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II. 8 Stability Constants of Chloro and Bromo Complexes of Some Lanthanoids(III) and Actinoids(III)

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Tripositive actinoids can be separated from lanthanoids by the anion exchange method using high concentrated chloride solution as an eluent. This phenomenon has been explained by the difference in the complex formation between actinoids (III) and lanthanoids(III). In this work, we try to determine the stability constants ( $\beta_1$  and  $\beta_2$ ) of the chloro and bromo complexes of trivalent Sm, Eu, Gd, Tb, Ac, Am, Cm, Bk and Cf in the relatively lower ionic concentrations by the solvent extraction method. In the aqueous phase, the ionic strength and the acidity were kept at 3.0 and 0.15 M respectively, while the chloride and bromide ions were varied from 0 to 2.85 M. Bis(2-ethylhexyl)hydrogenphosphate, HDEHP, was used as the extractant, and octane as solvent in the organic phase.

The radioactivities used in this work were obtained as follows:  $^{152,154}\text{Eu}$ ,  $^{153}\text{Gd}$ ,  $^{160}\text{Tb}$  and  $^{252}\text{Cf}$  were obtained from the Radiochemical Centre, Amersham, and  $^{241}\text{Am}$  from Oak Ridge National Laboratory.  $^{225}\text{Ac}$  was isolated from  $^{229}\text{Th}$  which was obtained from  $^{233}\text{U}$ .  $^{242,243,244}\text{Cm}$ , obtained and purified as reported previously,<sup>2,3)</sup> was used in this work. The mixture of  $^{243}\text{Bk}$  and  $^{244}\text{Bk}$  were produced by the bombardment of  $\alpha$ -particle on  $^{241}\text{Am}$  targets and purified as mentioned in the previous report.<sup>4)</sup>  $^{145}\text{Sm}$  was produced by means of  $\text{Nd}^+$  reaction, and was purified by successive extraction with HDEHP.

Distribution ratio (D) was calculated by equation (1).

$$D = M_{\text{org. total}} / M_{\text{aq. total}} \quad \dots\dots\dots(1)$$

In the presence of complexing anion  $\text{L}^-$  ( $\text{L}=\text{Cl}$  or  $\text{Br}$ ) in the aqueous phase, complexing formation reaction of tripositive cation succeeds:



where  $\beta_x = [\text{ML}_x^{3-x}] / [\text{M}^{3+}][\text{L}^-]^x$ . Therefore, the distribution ratio can be expressed as follows.

$$D = \frac{[\text{M}]_{\text{org. total}}}{[\text{M}^{3+}] + \sum_{x=1}^n [\text{ML}_x^{3-x}]} = D_0 \frac{1}{1 + \sum_{x=1}^n \beta_x [\text{L}^-]^x} \quad \dots\dots\dots(3)$$

And the equation,

$$(D_0/D) - 1 = \beta_1[\text{L}^-] + \beta_2[\text{L}^-]^2 + \dots \quad \dots\dots\dots(4)$$

is derived, where  $D_0$  is the distribution ratio in the absence of the ligand.

The relations between  $[L^-]$  and  $D$  are shown in fig. 1 and fig. 2. The values of  $\beta_1$  and  $\beta_2$ , shown in Table 1, were obtained from equation (4) by the least-mean-square fitting of the data points  $(D_0/D)-1$  vs.  $[L^-]$ , which were calculated from the data of fig. 1 and fig. 2. For actinoids(III),  $\beta_1$  of the chloro complexes are 0.4-0.6 and obviously larger than  $\beta_1$  of bromo complexes. And for lanthanoids(III),  $\beta_1$  of 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.

In order to examine the difference in the complexing ability between actinoids(III) and lanthanoids(III), we calculated the fraction of complex, i.e.,  $f_{12}=f_1+f_2$ , ( $f_x$  is a mole fraction of the species of  $ML_x^{3-x}$  in the aqueous phase) for chloride at  $[Cl^-]=2.85$  M. The result is shown in fig. 3, where  $f_{12}$  shows a minimum at Cm for actinoids(III) which may be due to the half-shell effect of 5f electrons, while for lanthanoids(III),  $f_{12}$  increases continuously with atomic number. However, 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.

#### References

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

Anion	Metal	$\beta_1$	$\beta_2$
Cl <sup>-</sup>	Sm	0.41 ± 0.04	0.25 ± 0.03
	Eu	0.52 ± 0.02	0.22 ± 0.02
	Gd	0.56 ± 0.02	0.21 ± 0.02
	Tb	0.45 ± 0.02	0.26 ± 0.02
	Ac	0.44 ± 0.02	0.31 ± 0.02
	Am	0.55 ± 0.03	0.22 ± 0.02
	Cm	0.56 ± 0.03	0.20 ± 0.02
	Bk	0.59 ± 0.02	0.25 ± 0.02
	Cf	0.61 ± 0.04	0.25 ± 0.03
Br <sup>-</sup>	sm	0.33 ± 0.04	0.24 ± 0.03
	Eu	0.38 ± 0.02	0.23 ± 0.01
	Gd	0.37 ± 0.02	0.26 ± 0.02
	Tb	0.41 ± 0.03	0.22 ± 0.01
	Ac	0.42 ± 0.02	0.29 ± 0.01
	Am	0.30 ± 0.03	0.28 ± 0.02
	Cm	0.39 ± 0.02	0.22 ± 0.02
	Bk	0.15 ± 0.04	0.29 ± 0.03
	Cf	0.30 ± 0.04	0.30 ± 0.03

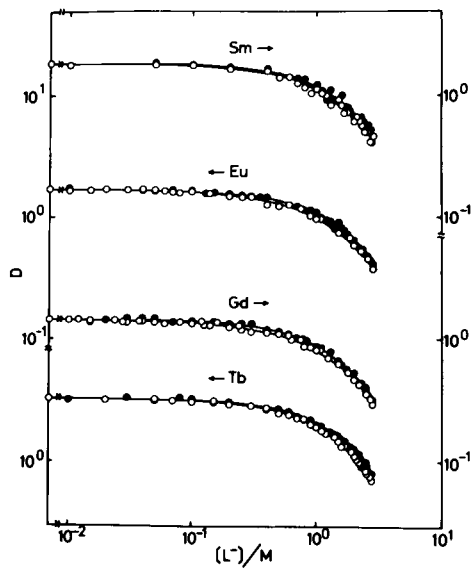


Fig. 1. Dependence of  $D$  of some lanthanoids(III) on chloride ion(o) and bromide ion(●).

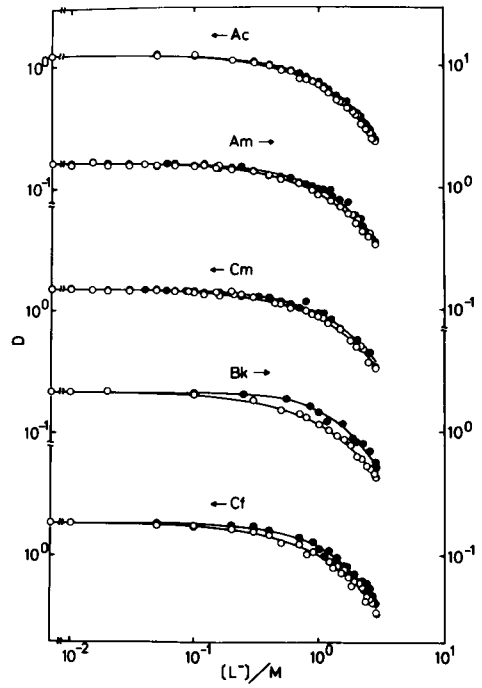


Fig. 2. Dependence of  $D$  of some actinoids(III) on chloride ion(o) and bromide ion(●).

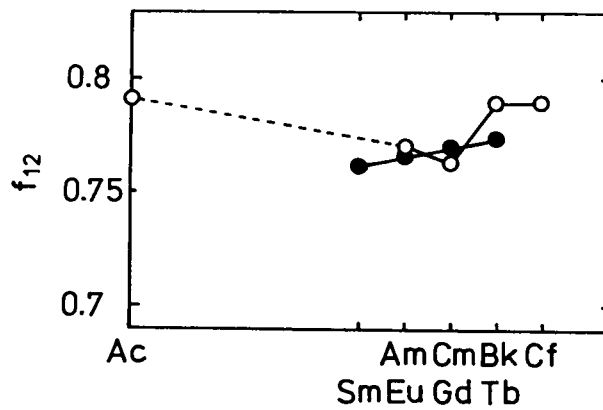


Fig. 3. Dependence of  $f_{12}$  of actinoids(o) and lanthanoids(●) on atomic number.