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Studies of Actinium(III) in Various Solutions. III. Actinium(III) Complexes with Oxalate, Sulfate, Chloride, and Thiocyanate Ions in Perchlorate Media

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In previous papers,[1–4] the stability of the complexes of lanthanum(III), europium(III), lutecium(III), and americium(III) with oxalate, sulfate, chloride, and thiocyanate ions has been determined by means of the metal chelate extraction method. The present paper studies the complex formation of actinium(III) in these aqueous systems in order to obtain further information about the stability of the complexes of trivalent lanthanides and actinides.

Experimental

All of the experiments were carried out in a thermostatted room at 25°C. The actinium-228 tracer was separated from radium-228 and purified by a solvent extraction method which was described in Paper I of this series.[5] Sodium salts of oxalate, sulfate, chloride, and thiocyanate were dissolved in water, and the concentration was analyzed by gravimetry or volumetry. The other reagents and the experimental procedures are the same as those described in Paper II of this series[6] or in other papers.[1–4]

Results and Discussion

As the statistical treatment of the experimental data was the same as in previous papers,[1–4,7] only the final form of the equations will be shown in this paper.

The stability constants for the "n-th" complex with the L^{l-} ligand are defined as;

$$\beta_n = \frac{[AcL_n^{3-nl}]}{[Ac^{3+}][L^{l-}]^n} \tag{1}$$

The net distribution ratio of the extraction with a chelating extractant, HA, in the absence of and in the presence of the complexing ligand is described as:

$$D_0 = \frac{[AcA_3]_{org}}{[Ac^{3+}]} \tag{2}$$

$$D = \frac{[AcA_3]_{org}}{[Ac^{3+}]+[AcL^{3-l}]+\cdots+[AcL_n^{3-nl}]} = \frac{D_0}{1+\beta_1[L^{l-}]+\cdots+\beta_n[L^{l-}]^n} \tag{3}$$

The extraction constant is defined as:

$$K_{ex} = D_0[H^+]^3[HA]_{org}^{-3} \tag{4}$$

When the extraction constant is determined in the absence of the complexing ligand, the stability constants are given by the following equation:

$$\frac{D[H^+]^3[HA]_{org}^{-3}}{K_{ex}} = (1+\beta_1[L^{l-}]+\cdots+\beta_n[L^{l-}]^n)^{-1} \tag{5}$$

When the $\log D[H^+]^3[HA]_{org}^{-3}K_{ex}^{-1}$ *vs.* $\log[L^{l-}]$ plot is made from the experimental data, the stability constants are determined by a curve-fitting method.[7]

The constants obtained from the experimental data are summarized in Table 1, together with the previous results on the other four ions. As the present results were analyzed by the graphic method, no range of error is included in the results.

It was reported in a previous work[6] that the extraction data of actinium(III) with TTA were reproducible only when a mixed extractant, TTA and TBP in a diluent, was used. This was confirmed in the present work. Moreover, it was also found that the formation of aqueous chelates could be prevented by the use of the mixed solvent.[8] The data on the experiments in the thiocyanate system scattered a little for some unknown reasons and so the constants for the thiocyanate complexes might be somewhat less accurate than the others.

Almost no work seems to have been done on the stabilities of the actinium(III) complexes.[9]

The results in Table 1 may be summarized as follows:

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[1] T. Sekine, *Acta Chem. Scand.*, **19**, 1435 (1965).

[2] T. Sekine, *ibid.*, **19**, 1469 (1965).

[3] T. Sekine, *ibid.*, **19**, 1477 (1965).

[4] T. Sekine, *ibid.*, **19**, 1519 (1965).

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

[6] T. Sekine, Y. Koike and Y. Hasegawa, This Bulletin, **42**, 432 (1969).

[7] T. Sekine, M. Sakairi and Y. Hasegawa, *ibid.*, **39**, 2141 (1966).

[8] T. Sekine, M. Sakairi, F. Shimada and Y. Hasegawa, *ibid*, **38**, 847 (1965).

[9] L. G. Sillén and A. E. Martell, "Stability Constants," *Spec. Pub.*, **17**, the Chemical Society, London (1964).

TABLE 1. STABILITY CONSTANTS OF COMPLEXES OF La(III), Eu(III), Lu(III), Ac(III) AND Am(III) WITH OXALATE, SULFATE, CHLORIDE AND THIOCYANATE IONS

The data of Ac(III) complexes were taken from the present work and the rests were taken from Refs. 1—4.

Ionic medium		Oxalate 1M $NaClO_4$	Sulfate 1M $NaClO_4$	Chloride 4M $NaClO_4$	Thiocyanate 5M $NaClO_4$
La^{3+}	$\log \beta_1$	4.26 ± 0.11	1.45 ± 0.07	-0.22 ± 0.11	0.24 ± 0.06
	$\log \beta_2$	7.85 ± 0.12	2.46 ± 0.08	-0.64 ± 0.11	(< -0.62)
	$\log \beta_3$	10.27 ± 0.21	—	—	-0.73 ± 0.12
Eu^{3+}	$\log \beta_1$	4.77 ± 0.10	1.54 ± 0.06	-0.15 ± 0.10	0.32 ± 0.09
	$\log \beta_2$	8.72 ± 0.09	2.69 ± 0.05	-0.72 ± 0.17	$\sim -0.1 (< 0.25)$
	$\log \beta_3$	11.39 ± 0.12	—	—	-0.36 ± 0.15
Lu^{3+}	$\log \beta_1$	5.11 ± 0.08	1.29 ± 0.23	-0.35 ± 0.07	0.45 ± 0.09
	$\log \beta_2$	9.18 ± 0.12	$\sim 1.9 (< 2.49)$	-0.57 ± 0.05	$\sim -1.3 (< -0.06)$
	$\log \beta_3$	12.79 ± 0.08	3.36 ± 0.18	—	-0.14 ± 0.23
Ac^{3+}	$\log \beta_1$	3.56[a]	1.36[a]	−0.04[b]	−0.75[c]
	$\log \beta_2$	6.16	2.68	−1.04	−0.46
	$\log \beta_3$	—	—	−1.26	—
Am^{3+}	$\log \beta_1$	4.63 ± 0.08	1.57 ± 0.09	-0.15 ± 0.07	0.85 ± 0.05
	$\log \beta_2$	8.35 ± 0.09	2.66 ± 0.08	-0.69 ± 0.10	—
	$\log \beta_3$	11.15 ± 0.07	—	—	0.55 ± 0.15
	$\log \beta_4$	—	—	—	0.00 ± 0.15

The range of the error is three times the standard deviation. The values in parentheses after $\log \beta_2$ give the value of $\log(\beta_2 \pm 3\sigma)$.

Composition of the organic phase and the extraction constant are as follows.

a) 0.03M TTA in CCl_4 with 0.2M TBP $\log K_{ex} = -5.04$
b) 0.2M TTA in CCl_4 with 0.3M TBP $\log K_{ex} = -5.55$
c) 0.015M TTA in CCl_4 with 0.1M TBP $\log K_{ex} = -5.93$

The dissociation constant of oxalic acid employed for the calculation is $pK_{a_2} = 3.54$ (Ref. 2). The hydrogen ion concentration was 1×10^{-3}—3×10^{-4} except for the chloride system which contained 0.01M H^+.

(i) The actinium(III) complexes are more stable in the order: thiocyanate<chloride<sulfate<oxalate. (ii) The oxalate complexes of actinium(III) are less stable than those of the other metal ions. (iii) No very remarkable differences are observed among the sulfate or chloride complexes of actinium and those of the other ions. (iv) The thiocyanate complexes of actinium(III) are much weaker than those with the other ions.

It may be generally assumed that the actinium(III) ion forms the least stable complexes among the trivalent metal ions presented in Table 1, because it is the largest and the least basic ion. This assumption seems to hold in the oxalate complexes. However, it is not obviously true in the sulfate or chloride complexes. This may be due to the fact that the stabilities of weak complexes of analogous metal ions are influenced by many other factors, such as the hydration. Surls and Choppin[10] pointed out, on the basis of their ion-exchange data, that the trivalent actinides form more stable thiocyanate complexes than the trivalent lanthanides; this agrees with the prediction of Diamond[11] based on the assumption of f-orbital hybridization that thiocyanate ions should complex more strongly with actinides than with lanthanides. Similar results were obtained for the complexes of americium(III), as may be seen in Table 1. Actinium(III), however, forms less stable thiocyanate complexes than does lanthanum(III). One possible explanation for the lower stabilities of the actinium(III) thiocyanate complexes may be that the fourteen 5f-electrons enter the actinides beginning at thorium (or that the 5f-electrons enter beginning with thorium).[12] If so, 5f-electrons, which are connected with the fact that the stability of the thiocyanate complexes of americium(III) is greater than that of europium(III), should not contribute the formation of the actinium(III) thiocyanate complexes.

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[10] J. P. Surls, Jr., and G. R. Choppin, *J. Inorg. Nucl. Chem.*, **4**, 62 (1957).

[11] R. M. Diamond, UCRL-1434 (1951).

[12] J. J. Katz and G. T. Seaborg, "The Chemistry of the Actinide Elements," Methuen, London (1957).