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Complex Formation of Lanthanide Ions with Sulfonated Crown Ethers in Aqueous Solution

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A new type of water-soluble crown ether (3′-sulfobenzo-12-crown-4 (SB12C4), 3′-sulfobenzo-15-crown-5 (SB15C5), 3′-sulfobenzo-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)) has been prepared. The complex formation constants (β) of lanthanide ions with sulfonated crown ethers in aqueous solution were determined via the solvent-extraction method. The stability of the resulting complexes increases with the number of sulfonic acid groups, 18C6 < SB18C6 < DSDB18C6. For mono and disulfonated crown ether complexes, the stability varies as SB18C6 < SB15C5 < SB12C4 and DSDB18C6 < DSDB21C7 < DSDB24C8. The β values of all the complexes of lanthanide ions decrease with the atomic number, which is a characteristic of macrocyclic ligands, and is quite opposite to the conventional complexing tendency. The extractive separability of lanthanide ions was found to improve by adding sulfonated crown ethers into the aqueous phase as ion-size selective masking reagents. The number of water molecules in the first coordination sphere of the central Eu^{3+} in the complex was determined by a laser-induced luminescence study. In addition, the fluorescence spectra were measured in order to evaluate the structure of the complexes. The stabilization of the complexes formed is discussed while taking into account an outer-sphere electrostatic attraction between the sulfonic acid group and the metal ion.

The introduction of donating side arms to the crown-ether derivatives often results in an improved complexing ability and separability for metal ions.[1—4] Especially, the attachment of carboxylic acid groups has been reported to be very effective in increasing the complex stabilities and selectivity.[5—8] The highly effective extraction of lanthanides with ionizable crown ethers was also reported.[9,10] These are inner-sphere interaction-type armed crown ethers (IS-ACE), which have donating atoms in the side arms coordinating directly to the central metal ion.

The authors have synthesized a novel armed crown ether, 3′-sulfobenzo-18-crown-6 (SB18C6), with a view to making it thoroughly water soluble in order to employ it as an ion size-selective masking reagent.[11] The complexation tendency of macrocyclic ligands for alkali, alkaline earth, and lanthanide metal ions is quite opposite to that of the conventional chelating ligands. The selectivity in the solvent extraction of these metal ions with the chelating reagents can be improved by adding the macrocyclic ligand to the aqueous phase.[12—14] It is necessary to minimize the partition of the macrocyclic ligands to the organic phase, since the adduct-formation reaction with a metal chelate and a macrocyclic ligand in the organic phase usually results in effective extraction, but poor selectivity. It was found that the complexation of lanthanide metal ions with SB18C6 is much more stable and selective than that with 18C6. The stabilization of the lanthanide metal ion–SB18C6 complex formed could be explained by taking into account an outer-sphere electrostatic attraction between the sulfonic acid group and the metal ion. This kind of ligand is an outer-sphere interaction-type armed crown ether (OS-ACE) with the side arm interacting with the metal ion via a long-range interaction. The complexation of armed crown ethers with lanthanide metal ions has not yet been studied in detail. In addition, little is known about the complexation reactions with OS-ACE.

In the present work, the authors synthesized a new type of sulfonated crown ether (3′-sulfobenzo-12-crown-4 (SB12C4), 3′-sulfobenzo-15-crown-5 (SB15C5), 3′-sulfobenzo-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 have investigated the complexation reaction of these crown ethers with lanthanide metal ions in aqueous solution. From the results of a number of water molecules in the first coordination sphere of the central metal ion of the complex determined by a laser-induced luminescence study and of fluorescence studies, the possible conformation of the complex was postulated. The principle concerning the stabilization of the lanthanide metal ion–crown ether complex in aqueous media, that is, the role of the crown ether ring and the present side arms, was elucidated.

Experimental

Materials and Standard Solutions. Standard solutions of 5×10^{-4} mol dm^{-3} lanthanide metal ions were prepared by dissolving high-purity lanthanide oxide (Shinetsu) with concentrated hydrochloric acid. Benzo-12-crown-4, benzo-15-crown-5, benzo-18-crown-6, dibenzo-18-crown-6, and dibenzo-24-crown-8 were purchased commercially from Tokyo Kasei and dibenzo-21-crown-7 from Wako. Di(2-ethylhexyl)phosphoric acid (D2EHPA) was commercially available from Aldrich and used as received. All other chemicals were of analytical reagent grade. Deionized and distilled water was used throughout. Figure 1 shows the structural formulas of the sulfonated crown ethers.

Synthesis of 3′-Sulfobenzo-12-crown-4 Tetramethylammonium Salt (SB12C4) and 3′-Sulfobenzo-15-crown-5 Tetramethylammonium Salt (SB15C5). SB12C4 and SB15C5 were prepared by an identical procedure as that for the synthesis of SB18C6, reported previously.[11] Benzo-12-crown-4 (22.3 mmol) or benzo-15-crown-5 (18.6 mmol) and acetonitrile (80 cm^3) were mechanically stirred in a round-bottom flask. An aliquot of sulfuric acid (97%, 22.3 mmol for benzo-12-crown-4 and 18.6 mmol for benzo-15-crown-5) was slowly added from a dropping funnel, and the mixture was stirred for 30 min at ca. 80 °C. The solvent was distilled away slowly. After complete evaporation of solvent, a 25% methanol solution of tetramethylammonium hydroxide (22.3 or 18.6 mmol) was added to the residue, precipitating a crude mixture. The mixture was first filtrated, and then recrystallized from 20% methanol–ethylacetate to give 7.6 g of SB12C4 (90%) or 7.5 g SB15C5 (95%). {Found: C, 50.3; H, 7.37; N, 3.78%. Calcd for $C_{16}H_{27}NO_7S$ (SB12C4): C, 50.9; H, 7.21; N, 3.71%}. {Found: C, 51.1; H, 7.62, N 3.65%. Calcd for $C_{18}H_{31}NO_8S$ (SB15C5): C, 51.3; H, 7.41; N 3.32%}. ^{1}H NMR (ppm, in D_2O) for SB12C4 $\delta=3.16$ (s, 12H, NCH_3), 3.70 (s, 4H, OCH_2CH_2O), 3.78—3.85 (m, 4H, CH_2O), 4.27—4.31 (m, 4H, $ArOCH_2$), 7.17, 7.21 (d, 1H, Ar-H), 7.48 (m, 2H, Ar-H); for SB15C5 $\delta=3.17$ (s, 12H, NCH_3), 3.68—3.77 (m, 8H, OCH_2CH_2O), 3.91—3.95 (m, 4H, CH_2O), 4.22—4.24 (m, 4H, $ArOCH_2$), 7.07, 7.11 (d, 1H, Ar-H), 7.36, 7.46 (d, 1H, Ar-H), 7.40, 7.41, 7.44, 7.45 (dd, 1H, Ar-H). FABMS for SB12C4 Found: *m*/*z* 378.1613 $(M+H)^+$. Calcd for $C_{16}H_{28}NO_7S$: M, 378.1587. FABMS for SB15C5 Found: *m*/*z* 422.1823 $(M+H)^+$. Calcd for $C_{18}H_{32}NO_8S$: M, 422.1850.

Synthesis of Di(3′-sulfo)dibenzo-18-crown-6 Bis(ditetramethylammonium Salt) (DSDB18C6), Di(3′-sulfo)dibenzo-21-crown-7 Bis(ditetramethylammonium Salt) (DSDB21C7), and Di(3′-sulfo)dibenzo-24-crown-8 Bis(ditetramethylammonium Salt) (DSDB24C8). Dibenzo-18-crown-6 (13.9 mmol), dibenzo-21-crown-7 (12.4 mmol) or dibenzo-24-crown-8 (11.1 mmol) and acetonitrile (80 cm^3) were mechanically stirred in a round-bottom flask. After sulfuric acid (97%, 30.6 mmol for dibenzo-18-crown-6, 27.3 mmol for dibenzo-21-crown-7, and 24.4 mmol for dibenzo-24-crown-8) was slowly added from a dropping funnel, the mixture was stirred for 45 min at ca. 80 °C. The solvent was distilled away slowly. After complete evaporation of the solvent, a 25% methanol solution of tetramethylammonium hydroxide (29.2, 26.0, and 23.3 mmol, respectively) was added to the residue, precipitating a crude mixture. The mixture was first filtrated, and then recrystallized from 20% methanol–ethylacetate to give a white solid; 8.5 g of DSDB18C6 (92%), 7.9 g DSDB21C7 (90%) or 7.5 g DSDB24C8 (90%). {Found: C, 50.4; H, 6.91; N 4.19%. Calcd for $C_{28}H_{46}N_2O_{12}S_2$ (DSDB18C6): C, 50.4; H, 6.95; N, 4.20%}. {Found: C, 50.9; H, 7.76; N, 4.07%. Calcd for $C_{30}H_{50}N_2O_{13}S_2$ (DSDB21C7): C 50.7; H 7.09; N 3.94%}. {Found: C, 50.3; H, 7.09; N, 3.70%. Calcd for $C_{32}H_{54}N_2O_{14}S_2$ (DSDB24C8): C, 50.9; H 7.21; N 3.71%}. ^{1}H NMR (ppm, in D_2O) for DSDB18C6 $\delta=3.16$ (s, 24H, NCH_3), 3.99 (m, 8H, CH_2O), 4.23—4.25 (m, 8H, $ArOCH_2$), 7.06, 7.10 (d, 2H, Ar-H), 7.34, 7.35 (d, 2H, Ar-H), 7.38, 7.39, 7.42, 7.46 (dd, 2H, Ar-H); for DSDB21C7 $\delta=3.17$ (s, 24H, NCH_3), 3.79 (s, 4H, OCH_2CH_2O), 3.91—3.94, 4.00—4.03 (m, 4H+4H, CH_2O), 4.27—4.30 (m, 8H, $ArOCH_2$), 7.01—7.13 (m, 2H, Ar-H), 7.39—7.45 (m, 4H, Ar-H); for DSDB24C8 $\delta=3.17$ (s, 24H, NCH_3), 3.79 (s, 8H, OCH_2CH_2O), 3.90—3.93 (m, 8H, CH_2O), 4.19—4.33 (m, 8H, $ArOCH_2$), 7.05—7.13 (m, 2H, Ar-H), 7.39—7.43 (m, 4H, Ar-H). FABMS for DSDB18C6 Found: *m*/*z* 667.2548 $(M+H)^+$. Calcd for $C_{28}H_{47}N_2O_{12}S_2$: M, 667.2572. for DSDB21C7 Found: *m*/*z* 711.2836 $(M+H)^+$. Calcd for $C_{30}H_{51}N_2O_{13}S_2$: M, 711.2834. for DSDB24C8 Found: *m*/*z* 755.3135 $(M+H)^+$. Calcd for $C_{32}H_{55}N_2O_{14}S_2$: M, 755.3097.

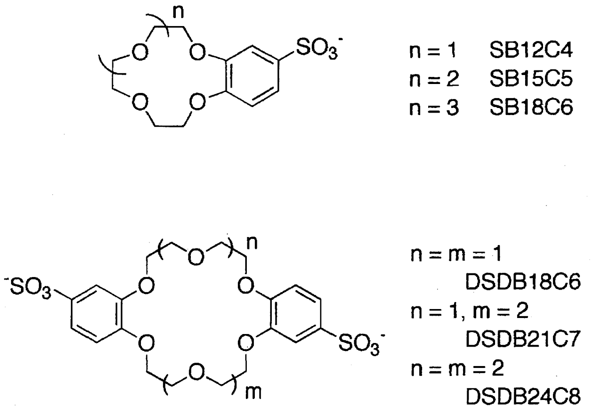


Fig. 1. The structural formulas of the sulfonated crown ethers.

Analytical data for SB18C6 can be found in a previous paper.[11] All of the sulfonated crown ethers are hygroscopic, and they should be kept in a desiccator to avoid taking up water.

Solvent Extraction of Lanthanides. The extraction was made in a 30 cm^3 glass-stoppered centrifuge tube with the aid of a mechanical shaker. A 5 cm^3 portion of an aqueous phase containing 0.1 mol dm^{-3} crown ether and 1×10^{-4} mol dm^{-3} lanthanide metal ion was adjusted to the desired pH with a hydrochloric acid or tetramethylammonium hydroxide solution. In the case of monosulfonated crown ethers, the ionic strength was adjusted to 0.12 with tetramethylammonium bromide. The aqueous phase was shaken with an equal volume of a cyclohexane phase containing 0.01 mol dm^{-3} D2EHPA at 25±1 °C. A shaking time of 1 h was found to be long enough to attain the extraction equilibrium. After centrifugation, the pH of the aqueous phase was measured by a Hitachi-Horiba F-22C pH meter and taken as the equilibrium pH. The metal concentration in the aqueous phase was determined by a Kyoto-Koken UOP-2 inductively coupled argon plasma atomic-emission spectrometer, and that in the organic phase was determined after stripping with a 1 mol dm^{-3} hydrochloric acid solution. The sum of the metal concentrations in the two phases was confirmed to agree well with the initial concentration.

Distribution of Sulfonated Crown Ethers. An aqueous phase containing 0.1 mol dm^{-3} crown ether was shaken with an equal volume of a cyclohexane phase in a 30 cm^3 centrifuge tube for 1 h at 25±1 °C. After centrifugation, the crown-ether concentration in the organic was determined spectrophotometrically by a Shimadzu UV-vis spectrophotometer UV-2200 at 237-8 nm after back-extraction into water. The crown-ether concentration in the aqueous phase was measured after dilution with water saturated cyclohexane.

Time-Resolved Laser-Induced Fluorescene Spectroscopy. The Eu^{3+} was excited to the $^5L_6$ state by a pulsed laser beam at 394 nm, and the emission from the $^5D_0$ state to the ground state ^7F manifold ($^7F_1$), 592 nm, was measured. The 394 nm pulsed laser beam was obtained with a pulsed 308 nm output of a Lambda Physik COMPex 201 XeCl excimer laser pumping PBBO (Lambda Physik) in a dioxane solution in a Lambda Physik SCANmate 2 dye laser head. The pulse power was typically 3—5 mJ for 394 nm and the pulse width was about 15 ns. The solution sample was taken in a standard 1 cm fluorimetry cell for a luminescence measurement. The emission light was collected at 90° into an Oriel 77257 monochrometer and detected by a Hamamatsu R928 photomultiplier tube. The whole emission wavelength range was observed. The signal was fed into a Hewlett Packard 54510A digitizing oscilloscope, which was connected to an NEC PC computer through a GP-IB interface. All of the luminescence decays observed in this work were single-exponential curves.

Fluorescence Spectroscopy. Fluorescence spectral measurements were performed at 25 °C using a Hitachi F-4500 spectrometer equipped with a xenon excitation source (394 nm with a band pass of 5 nm). The voltage of the photomultiplier was set at 750 V. The fluorescence readings were monitored at 540—720 nm.

NMR Spectroscopy. ^1H NMR spectra were obtained with a Varian 200 (200 MHz) spectrometer at 25 °C in D_2O with a Varian VXR 4000 data station.

Results and Discussion

Complex Formation Constants of Lanthanide ions with Sulfonated Crown Ethers in Aqueous Solution. The complex formation constants (β) of lanthanide ions (La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Dy^{3+}, Er^{3+}, and Yb^{3+}) 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 both the presence and absence of the crown ether. Because the partition constants for all of the crown ethers between cyclohexane and water are very low; $< 10^{-4}$ for the sulfonated crown ethers, $10^{-2.91}$ for 18C6 and $10^{-2.61}$ for 15C5,[15] the adduct formation reaction with the metal chelate and the macrocyclic ligand in the organic phase was negligible. Further, the distribution of lanthanide ions with the sulfonated crown ethers into cyclohexane in the absence of D2EHPA was confirmed to be less than 10^{-3}.

For the extraction of lanthanide ions (Ln^{3+}) with D2EHPA (HA), which was reported to exist as a dimer in an organic solvent of low polarity,[16] the extraction equilibrium and the extraction constant (K_{ex}) can be written as

$$Ln^{3+} + 3(HA)_{2,o} \rightleftharpoons LnA_3(HA)_{3,o} + 3H^+, \tag{1}$$

$$K_{ex} = [LnA_3(HA)_3]_o[H^+]^3/[Ln^{3+}][(HA)_2]_o^3, \tag{2}$$

where subscript o denotes the species in the organic phase. The distribution ratio of the metal ions in both the absence and presence of the crown ether (D^0 and D) can be expressed as in Eqs. 3 and 4, respectively, where β is the complex formation constant of lanthanide ions with the crown ether (CE) in the aqueous phase defined as $[Ln^{3+}(CE)]/[Ln^{3+}][CE]$:

$$\begin{aligned} D^0 &= [LnA_3(HA)_3]_o/[Ln^{3+}] \\ &= K_{ex}[(HA)_2]_o^3/[H^+]^3, \end{aligned} \tag{3}$$

$$\begin{aligned} D &= [LnA_3(HA)_3]_o/\{[Ln^{3+}] + [Ln^{3+}(CE)]\} \\ &= K_{ex}[(HA)_2]_o^3/[H^+]^3\{1+\beta[CE]\}. \end{aligned} \tag{4}$$

Diving D^0 by D gives

$$D^0/D = 1 + \beta[CE]. \tag{5}$$

The log D vs. pH plots for the extraction of lanthanide ions into cyclohexane with 0.01 mol dm^{-3} D2EHPA (a) in the absence and (b) in the presence of DSDB18C6 (0.1 mol dm^{-3}) are illustrated in Fig. 2. The plots are found to fall on straight lines with a slope of 3, in agreement with the power of the

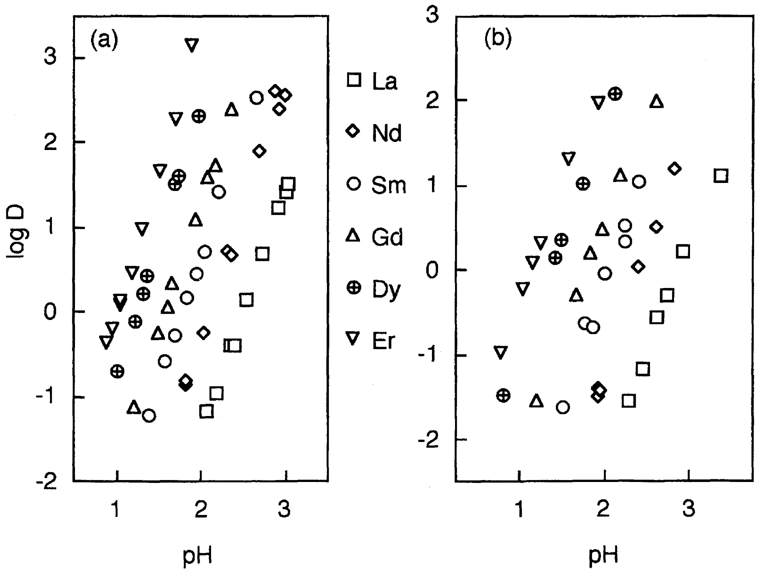


Fig. 2. Extraction of lanthanide ions into cyclohexane with 0.01 M D2EHPA (a) in the absence and (b) in the presence of DSDB18C6. $[D2EHPA]_o = 0.01$ mol dm^{-3} in cyclohexane, $[DSDB18C6] = 0.1$ mol dm^{-3}.

proton concentration in Eqs. 3 and 4. The slope of the plot of $\log D^0/D$ vs. log [CE] is almost unity in the [CE] range of 5×10^{-3}—1×10^{-1} mol dm^{-3}, indicating that a 1 : 1 complex is formed for all crown ethers in the aqueous phase.

The β values are summarized in Table 1. The difference between D^0 and D was too small ($\Delta pH_{1/2}<0.02$, that is, $\log D^0/D<0.06$) to obtain β of the complexes with 18C6 for the heavy lanthanide ions and with 15C5 for all of the ions. The previous investigations of lanthanide ions–crown ether complexes showed that no complexation reaction took place between 18-crown-6 and post-Gd^{3+} in methanol[17] and little or no complex formation took place between dibenzo-18-crown-6 and post-Nd^{3+} in acetone.[18] As shown in Table 1, all of the sulfonated crown ethers examined in the present work show the appreciable complexation with lanthanide ions. Due to the electron-withdrawing effects of the aromatic ring and the sulfonic acid group, the basicity of the aromatic ether oxygens is reduced in contrast to that of the other ether oxygens. Thus, it is presumed that the complexation of the metal ions with the present crown ethers could be weakened by this effect. The present results were unforeseen, and would support a significant contribution of the sulfonic acid group to complexation.

The stability of the resulting complex increases along with an 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. Further, 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 can not be explained only on the basis of the concept of a "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 the lighter lanthanide ions. The $\log\beta$ values are plotted against the reciprocal of the ionic radius[19] in Fig. 3. It is found that β for all of the sulfonated crown ether complexes with lanthanide ions gradually decreases along with an increase in the atomic number. This indicates that the cavity size is not the significant factor that governs the complexation behavior with lanthanide ions.

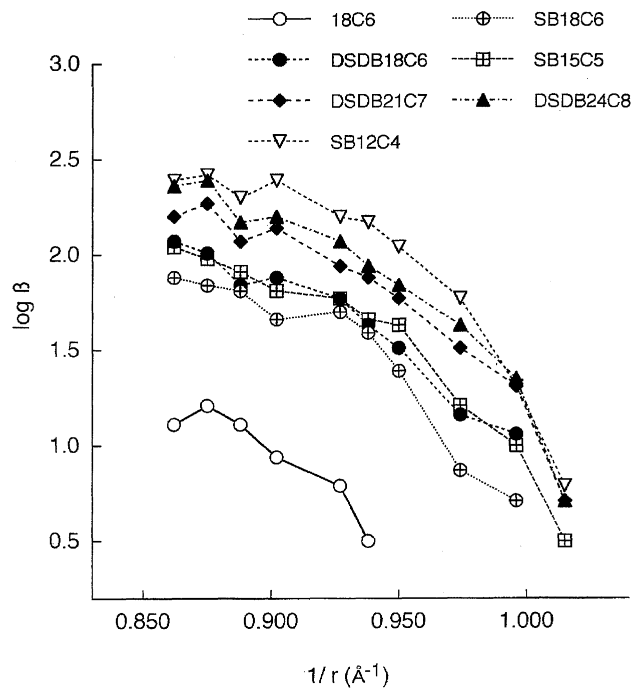


Fig. 3. Formation constants of the lanthanide complexes in aqueous solution.

Improved Extractive Separation of Lanthanides. The separation factor (SF) between two metal ions (M1 and M2) is defined in Eq. 6 as the difference in the logarithmic value of the respective distribution ratio.

$$SF = \log(D_{M1}/D_{M2}). \qquad (6)$$

The representative values are summarized in Table 2. The separation factor between La^{3+} and Yb^{3+} 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 effective for the heavier lanthanides.

Hydration States of the Eu^{3+} Complexes of Crown Ethers. The hydration number (n'_{H_2O}) of Eu^{3+} can be determined from the decay constants (k'_{obs}) of the luminescent excited state of Eu^{3+} in the crown ether complex using

Table 1. Log β Values for the Lanthanide–Crown Ether Complexes

Ln^{3+}	r(Å)	SB12C4	SB15C5	SB18C6	DSDB18C6	DSDB21C7	DSDB24C8	18C6	15C5
La^{3+}	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^{3+}	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^{3+}	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^{3+}	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^{3+}	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^{3+}	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^{3+}	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^{3+}	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^{3+}	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^{3+}	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 2. Separation Factors for the Extraction of Lanthanides in the Presence of Crown Ethers[a)]

	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

a) $[\mathrm{D2HEPA}]_0$=0.01 mol dm^{-3} in cyclohexane, [crown ether]=0.1 mol dm^{-3}.

Eq. 7,[20)] because the contribution from the ligand to the de-excitation of the luminescent excited state is negligible,[21)]

$$n'_{\mathrm{H_2O}} = 1.07k'_{\mathrm{obs}} - 0.62. \qquad (7)$$

The mole fraction (R) for the Eu^{3+}-complex in aqueous solution (0.01 mol dm^{-3} HCl) can be written as

$$R = \{\alpha - (\alpha^2 - 4\beta^2[\mathrm{Eu}^{3+}]_{\mathrm{tot}}[\mathrm{CE}]_{\mathrm{tot}})^{1/2}\}/2\beta[\mathrm{Eu}^{3+}]_{\mathrm{tot}}, \qquad (8)$$

where $\alpha = 1 + ([\mathrm{CE}]_{\mathrm{tot}} + [\mathrm{Eu}^{3+}]_{\mathrm{tot}})\beta$ and the subscript tot denotes the total concentration of the component.

The $n^0_{\mathrm{H_2O}}$ value is determined by extrapolating the $n'_{\mathrm{H_2O}}$ vs. R plot to R=1. Table 3 shows the calculated $n^0_{\mathrm{H_2O}}$ for the Eu^{3+} complexes of various crown ethers. The $n^0_{\mathrm{H_2O}}$ of the hydrated Eu^{3+} ion in H_2O was determined to be 9.0±0.5, which agrees well with the literature value.[20)] The $n^0_{\mathrm{H_2O}}$ of the 18C6 complex could not be obtained, since it was hard to set R at a proper value, owing to the low β value. In general, it could be expected that the number of hydrated water molecules around the central metal ion would decrease with the stronger binding of the IS-ACE to the metal ion. However, the opposite tendency is seen in our results; for the complexes of the 18-membered crown ethers and Eu^{3+}, $n^0_{\mathrm{H_2O}}$ increases along with an increase in the number of the sulfonic acid groups (SB18C6<DSDB18C6); that is, $n^0_{\mathrm{H_2O}}$ increases with an increase in the stability of the complex. The $n^0_{\mathrm{H_2O}}$ value also increases in the order SB18C6<SB15C5<SB12C4 for monosulfonated crown ethers, the same order in which their log β values increase. The $n^0_{\mathrm{H_2O}}$ value for the disulfonated crown-ether complex slightly increases with the cavity size.

Luminescence Spectroscopy of Eu^{3+}–Crown Ether Complexes in Aqueous Solution. The position of the Eu^{3+} complex emission bands in aqueous media did not depend on the existence and kind of the crown ether; however, changes in the relative intensities of the $^5D_0 \rightarrow {}^7F_1$ (592 nm) and $^7F_2$ (616 nm) emissions were observed (Fig. 4). The relative intensities are reported to be very sensitive to the detailed nature of the ligand environment, reflecting the hypersensitive character of the $^5D_0 \rightarrow {}^7F_2$ transition. Even in low-symmetry systems, the $^5D_0 \rightarrow {}^7F_1$ transition retains its magnetic dipole character, and its radiative transition probability is not much affected by the ligand environment. In contrast, the $^5D_0 \rightarrow {}^7F_2$ transitions are predominantly electric dipole in character, and their radiative transition probabilities are very sensitive to the detailed nature of the ligand environment.[22,23)]

The apparent relative intensity ratio between the $^5D_0 \rightarrow {}^7F_1$ and $^7F_2$ emissions (P') is defined as

$$P' = I'_{616\ \mathrm{nm}}/I'_{592\ \mathrm{nm}}, \qquad (9)$$

where I' denotes the peak area at 592 and 616 nm. The relative intensity ratio of the Eu^{3+}–crown ether complexes ($P_{\mathrm{(CE)}}$) can be calculated using Eqs. 8 and 9 as

Table 3. Luminescence Properties of the Eu^{3+}–Crown Ether Complexes in Aqueous Solution

CE	$n^0_{\mathrm{H_2O}}$ [a)]	$P_{\mathrm{(CE)}}$ [b)]
SB12C4	8.1±0.1	0.66
SB15C5	7.0±0.3	0.53
SB18C6	6.5±0.3	0.57
DSDB18C6	7.1±0.2	0.48
DSDB21C7	7.3±0.1	0.57
DSDB24C8	7.4±0.3	0.58
18C6	—	0.30

a) The hydration number. b) The relative intensity ratio of the Eu(III)–crown ether complexes.

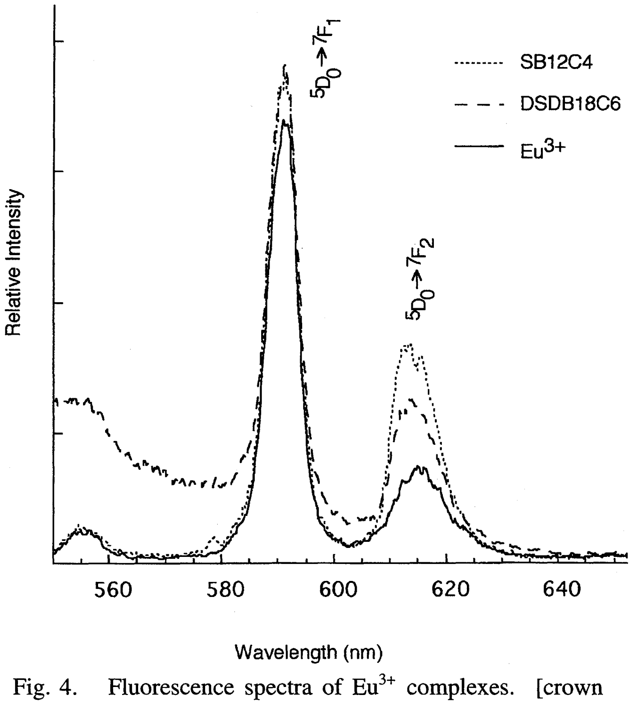


Fig. 4. Fluorescence spectra of Eu^{3+} complexes. [crown ether]=0.1 mol dm^{-3}, [$\mathrm{EuCl_3}$]=0.02 mol dm^{-3}.

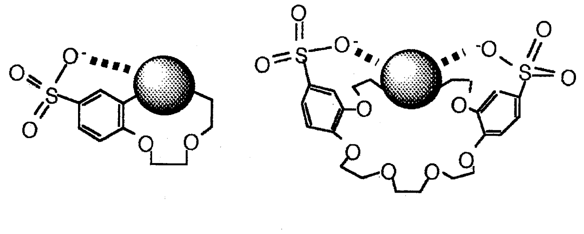
$$P' = P_{(\mathrm{Eu})^{3+}}\cdot(1-R)+P_{(\mathrm{CE})}\cdot R, \qquad (10)$$

where $P_{(\mathrm{Eu}^{3+})}$ is the intensity ratio in the absence of the crown ether (0.30). Table 3 gives the values of $P_{(\mathrm{CE})}$. Because $P_{(\mathrm{18C6})}$ is equal to $P_{(\mathrm{Eu}^{3+})}$, it can be considered that Eu^{3+} is incorporated in the cavity without diminishing symmetry. For SB18C6, which contains one sulfonic acid group, $P_{(\mathrm{SB18C6})}$ becomes larger due to an interaction between the Eu^{3+} and the sulfonic acid group, resulting in a lower symmetry than that of the 18C6 complex. The DSDB18C6 complex could recover symmetry due to the two sulfonic acid groups. The values of P for DSDB21C7 and DSDB24C8 are larger than that for DSDB18C6. In addition, $P_{(\mathrm{SB18C6})}$, being similar to $P_{(\mathrm{SB15C5})}$, is smaller than $P_{(\mathrm{SB12C4})}$. The symmetrical coordination would be reduced by the interaction ascribed to the sulfonic acid group and the larger or smaller cavity than that of the 18 membered macrocycle.

Stability. The unusual stability of lanthanide ions with sulfonated crown ethers, which have one or two binding sites, is dominated by two primary factors: (1) an ion-dipole interaction between the metal ion and the crown ether donating oxygens and (2) a long-range interaction between the metal ion and the sulfonic acid group. These synergistic effects should be taken into consideration. The sulfonic acid group and the crown-ether moiety do not work separately. A preliminary experiment shows that the complexation of lanthanide ions with 18C6 was not affected by the addition of benzenesulfonic acid (0.1 mol dm^{-3}).

On the basis of the results of the $n^0_{\mathrm{H_2O}}$ measurement and a luminescence study, the possible structures of the europium complexes with various sulfonated crown ethers have been postulated, and are illustrated in Fig. 5. It can be considered that $n^0_{\mathrm{H_2O}}$ decreases as the binding becomes stronger, that is, we assume that the europium ion with a lower value of $n^0_{\mathrm{H_2O}}$ would be located nearer to the cavity. The results of fluorescence spectroscopy also support the structure of the complexes. The symmetry of the coordination environment of the metal ion in aqueous solution depends on the extent of the interaction of the metal ions with the crown ether ring and the sulfonic acid groups.

The Eu^{3+} ion, which reacts with SB18C6 and DSDB18C6, is withdrawn from the cavity by the sulfonic acid group. The order of β is 18C6 < SB18C6 < DSDB18C6, although the hydration number increases as SB18C6 (6.5) < DSDB18C6 (7.1); in other words, the interaction of crown ether oxygens and the Eu^{3+} would be enhanced in the order SB18C6 > DSDB18C6. This tendency suggests that the contribution of the sulfonic acid group to the complexation stability is larger than that of the crown-ether moiety.



SB12C4 (n=8.1) DSDB24C8 (n=7.4)

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

For the monosulfonated crown ether complexes, $n^0_{\mathrm{H_2O}}$ increases in the order, SB18C6 (6.5) < SB15C5(7.0) < SB12C4 (8.1), as expected from the cavity size. Actually, the complexation stability with 15C5 was too low to obtain. However, the stability increases in the same order as $n^0_{\mathrm{H_2O}}$. The obtained results could not be anticipated from the cavity size. In the case of SB15C5 and SB12C4, the Eu^{3+} is not included in the cavity, and is located at a distance from the ring, which could enhance the interaction with the sulfonic acid group.

For the disulfonated crown ether complexes, $n^0_{\mathrm{H_2O}}$ increases slightly in the order DSDB18C6 < DSDB21C7 < DSDB24C8, while the stability increases as DSDB18C6 < DSDB21C7 < DSDB24C8. The binding with the crown-ether moiety would be comparable, as expected from the similar $n^0_{\mathrm{H_2O}}$. The ring conformation becomes more flexible as the ring size enlarges, which would enable a close contact of the sulfonic acid group with the central metal ion.

It could be concluded that the contribution of the long-range interaction between the metal ion and the sulfonic acid group would be more significant than the fitness of the ring size. The access of the sulfonic acid group to the central metal ion can facilitated by the appropriate size and flexibility of the crown ether ring.

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