the constants in Table 3. Aqueous phase: 1 M Na(ClO$_4$). Organic phase 0.2 M TTA in CHCl$_3$ containing 0.1 M TBP.
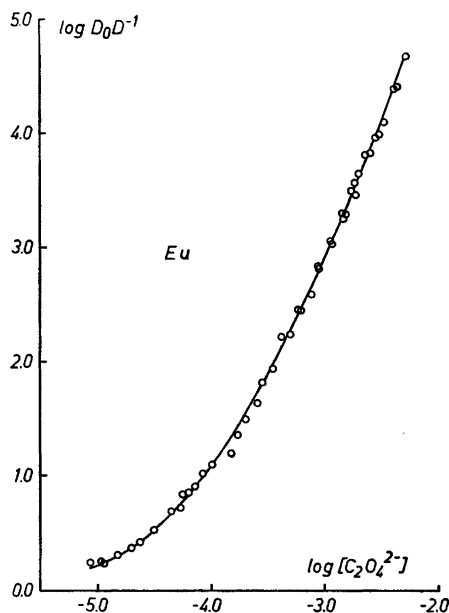
Fig. 2. The variation of the distribution ratio of europium(III) as a function of the concentration of oxalate ion. D_0D^{-1} gives $1 + \beta_1[\text{C}_2\text{O}_4^{2-}] + \beta_2[\text{C}_2\text{O}_4^{2-}]^2 + \beta_3[\text{C}_2\text{O}_4^{2-}]^3$ (*cf.* eqn. (5)). The curve gives the calculated curve from the constants in Table 3. Aqueous phase: 0.1 M TTA in CCl$_4$ containing 10 % (by volume) hexone.
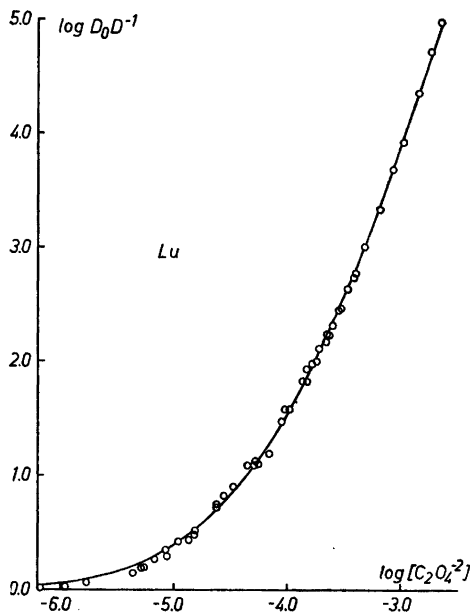
Fig. 3. The variation of the distribution ratio of lutetium(III) as a function of the concentration of oxalate ion. $D_0 D^{-1}$ gives $1 + \beta_1[C_2O_4^{2-}] + \beta_2[C_2O_4^{2-}]^2 + \beta_3[C_2O_4^{2-}]^3$ (*cf.* eqn. (5)). The curve gives the calculated curve from the constants in Table 3. Aqueous phase: 1 M Na(ClO$_4$). Organic phase: 0.1 M TTA in CCl$_4$ containing 10 % (by volume) hexone.
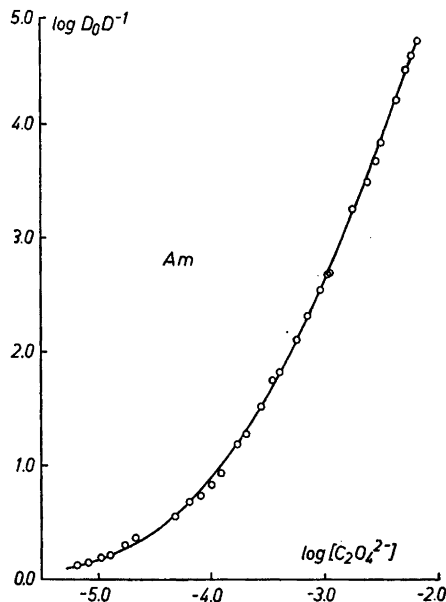
Fig. 4. The variation of the distribution ratio of americium(III) as a function of the concentration of oxalate ion. $D_0 D^{-1}$ gives $1 + \beta_1[C_2O_4^{2-}] + \beta_2[C_2O_4^{2-}]^2 + \beta_3[C_2O_4^{2-}]^3$ (*cf.* eqn. (5)). The curve gives the calculated curve from the constants in Table 3. Aqueous phase: 1 M Na(ClO$_4$). Organic phase: 0.1 M TTA in CCl$_4$ containing 10 % (by volume) hexone.

The assumptions made are:

(a) No complexes with the chelating acid, MA_n^{3-n}, and no hydrolyzed species are formed in the aqueous phase. (b) MA_3 and its adducts, MA_3N_n, are complexes of M^{3+} present in the organic phase.

$$\beta_n = [ML_n^{3-nl}]/[M^{3+}][L^{l-}]^n \tag{1}$$

$$D = [M(III)]_{\text{org, total}} / [M(III)]_{\text{aq, total}} \tag{2}$$

$$K_{\text{ex}} = [MA_3]_{\text{org}}[H^+]^3[HA]_{\text{org}}^{-3} [M^{3+}]^{-1} \tag{3}$$

$$K_{\text{ex}}' = [MA_3]_{\text{org}}[H^+]^3[HA]_{\text{org}}^{-3}[M^{3+}]^{-1}(1 + \sum_1^n \beta_{An}[N]_{\text{org}}^n)^{-1} \tag{4}$$

$$D_0 D^{-1} = 1 + \sum_1^n \beta_n[L^{l-}]^n \tag{5}$$

EXPERIMENTAL

Reagents. Analytical grade sodium oxalate was dried in an air-bath at 120°C. 0.0100 M Na$_2$C$_2$O$_4$ + 0.98 M NaClO$_4$ solution was made by dissolving 1.340 g of sodium oxalate in 1 l 0.98 M NaClO$_4$. Solutions of various oxalate concentration were made by dilution with 1 M NaClO$_4$. Other reagents were the same as in Paper II.[2]

Table 2. Metal distribution between the organic phase and 1 M $Na(ClO_4)$, at 25°C.

The composition of the organic phases are given in Table 1. The data are given as $-\log$ $[H^+]$, $-\log [C_2O_4^{2-}]$, $(\log D_0 D^{-1})$; where $\log D_0 D^{-1} = 1 + \sum_1^n \beta_n [C_2O_4^{2-}]^n$ (*cf.* eqn. (5)).

(a) La(III): 3.883, 2.191 (3.85); 3.826, 2.317 (3.52); 3.765, 2.416 (3.24); 3.711, 2.620 (2.91); 3.674, 2.697 (2.75); 3.647, 2.742 (2.61); 3.625, 2.815 (2.47); 3.587, 2.883 (2.27); 3.584, 2.947 (2.20); 3.532, 3.054 (1.92); 3.513, 3.143 (1.77); 3.522, 3.200 (1.66); 3.518, 3.272 (1.45); 3.476, 3.429 (1.26); 3.478, 3.457 (1.19); 3.466, 3.492 (1.16); 3.456, 3.569 (1.04); 3.474, 3.642 (0.85); 3.427, 3.759 (0.78); 3.435, 3.870 (0.65); 3.407, 3.900 (0.62); 3.434, 4.046 (0.55); 3.439, 4.126 (0.60); 3.395, 4.178 (0.43); 3.391, 4.256 (0.37); 3.445, 4.347 (0.32); 3.434, 4.458 (0.31); 3.427, 4.668 (0.18); 3.378, 4.733 (0.17); 3.430, 4.889 (0.14); 3.369, 4.921 (0.08); 3.418, 5.065 (0.08); 3.361, 5.403 (0.02).

(b) Eu(III): 3.743, 2.286 (4.67); 3.746, 2.365 (4.41); 3.623, 2.394 (4.39); 3.528, 2.487 (4.10): 3.518, 2.523 (3.99); 3.533, 2.559 (3.96); 3.538, 2.604 (3.83); 4.029, 2.648 (3.81); 3.976, 2.705 (3.65); 4.017, 2.726 (3.66); 3.562, 2.740 (3.57); 3.959, 2.775 (3.50); 3.953, 2.821 (3.29); 3.953, 2.842 (3.25); 3.495, 2.848 (3.30); 3.474, 2.939 (3.03); 3.964, 2.959 (3.07); 3.948, 3.063 (2.82); 3.425, 3.063 (2.84); 3.895, 3.126 (2.59); 3.919, 3.219 (2.45); 3.944, 3.240 (2.46); 3.229, 3.316 (2.24); 3.246, 3.384 (2.20); 3.855, 3.468 (1.94); 3.868, 3.559 (1.82); 3.214, 3.600 (1.64); 3.821, 3.697 (1.50); 3.836, 3.770 (1.36); 3.846, 3.833 (1.20); 2.886, 4.002 (1.10); 3.145, 4.080 (1.02); 3.163, 4.147 (0.91); 2.756, 4.204 (0.86); 3.187, 4.260 (0.84); 2.784, 4.274 (0.72); 2.822, 4.361 (0.69); 3.342, 4.511 (0.53); 3.342, 4.636 (0.42); 3.361, 4.708 (0.37); 3.327, 4.824 (0.31); 3.336, 4.943 (0.23); 2.784, 4.975 (0.25); 2.817, 5.066 (0.24).

(c) Lu(III): 4.024, 2.643 (4.97); 3.976, 2.737 (4.71); 3.932, 2.846 (4.35); 3.892, 2.981 (3.92); 3.850, 3.076 (3.68); 3.784, 3.194 (3.33); 3.763, 3.329 (3.00); 3.643, 3.407 (2.77); 3.730, 3.421 (2.73); 3.635, 3.474 (2.63); 3.697, 3.532 (2.46); 3.630, (3.553 (2.45); 3.626, 3.605 (2.31); 3.680, 3.636 (2.23); 3.303, 3.660 (2.24); 3.621, 3.665 (2.17); 3.615, 3.723 (2.11); 3.295, 3.745 (1.99); 3.609, 3.790 (1.97); 3.305, 3.830 (1.82); 3.303, 3.836 (1.93); 3.610, 3.870 (1.82); 3.283, 3.979 (1.58); 3.549, 4.000 (1.57); 3.033, 4.036 (1.58); 3.290, 4.051 (1.47); 3.261, 4.167 (1.19); 3.014, 4.260 (1.10); 3.591, 4.284 (1.13); 3.261, 4.292 (1.09); 3.535; 4.301 (1.09); 3.014, 4.356 (1.09); 3.006, 4.481 (0.90); 3.006, 4.561 (0.82); 3.501, 4.620 (0.72), 3.256, 4.623 (0.76); 3.006, 4.812 (0.52); 3.559, 4.818 (0.48); 3.256, 4.866 (0.43); 3.006, 4.959 (0.42); 3.006, 5.055 (0.29); 3.256, 5.071 (0.35); 3.256, 5.167 (0.26); 3.006, 5.260 (0.19); 3.559, 5.292 (0.19); 3.006, 5.356 (0.14); 3.256, 5.770 (0.06); 3.006, 5.959 (0.02); 3.256, 6.167 (0.01).

(d) Am(III): 4.254, 2.173 (4.71); 4.243, 2.233 (4.58); 4.419, 2.280 (4.46); 4.347, 2.367 (4.19); 4.103, 2.503 (3.82); 4.130, 2.547 (3.66); 4.145, 2.623 (3.48); 4.085, 2.745 (3.24); 3.986, 2.960 (2.68); 3.594, 2.975 (2.67); 3.975, 3.041 (2.53); 3.915, 3.156 (2.30); 3.904, 3.256 (2.09); 3.851, 3.398 (1.81); 3.875, 3.465 (1.74); 3.872, 3.565 (1.50); 3.858, 3.692 (1.27); 3.850, 3.775 (1.18); 4.156, 3.917 (0.93); 4.149, 4.000 (0.83); 4.149, 4.095 (0.732); 4.135, 4.195 (0.68); 4.135, 4.321 (0.55); 3.427, 4.670 (0.36); 3.422, 4.764 (0.30); 3.418; 4.893 (0.21); 3.413, 4.975 (0.19); 3.395, 5.089 (0.14); 3.429, 5.185 (0.12).

Table 3. Stability constants of oxalate complexes.

	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$
La^{3+}	4.26 ± 0.11	7.85 ± 0.12	10.27 ± 0.21
Eu^{3+}	4.77 ± 0.10	8.72 ± 0.09	11.39 ± 0.12
Lu^{3+}	5.11 ± 0.08	9.18 ± 0.12	12.79 ± 0.08
Am^{3+}	4.63 ± 0.08	8.35 ± 0.09	11.15 ± 0.07

The range of error gives three times the standard deviation, 3σ.

Table 4. Stability constants and solubility constants of oxalate complexes of trivalent lanthanide ions from other studies.

(a) Stability constants at $I = 0$, 25°C (Ref. 6)

	$\log K_1$	$\log K_2$	$\log \beta_2$	$\log K_3$	$\log \beta_3$
Ce(III)	6.52	3.96	10.48	0.82	11.30
Nd(III)	7.21	4.30	11.51	>1.96	—
Yb(III)	7.30	4.59	11.89	>1.96	—

(b) Solubility constants in 0.1 M $KClO_4$ + $K_2C_2O_4$ (Ref. 7)

	"$\log K_1$"	"$\log K_2$"	"$\log K_3$"
Er(III)	−4.82	−8.21	−10.03

Tracers. [140]La, [152+154]Eu, ^{177}Lu, and [241]Am were used as radioactive tracers. The tracers were prepared as in Paper I. The initial concentration of the metal ions in the aqueous phase was at most 5×10^{-7} M, so that complex formation would practically not change the concentration of the free oxalate ion.

Procedures. Sulfanilic acid was used as buffering reagent. The experimental procedure was the same as in Paper II. The recovery of the tracer from both phases was always checked, and no third phase was observed in the system.
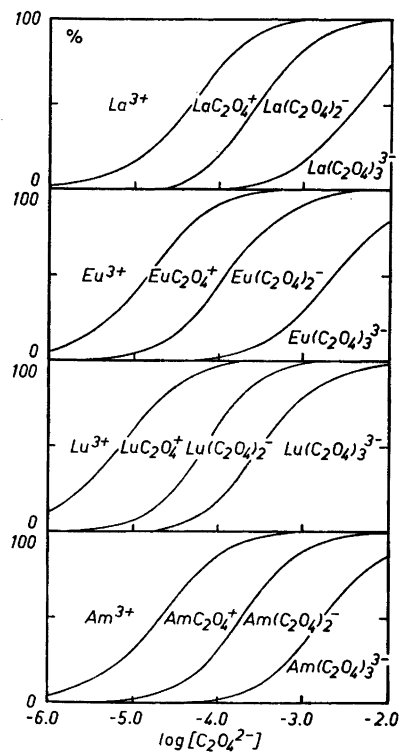

Fig. 5. The distribution of oxalate complexes as a function of log $[C_2O_4^{2-}]$.

RESULTS AND DISCUSSION

Tables 1 and 2 give the distribution data of La(III), Eu(III), Lu(III), and Am(III). Figs. 1 to 4 give the plot log $D_0 D^{-1}$ *versus* log $[C_2O_4{}^{2-}]$. The curves given in the figures are calculated values of log $D_0 D^{-1}$ *versus* log $[C_2O_4{}^{2-}]$ using the stability constants calculated below. As is seen in the figures, the limiting slope of the plot in the higher oxalate concentration region is three. This indicates that the highest complex is $M(C_2O_4)_3{}^{3-}$. No acid complex was indicated in this $-$log $[H^+]$ region.

The stability constants were first obtained by a graphical method and then they were refined by a generalized least squares method using the LETA-GROP VRID computer program. The final results are given in Table 3. The distribution of the oxalate complexes as a function of log $[C_2O_4{}^{2-}]$ is given in Fig. 5.

Table 4 gives results from earlier studies on the stability constants and the solubility constants of the oxalate complexes of trivalent lanthanide ions.[8]

From the results of present work, we may conclude that (1) all three stability constants, β_1, β_2, and β_3, show an order $La^{3+} < Eu^{3+} < Lu^{3+}$ which is parallel to the atomic number or inverse to the ionic size. (2) The stepwise stability constants show a regular order $K_1 > K_2 > K_3$. 3) The stability constants are a little larger for Eu^{3+} than Am^{3+} but the differences are not very large.

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