

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

II. Sulfate Complexes of La(III), Eu(III), Lu(III), and Am(III) in 1 M Na(ClO₄)

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The complex formation of La(III), Eu(III), Lu(III), and Am(III) with sulfate ion has been studied in 1 M Na(ClO₄) at 25°C by a distribution method.

The metal ions in aqueous solution were equilibrated with 2-thenoyltrifluoroacetone in chloroform, in chloroform containing tributylphosphate, or in carbon tetrachloride containing methylbutylketone, and the complex formation was determined from the decrease of the distribution ratio when various amounts of sulfate ion were introduced in the solution.

The stability constants of the sulfate complexes were calculated by a generalized least squares method, using the LETAGROP VRID computer program. The results are as follows:

$$\beta_n = [M(SO_4)_n^{3-2n}] / [M^{3+}] [SO_4^{2-}]^n$$

	log β_1	log β_2	log β_3
La(III)	1.45 ± 0.07	2.46 ± 0.08	—
Eu(III)	1.54 ± 0.06	2.69 ± 0.05	—
Lu(III)	1.29 ± 0.23	≈ 1.9 (< 2.5)	3.36 ± 0.18
Am(III)	1.57 ± 0.09	2.66 ± 0.08	—

Limits given are 3 σ , the value in the parentheses is log ($\beta_2 + 3\sigma$)

The chemical behavior of the rare earth elements in sulfate solution has been studied by many workers.² Since sulfuric acid is commonly used to attack rare earth minerals, the separation of rare earth elements often starts with a sulfate solution. The solubility of sulfates and the formation of rare earth double sulfates with alkali metals have been very extensively studied, mainly from the point of view of a separation process.

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Recent studies by many techniques have given indications of the complex formation of the trivalent lanthanides and the actinides in sulfate solutions. For example, it has been reported that these metal ions are adsorbed from sulfate solutions by an anion exchange resin. This may indicate the existence of anionic sulfate complexes.³⁻⁶

The first edition of "Stability Constants"⁷ lists several studies of sulfate complexes of La(III) and Ce(III) and some for Pr(III), Nd(III), Sm(III), Gd(III), Ho(III), Er(III), and Yb(III). Recently, stability constants of sulfate complexes have been determined for Ce(III),⁸ Eu(III),^{9,10} Am(III), and Cm(III).¹¹

The present author has studied the sulfate complex formation of La(III), Eu(III), Lu(III), and Am(III) in 1 M Na(ClO₄) at 25°C by a distribution method. The metal ions in the aqueous phase were equilibrated with 2-thenoyl-trifluoroacetone (TTA) in CHCl₃ or in CCl₄. In some cases, tributylphosphate (TBP) or methylisobutylketone (hexone) was added to the organic phase since these compounds may form adducts with the TTA chelates. The stability constants of the sulfate complexes were determined from the decrease of the distribution ratio when various amounts of sulfate ion were added.

APPLICATION OF THE LAW OF MASS ACTION

The equations used for the calculation of the stability constants were as follows. (For more 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 n th 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 n th 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 $[L^-]$.

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 the only complexes of M^{3+} present in the organic phase.

$$\beta_n = \frac{[ML_n^{3-n}]}{[M^{3+}][L^-]^n} \quad (1)$$

$$D = \frac{[M(III)]_{org, total}}{[M(III)]_{aq, total}} \quad (2)$$

$$K_{ex} = \frac{[MA_3]_{org}[H^+]^3[HA]_{org}^{-3}[M^{3+}]^{-1}}{[M^{3+}]} \quad (3)$$

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

$$D_0D^{-1} = 1 + \sum_1^n \beta_n [L^-]^n \quad (5)$$

EXPERIMENTAL

Radioactive tracers. The radioactive tracers used in this study were ^{140}La , $^{152+154}\text{Eu}$, ^{177}Lu , and ^{241}Am . The tracers were prepared in the same way as described in Paper I.¹ The tracer solutions were finally made to contain 0.9 M NaClO_4 + 0.1 M HClO_4 .

Reagents. All reagents used in this study were of analytical grade. Sodium sulfate recrystallized from water, and 0.5 M Na_2SO_4 stock solution was made by dissolving Na_2SO_4 which had been dried in an air bath at 120°C. The content of SO_4^{2-} in this solution was determined by weighing BaSO_4 precipitated from the solution. Methylisobutylketone was washed first with dilute perchloric acid, then with sodium hydroxide solution and finally repeatedly with water. The purifications of tributylphosphate, chloroform and sodium perchlorate were made in the same way as described in Paper I. Other reagents were used without further purification.

Procedures. All procedures were carried out in a thermostated room at 25°C. The phases were equilibrated in 50 ml stoppered glass tubes. A 0.1 ml portion of the tracer solution, and various amounts of 0.5 M Na_2SO_4 or 0.05 M Na_2SO_4 + 0.9 M NaClO_4 , were added to the tubes. The solution was buffered at $-\log [\text{H}^+] 3$ to 4 by sulfanilic acid-sulfanilate buffer at 0.01 M. By separate experiments, changing the concentration from 0.005 M to 0.02 M, it was proved that this amount of sulfanilate did not change the distribution ratio of the metal. The metal ion was always added to the aqueous phase as a radioactive tracer. The organic solutions were left standing overnight before the use, and added to the tubes. The initial volume of each phase was always 10.0 ml.

The tubes with the two phases were placed in a mechanical rotating framework and the phases were agitated for one hour, which according to our experience is sufficient for the distribution equilibrium to be reached. By centrifugation, two phases were separated completely. A 2 ml portion of each phase was transferred into small polyethylene tubes to measure the activity of the solutions. These procedures were carried out carefully to avoid any contamination from the other phase. A portion of the aqueous phase was transferred into a small plastic vessel with a glass cover to measure the hydrogen ion concentration. The radioactivity in the polyethylene tubes was measured with a well-type scintillation counter. The recovery of metal ions from both phases was always practically quantitative, and it was concluded that the sorption loss of the ions was negligible. The hydrogen ion concentration was measured potentiometrically with a glass electrode, using 0.01 M HClO_4 + 0.99 M NaClO_4 solution as the standard, with $\log [\text{H}^+] = -2.00$ and $I = 1.0$.

Table 1. Metal distribution between the organic phase and 1 M NaClO_4 at 25°C.

The organic phase

La(III): 0.2 M TTA in CHCl_3 containing 0.1 M TBP.

Eu(III): 0.1 M TTA in CCl_4 containing 10 % (by volume) hexone.

Lu(III): 0.2 M TTA in CHCl_3 .

Am(III): 0.1 M TTA in CCl_4 containing 10 % (by volume) hexone.

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 the $[\text{HA}]_{\text{org}}$ 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): 2.948, -1.078 (7.83); 3.173, -0.476 (7.90); 3.334, 0.083 (7.82); 3.559, 0.618 (7.96); 3.559, 0.643 (7.94); 3.895, 1.639 (7.95);

(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);

Table 2. Metal distribution between the organic phase and 1 M Na(ClO₄) at 25°C.

The composition of the organic phases are given in Table 1. The data are given as $-\log [\text{SO}_4^{2-}] (\log D_0 D^{-1})$; where $D_0 D^{-1} = 1 + \sum_1^n \beta_n [\text{SO}_4^{2-}]^n$ (cf. eqn. (5)).

(a) La(III): 0.745(1.17); 0.796(1.09); 0.854(1.00); 0.886(1.01); 0.921(0.93); 0.959(0.88); 1.000(0.83); 1.022(0.83); 1.031(0.81); 1.046(0.77); 1.071(0.75); 1.071(0.77); 1.097(0.71); 1.125(0.69); 1.155(0.62); 1.187(0.60); 1.222(0.53); 1.260(0.54); 1.301(0.53); 1.374(0.44); 1.374(0.45); 1.398(0.39); 1.398(0.37); 1.456(0.36); 1.523(0.35); 1.609(0.26); 1.824(0.16); 2.000(0.13); 2.155(0.10); 2.301(0.04).

(b) Eu(III): 0.699(1.46); 0.721(1.43); 0.745(1.37); 0.770(1.38); 0.796(1.29); 0.824(1.24); 0.854(1.17); 0.886(1.16); 0.921(1.08); 0.959(1.02); 1.000(0.95); 1.022(0.94); 1.046(0.92); 1.071(0.87); 1.155(0.73); 1.187(0.71); 1.222(0.65); 1.222(0.65); 1.260(0.63); 1.301(0.59); 1.301(0.59); 1.398(0.50); 1.398(0.51); 1.456(0.45); 1.523(0.41); 1.602(0.36); 1.699(0.32); 1.745(0.26); 1.790(0.22); 1.824(0.21); 1.854(0.21); 1.921(0.19); 2.046(0.15); 2.097(0.11); 2.555(0.11).

(c) Lu(III): 0.523(1.92); 0.523(1.90); 0.602(1.66); 0.699(1.30); 0.796(1.21); 0.824(1.15); 0.921(0.95); 1.000(0.84); 1.155(0.53); 1.155(0.52); 1.301(0.37); 1.301(0.38); 1.398(0.32); 1.398(0.30); 1.523(0.26); 1.523(0.22); 1.699(0.19); 1.824(0.10); 1.824(0.12); 2.000(0.10); 2.301(0.04).

(d) Am(III): 0.699(1.42); 0.745(1.36); 0.796(1.25); 0.824(1.29); 0.854(1.20); 0.886(1.21); 0.903(1.05); 0.921(1.09); 0.939(1.01); 0.959(1.06); 1.000(0.92); 1.022(0.94); 1.046(0.87); 1.046(0.93); 1.071(0.88); 1.097(0.80); 1.097(0.87); 1.125(0.81); 1.155(0.74); 1.155(0.77); 1.222(0.72); 1.222(0.66); 1.301(0.59); 1.398(0.52); 1.523(0.40); 1.602(0.34); 1.699(0.31); 1.824(0.21); 2.000(0.20); 2.155(0.10); 2.301(0.07); 2.523(0.05).

RESULTS

The net distribution ratio of the metal ions was calculated as $D = (\gamma \text{ activity in 2 ml org. phase}) / (\gamma \text{ activity in 2 ml aq. phase})$.

Tables 1 and 2 give the measured metal distribution ratios D . Figs. 1 to 4 give the plots $\log D_0 D^{-1}$ versus $\log [\text{SO}_4^{2-}]$.

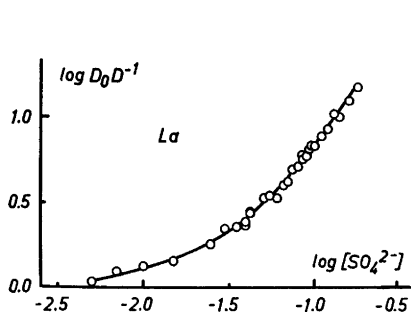


Fig. 1. Distribution ratio of lanthanum(III) as a function of the concentration of sulfate ion. $D_0 D^{-1}$ gives $1 + \beta_1 [\text{SO}_4^{2-}] + \beta_2 [\text{SO}_4^{2-}]^2$ (cf. eqn. (5)).

The curve gives the calculated curve from the constants in Table 3. Aqueous phase: 1 M Na(ClO₄). Organic phase: 0.2 M TTA in CHCl₃ containing 0.1 M TBP.

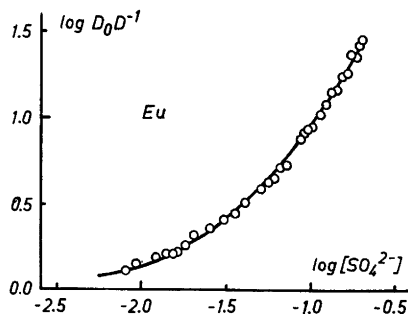


Fig. 2. The variation of the distribution ratio of europium(III) as a function of the concentration of sulfate ion. $D_0 D^{-1}$ gives $1 + \beta_1 [\text{SO}_4^{2-}] + \beta_2 [\text{SO}_4^{2-}]^2$ (cf. eqn. (5)). The curve gives the calculated curve from the constants in Table 3. Aqueous phase: 1 M Na(ClO₄). Organic phase: 0.1 M TTA in CCl₄ containing 10% (by volume) hexane.

Table 3. Stability constants of sulfate complexes of La(III), Eu(III), Lu(III), and Am(III) in 1 M Na(ClO₄) at 25°C.

$$\beta_n = [M(\text{SO}_4)_n^{3-2n}] / [M^{3+}] [\text{SO}_4^{2-}]^n$$

	log β_1	log β_2	log β_3
La ³⁺	1.45 ± 0.07	2.46 ± 0.08	—
Eu ³⁺	1.54 ± 0.06	2.69 ± 0.05	—
Lu ³⁺	1.29 ± 0.23	≈ 1.9 (<2.5) *	3.36 ± 0.18
Am ³⁺	1.57 ± 0.09	2.66 ± 0.08	—

(The limits of error give 3σ)

* β_2 for Lu(SO₄)₂⁻ was given as 77 ± 235 by the LETAGROP VRID calculation.

From these data, the stability constants were first estimated graphically and finally refined by a generalized least squares method using LETAGROP VRID which is an improved version of the LETAGROP computer program.¹⁴

The final stability constants are given in Table 3. The curves given in Figs. 1 to 4 are the calculated curves, log D_0D^{-1} versus log [SO₄²⁻], using these stability constants.

DISCUSSION

We can see from Table 1 that $-\log D [\text{H}^+]^3 [\text{HA}]_{\text{org}}^{-3}$ is practically constant when [HA]_{org} is constant. From this, we may conclude that chelate

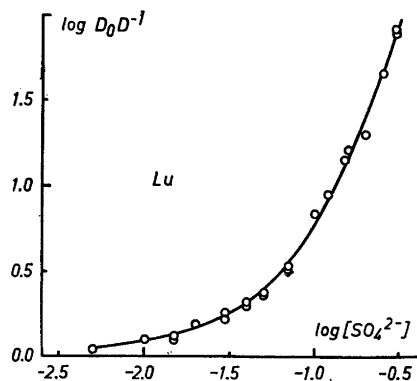


Fig. 3. The variation of the distribution ratio of lutetium(III) as a function of the concentration of sulfate ion. D_0D^{-1} gives $1 + \beta_1[\text{SO}_4^{2-}] + \beta_2[\text{SO}_4^{2-}]^2 + \beta_3[\text{SO}_4^{2-}]^3$ (cf. eqn. (5)). The curve gives the calculated curve from the constants in Table 3. Aqueous phase: 1 M Na(ClO₄). Organic phase: 0.2 M TTA in CHCl₃.

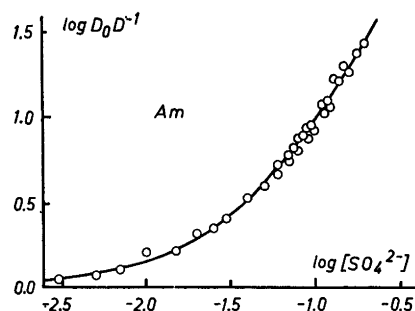


Fig. 4. The variation of the distribution ratio of americium(III) as a function of the concentration of sulfate ion. D_0D^{-1} gives $1 + \beta_1[\text{SO}_4^{2-}] + \beta_2[\text{SO}_4^{2-}]^2$ (cf. eqn. (5)). The curve gives the calculated curve from the constants in Table 3. Aqueous phase: 1 M Na(ClO₄). Organic phase: 0.1 M TTA in CCl₄ containing 10% (by volume) hexone.

Table 4. Stability constants of sulfate complexes of some trivalent lanthanide and actinide ions from other studies.

Metal ion	Medium	Temperature	$\log \beta_1$	$\log \beta_2$	Reference
La ³⁺	1 M (NaClO ₄)	25°	1.40		16
Ce ³⁺	0.5 M (NaClO ₄)	25°	1.78		17
	0.5 M (NaClO ₄)		1.75	2.90	8
	1 M (NaClO ₄)	25°	1.25		18
	1 M Na(ClO ₄)	20°	1.63	2.34	15
				($\log K_3 = 0.74$)	
Pu ³⁺	2 M (NaClO ₄)	25°	(1.0)	($\log K_2 = 0.62$)	19
Am ³⁺	1 M (NH ₄ Cl, ClO ₄)	20–25°	1.76	2.11	11
	0.75 M (NH ₄ Cl, ClO ₄)	20–25°	1.78		11
Cm ³⁺	0.75 M (NH ₄ Cl, CClO ₄)	20–25°	1.75	1.93	11

complexes in the aqueous phase or the extraction of any mixed chelate complex are negligible under these experimental conditions.

We may conclude from Table 3 that sulfate complexes of Lu(III) are different from those of other three ions. The β_2 for Lu(SO₄)₂⁻ is smaller than the β_2 for the other M(SO₄)₂⁻ complexes and the error σ given by the calculation is too large to establish this species definitely. On the other hand, the existence of Lu(SO₄)₃⁻³ which has not been found in other cases seems to be confirmed. We can see this also in Fig. 3 from the fact that the limiting slope of the plot is more than two.

Table 4 gives some results of other work. The β_1 for LaSO₄⁺ in 1 M NaClO₄ by Mattern¹⁶ and for AmSO₄⁺ by Lebedev *et al.*¹¹ agree with the results of the present work but the β_2 given by the latter is smaller than the present results.

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