726 © *1982 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **55**, *726—729 (1982)* [Vol. 55, No. 3

# Investigation on the Complex Formation of Some Lanthanoids(III) and Actinoids(III) with Chloride and Bromide

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(Received April 17, 1981)

Stability constants ($\beta_1$ and $\beta_2$) of the chloro and bromo complexes of tervalent Sm, Eu, Gd, Tb, Ac, Am, Cm, Bk, and Cf were determined by a solvent extraction method under the conditions of ionic strength and acidity to be 3.0 and 0.15 M (1 M=1 mol/dm$^3$), respectively. Stability constants obtained were discussed with respect to the formation mechanism. A much larger contribution from the inner sphere complex formation was observed in chloro complexes than bromo complexes on tripositive actinoids.

Diamond *et al.*[1)] reported the difference in the distribution behavior between tripositive actinoids and lanthanoids on the cation exchange resin at high concentrations of HCl. Hulet *et al.*[2)] presented the anion exchange method using 10 M LiCl as an eluent to separate tripositive actinoids from lanthanoids, and showed that the distribution ratio($D_v$) of actinoids were higher than those of lanthanoids. These phenomena have been explained by the difference in the complex formation between actinoids(III) and lanthanoids(III). Only a few studies have been carried out to determine the stability constants for many actinoids(III) under those conditions.[3)] Therefore, the pronounced difference in the complex formation between actinoids(III) and lanthanoids(III) can not be discussed in detail from the available data on stability constants. In this paper, we prepared the adequate tracers of Sm, Ac, Cm, and Bk which are not available in general, determined the stability constants accurately under the same conditions by a solvent extraction method with bis(2-ethylhexyl)hydrogenphosphate, HDEHP, and discussed the phenomena mentioned above.

## Experimental

*Radioisotopes.* $^{152,154}$Eu, $^{153}$Gd, $^{160}$Tb, and $^{252}$Cf were obtained from The Radiochemical Centre, Amersham, and $^{241}$Am from Oak Ridge National Laboratory. $^{225}$Ac was isolated from $^{229}$Th which was obtained from $^{233}$U.[4)] $^{242,243,244}$Cm, obtained and purified as reported previously,[5,6)] was used in this experiment. $^{145}$Sm and the mixture of $^{243}$Bk and $^{244}$Bk[7)] were produced by means of $^{142,143,144}$Nd+$\alpha$ and $^{241}$Am+$\alpha$ reaction, respectively. For the bombardment, A. V. F. cyclotron at the Cyclotron and Radioisotope Center, Tohoku University, was used. $^{145}$Sm was purified by successive extraction with HDEHP. $^{243,244}$Bk was separated from irradiated $^{241}$Am and fission products by HDEHP extraction of quadrivalent Bk. These tracers were dissolved into 3.0 M HClO$_4$ solutions and stored in Pyrex vessels.

*Reagents.* The organic extractant HDEHP was purified by the copper-salt precipitation method,[8)] and stored as copper salt. LiCl and LiClO$_4$ were prepared from a reagent grade Li$_2$CO$_3$. LiBr was obtained in 99.9% purity from MITSUWA Chemical Reagents Co., Ltd. These lithium salts were recrystallized twice before use. All the other chemicals were of the highest grade available.

*Apparatus.* Gamma-rays of $^{152,154}$Eu, $^{153}$Gd, $^{160}$Tb, $^{241}$Am, and $^{243}$Cm were counted by means of an auto-well scintillation counter, Packard model 5230. $^{225}$Ac, in radioequilibrium with the decay series nuclides, was assayed by the same apparatus. $^{252}$Cf was assayed by the prompt fission $\gamma$-rays. For the counting, another well type NaI(Tl) ($1.5\phi \times 2''$) counting system was used with a discriminator adjusted to 2.8 MeV with respect to $\gamma$-energy. For $^{145}$Sm, 61 keV $\gamma$-ray was counted by a $\gamma$-ray spectrometry system; Tracor Northern TN-11, using an intrinsic Ge(PGT model IGC13) and a Ge(Li) (ORTEC model 8101-1820) detectors. For mixture of $^{243}$Bk and $^{244}$Bk, the KX-rays of Cm and 218 keV $\gamma$-ray were counted by the same $\gamma$-ray spectrometry system.

*Procedures.* Six ml of sample solution was prepared by mixing of appropriate amounts of the stock solution, 3.0 M LiClO$_4$ solution, and 3.0 M LiCl or LiBr solution in a separatory funnel. The sample solution was equilibrated with an equal volume of the HDEHP/octane solution pre-equilibrated by a solution of the same composition as the sample solution. The HDEHP/octane solution was prepared just before the experiment converting the Cu(DEHP)$_2$ to acid form. To determine the relation between distribution ratio and ligand concentration, the acidity was fixed at 0.15 M and the concentration of HDEHP was controlled so that the distribution ratio in the absence of the ligand was to be 1.5—1.8. Extraction equilibrium was reached by shaking for 20 min at about 20 °C. From each phase in equilibrium, a 2 ml portion was taken into a polyethylene test tube and the radioactivity was counted. For the bromide solution, values were corrected for self-absorption of $\gamma$-rays by preliminary determined absorption data.

*Calculation of the Overall Stability Constants $\beta_1$ and $\beta_2$.* Distribution ratio was calculated by Eq. 1.

$$D = \frac{[\mathrm{M}]_{\mathrm{org,\ total}}}{[\mathrm{M}]_{\mathrm{aq,\ total}}} \tag{1}$$

In the presence of complexing anion L$^-$ (L=Cl or Br) in the aqueous phase, complex formation reaction of tripositive cation exists

$$\mathrm{M}^{3+} + x\mathrm{L}^- \overset{\beta_x}{\rightleftharpoons} \mathrm{ML}_x{}^{3-x},\ (x=1—n), \tag{2}$$

where $\beta_x=[\mathrm{ML}_x{}^{3-x}]/[\mathrm{M}^{3+}][\mathrm{L}^-]^x$. HDEHP is a cation exchange extractant and the extraction of the complex species can be neglected because of the decrease in the positive charge on the complex species. For example, tervalent lanthanoids and actinoids ions show a distribution ratio a few order of magnitude higher (>10$^3$) than the divalents.[9)] Therefore, the distribution ratio can be expressed as follows:

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$$D = \frac{[\mathrm{M}]_{\mathrm{org,\,total}}}{[\mathrm{M}^{3+}] + \sum\limits_{x=1}^{n}[\mathrm{ML}_x{}^{3-x}]} = D_0\frac{1}{1+\sum\limits_{x=1}^{n}\beta_x[\mathrm{L}^-]^x}. \qquad (3)$$

And the equation,

$$(D_0/D) - 1 = \beta_1[\mathrm{L}^-] + \beta_2[\mathrm{L}^-]^2 + \cdots \qquad (4)$$

is derived, where $D_0$ is the distribution ratio in the absence of the ligand. From Eq. 3, the slope of $\log D$ *vs.* $\log\,[\mathrm{L}^-]$ curve is represented as

$$\frac{\partial \log D}{\partial \log\,[\mathrm{L}^-]} = -\sum_{x=1}^{n} x\frac{\beta_x[\mathrm{L}^-]^x}{1+\sum\limits_{x=1}^{n}\beta_x[\mathrm{L}^-]^x} = -\sum_{x=1}^{n} xf_x. \qquad (5)$$

Where, $f_x$ is a mole fraction of $\mathrm{ML}_x{}^{3-x}$ in the aqueous phase. Equation 4 was used to calculate $\beta_x$ by the least mean squares fitting of the data points $(D_0/D)-1$ *vs.* $[\mathrm{L}^-]$. In order to determine the maximum ligand number, $n$, a graphic method was applied using the relation of (5).

## Results and Discussion

The relation between $\log D$ and $\log\,[\mathrm{HDEHP}]_{\mathrm{org}}$ for Bk is shown in Fig. 1. And for Gd, the relation between $\log D$ and $\log\,[\mathrm{HDEHP}]_{\mathrm{org}}$ at various ligand concentration is shown in Fig. 2. In these figures, it is shown that $D$ is proportional to the 2.5 power of $[\mathrm{HDEHP}]_{\mathrm{org}}$ and the relation is not affected by the addition of $\mathrm{Cl}^-$ or $\mathrm{Br}^-$. The dependence of $\log D$ on $\log\,[\mathrm{H}^+]_{\mathrm{aq}}$ is shown in Fig. 3 for Bk. As shown in Fig. 3, $D$ is inversely proportional to the third power of $[\mathrm{H}^+]_{\mathrm{aq}}$. The other lanthanoids(III) and actinoids (III) examined in this investigation exhibit the same dependency of $D$ on $[\mathrm{HDEHP}]_{\mathrm{org}}$ and $[\mathrm{H}^+]_{\mathrm{aq}}$. HDEHP exists as dimer, $(\mathrm{HA})_2$, in the organic solution. Then the extraction reaction can be written as

$$\mathrm{M}^{3+}{}_{\mathrm{aq}} + 2.5(\mathrm{HA})_{2\,\mathrm{org}} \rightleftharpoons \mathrm{MA}_3(\mathrm{HA})_{2\,\mathrm{org}} + 3\mathrm{H}^+{}_{\mathrm{aq}}. \qquad (6)$$

The relations between $\log D$ and $\log\,[\mathrm{Cl}^-]_{\mathrm{aq}}$ or $\log\,[\mathrm{Br}^-]_{\mathrm{aq}}$ are shown in Figs. 4 and 5. As shown in these figures, the values of $\partial \log D/\partial \log[\mathrm{L}^-]$ at maximum ligand concentration, $[\mathrm{L}^-]=2.85$ M, are around $-1.5$. It is reasonable that $f_3$, the fraction of the species $\mathrm{ML}_3$, is negligible under the experimental conditions employed in this work. Therefore, we determined the overall stability constants $\beta_1$ and $\beta_2$ by the least mean squares method based Eq. 4. Some examples of fitting are shown in Figs. 6 and 7. The values of $\beta_1$ and $\beta_2$ are given in Table 1.

As shown in Table 1, $\beta_1$ of the chloro complexes of actinoids(III) are 0.4—0.6 and obviously larger than $\beta_1$ of actinoids(III) bromo complexes. And for lanthanoids(III), $\beta_1$ of the chloro complexes are also 0.4—0.6 and slightly larger than $\beta_1$ of bromo complexes. But for $\beta_2$, no significant difference between chloro and bromo complexes was recognized. This means that the second formation constants $K_2$, calculated as $\beta_2/\beta_1$, of actinoids(III) bromo complexes are obviously larger than those of the others. Moreover, $K_2$ of the chloro complexes of actinoids(III) and lanthanoids(III) are 0.5—0.7, *i.e.*, almost similar values to $K_1(\beta_1)$. But for Am, Bk, and Cf, $K_2$ values of the bromo complexes are larger than $\approx 1$, as is shown in Table 1.

Tanaka and Yamada[10] proposed that the complex

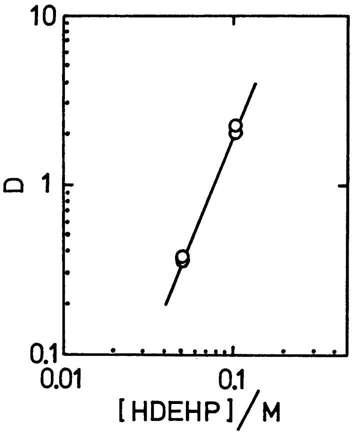

Fig. 1. Dependence of $D$ of Bk on [HDEHP]. $[\mathrm{H}^+]=0.15$ M, slope=2.5.

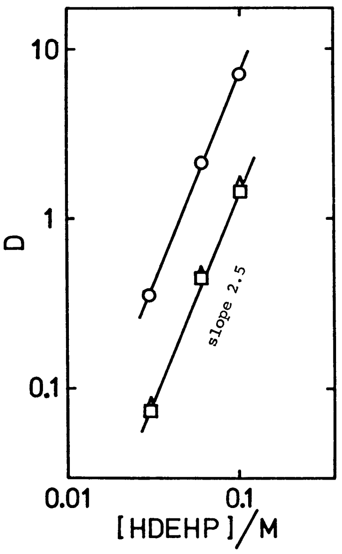

Fig. 2. Dependence of $D$ of Gd on [HDEHP]. ○: 3.0 M $(\mathrm{H,Li})\mathrm{ClO_4}$, □: 3.0 M $(\mathrm{HClO_4,LiCl})$, △: 3.0 M $(\mathrm{HClO_4,LiBr})$.

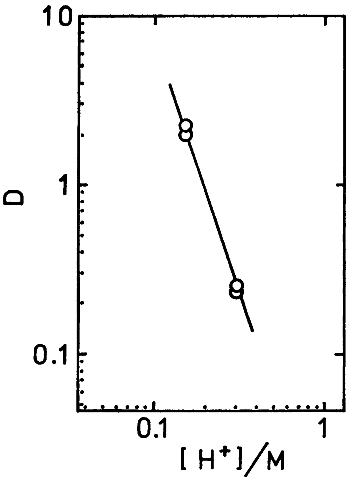

Fig. 3. Dependence of $D$ of Bk on $[\mathrm{H}^+]$. $[\mathrm{HDEHP}]=0.1$ M, slope$=-3.0$.

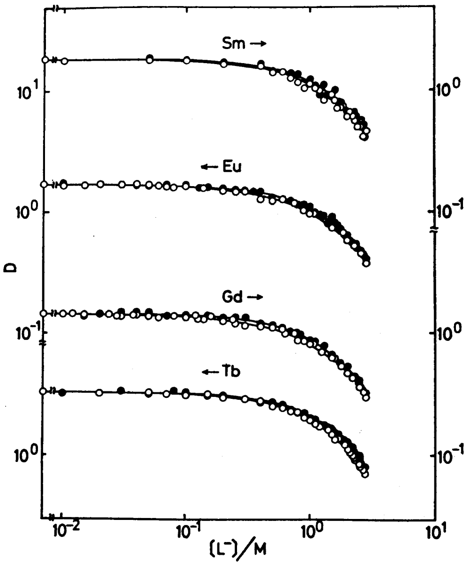

Fig. 4. Dependence of $D$ of some lanthanoids(III) on chloride ion(○) and bromide ion(●).

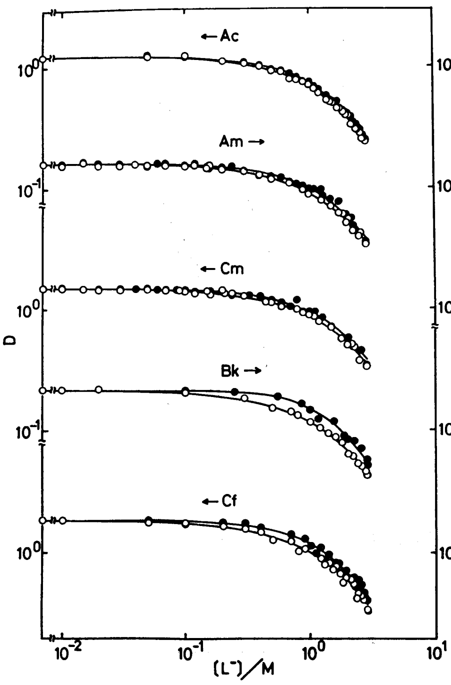

Fig. 5. Dependence of $D$ of some actinoids(III) on chloride ion(○) and bromide ion(●).

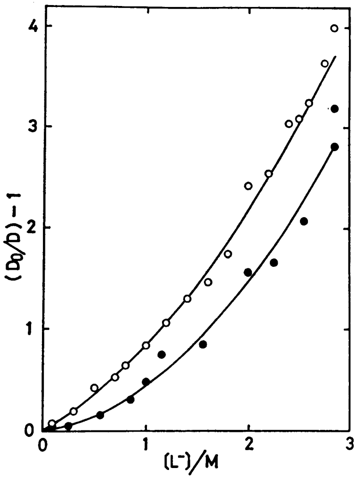

Fig. 6. Dependence of $D_0/D-1$ of Bk on chloride ion(○) and bromide ion(●).

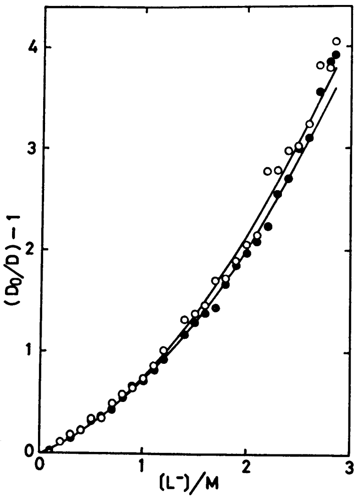

Fig. 7. Dependence of $D_0/D-1$ of Ac on chloride ion(○) and bromide ion(●).

formation reaction proceeds along with the Eigen mechanism[11] and the apparent formation constant $K$ is expressed as follows:

$$K = K_{os}(1+K_{is}), \qquad (7)$$

where $K_{os}$ is an outer sphere formation constant and $K_{is}$ is a transformation constant of an inner sphere complex. Fuoss[12] proposed an equation which has been applied frequently to the calculation of $K_{os}$;

$$K_{os} = \frac{4\pi Na^3}{3000}\exp[\mu/kT], \qquad (8)$$

where $4\pi a^3/3$ is exclusive volume of a cation and $\mu$ is the electrostatic energy. This equation gives calculated formation constants for the bromo complexes of actinoids(III) and lanthanoids(III) of 0.34—0.35 in good agreement with the experimental values of $\beta_1$, *i.e.*, $K_1$. On the other hand for the chloro complexes of actinoids(III), the experimental values of $\beta_1$ are obviously higher than the calculated values by Eq. 8, *i.e.*, $K_{os}$=0.35—0.36. According to Eq. 7, this implies that an inner sphere mechanism can not be neglected for the formation of actinoids (III) chloro complexes.

As was mentioned before, in high concentration of LiCl solution actinoids(III) were absorbed by anion exchange resin more strongly than lanthanoids(III), and the distribution ratio($D_v$) for actinoids(III) series showed a distinct minimum at Cm, whereas for lanthanoids(III) such trend was not observed.[2] These two facts have been explained by the different complexing ability between two *f*-series elements and it is widely recognized that actinoids(III) have a much larger ability for complex formation than lanthanoids (III). In order to examine this difference from the data obtained in this work, we calculated the fraction

Table 1. Stability constants of the chloride and bromide complexes of some lanthanoids and actinoids

| Anion | Metal | $\beta_1$ | $\beta_2$ | $K_2$ | $K_{\mathrm{os\ calcd}}$ |
|---|---|---|---|---|---|
| $Cl^-$ | Sm | 0.41±0.04 | 0.25±0.03 | 0.60±0.07 | 0.36 |
| | Eu | 0.52±0.02 | 0.22±0.02 | 0.41±0.04 | 0.35 |
| | Gd | 0.56±0.02 | 0.21±0.02 | 0.38±0.04 | 0.35 |
| | Tb | 0.45±0.02 | 0.26±0.02 | 0.58±0.04 | 0.35 |
| | Ac | 0.44±0.02 | 0.31±0.02 | 0.72±0.05 | 0.38 |
| | Am | 0.55±0.03 | 0.22±0.02 | 0.40±0.05 | 0.36 |
| | Cm | 0.56±0.03 | 0.20±0.02 | 0.35±0.05 | 0.36 |
| | Bk | 0.59±0.02 | 0.25±0.02 | 0.42±0.03 | 0.36 |
| | Cf | 0.61±0.04 | 0.25±0.03 | 0.40±0.04 | 0.36 |
| $Br^-$ | Sm | 0.33±0.04 | 0.24±0.03 | 0.71±0.11 | 0.34 |
| | Eu | 0.38±0.02 | 0.23±0.01 | 0.59±0.05 | 0.34 |
| | Gd | 0.37±0.02 | 0.26±0.02 | 0.69±0.07 | 0.34 |
| | Tb | 0.41±0.03 | 0.22±0.01 | 0.53±0.03 | 0.34 |
| | Ac | 0.42±0.02 | 0.29±0.01 | 0.71±0.03 | 0.37 |
| | Am | 0.30±0.03 | 0.28±0.02 | 0.93±0.11 | 0.35 |
| | Cm | 0.39±0.02 | 0.22±0.02 | 0.57±0.05 | 0.35 |
| | Bk | 0.15±0.04 | 0.29±0.03 | 1.95±0.46 | 0.35 |
| | Cf | 0.30±0.04 | 0.30±0.03 | 0.99±0.13 | 0.34 |

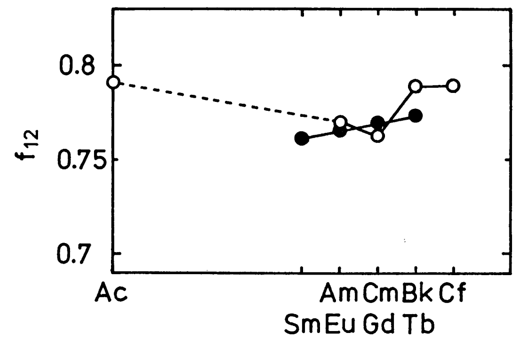

Fig. 8. Variation of $f_{12}$ with atomic number.

of complex species, *i.e.*, $f_{12}=f_1+f_2$, for chloride at $[Cl^-]=2.85$ M, where no anionic complexes are formed. The result is shown in Fig. 8, where $f_{12}$ shows the similar trend as the behavior of $D_v$ for anion exchange and shows a minimum at Cm for actinoids (III), whereas for lanthanoids(III) $f_{12}$ increases continuously with atomic number. However, there is no significant difference in the magnitude of $f_{12}$ between actinoids(III) and lanthanoids(III), thought it has been observed for $D_v$ of anion exchange system. This implies that the large difference in the complex formation between actinoids(III) and lanthanoids(III), which should be observed in the anionic complex formation and gives the experimental basis on the group separation, can not be observed in $\beta_1$ and $\beta_2$ values experimentally determined in the aqueous system of $\mu=3.0$ and $[Cl^-]\leq 2.85$ M.

The authors wish to thank the members of Cyclotron and Radioisotope Center, Tohoku University, for their handling the cyclotron and monitoring the irradiated sample in the production of Sm and Bk tracers. A part of the expenses for this investigation has been defrayed by a Grant-in-Aid for Scientific Research No. 505002 from the Ministry of Education, Science and Culture.

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