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Studies of Actinium(III) in Various Solutions. II. Distribution Behavior of Lanthanum(III) and Actinium(III) in Some Chelate Extraction Systems

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Distribution behavior of lanthanum(III) and actinium(III) at tracer concentrations was studied in metal chelate extraction systems where the organic phase was chloroform containing dibutylphosphate, thenoyltrifluoroacetone (TTA), β-isopropyltropolone or 5,7-dichloroxine. The separation factors for this pair of ions by extraction with these four chelating ligands were determined. The distribution behavior was also studied in the adduct chelate extraction systems where the organic phase was carbon tetrachloride containing mixed ligands, TTA-tributylphosphate (TBP) or TTA-methyl isobutyl ketone (MIBK). The adduct formation constants for actinium(III)-tris-TTA chelate with these neutral ligands were determined. Results were compared with previous results on the distribution behavior of other trivalent actinide and lanthanide ions in these systems. It was concluded that the separation of lanthanum-actinium was somewhat different from the separation of europium-americium in the same chelate extraction systems. The stabilities of the first adducts with TBP or MIBK of actinium TTA chelate were smaller than those of americium TTA chelate, but the stabilities of the second adducts showed just the reverse order. This tendency in adduct formation is the same as that observed among the lanthanum and europium adduct TTA chelates in previous work. Finally, the use of TTA-TBP mixture was recommended for the extraction of lanthanum(III) or actinium(III) at tracer concentrations based on the fact that the use of these mixed ligands resulted in much better recovery of material and better reproducibility of results than a single chelating ligand.

Little is known about the solvent extraction behavior of actinium except for the early studies of Hagemann,[1] who prepared actinium-227 using a TTA (thenoyltrifluoroacetone) extraction method, and of Peppard, Mason, Gray and Mech,[2] who studied the extraction of this element with TBP (tributylphosphate).

In the present paper, the authors measured the liquid-liquid distribution behavior of actinium(III) and lanthanum(III) in some metal chelate extraction systems in which Sekine and Dyrssen[3,4] previously studied the solvent extraction of europium(III) and americium(III). It was further intended to compare the liquid-liquid distribution behavior of the trivalent lanthanides and actinides.

Experimental

Tracer. Actinium-228 tracer was prepared by the method described in Part I of this series[5] just before use. Lanthanum-140 tracer was prepared from barium-140 by a method similar to actinium-228 as follows: A carrier-free barium-140 solution was stored a few days and adjusted to pH 5—6 using acetate buffer. The lanthanum-140 produced in the solution was extracted with 0.1 M TTA in chloroform. The organic layer was once washed with a fresh buffer solution at pH 5—6 and then the lanthanum-140 was back-extracted by shaking the organic layer with 0.1 M perchloric acid. The aqueous layer thus obtained was then washed with chloroform and used as a stock solution of this isotope.

Reagents. A mixture of DBP (dibutylphosphate) and monobutylphosphate was obtained from Tokyo Kasei Co. DBP was separated and purified by a solvent extraction method.[6] TTA was obtained from Dojindo & Co., IPT (β-isopropyltropolone) from Takasago Perfumery Co. and 5,7-dichloroxine from Tokyo Kasei Co. These chelating reagents were used without further purification. TBP and MIBK (methyl isobutyl ketone) were obtained from Tokyo Kasei Co. They were washed with 0.1 M perchloric acid, water and 0.1 M sodium hydroxide, in that order, and then

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[1] F. T. Hagemann, *J. Am. Chem. Soc.*, **72**, 768 (1950).

[2] D. E. Peppard, G. W. Mason, P. R. Gray and J. F. Mech, *ibid.*, **74**, 6081 (1952).

[3] T. Sekine and D. Dyrssen, *Talanta*, **11**, 867 (1964).

[4] T. Sekine and D. Dyrssen, *J. Inorg. Nucl. Chem.*, **29**, 1481 (1967).

[5] T. Sekine, Y. Koike and M. Sakairi, *J. Nucl. Sci. and Tec.*, **4**, 308 (1967).

[6] D. Dyrssen and L. D. Hay, *Acta Chem. Scand.*, **14**, 1100 (1960).

several times with water. Chloroform was washed three times with water. Other reagents were of an analytical grade.

Procedures. All procedures were carried out in a thermostatted room at 25±0.5°C. Lanthanum(III) carrier (initial concentration in the aqueous phase, 5×10^{-5} M) was added to the aqueous phase except for the TBP adduct experiments when the TBP concentration was low. A small amount of sulfanilate, acetate or carbonate (initial concentration in the aqueous phase, 0.01 M) was added to the aqueous phase when a buffer was necessary. It was confirmed that no change in extraction was caused by these buffers at this concentration. A 5 m*l* portion of the aqueous phase and a 5 m*l* portion of the organic phase were placed in tubes with glass stoppers (volume 20 m*l*) and agitated mechanically for 30 min and centrifuged. A 2 m*l* portion was pipetted from each phase and transferred to small glass test tubes and the γ-radioactivity measured with a well-type (NaI) scintillation counter. A small portion was also taken from the aqueous phase and the hydrogen ion concentration measured potentiometrically using a standard solution containing 0.0100 M perchloric acid and 0.09 M or 0.99 M sodium perchlorate as the standard of $-\log[\mathrm{H^+}]$ 2.00 in 0.1 M or 1 M perchlorate media. When the hydrogen ion concentration exceeded 0.01 M, it was determined by a titration method.

The net distribution ratio of the trivalent metal ions M^{3+} was defined and determined as follows;

$$D=[\mathrm{M(III)}]_{org,\,total}/[\mathrm{M(III)}]_{total}=\frac{\gamma\text{-count-rate per m}l\text{ org. phase}}{\gamma\text{-count-rate per m}l\text{ aq. phase}}$$

Results

A) Extraction of Metal Chelates. In the extraction of metal chelates, the aqueous phase was kept at 0.1 M perchlorate. The organic phase was chloroform containing 0.1 M DBP, TTA or IPT, or chloroform containing 0.05 M 5,7-dichloroxine.

Assuming that extraction takes place by the following reaction (HA denotes the chelating acid),

$$\mathrm{M^{3+}}+(3+n)\mathrm{HA(org)}\rightleftarrows \mathrm{MA_3(HA)}_n\mathrm{(org)}+3\mathrm{H^+} \quad (1)$$

$$D=\sum[\mathrm{MA_3(HA)}_n]_{org}/[\mathrm{M^{3+}}] \quad (2)$$

an equilibrium constant for the extraction may be defined if the chelate concentration is kept constant as

$$K=D[\mathrm{H^+}]^3 \quad (3)$$

However, when the chelate concentration is not constant, a more involved equation[7] should be used.[*1] In the present study, the chelate concentration was kept constant in each series of experiments, and thus Eq. (3) could be used.

Table 1 summarizes the separation of lanthanum(III) and actinium(III) by chelate extraction into chloroform. This table also summarizes previously reported data on the separation of europium(III) and americium(III).[3] The constants $D[\mathrm{H^+}]^3$ were calculated from data obtained from the range of the distribution ratio $10>D>0.1$, because the values $D[\mathrm{H^+}]^3$ for all the chelate extraction systems were approximately constant only in this range.

In the hydrogen ion concentration region where the distribution ratio is greater than 10, some decrease in the slope of the extraction curve from +3 was observed in the IPT system. This discrepancy was assumed due to aqueous chelate formation.[9] When the distribution ratio is less than 0.1, some decrease in the slope from +3 was also observed in actinium(III) chelate extraction systems, but no explanation can be given for this deviation.

The slope $\log D$ *vs.* $-\log[\mathrm{H^+}]$ plot for the 5,7-dichloroxine system was found to be +3 at least when $-\log[\mathrm{H^+}]$ was below 7. This indicates that the hydrolysis of these ions is not very important

Table 1. Separation of La^{3+} and Ac^{3+} in 0.1 M (Na, H)ClO_4 at 25°C by solvent extraction with some chelating acids in chloroform together with previous data on that of Eu^{3+} and Am^{3+} under the similar conditions[3]

Reagent (HA)	$[\mathrm{HA}]_{org}$	$\log SF_{\mathrm{La^{3+}-Ac^{3+}}}$	$\log SF_{\mathrm{Eu^{3+}-Am^{3+}}}$	$\log D_{\mathrm{La^{3+}}}[\mathrm{H^+}]^3$	$\log D_{\mathrm{Ac^{3+}}}[\mathrm{H^+}]^3$	$\log SF_{\mathrm{Eu^{3+}-La^{3+}}}$	$\log SF_{\mathrm{Am^{3+}-Ac^{3+}}}$
Dibutylhydrogenphosphate (DBP)	0.1 M	+0.64	+1.36	−4.92	−5.56	+2.01	+1.29
2-Thenoyltrifluoroacetone (TTA)	0.1 M	+1.84	+0.48	−14.06	−15.90	+2.38	+3.70
β-Isopropyltropolone (IPT)	0.1 M	+1.82	−0.01	−13.60	−15.42	+3.70	+5.53
5,7-Dichloroxine (DCOX)	0.05 M	+1.71	−0.99	−17.81	−19.52	+4.08	+6.78

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[7] T. Sekine and D. Dyrssen, *J. Inorg. Nucl. Chem.*, **26**, 1727 (1964).

[*1] Actually the chelate complex of europium(III) with IPT in chloroform was found to be of the form $\mathrm{EuA_3HA}$,[8] and it is most probable that the actinium IPT complex also exists in the form $\mathrm{AcA_3HA}$.

[8] T. Sekine and D. Dyrssen, *ibid.*, **29**, 1457 (1967).

[9] T. Sekine, A. Koizumi and M. Sakairi, This Bulletin, **39**, 2681 (1966).

[10] F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Co., Inc., New York (1961), p. 233.

[11] G. Biedermann and L. Ciavatta, *Acta Chem. Scand.*, **15**, 1347 (1961).

if the hydrogen ion concentration is kept above 10^{-7} M.[10,11]

B) Extraction of Adduct Metal Chelates. The adduct formation of actinium(III)-tris-TTA chelate with TBP or MIBK was studied in carbon tetrachloride. In these experiments, the aqueous phase was adjusted to 1 M (H, Na)ClO_4 in order to compare results with the previous data.[4]

As a statistical treatment of adduct chelate formation in a solvent extraction system has been already given in a previous paper,[12] only a brief description will be given here. When metal tris-TTA chelate MA_3 forms adduct chelate complexes with an organophilic neutral ligand L, the reaction and formation constants may be described by

$$MA_3(\text{org}) + n\text{L}(\text{org}) \rightleftarrows MA_3L_n(\text{org}) \qquad (4)$$

$$\beta_n = [MA_3L_n]_{org}/[MA_3]_{org}[L]^n_{org} \qquad (5)$$

When these adduct chelates are formed in the organic phase and M^{3+} is the only metal species in the aqueous phase, the net distribution ratio may be generally written.

$$D = \frac{[MA_3]_{org} + [MA_3L]_{org} + [MA_3L_2]_{org} + \cdots}{[M^{3+}]} \qquad (6)$$

When the net distribution ratio of the metal chelate extraction in the absence of the adduct forming ligand can be described as $D_0 = [MA_3]_{org}/[M^{3+}]$, the following equation is obtained from Eqs. (5) and (6) if the chelating ligand and hydrogen ion concentrations are kept constant;

$$D/D_0 = 1 + \beta_1[L]_{org} + \beta_2[L]^2_{org} + \cdots \qquad (7)$$

Figure 1 shows the $\log D/D_0$ *vs.* $\log[L]_{org}$ plot of actinium(III)-tris-TTA chelate in carbon tetrachloride when the neutral ligand was TBP or MIBK.

The formation constants were determined in the same manner as described in Ref. 12 and are given in Table 2 together with the formation constants of lanthanum(III), europium(III), lutetium(III) and americium(III) tris-TTA chelates under the same experimental conditions as in Ref. 7. The solid curves in Fig. 1 are calculated from the formation constants given in Table 2.

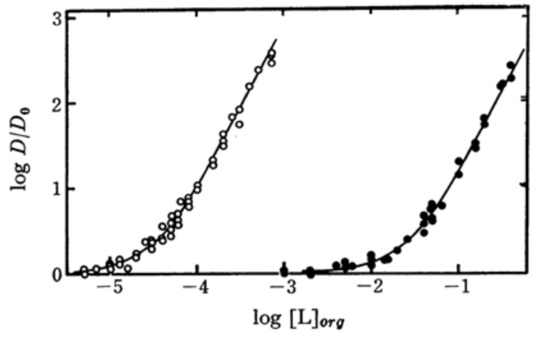

Fig. 1. The increase in the TTA extraction of actinium(III) by the adduct fromation shown as a function of the concentration of the adduct forming ligand.
Organic phase: Carbon tetrachloride containing 0.1 M TTA and TBP (open circles) or MIBK (closed circles).
Aqueous phase: 1M $NaClO_4$.
The solid curves were drawn as follows.
TBP: $Y = \log(1 + 10^{4.2}[L]_{org} + 10^{8.9}[L]^2_{org})$
MIBK: $Y = \log(1 + 10^{1.3}[L]_{org} + 10^{3.1}[L]^2_{org})$

TABLE 2. ADDUCT FORMATION OF TRIS-TTA CHELATES IN CARBON TETRACHLORIDE AT 25°C
(AQUEOUS PHASE, 1M $NaClO_4$)

(a) Extraction constants with pure TTA in carbon tetrachloride
$K_{ex_0} = [MA_3]_{org}[H^+]^3/[M^{3+}][HA]^3_{org}$

Metal ion	log K_{ex_0}	Ionic radius Å**
Ac^{3+}	−12.90	1.11
La^{3+}*	−10.95	1.04
Am^{3+}*	−8.88	0.99
Eu^{3+}*	−8.57	0.96

(b) Adduct formation constants of tris-TTA chelate in carbon tetrahcloride at 25°C
$\beta_1 = [MA_3L]_{org}/[MA_3]_{org}[L]_{org}$
$\beta_2 = [MA_3L_2]_{org}/[MA_3]_{org}[L]^2_{org}$
$K_2 = \beta_2/\beta_1 = [MA_3L_2]_{org}/[MA_3L]_{org}[L]_{org}$

Metal chelate	MIBK			TBP		
	logβ_1	logβ_2	logK_2	logβ_1	logβ_2	logK_2
AcA_3	1.3	3.1	1.8	4.2	8.9	4.7
LaA_3*	2.0	2.9	0.9	4.8	9.3	4.5
AmA_3*	1.8	2.5	0.7	5.1	8.9	3.8
EuA_3*	1.8	2.4	0.6	5.2	8.9	3.7

* taken from Ref. 4.
** taken from W. H. Zachariesen, "The Actinide Elements," NNES-14A McGraw-Hill, New York (1954).

It was found that the results on the extraction of carrier-free lanthanum(III) and actinium(III) were not very reproducible. The addition of non-radioactive lanthanum(III) (initial concentration in the aqueous phase, 5×10^{-5} M) improved the reproducibility very much, especially that of actinium extraction. The extraction of carrier-free actinium(III), however, was very reproducible when a mixture of TTA and TBP in carbon tetrachloride was employed as extractants instead of a single chelating agent.

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[12] T. Sekine and M. Ono, This Bulletin, **38**, 2087 (1965).

Discussion

The results are summarized as follows;

A) The extraction of actinium(III) with the four chelating reagents was always inferior to that of lanthanum(III). The separation of lanthanum(III) from actinium(III) using TTA, IPT or 5,7-dichloroxine was better than that of europium(III) from americium(III) with the same reagent, but the difference in extraction of lanthanum(III) and actinium(III) using DBP was inferior to that of europium(III) and americium(III). In a previous study,[3] americium(III) was extracted with 5,7-dichloroxine ten times better than europium(III), but the separation of actinium(III) from lanthanum(III) with this reagent, on the other hand, showed just the reverse tendency; lanthanum(III) extracted fifty times better than actinium(III).

B) In a previous work,[4] it was pointed out that the stability of the first adducts MA_3L was greater in the increasing order of extractability of the tris-TTA metal complexes $LaA_3L < EuA_3L < LuA_3L$, but the stability of the second complexes MA_3L_2 was greater in the reverse order $LaA_3L_2 > EuA_3L_2 > LuA_3L_2$. A similar tendency of stability was also observed in TBP adducts of actinide TTA chelates; the formation constants of the first adducts of actinium TTA chelate were smaller than those of americium TTA chelate. On the other hand, the stepwise formation constants K_2 of actinium adducts were larger than those of americium adducts.

The similarity in chemical properties of lanthanides and actinides has been explained in terms of their electronic configurations; the 4f orbitals (lanthanides) or 5f orbitals (actinides) are filled successively by electrons with increase in atomic number. In the case of lanthanum and actinium, however, a contribution from the 4f and 5f electrons to their chemical properties is not expected, and thus the chemical properties of these pairs of elements could be different to some extent.

Separation of two metal ions by a metal chelate extraction method is influenced by many factors. The separation factor (*SF* in Table 1) is defined,

$$SF = \frac{D_{\mathrm{La}^{3+}}[\mathrm{H}^+]^3}{D_{\mathrm{Ac}^{3+}}[\mathrm{H}^+]^3} \quad \text{(when } [\mathrm{HA}]_{org} \text{ is the same)}$$

this equation can be altered as follows (*cf.* also Ref. 13).

The distribution ratio in a metal chelate extraction system can generally be written,

$$D = \frac{[\mathrm{MA_3}]_{org} + [\mathrm{MA_3(HA)}]_{org} + \cdots + [\mathrm{MA_3(HA)}_n]_{org}}{[\mathrm{M}^{3+}] + [\mathrm{MA}^{2+}] + [\mathrm{MA_2}^+] + [\mathrm{MA_3}] + \cdots + [\mathrm{MA}_n{}^{3-n}]} \tag{8}$$

Let us discuss the case where only the MA_3 species is extracted into the organic phase for simplicity (a general discussion will also be possible). When we define the stability constants of metal chelates produced in the aqueous phase and the distribution constant of the non-charged metal chelate as follows,

$$\beta_n = \frac{[\mathrm{MA}_n{}^{3-n}]}{[\mathrm{M}^{3+}][\mathrm{A}^-]^n} \tag{9}$$

$$K_{DM} = \frac{[\mathrm{MA_3}]_{org}}{[\mathrm{MA_3}]} \tag{10}$$

the distribution ratio can be described as

$$D = \frac{K_{DM}\beta_3[\mathrm{A}^-]^3}{1 + \beta_1[\mathrm{A}^-] + \beta_2[\mathrm{A}^-]^2 + \beta_3[\mathrm{A}^-]^3 + \cdots + \beta_n[\mathrm{A}^-]^n} \tag{11}$$

The separation factor of two metal ions (denoted M_a and M_b) can be written from Eq. (11) as (the subscripts "*a*" and "*b*" denote the constants for M_a and M_b);

$$\frac{Da}{Db} = \frac{K_{DMa}\beta_{3a}}{K_{DMb}\beta_{3b}} \times \frac{1 + \beta_{1b}[\mathrm{A}^-] + \beta_{2b}[\mathrm{A}^-]^2 + \beta_{3b}[\mathrm{A}^-]^3 + \cdots}{1 + \beta_{1a}[\mathrm{A}^-] + \beta_{2a}[\mathrm{A}^-]^2 + \beta_{3a}[\mathrm{A}^-]^3 + \cdots} \tag{12}$$

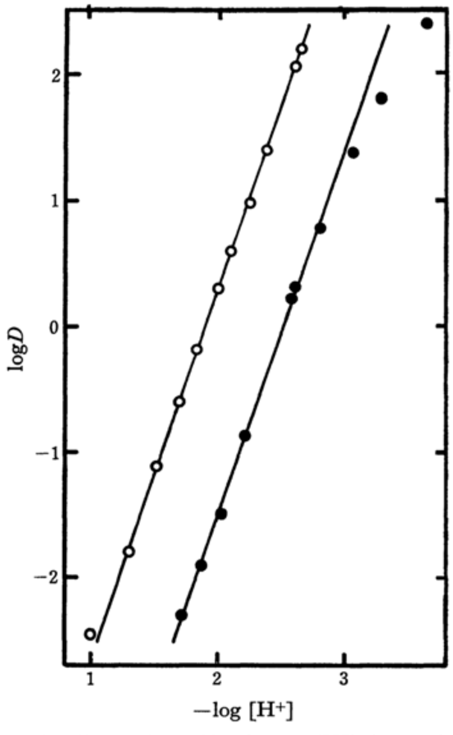

Fig. 2. Extraction of lanthanum(III) (open circles) and actinium(III) (closed circles) with mixed solvents as a function of the hydrogen ion concentration.

Organic phase: carbon tetrachloride containing 0.2 M TTA and 0.2 M TBP.

Aqueous phase: 1 M aqueous sodium perchlorate.

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[13] T. Wakahayashi *et al.*, *J. Inorg. Nucl. Chem.*, **26**, 2255, 2265 (1964); **27**, 1141 (1965).

We see from Eq. (12) that the separation factor will not be constant over all hydrogen ion concentrations, but in the region where no aqueous chelate complexes are formed (where the slope of the plot log$D$ *vs.* $-\log[\mathrm{H}^+]$ is $+3$), the separation factor can be written

$$SF=\frac{Da}{Db}=\frac{K_{DMa}\beta_{3a}}{K_{DMb}\beta_{3b}} \tag{13}$$

Equation (13) shows that the separation of these two metal ions is concerned only with the stability and the extractability of the third chelate complexes.

No previous information on these factors for lanthanide and actinide chelate seems to have been reported. Further discussion on the separation of lanthanides and actinides by metal chelate extraction would be possible if we could obtain the K_{DM} and β_3 values of the chelates.

In Ref. 4, the general tendency of the stability of the adduct metal chelates was explained in terms of the residual coordination power of metal ions which is decreased if they form more stable complexes with the chelating ligands. This tendency is again found in the present results. The extractability of actinium(III) with TTA is smaller than that of lanthanum(III) or americium(III). This fact indicates a smaller β_3 value for actinium(III) than for the others.[*2] Thus we may expect a larger residual coordination power in actinium tris-TTA chelate than in the other which causes the actinium tris-TTA chelates to form less stable first adducts and more stable second adducts.

As described, the extraction of carrier-free lanthanum or actinium in liquid-liquid systems containing only a chelating acid is not reproducible. When it is necessary to treat these ions at tracer concentrations, we recommend the use of mixed extractant systems. The extraction of carrie-free actinium was conveniently carried out with the use of TTA-TBP mixtures. Figure 2 shows the log$D$ *vs.* $-\log[\mathrm{H}^+]$ plot of these ions when the organic phase was carbon tetrachloride containing 0.2 M TTA and 0.2 M TBP. In this system, the separation factor is 1.80 and the recovery of the materials almost quantitative. The reproducibility of the experimental results was excellent.

[*2] As no information on the magnitude of K_{DM} values is available, we can not discuss the stabilities of these tris-TTA chelate, β_3, except from the extraction constants as seen from Eq. (13). However, it would not be unreasonable to assume that the separation factor is concerned more with β_3 than with K_{DM}, or the organophilic tendencies of the metal chelates would resemble each other because the metal ions in the chelate complex molecules are surrounded by three common organophilic molecules.