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

I. Chloride Complexes of La(III), Eu(III), Lu(III), and Am(III) in 4 M Na(ClO$_4$)

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The complex formation of La(III), Eu(III), Lu(III) and Am(III) with chloride ions has been studied in 4 M Na(ClO$_4$) at 25°C by a distribution method.

The metal distribution ratio D between an organic phase containing a chelating acid and aqueous phases of various chloride concentrations was measured and the stability constants were calculated from the decrease of the distribution ratio caused by the formation of chloride complexes. The constants were finally refined by a generalized least squares method using the LETAGROP VRID computer program. The stability constants thus obtained are as follows:

$$\beta_1 = [\text{MCl}^{2+}]/[\text{M}^{3+}][\text{Cl}^-]; \quad \beta_2 = [\text{MCl}_2^+]/[\text{M}^{3+}][\text{Cl}^-]^2$$

	La(III)	Eu(III)	Lu(III)	Am(III)
log β_1	-0.22 ± 0.11	-0.15 ± 0.10	-0.35 ± 0.07	-0.15 ± 0.07
log β_2	-0.64 ± 0.11	-0.72 ± 0.17	-0.57 ± 0.05	-0.69 ± 0.10

The range of error gives three times the standard deviation, $\pm 3\sigma$.

It is common for highly charged metal ions to undergo strong interaction with anions in aqueous solution and give many kinds of metal complexes. Trivalent lanthanide and actinide ions are thus expected to form strong complexes with many anionic ligands.

The ions in each series of these elements are quite similar to each other, and this has been explained by the fact that the 4f orbitals (for lanthanides) or the 5f orbitals (for actinides) are filled successively by electrons. It has been

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pointed out that the chemical behavior of the actinide ions is quite similar to that of the lanthanide ions especially for pairs of ions which have the same number of electrons in their outermost f orbitals.

The chemical similarities of these ions have been shown by many techniques. The differences between them in various aqueous solutions have also been studied very often, mainly from the point of view of their separation.

In this series of papers, the author has studied the complex formation of some trivalent lanthanide and actinide ions in aqueous solution to make a quantitative comparison of their complex formation under the same experimental conditions. La(III), Eu(III), and Lu(III) have been chosen as representatives of the lanthanides because they are the first, middle, and last elements of this series. Am(III) has been chosen to represent the actinides because it has the same position as has Eu(III) among the lanthanides.

Four very common anions were chosen as the complex-forming ligands. Oxalate ion is often used as a precipitant for these metal ions and is known to form very strong complexes with them. Sulfuric acid is very often used to attack minerals of rare earths, and sulfate ion is known to form moderately stable complexes with these metal ions. Both chloride and thiocyanate ions are known as to be very effective ligands to separate the actinides and the lanthanides by ion-exchange techniques. The complexes formed with these ions are rather weak.

Paper I of this series deals with the chloride complexes, Paper II with sulfate complexes, Paper III with oxalate complexes and Paper IV with thiocyanate complexes.

There has been some earlier work on the stability constants of the chloride complexes of trivalent lanthanides and actinides. Studies published before 1957 [1-7] have been summarized by Bjerrum, Schwarzenbach and Sillén.[8] Recently a few more papers on this subject have appeared. The stability constants of the MCl^{2+} complexes of La(III), Ce(III), Pr(III), Eu(III), Tm(III) Yb(III), Lu(III), and Am(III) were determined by a distribution method,[9] those of $AmCl^{2+}$ and $AmCl_2^+$ were determined by a cation exhange method,[10] those of YCl^{2+}, $ScCl^{2+}$ and $ScCl_2^+$ were determined by emf measurements,[11] and the MCl^{2+} and MCl_2^+ complexes of Ce(III) and Eu(III) and the YCl^{2+} complex were studied by a distribution method.[12]

The ion exchange behavior of these ions in chloride medium has been studied by many workers and has been reviewed by Katz and Seaborg.[13] The elution of trivalent actinide ions from a cation exchange resin with hydrochloric acid indicates that the actinides form chloride complexes to a greater extent than the lanthanides. The adsorption of these ions on an anion exchange resin from hydrochloric acid or lithium chloride media also indicates that the actinides form anionic chloride complexes to a much greater extent than the lanthanides, especially if the concentration of chloride ion is very high.

In the present work, the complex formation of La(III), Eu(III), Lu(III), and Am(III) with chloride ion in 4 M Na(ClO_4) has been studied by a distribution method at 25°C.

An ionic medium of 4 M Na(ClO_4) was chosen because the chloride complexes of these ions are so weak that one must make experiments at a high chloride concentration especially in order to study the higher complexes. The

stability constants were determined from the decrease of the distribution ratio of metal ions between an organic phase which contained a chelating acid and aqueous phases which contained various amounts of chloride ion. Except for the Eu(III) extraction, which had been carried out in the early stage of this work, mixtures of 2-thenoyltrifluoroacetone (TTA) and tributylphosphate (TBP) in carbon tetrachloride were used as the extractant. These mixtures give much higher metal extraction than does TTA alone, due to adduct chelate complex formation. This increase of the metal extraction is very often called a "synergetic effect" and it has been reported by many authors. Sekine and Dyrssen have studied the extraction of Cu(II), Zn(II), Th(IV), In(III), Sc(III), La(III), Eu(III), Lu(III), and Am(III) with mixtures of TTA and TBP or TTA and methylisobutylketone (hexone) and deduced the composition of the adducts; they also gave a short review of previous work.[14]

The use of a mixture of a chelating acid and a neutral ligand is sometimes very favorable for a distribution study because one can get a very large variation of the ability to extract metal ions at a certain concentration of the chelating acid merely by changing the concentration of the adduct-forming ligand in the organic phase. Moreover, by decreasing the concentration of the chelating acid, one can decrease the concentration of metal chelate complexes in the aqueous phase, which otherwise complicates the results.

The $-\log [H^+]$ was kept at 2.00 because no buffering agent was necessary in this region and practically no $HClO_4$ or HCl is extracted into the organic phase.

The stability constants were first estimated graphically and the estimates were then refined by a generalized least squares method using LETAGROP VRID which is an improved version of the LETAGROP computer program.[15]

A short note on the stability constants of La(III), Eu(III), Lu(III), and Am(III) complexes which contained the results of this work has been published.[16]

APPLICATION OF THE LAW OF MASS ACTION

When a trivalent metal ion, M^{3+}, forms the nth complex with an anionic ligand, L^-, as in the reaction

$$M^{3+} + nL^- \rightleftharpoons ML_n^{3-nl} \qquad (1)$$
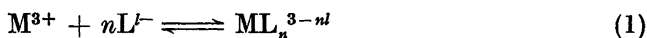
the equilibrium constant, the overall stability constant for the complex, is defined as

$$\beta_n = [ML_n^{3-n}]/[M^{3+}] [L^-]^n \qquad (2)$$

In an aqueous solution where the successive complexes with L^- but no other complexes of M^{3+} are formed, the total metal concentration can be written as

$$[M(III)]_{aq, \; total} = [M^{3+}] + [ML^{3-l}] + \ldots + [ML_n^{3-nl}]$$
$$= [M^{3+}] (1 + \sum_1^n \beta_n [L^-]^n) \qquad (3)$$

We will make the following assumptions for the distribution of a trivalent metal ion between an aqueous phase and an organic phase: (a) No complexes

with the chelating acid, MA_n^{3-n}, and no hydrolyzed species are formed in the aqueous phase. (b) Only MA_3 and its adducts MA_3N_n (N is a neutral ligand) are present in the organic phase.

The main distribution equilibrium is then

$$M^{3+} \text{ (aq)} + 3 \text{ HA (org)} \rightleftharpoons MA_3 \text{ (org)} + 3 \text{ H}^+ \text{ (aq)} \qquad (4)$$

The equilibrium constant, the "extraction constant" is

$$K_{ex} = [MA_3]_{org} [H^+]^3/[M^{3+}] [HA]_{org}^3 \qquad (5)$$

The extraction of MA_3 complexes is sometimes enhanced very much by the addition of a neutral ligand, N, such as TBP (synergetic effect).

The formation of the adduct chelate complex is written as

$$MA_3(\text{org}) + n N(\text{org}) \rightleftharpoons MA_3N_n(\text{org}) \qquad (6)$$

The overall adduct formation constant for the nth adduct is

$$\beta_{An} = [MA_3N_n]_{org}/[MA_3]_{org}[N]_{org}^n \qquad (7)$$

and the total metal concentration is

$$[M(III)]_{org, \text{ total}} = \sum_0^n [MA_3N_n]_{org} = [MA_3]_{org} (1 + \sum_1^n \beta_{An}[N]_{org}^n)$$
$$= K_{ex}'[M^{3+}][HA]_{org}^3[H^+]^{-3} \qquad (8)$$

We have introduced here K_{ex}', which is constant as long as $[N]_{org}$ is kept constant:

$$K_{ex}' = K_{ex} (1 + \sum_1^n \beta_{An} [N]_{org}^n) \qquad (9)$$

The net distribution ratio is defined as

$$D = [M(III)]_{org, \text{ total}}/[M(III)]_{aq, \text{ total}} \qquad (10)$$

We introduce into (10) the expressions (3) and (8) which contain our assumptions (a) and (b) above, and find

$$D = K_{ex}'[HA]_{org}^3[H^+]^{-3} (1 + \sum_1^n \beta_n[L^-]^n)^{-1} \qquad (11)$$

We shall denote by D_0 the distribution ratio of the metal when no complex-forming ligand, L^-, is in the aqueous solution but $[HA]_{org}$ and $[H^+]$ are the same as when D is measured. Then D_0, and the ratio of the distribution ratios D_0D^{-1} are

$$D_0 = K_{ex}'[HA]_{org}^3[H^+]^{-3} \qquad (12)$$
$$D_0D^{-1} = 1 + \sum_1^n \beta_n[L^-]^n \qquad (13)$$

Thus we can determine the overall stability constants from the decrease of the distribution ratio when various amounts of the ligand are present.

The overall stability constants were first estimated graphically. The plot log D_0D^{-1} *versus* log [L] can be fitted with a family of normalized curves

$$Y = \log (1 + \sum_1^n p_n v^n)$$
$$X = \log v \qquad (14)$$

where the parameters p_n contain the β_n, and one of them is set $= 1$. The procedure is described in Refs. 17—18.

EXPERIMENTAL

Reagents. All the reagents used were of analytical grade. The sodium perchlorate was prepared from sodium carbonate and perchloric acid and was recrystallized twice. The chloroform was shaken three times with the same volume of water in order to remove alcohol. The TBP was shaken first with 0.1 M $HClO_4$, then with 0.1 M NaOH and then several times with water until the aqueous phase gave a neutral color with pH paper.

Table 1. Dependence of the distribution ratio on the hydrogen ion concentration when chloride ion is absent and present.

Aqueous phase: 4M $Na(ClO_4)$
Organic phase for La(III): 0.1 M TTA in CCl_4 containing 0.1 M TBP;
           for Eu(III): 0.1 M Dioctylhydrogenphosphate in $CHCl_3$;
           for Lu(III): 0.1 M TTA in CCl_4 containing 0.034 M TBP;
           for Am(III): 0.1 M TTA in CCl_4 containing 0.01 M TBP.

(a) La(III)

$\log [Cl^-]$	$-\log [H^+]$	$\log D$	$-\log D [H^+]^3 [HA]_{org}^{-3}$
—	2.222	0.970	2.70
—	2.000	0.277	2.72
—	1.745	−0.504	2.74
—	1.523	−1.157	2.73
0.505	2.222	0.250	3.42
0.505	2.000	−0.442	3.44
0.505	1.854	−0.860	3.42

(b) Eu(III)

$\log [Cl^-]$	$-\log [H^+]$	$\log D$	$-\log D [H^+]^3 [HA]_{org}^{-3}$
—	2.523	2.467	2.10
—	2.301	1.791	2.11
—	2.000	1.033	1.97
—	1.699	0.170	1.93
0.505	2.222	0.938	2.73
0.505	2.000	0.305	2.70
0.505	1.854	−0.119	2.68

(c) Lu(III)

$\log [Cl^-]$	$-\log [H^+]$	$\log D$	$-\log D [H]^3 [HA]_{org}^{-3}$
—	2.301	−0.112	4.02
—	2.000	−1.031	4.03
—	1.699	−1.854	3.95
0.511	2.222	−1.201	4.87
0.511	2.000	−1.833	4.83
0.511	1.824	−2.308	4.78

(d) Am(III)

$\log [Cl^-]$	$-\log [H^+]$	$\log D$	$-\log D [H^+]^3 [HA]_{org}^{-3}$
—	2.523	+0.100	4.47
—	2.301	−0.583	4.49
—	2.000	−1.433	4.43
—	1.699	−2.295	4.39
0.516	2.222	−1.509	5.18
0.516	2.000	−2.183	5.18
0.516	1.854	−2.523	5.08

Other reagents were used with no further purification. Solutions of NaCl were prepared by weighing dry NaCl. 4 M $NaClO_4$ was prepared by diluting the stock solution and its sodium perchlorate content had been determined by weighing the residue $NaClO_4$ after evaporation of a measured amount of the solution in an air bath at 120°C.

Tracers. [140]La, [152+154]Eu, ^{177}Lu were prepared as follows: Very pure oxides of these metals were irradiated with thermal neutrons in the Swedish heavy water reactor R1. The metal oxides were then dissolved in hot concentrated HNO_3 and the solutions were evaporated to dryness under an infrared lamp to expel the excess acid. The residues were then dissolved in 0.1 M $HClO_4$ + 3.9 M $NaClO_4$ or in 0.1 M HCl + 3.9 M NaCl solutions and these were used as stock solutions. [241]Am was obtained from the Radiochemical Center, Amersham, England, as a chloride solution. The solution was evaporated under an infrared lamp to dryness and the residue was dissolved in 0.1 M $HClO_4$ + 3.9 M $NaClO_4$ or 0.1 M HCl + 3.9 M NaCl solutions and these solutions were then used as stock solutions.

Procedures. All procedures were carried out in a thermostated room at 25°C. The two phases were equilibrated in 50 ml stoppered glass tubes. The initial volume of both the organic and the aqueous phases was 5.0 ml and the hydrogen ion concentration was always 0.01 M except for the experiments listed in Table 1. Both phases in the tubes were agitated by a mechanical rotator for about 2 h and were separated by centrifugation. A 2 ml sample was pipetted off from each phase and transferred into a small polyethylene tube. The γ-activity of the solution was measured with a well-type scintillation counter.

RESULTS

The net distribution ratio of the metal was calculated as $D = (\gamma$ activity in 2 ml of organic phase)/(γ activity in 2 ml of aqueous phase).

Table 1 gives the dependence of the metal distribution on $-\log [H^+]$ when chloride ion is absent and present. Table 2, parts (a) to (d), gives $\log D_0 D^{-1}$

Table 2. Metal distribution between the organic phase (composition as in Table 1) and the aqueous phase with various concentrations of chloride ion at $-\log [H^+] = 2.00$. The data are given as $\log [Cl^-]$ ($\log D_0 D^{-1} = 1 + \sum_1^n \beta_n [Cl^-]^n$) (*cf.* eqn. (13)).

(a) La(III). 0.551 (0.78); 0.542 (0.75); 0.526 (0.74); 0.521 (0.73); 0.511 (0.75); 0.494 (0.68); 0.483 (0.71); 0.453 (0.66); 0.435 (0.64); 0.422 (0.61); 0.395 (0.59); 0.373 (0.57); 0.350 (0.55); 0.326 (0.54); 0.292 (0.49); 0.274 (0.47); 0.225 (0.40); 0.158 (0.37); 0.121 (0.36); 0.049 (0.28); 0.017 (0.29); −0.036 (0.30); −0.097 (0.29); −0.119 (0.17); −0.167 (0.15); −0.222 (0.13); −0.252 (0.12); −0.284 (0.10); −0.356 (0.10); −0.495 (0.09); −0.620 (0.06); −0.796 (0.04); −0.921 (0.01); −1.398 (0.02);

(b) Eu(III). 0.556 (0.81); 0.547 (0.78); 0.526 (0.79); 0.516 (0.77); 0.494 (0.73); 0.489 (0.68); 0.477 (0.69); 0.471 (0.66); 0.459 (0.64); 0.447 (0.66); 0.435 (0.62); 0.422 (0.58); 0.401 (0.57); 0.395 (0.53); 0.358 (0.52); 0.322 (0.48); 0.335 (0.53); 0.310 (0.52); 0.283 (0.51); 0.265 (0.49); 0.255 (0.45); 0.246 (0.45); 0.236 (0.45); 0.225 (0.42); 0.215 (0.42); 0.193 (0.38); 0.182 (0.43); 0.170 (0.40); 0.158 (0.44); 0.146 (0.38); 0.136 (0.44); 0.121 (0.36); 0.107 (0.43); 0.093 (0.34); 0.079 (0.37); 0.065 (0.31); 0.000 (0.24); −0.055 (0.22); −0.097 (0.25); −0.143 (0.20); −0.222 (0.11); −0.495 (0.07); −0.620 (0.04); −0.796 (0.04);

(c) Lu(III). 0.537 (0.77); 0.526 (0.74); 0.505 (0.73); 0.505 (0.75); 0.505 (0.72); 0.494 (0.69); 0.471 (0.65); 0.447 (0.63); 0.422 (0.59); 0.395 (0.57); 0.366 (0.52); 0.335 (0.50); 0.301 (0.47); 0.265 (0.43); 0.246 (0.43); 0.225 (0.41); 0.204 (0.40); 0.182 (0.36); 0.158 (0.37); 0.134 (0.33); 0.107 (0.31); 0.079 (0.28); 0.049 (0.27); 0.017 (0.24); −0.018 (0.22); −0.055 (0.22); −0.055 (0.19); −0.097 (0.19); −0.143 (0.17); −0.194 (0.13); −0.252 (0.12); −0.398 (0.08);

(d) Am(III). 0.556 (0.81); 0.556 (0.81); 0.547 (0.77); 0.537 (0.79); 0.526 (0.75); 0.516 (0.75); 0.483 (0.73); 0.459 (0.67); 0.435 (0.66); 0.422 (0.62); 0.408 (0.61); 0.395 (0.60); 0.380 (0.58); 0.366(0.57); 0.350 (0.54); 0.335 (0.51); 0.318 (0.50); 0.301 (0.49); 0.283 (0.47); 0.265 (0.46); 0.225 (0.47); 0.017 (0.33); −0.018 (0.31); −0.055 (0.27); −0.097 (0.25); −0.097 (0.25); −0.143 (0.20); −0.194 (0.19); −0.252 (0.16); −0.319 (0.13); −0.398 (0.10);

(*cf.* eqn. 13) *versus* log [Cl⁻] when the aqueous phase contains various amounts of chloride ion. Figs. 1 to 4 give the plots of log D_0D^{-1} *versus* log [Cl⁻].

By a curve-fitting method, the stability constants for the MCl^{2+} and the MCl_2^{+} complexes, β_1 and β_2, were estimated and these estimates were then
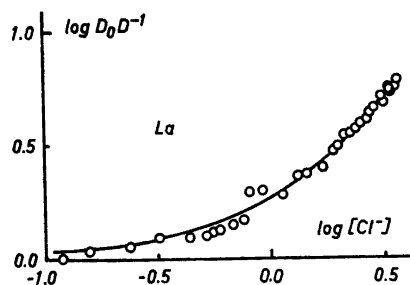

Fig. 1. The variation of the distribution of lanthanum(III) as a function of the concentration of chloride ion. D_0D^{-1} gives $1 + \beta_1$ [Cl⁻] + β_2 [Cl⁻]² (*cf.* eqn. (13)). The curve gives the calculated curve from the constants in Table 3. Aqueous phase: 4 M Na(ClO₄) at −log [H⁺] = 2.00. Organic phase: 0.1 M TTA in CCl₄ containing 0.1 M TBP.
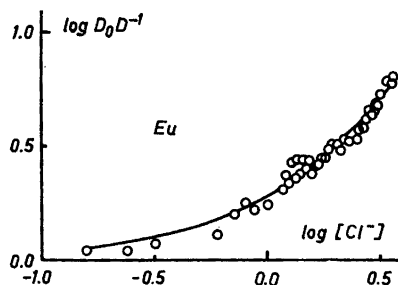
Fig. 2. The variation of the distribution of europium(III) as a function of the concentration of chloride ion. D_0D^{-1} gives $1 + \beta_1$ [Cl⁻] + β_2 [Cl⁻]² (*cf.* eqn. (13)). The curve gives the calculated curve from the constants in Table 3. Aqueous phase: 4 M Na(ClO₄) at −log [H⁺] = 2.00. Organic phase: 0.1 M dioctylhydrogenphosphate in CHCl₃.

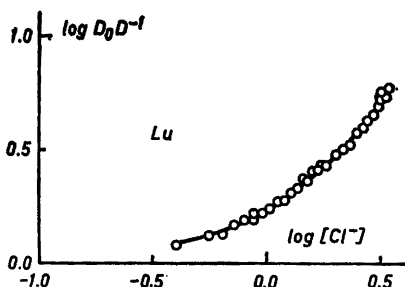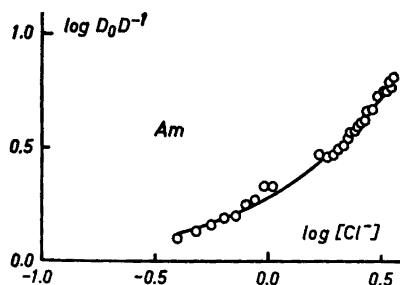*Fig. 3.* The variation of the distribution of lutetium(III) as a function of the concentration of chloride ion. D_0D^{-1} gives $1 + \beta_1$ [Cl⁻] + β_2 [Cl⁻]² (*cf.* eqn. (13)). The curve gives the calculated curve from the constants in Table 3. Aqueous phase: 4 M Na(ClO₄) at −log [H⁺] = 2.00. Organic phase: 0.1 M TTA in CCl₄ containing 0.034 M TBP.

Fig. 4. The variation of the distribution of americium(III) as a function of the concentration of chloride ion. D_0D^{-1} gives $1 + \beta_1$ [Cl⁻] + β_2 [Cl]² (*cf.* eqn. (13)). The curve gives the calculated curve from the constants in Table 3. Aqueous phase: 4 M Na(ClO₄) at −log [H⁺] = 2.00. Organic phase: 0.1 M TTA in CCl₄ containing 0.001 M TBP.

refined by a generalized least squares method using LETAGROP VRID which is an improved version of the LETAGROP computer program,[15] so as to minimize the error square sum

$$U = \sum(\log D_0D^{-1}_{(exp)} - \log (1 + \beta_1[Cl^-] + \beta_2[Cl^-]^2)_{(calc)})^2 \qquad (16)$$

The "best fit" stability constants thus obtained are listed in Table 3. The range of error in Table 3 gives three times the standard deviation, $\pm 3\sigma$.

The solid curves in Figs. 1 to 4 give the calculated values of log $D_0 D^{-1}$ versus log [Cl$^-$] using these constants.

Fig. 5 gives the distribution of the M^{3+}, the MCl^{2+}, and the MCl_2^+ species as a function of log [Cl$^-$] which has been calculated from the constants in Table 3.

Table 3. Stability constants of the complexes of lanthanum(III), europium(III), lutetium(III), and americium(III) with chloride ion.

$$\beta_1 = [MCl^{2+}] / [M^{3+}] [Cl^-]$$

$$\beta_2 = [MCl_2^+] / [M^{3+}] [Cl^-]^2$$

	La(III)	Eu(III)	Lu(III)	Am(III)
log β_1	-0.22 ± 0.11	-0.15 ± 0.10	-0.35 ± 0.07	-0.15 ± 0.07
log β_2	-0.64 ± 0.11	-0.72 ± 0.17	-0.57 ± 0.05	-0.69 ± 0.10

(The range of error gives three times the standard deviation, $\pm 3\sigma$)

DISCUSSION

Table 1 indicates that the extraction constant, K_{ex} or K_{ex}', is practically constant at a certain [HA]$_{org}$ and [N]$_{org}$ in all the systems both when chloride ion is present and absent. If chelate complexes had formed in the aqueous phase, or mixed complexes of the metal with Cl$^-$ or ClO$_4^-$ and with A$^-$ had been extracted, the extraction constant, K_{ex} in eqn. (5), or K_{ex}' in eqn. (11), should decrease when [H$^+$] is decreased. We conclude from Table 1 that the extraction of mixed complexes is negligible in these experiments.

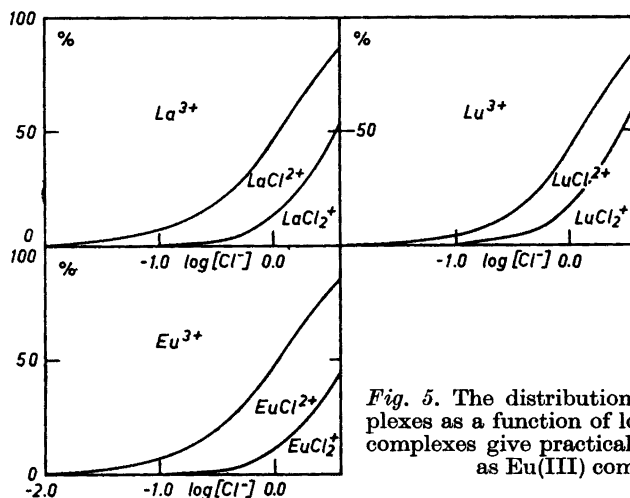Fig. 5. The distribution of chloride complexes as a function of log [Cl$^-$]. (Am(III) complexes give practically the same curve as Eu(III) complexes.)

Table 4. Stability constants of chloride complexes of various trivalent lanthanide and actinide ions from other studies.

Metal ion	I	Temperature °C	log β_1	log β_2	Reference
La^{3+}	1.0	25	−0.15		1
	1.0	25	−0.12		2
	1.0	22	−0.05		8
Ce^{3+}	0.6	25	0.10		3
	1.0	25	0.24		3
	1.0	22	−0.05		8
	1.0	25	−0.1	−0.7	11
Pr^{3+}	1.0	22	−0.05		8
Eu^{3+}	2.0	—	0.3		5
	1.0	22	−0.10		8
	1.0	25	−0.1	−0.7	11
Tm^{3+}	1.0	22	−0.10		8
Yb^{3+}	1.0	22	−0.23		8
Lu^{3+}	0.1	20	1.45		6
	1.0	22	−0.40		8
Pu^{3+}	1.0	25	−0.15		4
	0.5	—	−0.24		7
	1.0	—	−0.05		7
Am^{3+}	0.5	—	−0.24		7
	1.0	22	−0.05		8
	4.0	20	−0.16	−0.74	9
Cm^{3+}	0.5	—	−0.18		7

No correction was made for a change in the ion activity factors which might be expected to occur when the relative concentrations of the anions in the solution are changed so much.

Table 4 gives a summary of previous work in this area. The present study can be compared directly with the constants given by Grenthe.[9]

The agreement of the constants for the Am(III) complexes in 4 M Na(ClO$_4$) is very good. The agreement is also fairly good with the constants in $I = 1.0$ M given in Refs. 1, 2, 8, and 11.

A chloride medium is very often used for the ion exchange separation of trivalent actinide and lanthanide ions as can be seen in the review by Katz and Seaborg.[13] The cation exchange behavior of Eu(III) and Am(III) in solutions of lower HCl concentration is nearly the same, but Am(III) is more easily eluted with 9.3 M or 12.2 M HCl than is Eu(III). On the other hand, Am(III) is adsorbed on an anion exchange resin from a concentrated HCl or LiCl solution while Eu(III) is adsorbed much less strongly. The close similarity of β_1 and β_2 for Eu (III) and Am(III) shows that there is practically no difference between the stability of AmCl^{2+} and EuCl^{2+}, or between AmCl$_2^+$ and EuCl$_2^+$, and thus, a large difference in the stability of the complexes of these ions may occur in the higher complexes.

Among the three lanthanide ions, Lu(III) showed the smallest β_1 and the largest β_2. This may be caused by many factors and further investigation seems to be necessary in order to explain the variation of the stability of the complexes with the order of the atomic number or with the ionic size.

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