Studies of the Liquid-Liquid Partition Systems. III. The Solvent Extraction of Americium(III) and Europium(III) Thiocyanate Complexes with Tributylphosphate

By Tatsuya SEKINE

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Two different liquid-liquid partition methods have been applied to the determination of the stability constants of various metal complexes in aqueous solutions.

By the first method, the metal ion is extracted with an organophilic chelating acid in the organic phase. The complex formation is determined from the decrease in the chelate extraction caused by the complex formation in the aqueous phase.

By the second method, the metal ion is extracted, as an adduct of the neutral complex, with an organophilic neutral ligand in the organic phase. The complex formation is determined from the change in the metal extraction caused by the change in the relative concentration of the neutral complex in the aqueous phase.

The principles of these two methods are quite different, and the stability constants of metal complexes in an aqueous solution may be determined quite independently by the two methods.

The chelate extraction method has been applied to various complex formation systems; the stability constants thus determined have been found to agree with the constants determined by various other methods. On the other hand, the adduct extraction method has not often been applied except in some recent studies of the mononuclear hydrolysis of metal ions,[1] and no attempt seems to have been made to compare the results given by this method with the results given by the other methods.

The present work studied the thiocyanate complexes of trivalent americium and europium by the adduct extraction method.

As was reviewed in the previous paper,[2] a remarkable difference in ion-exchange behavior has been observed between the trivalent actinide and lanthanide ions in thiocyanate media; this has been explained in terms of the stronger complexing of actinides than of lanthanides with thiocyanate ions. The stability constants of these complexes in 5 M $Na(SCN, ClO_4)$ were determined by the chelate extraction method at 25°C.[2] The results showed that americium(III) forms more stable thiocyanate complexes than does europium(III).

The extraction of the neutral metal thiocyanate complexes as an adduct of various extractants has been reported by many authors.[3] Yoshida[4] reported that europium(III) was extracted with tributylphosphate (TBP) from ammonium thiocyanate solutions and that the distribution ratio was quite different when the inert diluent of TBP was different; he concluded that the metal complex in the organic phase was a tetrasolvate of TBP.

In the present work, the distribution of americium(III) and europium(III) between hexane solutions of TBP and aqueous solutions of sodium thiocyanate will be studied. The stability constants of the complexes will be calculated from the distribution data and compared with the results given in Ref. 2. Some discussion will also be made of the salting-out of the metal ions by the electrolytes in the aqueous phase.

Statistical Treatment

The formation of the metal thiocyanate complexes and the over-all stability constants can be described as follows:

$$M^{3+} + nSCN^- \rightleftarrows M(SCN)_n^{3-n} \qquad (1)$$

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

In the present paper, the net distribution ratio of the metal ions between the organic and aqueous phases is always defined as:

$$D = [M(III)]_{org,total}/[M(III)]_{total} \qquad (3)$$

The subscript " org " denotes a chemical species in the organic phase, while the absence of a

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[1] D. Dyrssen and T. Sekine, *J. Inorg. Nucl. Chem.*, **26** 981 (1964); D. Dyrssen and P. Lumme, *Acta Chem. Scand.*, **16**, 1785 (1962); T. Sekine, *Acta Chem. Scand.*, to be published.

[2] T. Sekine, *J. Inorg. Nucl. Chem.*, **26**, 1463 (1964). The full paper will be published in *Acta Chem. Scand.*

[3] The previous work is reviewed in G. H. Morrison and H. Freiser, " Solvent Extraction in Analytical Chemistry," John Wiley & Sons Inc., New York (1957); L. G. Sillén, and A. E. Martell, " Stability Constants," spec. pub. No. 17, The Chemical Society, London (1964). and revised edition to be published.

[4] H. Yoshida, *J. Inorg. Nucl. Chem.*, **24**, 1257 (1962).

subscript denotes a chemical species in the aqueous phase.

The Metal Chelate Extraction Method.—The details of this method were given in Ref. 2; only the final equation will be given in the present paper:

$$D_0/D=K_0/K=1+\sum_1^n \beta_n[\mathrm{SCN}^-]^n \qquad (4)$$

In Eq. 4, the subscript "0" denotes the net distribution ratio of the metal or the metal chelate extraction constant when no complexes are formed in the aqueous phase. The metal chelate extraction and the extraction constant are described as:

$$\mathrm{M}^{3+} + 3\mathrm{HA}_{(\mathrm{org})} \rightleftarrows \mathrm{MA}_{3(\mathrm{org})} + 3\mathrm{H}^+$$

$$K_0=D_0[\mathrm{H}^+]^3[\mathrm{HA}]^{-3}{}_{\mathrm{org}} \qquad (5)$$

where HA denotes an organophilic chelating acid.

Equation 4 shows that the stability constants of the thiocyanate complexes, MSCN^{2+}, $\mathrm{M(SCN)}_2{}^+$,$\cdots$ can be determined from the decrease in the metal chelate extraction and in the concentration of the ligand.

The Adduct Extraction Method.—In an aqueous solution where the metal complexes are formed with thiocyanate ions, the metal concentration can be written as:

$$\begin{aligned}[\mathrm{M(III)}]_{\mathrm{total}} &= [\mathrm{M}^{3+}] + [\mathrm{MSCN}^{2+}] \\ &+ [\mathrm{M(SCN)}_2{}^+] + [\mathrm{M(SCN)}_3] \\ &+ [\mathrm{M(SCN)}_4{}^-] + \cdots \qquad (6)\end{aligned}$$

When the neutral complex, $\mathrm{M(SCN)}_3$, is extracted with an organophilic neutral ligand, N, the equilibrium constant is described as:

$$\mathrm{M(SCN)}_3 + n\mathrm{N}_{(\mathrm{org})} \rightleftarrows \mathrm{M(SCN)}_3\mathrm{N}_{n(\mathrm{org})} \qquad (7)$$

$$K_n = [\mathrm{M(SCN)}_3\mathrm{N}_n]_{\mathrm{org}}/[\mathrm{M(SCN)}_3][\mathrm{N}]^n{}_{\mathrm{org}} \qquad (8)$$

The total metal concentration in the organic phase is written as:

$$\begin{aligned}[\mathrm{M(III)}]_{\mathrm{org,total}} &= [\mathrm{M(SCN)}_3\mathrm{N}]_{\mathrm{org}} \\ &+ [\mathrm{M(SCN)}_3\mathrm{N}_2]_{\mathrm{org}} + \cdots \qquad (9) \\ &= \sum_1^n K_n[\mathrm{M(SCN)}_3][\mathrm{N}]^n{}_{\mathrm{org}} \qquad (10)\end{aligned}$$

When the concentration of the extracting ligand, N, in the organic phase is constant, Eq. 10 can be written as:

$$[\mathrm{M(III)}]_{\mathrm{org,total}} = K_{\mathrm{DM}}[\mathrm{M(SCN)}_3] \qquad (11)$$

From Eqs. 6 and 10, the net distribution ratio of M(III) in Eq. 3 can be written as:

$$\begin{aligned}D=K_{\mathrm{DM}}[\mathrm{M(SCN)}_3]/([\mathrm{M}^{3+}] &+ [\mathrm{MSCN}^{2+}] \\ &+ [\mathrm{M(SCN)}_2{}^+] + [\mathrm{M(SCN)}_3] \\ &+ [\mathrm{M(SCN)}_4{}^-] + \cdots) \qquad (12)\end{aligned}$$

From Eqs. 2 and 12, the distribution of M(III) can be written as:

$$\begin{aligned}D = K_{\mathrm{DM}}\beta_3[\mathrm{SCN}^-]^3/(1 &+ \beta_1[\mathrm{SCN}^-] \\ &+ \beta_2[\mathrm{SCN}^-]^2 + \beta_3[\mathrm{SCN}^-]^3 \\ &+ \beta_4[\mathrm{SCN}^-]^4 + \cdots) \qquad (13)\end{aligned}$$

or it can also be written as:

$$\begin{aligned}D=K_{\mathrm{DM}}/(\beta_3{}^{-1}[\mathrm{SCN}^-]^{-3} &+ \beta_1\beta_3{}^{-1}[\mathrm{SCN}^-]^{-2} \\ &+ \beta_2\beta_3{}^{-1}[\mathrm{SCN}^-]^{-1} + 1 \\ &+ \beta_4\beta_3{}^{-1}[\mathrm{SCN}^-] + \cdots) \qquad (14)\end{aligned}$$

Thus we can determine the stability constants, β_n, from the net distribution ratio, *D*, and the concentration of thiocyanate ions if the concentration of the extracting ligand in the organic phase is kept constant.

Experimental

Reagents. — The europium 152+154 tracer was obtained from the Oak Ridge National Laboratory as a hydrochloric acid solution. The americium 241 tracer was obtained from the Radiochemical Center, Amersham, also as a hydrochloric acid solution. They were then diluted with 5 M sodium perchlorate or 5 M sodium thiocyanate and used as the stock solutions. All of the reagents used were of analytical grade. Sodium perchlorate was prepared from sodium carbonate and perchloric acid and recrystallized two times. Tributylphosphate (TBP) was washed with 0.1 M perchloric acid, water and 0.1 M sodium hydroxide, and then with water until the washed solution gave a neutral color on an indicator paper. Stock solutions of sodium perchlorate and sodium thiocyanate were also prepared. The concentration of the sodium perchlorate stock solution was determined from the difference in the weight of a portion of the stock solution before and after it had been dried in an air-bath at 120°C. The concentration of the thiocyanate stock solution was determined by argentimetry.

Procedures.—All of the procedures were carried out in a thermostatted room at 25±0.5°C. The tracer solution, various amounts of the sodium thiocyanate solution, the sodium perchlorate solution and the TBP hexane solution were placed in stoppered glass tubes. The aqueous phase was buffered at pH 4 to 5 with a small amount of acetate. The initial volume of both the organic and aqueous phases was 5.0 ml. The initial concentration of the tracer in the aqueous phase was less than 10^{-6} M.

The two phases in the tubes were agitated with a mechanical rotator at 20 r.p.m. for about two hours and centrifuged at 1500 r.p.m. for about three minutes. Two milliliters of the solution was then pipetted from both phases and transferred into small tubes. The γ-radioactivity of the solutions was determined with a well-type (NaI) scintillation counter, and the net distribution ratio of M(III) was determined to be:

$$D=\frac{\gamma\text{-count-rate per 2 ml. of the organic phase}}{\gamma\text{-count-rate per 2 ml. of the aqueous phase}} \qquad (15)$$

Results

In the present study, the hydrogen ion concentration of the aqueous solution was buffered at pH 4 to 5. This was enough to prevent the association of SCN^- with H^+ and the hydrolysis of the metal ion. In the preliminary experiments, is was confirmed that the change in the pH value within this range did not change the metal distribution. The expression " 5% TBP in hexane " will always mean a 5% TBP hexane solution as expressed by the volume percentage. The temperature was always 25± 0.5°C. The description " 5 M Na(SCN, ClO_4)" denotes that the concentration of sodium ions is always 5 M; the sum of the thiocyanate and perchlorate concentrations is also kept at 5 M.

The Extraction of Americium(III) and Europium(III) from Sodium Thiocyanate Solutions.—Figure 1 gives the plot of log D vs. log [SCN^-] when the organic phase was 5% TBP in hexane and when the aqueous phase was sodium thiocyanate solutions (the total electrolyte concentration was not kept constant). We may see in the figure that the distribution of the metal ions increases drastically with the increase in the thiocyanate concentration. The slope d log D/d log [SCN^-] also increases with the increase in the thiocyanate concentration. The separation factor of americium(III) and europium(III), D_{Am}/D_{Eu}, is largest in the lowest thiocyanate concentration region; it decreases to unity in the highest region.

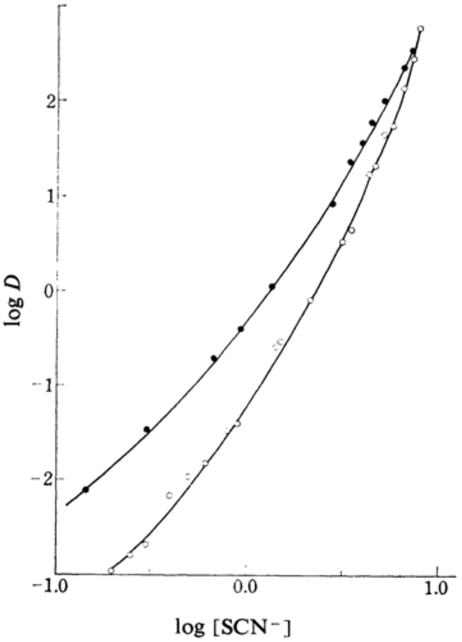

Fig. 1. Distribution of americium(III) (●) and europium(III) (○) between 5% TBP (by volume) in hexane and sodium thiocyanate solutions at pH 4 to 5 (total electrolyte concentration is not constant).

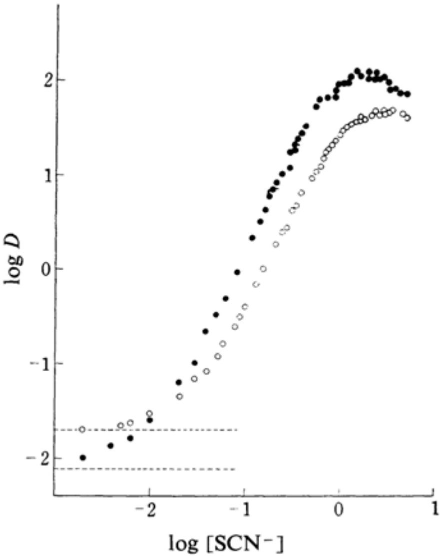

Fig. 2. Distribution of americium(III) (●) and europium(III) (○) between 5% TBP (by volume) in hexane and 5 M Na(SCN, ClO_4) at pH 4 to 5. The dotted lines give the distribution ratio of Am(III) (log D = −2.10) and Eu(III) (log D = −1.70) when the aqueous phase is 5 M $NaClO_4$ at pH 4 to 5.

The Extraction of Americium(III) and Europium(III) from 5 M Na(SCN, ClO_4).—Figure 2 gives the plot of log D vs. log [SCN^-] of americium(III) and europium(III) when the organic phase was 5% TBP in hexane and when the aqueous phase was 5 M Na(SCN, ClO_4). In the figure, we see that the distribution ratio of the metal ions is constant in the lowest thiocyanate concentration region. The distribution ratio increases with the increase in the thiocyanate concentration until it reaches a maximum, and then it decreases slightly in the highest concentration region.

From Eqs. 12 to 14 we may see that the slope d log D/d log [SCN^-] changes from +3 to $3-n$ with the change in the thiocyanate concentration corresponding to the dominant metal complex species, M^{3+}, $MSCN^{2+}$,···, $M(SCN)_n{}^{3-n}$ in the aqueous phase. It seems that the constancy of the distribution ratio in the lowest thiocyante concentration region can be explained by the extraction of the ion-pair of the metal ion with the perchlorate ion, $M^{3+}(ClO_4{}^-)_3\cdot(TBP)_n$. It may be also possible that mixed complexes are extracted from the aqueous solutions at a lower thiocyanate concentration and that the distribution ratio of the metal ions may generally be described as:

$$D=\sum_{0}^{3}[\mathrm{M(SCN)}_a(\mathrm{ClO_4})_{3-a}]_{\mathrm{org}}/\sum_{0}^{n}[\mathrm{M(SCN)}_n{}^{3-n}] \qquad (16)$$

The separation factor, $D_{\mathrm{Am}}/D_{\mathrm{Eu}}$, changes from 0.4 to 10 between a 0.1 M and a 1.0 M thiocyanate solution and decreases in the highest thiocyanate concentration region.

TABLE I. TWO PHASE DISTRIBUTION OF AMERICIUM(III) AND EUROPIUM(III)

Organic phase; 5% (by volume) TBP in hexane
Aqueous phase; 5 M Na(SCN, ClO_4) at pH 4 to 5
Temperature 25±0.5°C

log [SCN^-]	log D_{Am}	log [SCN^-]	log D_{Eu}
0.681	1.86	0.681	1.64
0.644	1.87	0.644	1.65
0.623	1.86	0.501	1.68
0.602	1.87	0.477	1.68
0.556	1.91	0.477	1.71
0.532	1.91	0.415	1.66
0.505	1.94	0.398	1.65
0.501	1.90	0.362	1.64
0.477	2.01	0.342	1.65
0.477	2.01	0.322	1.63
0.477	2.01	0.301	1.64
0.415	2.00	0.279	1.62
0.398	2.08	0.255	1.65
0.362	2.07	0.230	1.58
0.342	2.03	0.230	1.60
0.301	2.02	0.176	1.56
0.279	2.07	0.146	1.56
0.230	2.03	0.146	1.58
0.176	2.08	0.114	1.53
0.176	2.06	0.114	1.56
0.114	2.03	0.079	1.51
0.079	1.99	0.079	1.51
0.000	1.96	0.041	1.53
−0.036	1.90	0.000	1.43
−0.046	1.87	0.000	1.48
−0.076	1.83	−0.046	1.37
−0.131	1.84	−0.097	1.33
−0.155	1.81	−0.119	1.30
−0.208	1.80	−0.143	1.26
−0.268	1.73	−0.167	1.23
−0.366	1.54	−0.194	1.20
−0.409	1.47	−0.222	1.14
−0.444	1.38	−0.222	1.13
−0.468	1.33	−0.252	1.07
−0.495	1.26	−0.301	0.99
−0.523	1.25	−0.398	0.82
−0.585	1.09	−0.468	0.70
−0.620	1.08	−0.509	0.64
−0.658	0.90	−0.553	0.49
−0.699	0.86	−0.602	0.42
−0.745	0.79	−0.658	0.30
−0.796	0.66	−0.796	0.01
−0.854	0.52	−0.886	−0.14
−0.921	0.36	−1.000	−0.38

The Calculation of the Stability Constants.—From the results in the Fig. 2, we can calculate the stability constants of the metal thiocyanate complexes in 5 M Na(SCN, ClO_4).

For the calculation of the stability constants, the data should be taken from the thiocyanate concentration region, where the extraction of the mixed complexes is practically negligible. In Fig. 2, we see that the slope $d \log D/d \log[\mathrm{SCN^-}]$ is about +2 above $\log[\mathrm{SCN^-}]=-1.3$, and so it may be possible to say that the $MSCN^+$ complex is dominant in this region and that only the $M(SCN)_3$ species is extracted into the organic phase. The results in Ref. 2 also seem to support this estimate.

From this, the data used for the calculation were taken from the thiocyanate concentration region above 0.1 M. The data are given in Table I.

In the present study, Eq. 14 was used for the calculation because it is not possible to calculate the β_1 without the distribution data in the region where both of the M^{3+} and the $MSCN^{2+}$ species exist in the aqueous phase (and where the slope in Fig. 2 should be from

TABLE II. EQUILIBRIUM CONSTANTS OF AMERICIUM(III) AND EUROPIUM(III) THIOCYANATE COMPLEXES IN 5 M Na(SCN, ClO_4) AT 25°C

$\beta_n=[\mathrm{M(SCN)}_n{}^{3-n}]/[\mathrm{M^{3+}}][\mathrm{SCN^-}]^n$
$\beta_1\beta_3{}^{-1}=[\mathrm{MSCN^{2+}}][\mathrm{SCN^-}]/[\mathrm{M(SCN)_3}]$
$\beta_2\beta_3{}^{-1}=[\mathrm{M(SCN)_2{}^+}][\mathrm{SCN^-}]/[\mathrm{M(SCN)_3}]$
$\beta_4\beta_3{}^{-1}=[\mathrm{M(SCN)_4{}^-}]/[\mathrm{M(SCN)_3}][\mathrm{SCN^-}]$
$K_{\mathrm{DM}}=[\mathrm{M(SCN)_3}]_{\mathrm{org}}/[\mathrm{M(SCN)_3}]$
(organic phase: 5% (by volume) TBP in hexane)

(A) Equilibrium constants obtained by the adduct extraction method (present work).

	Am(III)	Eu(III)
$\beta_1\beta_3{}^{-1}$	1.68±0.84	2.48±0.24
$\beta_2\beta_3{}^{-1}$	no evidence	∼0.9(<0.75)
$\beta_4\beta_3{}^{-1}$	0.74±0.51	0.34±0.07
K_{DM}	321±146	113±10

(B) Equilibrium constants obtained by the chelate extaction method in Ref. 2.

	Am(III)	Eu(III)
β_1	7.02±0.28	2.08±0.14
β_2	no evidence	∼0.9(<1.5)
β_3	3.57±0.41	0.44±0.15
β_4	1.00±0.12	no evidence
$\beta_1\beta_3{}^{-1}$	2.0	4.7
$\beta_2\beta_3{}^{-1}$	no evidence	erroneous
$\beta_4\beta_3{}^{-1}$	0.28	no evidence

(the limit of error is 3σ)

+3 to +2). The equilibrium constants thus calculated show the following:

$$\beta_1\beta_3^{-1}=[\mathrm{MSCN}^{2+}][\mathrm{SCN}^-]^2/[\mathrm{M(SCN)_3}]$$

$$\beta_2\beta_3^{-1}=[\mathrm{M(SCN)_2}^+][\mathrm{SCN}^-]/[\mathrm{M(SCN)_3}]$$

$$\beta_4\beta_3^{-1}=[\mathrm{M(SCN)_4}^{-1}]/[\mathrm{M(SCN)_3}][\mathrm{SCN}^-]$$

The constants were first estimated graphically, and then the estimates were refined by a generallized least-squares method using the computer program "LETAGROP VRID."[5] The details of the calculation were the same as those given in previous work.[1,2] The equilibrium constants thus determined are given in Table II, together with the constants calculated from the results in Ref. 2. In the table, the limit of the error is 3σ. The expression for the $\beta_2\beta_3^{-1}$ of europium(III), ~0.3 (<0.75), means that the calculated value is 0.3 but it may range in the region $0 \leq \beta_2\beta_3^{-1} < 0.75$ if 3σ is employed as the limit of the error.

The Change in the Distribution Ratio upon the Addition of Perchlorate.—Figure 3 gives the plot of the distribution of europium(III), log *D* vs. log [SCN⁻], when the organic phase was 5% TBP in hexane and when the aqueous phase was (i) sodium thiocyanate, (ii) 3 M Na(SCN, ClO₄) and (iii) 5 M Na(SCN, ClO₄).

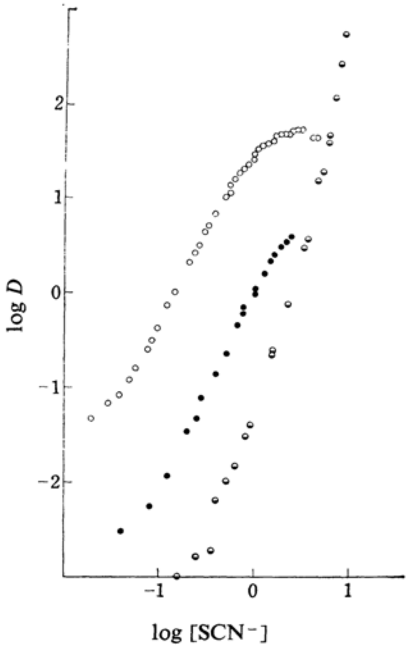

Fig. 3. Distribution of europium(III) between 5% TBP hexane (by volume) and (i) sodium thiocyanate (◒), (ii) 3 M Na(SCN, ClO₄) (●), (iii) 5 M Na(SCN, ClO₄) (○). pH of the aqueous phase is 4 to 5.

In the figure we can see that the slope d log *D*/d log [SCN⁻] increases drastically with the increase in the thiocyanate concentration when the aqueous phase contains only sodium thiocyanate, but that the slope changes only gradually when the total electrolyte concentration is kept constant at 3 M Na(SCN, ClO₄) or 5 M Na(SCN, ClO₄). This indicates that the metal distribution is very much increased

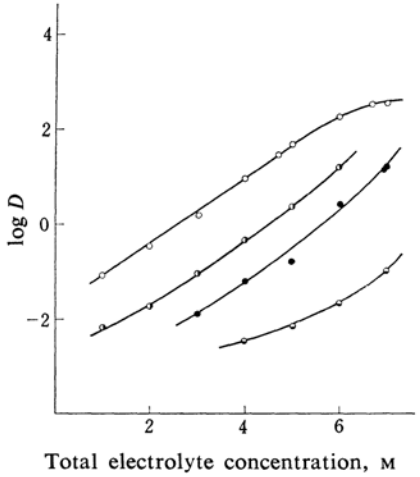

Fig. 4. Increase of the distribibution ratio of europium(III) by addition of sodium perchlorate. Organic phase: TBP 5% (by volume) in hexane. Aqueous phase: at pH 4 to 5 ○ [SCN⁻]=1.0 M, ◑ [SCN⁻]=0.28 M, ● [SCN⁻]=0.10 M, ◒ [SCN⁻]=0 M.
The abscissa gives the total electrolyte concentration in the aqueous phase (the sum of the concentrations of sodium perchlorate and sodium thiocyanate).

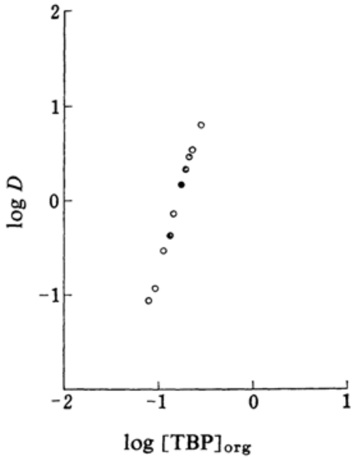

Fig. 5. Dependency of the distribution ratio of europium(III) on the concentration of tributylphosphate.
Organic phase: TBP in hexane.
Aqueous phase: 1 M NaSCN+2 M NaClO₄ at pH 4 to 5.

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[5] N. Ingri and L. G. Sillén, *Acta Chem. Scand.*, **16**, 173 (1962); *Arkiv Kemi*, **23**, 97 (1964).

by the addition of sodium perchlorate, even when the concentration of thiocyanate ions is kept constant.

Figure 4 gives the change in the log D when various amounts of sodium perchlorate are added to the solutions while the concentration of thiocyanate ion is kept constant.

In the figure we can see that the addition of perchlorate increases the distribution greatly.

Europium(III) is extracted with TBP, even from a sodium perchlorate solution, and the distribution ratio is also greatly increased by the increase in the perchlorate concentration.

The TBP Dependency of the Metal Distribution.—Figure 5 gives the plot of log D vs. log [TBP]$_{org}$ when the aqueous phase contains 1 M sodium thiocyanate and 2 M sodium perchlorate. In this figure we can see that the TBP dependency of the metal distribution is between 3 and 4 in the TBP concentration range.

Discussion

The Stability Constants of the Metal Thiocyanate Complexes.—The results in Fig. 2 and the equilibrium constants in Table II may be summarized as follows.

The constants determined by the chelate extraction method in Ref. 2 indicate that:

(i) The americium(III) thiocyanate complexes are always more stable than the europium(III) thiocyanate complexes.

(ii) No evidence of the complex $Am(SCN)_2^+$ can be observed. The stability constants for the $Eu(SCN)_2^+$ is erroneous, and it is not possible to recognize this species definitely.

(iii) The stability constants for the $Am(SCN)_4^-$ species can be determined, but no evidence of the $Eu(SCN)_4^-$ complex is observed when the thiocyanate concentration is below 5 M.

On the other hand, the results obtained by the present TBP adduct extraction method indicate that:

(i) In the lower thiocyanate concentration region, both americium(III) and europium(III) are extracted with perchlorate ions, and it is not possible to determine the constant for the equilibrium, $M^{3+} + SCN^- \rightleftarrows MSCN^{2+}$.

(ii) It is also not possible to determine the stability constants of the other complexes in Eq. 2. The equilibrium constants obtained are only for the formation of the $M(SCN)_3$ complex from the $MSCN^{2+}$, $M(SCN)_2^+$ and $M(SCN)_4^-$ complexes.

(iii) No evidence of the complex $Am(SCN)_2^+$ can be observed. The equilibrium constant, $\beta_2\beta_3^{-1} = [Eu(SCN)_2^+][SCN^-]/[Eu(SCN)_3]$, is very erroneous, and it is not possible to confirm this complex definitely.

(iv) The formation of the $Eu(SCN)_4^-$ complex, which was not observed in the chelate extraction method, is here observed in the heighest thiocyanate concentration region. The stability constant for the $Am(SCN)_4^-$ complex is higher than that obtained by the chlate extraction method.

(v) The distribution constant of the $Am(SCN)_3$ species between the aqueous and the organic phases, K_{DM} in Eq. 11, is higher than that of the $Eu(SCN)_3$ species.

Thus, from Table II, we may conclude that the equilibrium constants as determined by these two methods nearly agree with each other except for the constant for the formation of the $Eu(SCN)_4^-$ complex.

In the highest thiocyanate concentration region, the anion in the aqueous phase is almost entirely changed from ClO_4^- to SCN^-; this may cause some change in the activity of the chemical species in the aqueous phase, even when the total electrolyte concentration is kept constant.

However further information on these systems seems to be necessary in order for us to be able to explain the difference in the constants obtained by these two methods.

The Effect of the Electrolyte Concentration on the Metal Distribution.—The increase in the distribution of the metal ions by the addition of various amounts of perchlolate is very remarkable. The increase can be caused by: (i) the extraction of the mixed complexes with thiocyanate and perchlorate ions; (ii) the increase in the stability of the $M(SCN)_3$ species in the aqueous phase, or (iii) the increase in the distribution constant of the $M(SCN)_3$ complex, K_{DM} in Eq. 11.

The extraction of the mixed complexs may not always be important, because the stability constants in Table II, obtained by calculations which neglect the mixed complexs, seem to be reasonable.

The increase in the stability of the $M(SCN)_3$ may also not be very important, because we see in Fig. 3 that the plot of log D vs. log $[SCN^-]$ of the metal extraction from 3 M $Na(SCN, ClO_4)$ is nearly parallel to that of the extraction from 5 M $Na(SCN, ClO_4)$. If the difference in the distribution ratio is caused by the increase in the relative concentration of the $M(SCN)_3$, the shape of the extraction curve should be different (cf. Eqs. 12 to 14). However, it is not possible to discuss this problem in more detail before we know the equilibrium constants in 3 M $Na(SCN, ClO_4)$.

The final explanation, that the addition of sodium perchlorate increases the K_{DM} in Eq. 11, seems to be most reasonable. The increase in the K_{DM} can be caused both by the increase in the thermodynamical activity of the $M(SCN)_3$ species and by the decrease in the activity of water in the aqueous phase. The decrease in the activity of water may be favorable for the dissociation of the hydrated water of the $M(SCN)_3$ moleculces when they pass through the intersurface between the two phases. However, further information seems to be necessary before we can discuss this problem further.

In Fig. 1 we see that the distribution ratios always increase with the increase in the thiocyanate concentration. When the total electrolyte concentration is kept constant with sodium perchlorate, a slight decrease is observed in the highest thiocyanate concentration region for both americium and europium; this can be explained in terms of the formation of the negative charged species, $M(SCN)_4^-$. The continuous increase in the distribution ratios in Fig. 1, even above 5 M sodium thiocyanate, may be explained in terms of the salting-out effect of the sodium thiocyanate. The formation of the negative charged species by the increase in the thiocyanate concentration should decrease the relative concentration of the $M(SCN)_3$ species in the aqueous phase, and this in turn should decrease the metal distribution. However, as we see in Figs. 3 and 4, the salting-out in these systems is very large, and even though the relative concentration of the $M(SCN)_3$ is decreased by the increase in the thiocyanate concentration (which is not favorable for the metal distribution), the increase in the distribution constant of the $M(SCN)_3$, K_{DM}, by the salting-out exceeds the decrease by the former.

Thus, we may conclude that the addition of sodium thiocyanate in the experiment in Fig. 1 causes both the complex formation and the salting-out effect.

The Solvation Number of TBP in the Adduct Complexes.—The TBP dependency of the distribution ratio of europium(III) was estimated to be between 3 and 4. This means that if the activity coefficient of TBP in the organic phase can be assumed to be constant, the adduct complexes in the organic phase are a mixture of $Eu(SCN)_3(TBP)_3$ and $Eu(SCN)_3(TBP)_4$. This is a little different from the conclusion of Yoshida.[4] The difference in the composition of the aqueous phase can cause this difference.

Summary

The two-phase distribution of americium(III) and europium(III) has been studied between the hexane solution of tributylphosphate (TBP) and the aqueous solution of sodium thiocyanate at 25°C. From the distribution data when the organic phase was 5% (by volume) TBP in hexane and the aqueous phase was 5 M $Na(SCN, ClO_4)$, the following equilibrium constants have been obtained by a least-squares method:

	Am(III)	Eu(III)
$\beta_1\beta_3^{-1}$	1.68 ± 0.84	2.53 ± 0.24
$\beta_2\beta_3^{-1}$	no evidence	~0.3 (<0.75)
$\beta_4\beta_3^{-1}$	0.74 ± 0.51	0.34 ± 0.07
K_{DK}	321 ± 146	113 ± 10

(The limit of error is 3σ)

A remarkable salting-out effect has been observed when sodium perchlorate is added to the aqueous phase. This salting-out effect has been discussed, as has the solvation number of TBP in the adduct complexes in the organic phase.

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Department of Chemistry
Tokyo College of Science
Kagurazaka, Shinjuku-ku, Tokyo