

# Macrocyclic ligand as ion size selective masking reagent in metal ion separation

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The extraction-separation of alkali, alkaline earth, and rare earth metal ions could be improved by using macrocyclic ligands as ion size selective masking reagents. By adding a macrocyclic ligand to the aqueous phase of a conventional chelate extraction system, the extraction of metal ions with larger ionic radii was shifted to a higher pH region. Consequently, the separation among the metal ions was enhanced. Diazapolyoxabicyclic ligands (cryptand) exhibited a prominent separation ability for alkali and alkaline earth metal ions. Quantitative separation systems were successfully developed in the synergistic extraction of alkali and alkaline earth metal ions in the presence of a cryptand. A new type of water-soluble sulfonated crown ethers was prepared. The separability of lanthanide ions was found to improve by adding the sulfonated crown ethers into the aqueous phase. The number of water molecules in the first coordination sphere of the central  $\text{Eu}^{3+}$  in the complex was determined by a laser-induced luminescence study. In addition, fluorescence spectra were measured to evaluate the structure of the complexes. The stabilization of the complexes formed is discussed, taking into account an outer-sphere electrostatic attraction between the sulfonic acid group and the metal ion.

Much effort has been exerted in the design of organic ligands and extraction-separation systems of high selectivity. The application of a masking effect to the solvent extraction method is effective for the selective separation of metal ions. In general, the extractability of metal ions using conventional chelating reagents such as  $\beta$ -diketones is governed by the stability of the metal complexes. In the solvent extraction of alkali, alkaline earth and lanthanide metal ions with the chelating reagents, metal ions having smaller ionic radii exhibit higher extractability. On the other hand, the stability in the complex formation between macrocyclic ionophores such as crown ethers and the above-mentioned metal ions exhibits a quite different tendency.<sup>1,2)</sup> Thus, a solvent extraction system of high selectivity could be developed by the combination of chelating reagents and macrocyclic ionophores (Scheme 1).

## Extraction of alkaline earths in the presence of 18-crown-6<sup>3)</sup>

The results for the extraction of alkaline earths into cyclohexane with 0.05 M HPMBP and 0.01 M TOPO in the absence (blank symbols) and presence (solid symbols) of 18-crown-6 (0.03 M) are shown in Fig. 1. Alkaline earths were extracted in the order,  $\text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$ , which is the same order as that of decreasing ionic radius. When 0.03 M 18-crown-6 was added to the aqueous phase, the extractions shifted to a higher pH region. The larger the ionic radius is, the higher the pH region the extraction shifts to. As a result, the separation among alkaline earths, especially for Ca-Sr and Sr-Ba was improved. It is clear that 18-crown-6 works as an ion-size selective masking reagent in the aqueous phase. The distribution ratio of 18-crown-6 between cyclohexane and water is reported<sup>4)</sup> to be  $10^{-2.91}$ , indicating that the concentration of 18-crown-6 in the cyclohexane phase is negligible.

In the synergistic extraction of alkaline earths ( $\text{M}^{2+}$ ) with HPMBP (HA) and TOPO (L), the extraction equilibrium and the extraction constant,  $K_{\text{ex},s}$ , can be written as follows:

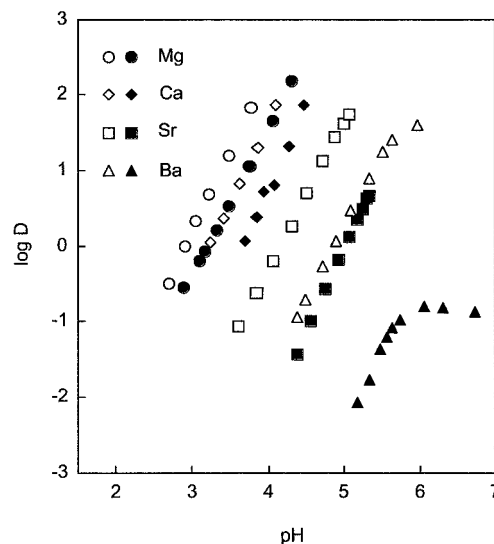
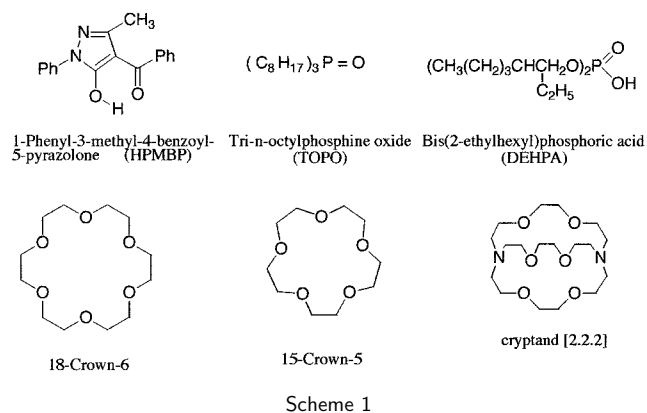


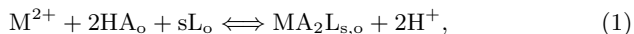
Fig. 1. Extraction of alkaline earths into cyclohexane with HPMBP and TOPO in the absence (blank symbols) and presence (solid symbols) of 18-crown-6.  $[\text{HA}]_0 = 0.05 \text{ M}$ ,  $[\text{L}]_0 = 0.01 \text{ M}$  in cyclohexane,  $[\text{CE}] = 0.03 \text{ M}$  in an aqueous phase.

Table 1. Extraction parameters for alkaline earths in the cyclohexane system.

	r(Å) <sup>a</sup>	log K <sub>ex,L</sub>	s	15-crown-5		18-crown-6	
				SF	log β	SF*	log β
Mg	0.72	0.80	2		–		2.25
Ca	1.00	0.16	2	0.64		0.64	
					–		2.30
Sr	1.18	–1.74	2	1.90		1.90	
					–		3.06
Ba	1.35	–1.16	3	1.42		2.06 <sup>b</sup>	
					2.05		3.82

<sup>a</sup> Ionic radius for a coordination number of six. Taken from Ref. 11.

<sup>b</sup> At [TOPO]<sub>o</sub> = 0.01 M.



$$K_{ex,s} = \frac{[MA_2L_s]_o [H^+]^2}{[M^{2+}] [HA]_o^2 [L]_o^s} = D [H^+]^2 / [HA]_o^2 [L]_o^s, \quad (2)$$

where subscript o denotes the species in the organic phase and D is defined as  $[MA_2L_s]_o / [M^{2+}]$ . The number of TOPO units in the adduct is two per metal for Mg, Ca, and Sr, and three for Ba.<sup>5)</sup> The log K<sub>ex,s</sub> values were obtained from Fig. 1 using Eq. (2) on the basis of known s values and are summarized in Table 1.

The distribution ratio in the presence of 18-crown-6 (CE), D\*, can be expressed in Eq. (3).

$$D^* = \frac{[MA_2L_s]_o}{\{[M^{2+}] + [M(CE)^{2+}]\}} = K_{ex,s} [HA]_o^2 [L]_o^s / [H^+]^2 \{1 + \beta [CE]\}, \quad (3)$$

where β is the complex formation constant between alkaline earths and 18-crown-6 in the aqueous phase defined as  $[M(CE)^{2+}] / [M^{2+}] [CE]$ . Dividing D by D\* gives Eq. (4).

$$D/D^* = 1 + \beta [CE]. \quad (4)$$

The log β values are summarized in Table 1. The separation factor, SF, between two metal ions, M1 and M2, is defined as the difference between the logarithmic values of the respective distribution ratios.

$$SF = \log(D_{M1}/D_{M2}) = \log(K_{ex,s,M1}/K_{ex,s,M2}). \quad (5)$$

The separation factor in the presence of crown ether, SF\*, is written in Eq. (6) when s1 and s2 are the same and [CE] is sufficiently high.

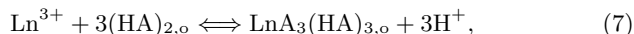
$$SF^* = \log(D_{M1}^*/D_{M2}^*) = \log(K_{ex,s,M1}/K_{ex,s,M2}) (\beta_{M2}/\beta_{M1}). \quad (6)$$

Comparing Eqs. (5) and (6), the separation factor can be improved by as much as  $\beta_{M2}/\beta_{M1}$ . Separation factors in the presence and absence of crown ether are summarized in Table 1. Since the separation factor for Sr-Ba depends on [TOPO]<sub>o</sub>, it was obtained under the condition, [TOPO]<sub>o</sub> = 0.01 M.

### Extraction of lanthanides in the presence of 18-crown-6<sup>3)</sup>

The application of 18-crown-6 to the solvent extraction of lanthanides into cyclohexane was examined. While the pH<sub>1/2</sub> values for heavy lanthanides, Dy, Ho, and Yb, did not change on adding 0.1 M 18-crown-6 into the aqueous phase, those for light lanthanides, La, Nd, Sm, and Eu, increased. The difference in pH<sub>1/2</sub> value in the presence and absence of 18-crown-6, ΔpH<sub>1/2</sub>, increases linearly as the ionic radius increases.

In the extraction of lanthanides (Ln<sup>3+</sup>) with DEHPA (HA), the extraction equilibrium and the extraction constant, K<sub>ex</sub>, can be written as follows:



$$K_{ex} = \frac{[LnA_3(HA)_3]_o [H^+]^3}{[Ln^{3+}] [(HA)_2]_o^3}. \quad (8)$$

The log K<sub>ex</sub> values were obtained on the basis of Eq. (8) and are summarized in Table 2. We obtained log β values by substituting the D/D\* values read from the figure into Eq. (4) and they are summarized in Table 2 together with SF and SF\* values. Owing to the small β values, a high concentration of 18-crown-6 was required. However, it is obvious that the addition of an ion size selective masking reagent improves the separation of lanthanides whose separation has been known to be very difficult due to the similar nature as metal cations. SF for lanthanum-dysprosium increased from 3.06 to 4.02. This improvement is significant. 18-Crown-6 was found to be an effective masking reagent for light lanthanides.

Table 2. Extraction parameters for lanthanides.

	log K <sub>ex</sub>	ΔpH <sub>1/2</sub> <sup>a</sup>	log β	r(Å) <sup>b</sup>	SF	SF*
La	0.57	0.32	1.91	1.160		
Nd	0.90	0.18	1.39	1.109	0.33	0.75
						0.66
Sm	1.56	0.13	1.16	1.079	0.72	0.78
						1.35
Eu	2.28	0.11	1.06	1.066	0.15	0.15
						0.36
Dy	3.63	–	–	1.027		
Ho	3.78	–	–	1.015		
Yb	4.14	–	–	0.985		

<sup>a</sup> [DEHPA]<sub>o</sub> = 0.01 M in cyclohexane, [18C6] = 0.1 M. <sup>b</sup> Ionic radius for a coordination number of eight. Taken from Ref. 11.

### Extraction of alkaline earths in the presence of cryptand<sup>6,7)</sup>

The stability constants of cryptate inclusion complexes between several kinds of cryptands and, alkali and alkaline earth metal cations were reported by Lehn and Sauvage in 1975.<sup>8)</sup> These stability constants show the considerable differences between two neighboring metals, for example, between Mg and Ca, and Li and Na with cryptand [2.2.1] and between Ca and Sr with cryptand [2.2.2]. They are soluble in water and their stability on complexation is sufficiently high for use as practical masking reagents. Due to the presence of elemental nitrogens in the ring structure, the masking effect of cryptands depends on pH unlike crown ethers such as 18-

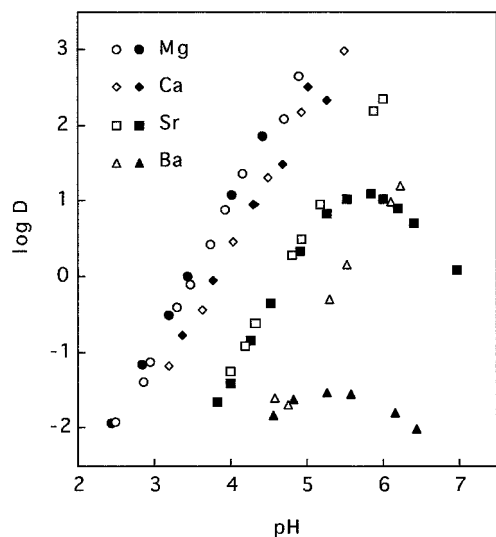


Fig. 2. Extraction of alkaline earths with HPMBP and TOPO in the absence (blank symbols) and presence (solid symbols) of cryptand [2.2.2].  $[\text{HPMBP}]_0 = [\text{TOPO}]_0 = 0.01 \text{ M}$  in cyclohexane,  $[\text{cryptand}] = 0.01 \text{ M}$  in an aqueous phase.

crown-6. Cryptand [2.2.2] should be the most suitable masking reagent for separating Ca and Sr in the series of alkaline earth metals. Figure 2 shows the results for the extraction with 0.01 M HPMBP and 0.01 M TOPO into cyclohexane in the absence (blank symbols) and presence (solid symbols) of 0.01 M cryptand [2.2.2]. The extraction behavior for Mg and Ca in the presence of cryptand [2.2.2] is similar to that in the absence of cryptand [2.2.2]. The log D values for Sr in the presence of cryptand [2.2.2] increase as pH increases, similar to those in the absence of cryptand [2.2.2], then begin to decrease above pH 5. The log D values for Ba in the presence of cryptand [2.2.2] deviate from those in the absence of cryptand [2.2.2] above pH 4.5.

The results obtained indicate that the masking effect by a cryptand depends on the stability on complexation and on the pH. The extraction behavior in the presence and absence of a cryptand can be predicted by taking the above equilibrium and the concentrations of the reagents into consideration. In order to establish a quantitative extraction-separation system for Ca and Sr, the extraction was conducted by reducing the concentrations of HPMBP and TOPO to  $4 \times 10^{-3} \text{ M}$  while keeping the initial concentration of cryptand at  $1 \times 10^{-2} \text{ M}$ . As shown in Fig. 3, the distribution ratio of Sr decreases rapidly above pH 5.6 as expected, while that of Ca still increases by pH 7.5. Ca can be separated from Sr quantitatively in the pH range of 7.2 to 8.6 where more than 99% of Ca ( $\log D > 2$ ) is extracted into cyclohexane, while more than 99% of Sr ( $\log D < -2$ ) remains in the aqueous phase at the same time. Careful control of pH at 7.8 could lead to the best separation: 99.9% extraction of Ca ( $\log D > 3$ ) with 99.9% of Sr ( $\log D < -3$ ) remaining in the aqueous phase.

Cryptands exist in the protonated form in the lower pH region and release hydrogens stepwise to become neutral; this then reacts with metal ions as pH increases. The  $\text{pK}_{a1}$  and  $\text{pK}_{a2}$  values for cryptand [2.2.2] are reported to be 7.28 and 9.60.<sup>8)</sup> Accordingly, in order to utilize the masking effect of cryptands more effectively, it is desirable to employ them in the alkaline region. Benzoyltrifluoroacetone (BFA) and tri-

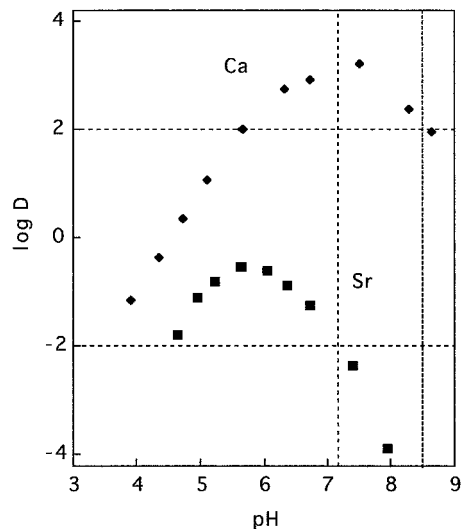


Fig. 3. Extraction of calcium and strontium with HPMBP and TOPO in the presence of cryptand [2.2.2].  $[\text{HPMBP}]_0 = [\text{TOPO}]_0 = 4 \times 10^{-3} \text{ M}$ ,  $[\text{cryptand}] = 1 \times 10^{-2} \text{ M}$ .

n-butylphosphate (TBP) have been used since the acidity of BFA is lower than that of HPMBP and TBP is a weaker Lewis base than TOPO; consequently, the extraction would be conducted in the higher pH region. In addition, cryptands [2.2.1] and [2.2.2] have been used properly according to the purpose.

Quantitative extraction of and separation between Mg and Ca into cyclohexane could be achieved with  $2.5 \times 10^{-3} \text{ M}$  BFA and TBP in the presence of 0.01 M cryptand [2.2.1]. Mg can be separated from Ca and Sr quantitatively in the pH range of 8.5–9.5 where more than 98% of Mg ( $\log D^* > 1.80$ ) is extracted into cyclohexane, while more than 99% of Ca ( $\log D^* < -2$ ) remains in the aqueous phase at the same time. The distribution of Sr was very low ( $\log D^* < -3$ ) in the pH range of 7.0–9.5. Quantitative extraction of and separation between Ca and Sr into cyclohexane could be achieved with 0.015 M BFA and TBP in the presence of 0.01 M cryptand [2.2.2]. The concentrations of BFA and TBP were increased in this system to shift the extraction to a lower pH region, in order to optimize the masking effect for Sr. Sr was separated from Mg and Ca quantitatively above pH 6.7 where more than 99% of Mg and Ca ( $\log D^* > 2$ ) were extracted into cyclohexane, while more than 99% of Sr ( $\log D^* < -2$ ) remained in the aqueous phase at the same time.

Taking the previous data into consideration, Cryptand [2.2.1] should be most suitable ion size selective masking reagent for the separation of Li from Na. Since the synergistic effect of TBP for alkali metals is too low, that is, the extraction of Li is not sufficient, TOPO has been used as a synergistic reagent instead of TBP. Quantitative extraction of and separation between Li and Na into cyclohexane could be achieved with 0.1 M BFA and 0.03 M TOPO in the presence of 0.01 M cryptand [2.2.1]. The distribution of Na decreases rapidly above pH 7.5, while that of Li is similar to those in the absence of cryptand [2.2.1]. From this results, Li can be separated quantitatively from Na over pH 8, where more than 99% ( $\log D^* > 2$ ) of Li is extracted into cyclohexane, while more than 99% ( $\log D^* < -2$ ) of Na remains in the aqueous phase at the same time.

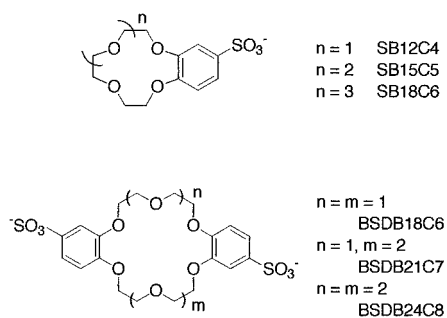
Table 3. Log  $\beta$  values for lanthanide - crown ether complexes.

$\text{Ln}^{3+}$	r(Å)	SB12C4	SB15C5	SB18C6	DSDB18C6	DSDB21C7	DSDB24C8	18C6	15C5
La <sup>3+</sup>	1.160	2.39±0.03	2.04±0.01	1.88±0.01	2.07±0.12	2.20±0.01	2.36±0.04	1.11±0.07	< 0.2
Ce <sup>3+</sup>	1.143	2.42±0.02	1.98±0.01	1.84±0.09	2.01±0.08	2.27±0.01	2.39±0.02	1.21±0.09	< 0.2
Pr <sup>3+</sup>	1.126	2.30±0.02	1.91±0.11	1.81±0.09	1.84±0.14	2.07±0.11	2.17±0.06	1.11±0.09	< 0.2
Nd <sup>3+</sup>	1.109	2.39±0.02	1.81±0.01	1.66±0.01	1.88±0.06	2.14±0.02	2.20±0.05	0.94±0.06	< 0.2
Sm <sup>3+</sup>	1.079	2.20±0.02	1.77±0.07	1.70±0.02	1.77±0.13	1.94±0.06	2.07±0.05	0.79±0.07	< 0.2
Eu <sup>3+</sup>	1.066	2.17±0.02	1.66±0.02	1.59±0.04	1.63±0.07	1.88±0.03	1.94±0.10	0.50±0.03	< 0.2
Gd <sup>3+</sup>	1.053	2.04±0.02	1.63±0.01	1.39±0.07	1.51±0.05	1.77±0.03	1.84±0.04	< 0.2	< 0.2
Dy <sup>3+</sup>	1.027	1.77±0.02	1.21±0.01	0.87±0.06	1.16±0.01	1.51±0.01	1.63±0.06	< 0.2	< 0.2
Er <sup>3+</sup>	1.004	1.31±0.02	1.00±0.01	0.71±0.06	1.06±0.04	1.31±0.01	1.35±0.08	< 0.2	< 0.2
Yb <sup>3+</sup>	0.985	0.79±0.02	0.50±0.01	< 0.2	< 0.2	0.71±0.01	0.71±0.05	< 0.2	< 0.2

Table 4. Separation factors for the extraction of lanthanides in the presence of crown ethers.<sup>a</sup>

	none	18C6	SB12C4	SB15C5	SB18C6	DSDB18C6	DSDB21C7	DSDB24C8
La / Pr	0.90	0.90	1.20	1.02	0.90	1.11	1.02	1.08
Pr / Eu	1.62	1.86	1.74	1.83	1.80	1.80	1.80	1.83
Eu / Dy	1.29	1.47	1.65	1.62	1.74	1.62	1.59	1.56
Dy / Yb	1.53	1.53	2.04	1.83	1.71	1.86	1.98	2.07
La / Yb	5.34	5.76	6.63	6.30	6.15	6.39	6.39	6.54

<sup>a</sup> [D2HEPA]<sub>o</sub> = 0.01 mol dm<sup>-3</sup> in cyclohexane, [crown ether] = 0.1 mol dm<sup>-3</sup>.



Scheme 2

### Sulfonated crown ethers<sup>9)</sup>

The novel armed crown ether, 3'-sulfo-18-crown-6 (SB18C6), was synthesized with the aim of making it thoroughly water-soluble in order to employ it as an ion size-selective masking reagent.<sup>10)</sup> It is necessary to minimize the partition of macrocyclic ligands to the organic phase, as the adduct formation reaction with the metal chelate and the macrocyclic ligand in the organic phase usually results in effective extraction but poor selectivity.

New types of sulfonated crown ethers (Scheme 2) have been synthesized: 3'-sulfo-12-crown-4 (SB12C4), 3'-sulfo-15-crown-5 (SB15C5), 3'-sulfo-18-crown-6 (SB18C6), di(3'-sulfo)-dibenzo-18-crown-6 (DSDB18C6), di(3'-sulfo)-dibenzo-21-crown-7 (DSDB21C7) and di(3'-sulfo)-dibenzo-24-crown-8 (DSDB24C8), and the complexation reaction of these crown ethers with lanthanide metal ions in aqueous solution has been investigated. The complex formation constants,  $\beta$ , of lanthanide ions with the sulfonated crown ethers in aqueous solution were determined by analyzing the distribution of lanthanide ions in the D2EHPA / cyclohexane solvent extraction system in the presence and absence of the crown ethers. Because the partition constants for all of the crown ethers between cyclohexane and water

are very low,  $< 10^{-4}$  for sulfonated crown ethers,  $10^{-2.91}$  for 18C6 and  $10^{-2.61}$  for 15C5,<sup>4)</sup> the adduct formation reaction with the metal chelate and the macrocyclic ligand in the organic phase was negligible. The  $\beta$  values are summarized in Table 3. As shown in Table 3, all of the sulfonated crown ethers show appreciable complexation with lanthanide ions. The present results are unforeseen and would support the significant contribution of the sulfonic acid group to the complexation.

The stability of the resulting complex increases with the increase in the number of sulfonic acid groups in the following order: 18C6 < SB18C6 < DSDB18C6. It can be considered that the outer-sphere interaction between the sulfonic acid group and the metal ion can contribute to the complexation stability. Furthermore, for mono- and disulfonated crown ether complexes, the stability varies in the order, SB18C6 < SB15C5 < SB12C4 and DSDB18C6 < DSDB21C7 < DSDB24C8. The stability of the complexes cannot be explained only on the basis of the concept of "size fitting effect," though it is known that the cavity size of 18C6 (radius: 1.34–1.43 Å) is similar to the ionic size of lighter lanthanide ions. The log  $\beta$  values are plotted against the reciprocal of ionic radius<sup>11)</sup> in Fig. 4. It is found that  $\beta$  for all of the sulfonated crown ether complexes with lanthanide ions decreases gradually with an increase in the atomic number. This indicates that the cavity size is not a significant factor that governs the complexation behavior with lanthanide ions.

The separation factor defined in Eq. (6) is summarized in Table 4. The separation factor between La<sup>3+</sup> and Yb<sup>3+</sup> in the absence of any crown ether is 5.34, and increases when the crown ethers are added to the aqueous phase as ion-size selective masking reagents. It is clear that the sulfonated crown ethers are much more effective ion-size selective masking reagents than 18C6. The best value is given by SB12C4 to be 6.63. It is also found that the sulfonated crown ethers are more effective for heavier lanthanides.

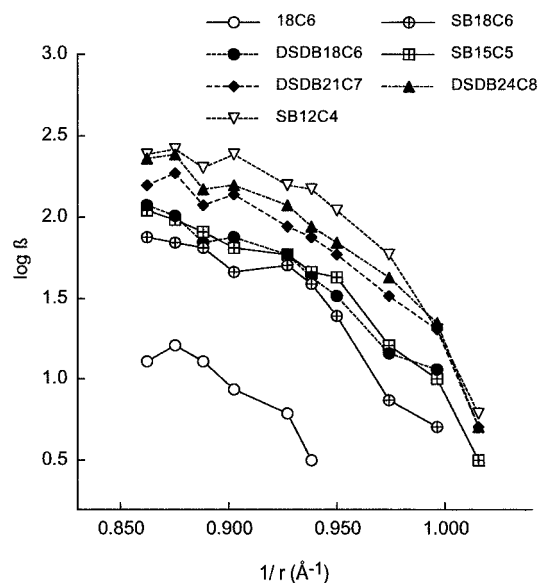


Fig. 4. Formation constants of lanthanide complexes in aqueous solution.

Table 5. Luminescence properties of  $\text{Eu}^{3+}$ -crown ether complexes in aqueous solution.

CE	$n_{\text{H}_2\text{O}}^{\circ}$ <sup>a</sup>	$P_{(\text{CE})}$ <sup>b</sup>
SB12C4	$8.1 \pm 0.1$	0.66
SB15C5	$7.0 \pm 0.3$	0.53
SB18C6	$6.5 \pm 0.3$	0.57
DSDB18C6	$7.1 \pm 0.2$	0.48
DSDB21C7	$7.3 \pm 0.1$	0.57
DSDB24C8	$7.4 \pm 0.3$	0.58
18C6	—	0.30

<sup>a</sup> The hydration number. <sup>b</sup> The relative intensity ratio of the  $\text{Eu}(\text{III})$ -crown ether complexes.

The hydration number,  $n_{\text{H}_2\text{O}}^{\circ}$ , of  $\text{Eu}^{3+}$  can be determined from the decay constants of the luminescent excited state of  $\text{Eu}^{3+}$  in the crown ether complex.<sup>12)</sup> Table 5 shows the calculated  $n_{\text{H}_2\text{O}}^{\circ}$  for the  $\text{Eu}^{3+}$  complexes of various crown ethers. In general, it can be expected that the number of hydrated water molecules around the central metal ion decreases with the stronger binding of the inner-sphere interaction type armed crown ethers to the metal ion. However, an opposite tendency is seen in the results: for complexes of 18-membered crown ethers and  $\text{Eu}^{3+}$ ,  $n_{\text{H}_2\text{O}}^{\circ}$  increases with an increase in the number of sulfonic acid groups ( $\text{SB18C6} < \text{DSDB18C6}$ ); that is,  $n_{\text{H}_2\text{O}}^{\circ}$  increases with an increase in the stability of the complex. The  $n_{\text{H}_2\text{O}}^{\circ}$  value also increases in the order,  $\text{SB18C6} < \text{SB15C5} < \text{SB12C4}$  for the monosulfonated crown ethers, which is the same as the order in which their  $\log \beta$  values increase. The  $n_{\text{H}_2\text{O}}^{\circ}$  value for the disulfonated crown ether complex slightly increases with the cavity size. On the basis of the results of  $n_{\text{H}_2\text{O}}^{\circ}$  measurement and luminescence study, the possible structures of europium

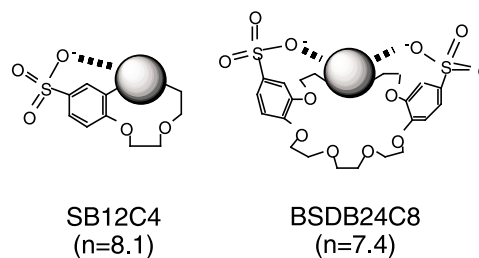


Fig. 5. Possible structures of  $\text{Eu}^{3+}$  complexes in aqueous solution.

complexes with various sulfonated crown ethers are postulated and illustrated in Fig. 5.

The unusual stability of lanthanide ions with sulfonated crown ethers that have one or two binding sites is dominated by two primary factors: (1) ion-dipole interaction between the metal ion and the crown ether donating oxygens and (2) long-range interaction between the metal ion and the sulfonic acid group. These synergistic effects should be taken into consideration.

The combination of conventional chelating reagents and ion-size selective masking ligands having an opposite complexation tendency was proven to improve the extraction and separation of alkaline earths and lanthanides. The equilibrium study revealed that the separation factor for two metal ions can be enhanced as much as the difference between the complexation stabilities of the respective metal ions with crown ethers. This concept is universal and is of particular interest because it generates many opportunities for analytical and separation chemistry.

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