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Stability Constants and Some Other Properties of the Lanthanoid Nitrate Complexes with Tri-, Tetra-, and Pentaethylene Glycols

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The lanthanoid nitrate complexes of tri-, tetra-, and pentaethylene glycols (EO3, EO4, and EO5) exhibited anomalous stability trends attributed to structures similar to those of crown complexes. The stability constants of the EO4 and the EO5 complexes decreased with an increase in the atomic number of the lanthanoid in contrast to the lanthanoid complexes with most other ligands. A maximum stability was found at europium for EO3 complexes. The decomposition temperatures of EO3 complexes were higher than those of the corresponding EO4 and EO5 complexes. The yields of the solid complexes in reactions of the lanthanoids with EO5 decreased with an increase in the atomic number of the lanthanoid (with some exceptions). The separation factors observed for fractional precipitation using EO5 as the separating reagents were comparable to those reported regarding reagents practically used for lanthanoid separation.

Macrocyclic polyethers, so-called crown ethers and so on, have received increasing attention in recent years because of their specific interaction with several cations. Relatively few reports[1–5] are concerned with the interaction of noncyclic polyethers with cations. The lanthanoid complexes of polyethylene glycols and glymes have been synthesized by the present authors.[6–8] The mutual separation of lanthanoids by fractional precipitation using tetraethylene glycol has also been reported.[9] According to structure analyses,[10–12] polyethylene glycols in lanthanoid complexes form ring-like structures similar to those of crown compounds, and the mode of coordination of a nitrate ion varies with a change in the number of oxygen atoms in the polyethylene glycols.

It would be interesting to investigate the stability of lanthanoid nitrate complexes with polyethylene glycols since the selectivities of the glycols are expected to be unique, as those of the crown compounds.[13–15] This is due to a similar structure. This paper reports on the stability constants and some other properties of lanthanoid complexes with tri-, tetra-, and pentaethylene glycols.

Experimental

Materials. The lanthanoid nitrates and their complexes were prepared by the method described in a previous report.[8] The composition of the complexes used in this investigation was $Ln(NO_3)_3 \cdot HO(CH_2CH_2O)_nH$ (Ln: lanthanoid element, n=3, 4, or 5). Tri-, tetra-, and pentaethylene glycols were the same as those in the previous paper,[8] and are denoted as EO3, EO4, and EO5, respectively.

Measurements of Decomposition Temperature and Solubility of the Complexes. The decomposition temperatures of the complexes were determined on a Yanagimoto micro melting-point apparatus. The procedure for solubility measurements was as previously described.[8]

Determination of Stability Constants. **The EO4 and EO5 Complexes**: The stability constants of the EO4 and EO5 complexes were determined by measuring the solubilities of the complexes in ethyl acetate containing different concentrations of EO4 and EO5. The following equilibrium was attained in solutions. The complex partly dissociated into the parent nitrate and EOn (n=4 or 5).

$$Ln(NO_3)_3 \cdot EOn \rightleftharpoons Ln(NO_3)_3 + EOn \quad (1)$$

Therefore, the apparent solubility (S), which was observed directly, is regarded to be the sum of the solubility of the undissociated complex (S_0) and the concentration of $Ln(NO_3)_3$ ([M]) arising from the dissociation, that is S=S_0+[M]. The value of S was varied with a change in the concentration of EO4 or EO5 because [M] is related to the concentration of EOn by Eq. 2 though S_0 is invariant.

$$K = \frac{S_0}{[M] \cdot [EOn]}, \quad (2)$$

where K and [EOn] represent the stability constant and the concentration of EOn, respectively. Equation 2 can be rewritten as Eq. 3 since [M]=S−S_0 and [EOn]=[M]+L.

$$K = \frac{S_0}{(S-S_0)(S-S_0+L)}, \quad (3)$$

where L is the initial concentration of EOn. Equation 4 is derived from Eq. 3.

$$S^2 + L \cdot S = S_0(2S+L) + (S_0/K - S_0^2) \quad (4)$$

A plot of (S^2+$L \cdot S$) against (2S+L) gave values for S_0 and K.

The EO3 Complexes: The stability constants of the EO3 complexes were determined by measurements of apparent molecular weights in solutions, since a determination of stability by measuring the solubility was difficult, owing to the very large solubilities of the complexes. The measurement of the molecular weights were carried out by vapor osmometry. The stability constant was calculated using Eq. 5.

$$K = \frac{\alpha^2 \cdot C_0}{1-\alpha}, \quad (5)$$

where α and C_0 represent the degree of dissociation and the formal concentration of the complex dissolved in acetone, respectively. The value of α was calculated from the observed molecular weight (M_o) and the formula weight (FW) of the complex using the equation $\alpha=(FW/M_o)-1$.

The stability constants of the EO3 complexes of some lanthanoids (La, Eu, and Lu) and yttrium were also determined by measurements of the proton NMR spectra of acetone-d_6 solutions. The signals of the oxyethylene protons of EO3 shifted upon complexing with metals. The relation between the dissociation degree of the complex (α) and the shift is expressed in Eq. 6.

$$\Delta a = (1-\alpha)\cdot\Delta A, \tag{6}$$

where Δa is the magnitude of the actually observed shift and ΔA is a value to be observed when all of the EO3 is complexed. A combination of Eq. 6 with Eq. 5 gives Eq. 7.

$$\Delta a = \Delta A - \sqrt{\Delta A/K}\cdot\sqrt{\Delta a/C_0} \tag{7}$$

A plot of Δa against $\sqrt{\Delta a/C_0}$ gave values for K and ΔA. The stability constants obtained by NMR measurement were roughly in accordance with those obtained by measurements of the molecular weight.

Determination of the Yield of the Solid Complexes. Ten cm^3 of a 0.05-M ethyl acetate solution of a hydrated lanthanoid nitrate was added to an equal volume of an ethyl acetate solution of EO5 in a 50-cm^3 flask with a glass stopper (1 M=1 mol dm^{-3}). The concentration of the EO5 solution was 0.025, 0.05, or 0.1 M. The water content of the mixed solution was adjusted to the desired value by dehydration or by the addition of water. The flask was shaken for 2 h in a water bath thermostatted at 25.0+0.5 °C. The complex was then deposited immediately after mixing or during the shaking. A solid complex was filtered out with sintered glass. The amounts of lanthanoid in the filtrate and in the solid complex were determined separately by EDTA titration. The yield of the solid complex (Y) was defined as

$$Y = (\mathrm{Ln})_s/((\mathrm{Ln})_s + (\mathrm{Ln})_f),$$

where $(\mathrm{Ln})_s$ and $(\mathrm{Ln})_f$ are the amounts of lanthanoid in the solid complex and filtrate, respectively.

Determination of the Separation Factor. The procedure for the determination of the separation factor was nearly the same as that for the determination of the yield, except the former treated the two-lanthanoid systems, which contained two different lanthanoids. The initial concentrations of individual lanthanoids and EO5 were all 0.0125 M. The separation factor between two lanthanoids (Ln1 and Ln2), $S_{\mathrm{Ln1,Ln2}}$ is defined as follows:

$$S_{\mathrm{Ln\,1,Ln\,2}} = \left(\frac{\mathrm{Ln\,1}}{\mathrm{Ln\,2}}\right)_s \Big/ \left(\frac{\mathrm{Ln\,1}}{\mathrm{Ln\,2}}\right)_f, \tag{8}$$

where (Ln1/Ln2) is the molar ratio of the two lanthanoids in the solid complex or filtrate. The amounts of individual lanthanoids in each phase were determined by absorption spectrophotometry, fluorescent X-ray analysis, or atomic absorption analysis.

Results and Discussion

Stability Constants of the Complexes. Figure 1 indicates that the stability constants of the EO4 and the EO5 complexes decreased with increasing atomic number of the lanthanoid and that those of the EO3 complexes exhibited a maximum at europium. The stability trends are considerably different from those of lanthanoid complexes, most other ligands showing higher stabilities for the heavier lanthanoids. Similar trends have been reported for complexes of crown compounds by Izatt et al.[13] and Massaux et al.[14,15] The stabilities of most other lanthanoid complexes depend mainly on the charge density of the lanthanoid ion, and accordingly increase with a decrease in the ionic radius. On the other hand, the specific selectivities of crown compounds for several cations have been explained on the basis of the concept of the fitness between the size of the cation and the cavity of the crown ether. The unique stability trends observed here are also considered to be attributed to the ring-like structures formed by the ligands.[10–12] The diameter of the cavity of the ring-like structure in an EO4 or EO5 complex was estimated to be about 270 pm by assuming that the conformation for C-C-O-C-C in the glycol is G-T-T-G (G: gauche, T: trans), which was reported to be the most stable one for poly(oxyethylene) derivatives in the metal complexes.[16] The cavity size is larger than the diameter of a La^{3+} ion (ca. 250 pm) which is the largest among the lanthanoid ions; correspondingly, the EOn chain in a lanthanoid complex is deformed from an ideal structure and is strained to maintain the Ln–O distance at a length suitable for coordination. The decrease in the ionic radius of the

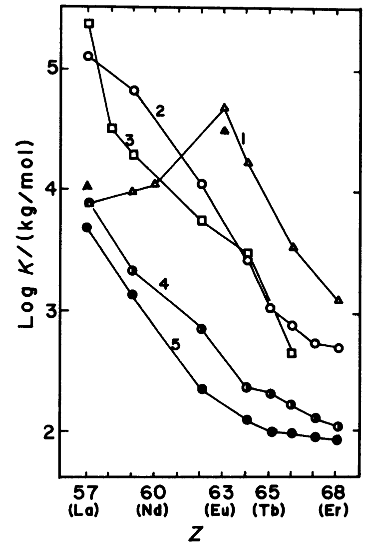

Fig. 1. Stability constants (K) of the lanthanoid nitrate complexes with EO3, EO4, and EO5.
1(△): EO3 complex (in acetone, ▲: Determined by NMR), 2(○): EO4 complex (in ethyl acetate), 3(□): EO5 complex (in ethyl acetate), 4(◑): EO4 complex (in ethyl acetate), 5(●): EO4 complex (in ethyl acetate). 1,2,3: [H_2O]=0.0 mol/kg, 4: [H_2O]=0.14 mol/kg, 5: [H_2O]=0.28 mol/kg. Z: atomic number.

lanthanoid increases the strain in the EO*n* chain and, hence, reduces the stability of the complex.

Triethylene glycol (EO3) in the complex surrounds only half of the lanthanoid ion and forms a ring-like structure with a bidentate nitrate. In addition, the distance between the two coordinating oxygens of the nitrate is rather short compared with those between the adjacent oxygens of EO*n*'s in the complexes. These situations make it possible for the coordinating oxygen atoms in the EO3 complexes to be located closer to the central metal ions without significant repulsion among the oxygen atoms or a serious strain in the glycol chain, than those in the EO4 or EO5 complexes. The contribution of the effect of charge density is, therefore, relatively large in the EO3 complexes as in the lanthanoid complexes with most other ligands. This is especially true for those of the lighter lanthanoids, while the effect of the strain in the EO3 chain becomes significant for complexes of heavier lanthanoids. The former effect increases and the latter decreases the stability with a decrease in the ionic radius of the lanthanoid. A maximum stability at europium is considered to result from a balancing of the above opposing effects.

The above results suggest that other noncyclic compounds, which would form ring-like structures in the complexes, could also exhibit specific selectivities for lanthanoids. The stability trends of the EO*n* complexes are different from those of many other lanthanoid complexes and demonstrate that the polyethylene glycols can be useful for lanthanoid separation, especially in a combined use with other separating reagents.

Figure 1 also demonstrates that the stability constants of the EO4 complexes decrease with an increase in the water concentration in a solution (curves 2, 4, and 5). A similar stability drop was also observed for EO3 and EO5 complexes, though only a qualitative investigation was carried out for a few of the complexes. The decrease in the stability is attributed to a competitive coordination of the water and the glycol to the lanthanoid, and necessitates the dehydration of the solution for a syntheses of some of the complexes.

Decomposition Temperature. All the complexes were decomposed to evolve gas (explosively) and to be blackened upon heating. As shown in Fig. 2, the decomposition temperature, T_d, of an EO3 complex is higher than those of the corresponding EO4 and EO5 complexes. This temperature became lower with an increase in the atomic number of the lanthanoid, except for lanthanum and praseodymium. The T_d of the EO4 complex became lower with an increasing atomic number of the lanthanoid from lanthanum to dysprosium (Z=66). It remained nearly constant for elements between dysprosium and lutetium. On the other hand, the T_d of the EO5 complex between lanthanum and gadolinium is nearly constant, and it lowers from gadolinium complex to the heavier lanthanoid complexes. The difference in the decomposition trends of EO4 and EO5 complexes between the lighter and heavier lanthanoids is probably related to different crystal structures. This was previously suggested by a powder X-ray analysis.[8]

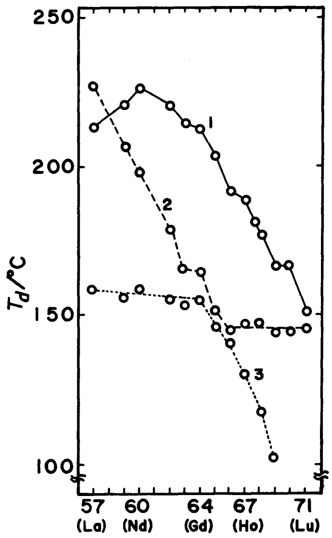

Fig. 2. Decomposition temperatures (T_d) of the lanthanoid nitrate complexes with EO3, EO4, and EO5. 1: EO3 complex, 2: EO4 complex, 3: EO5 complex. Z: atomic number.

Fractional Precipitation. The use of tetraethylene glycol (EO4) in the fractional precipitation of lanthanoids was reported by the present authors.[9] From data regarding the solubilities and stability constants of the complexes, pentaethylene glycol (EO5) was also expected to be useful for the separation of lanthanoids. Figure 3 shows the yields of the solid complexes in a reaction of lanthanoid nitrates with EO5. The yield generally decreased with an increase in the atomic number of the lanthanoid, with a few exceptions, and increased with an increasing initial molar ratio of EO5 to the lanthanoid (EO5/Ln). When the molar ratio was two or unity the yields were nearly the same. They were higher than 95% for elements between lanthanum and gadolinium ((EO5/Ln)=2) or for elements from lanthanum to neodymium ((EO5/Ln)=1). When the molar ratio was 1/2, the yield for cerium, praseodymium, neodymium, and samarium was higher than 50% (ca. 60%), though the yield was not expected to exceed 50% assuming that only a 1:1 complex was deposited. The actual Ln/EO5 ratios in the solid complexes of these elements were larger than 1.0. It was in accordance with the report[8] that the ratio in the solid complex was larger than unity unless EO5 was always in excess. The yield for lanthanum was lower than 50% in contrast to those for the other elements (Ce–Sm). The unique behavior of the lanthanum complex is attributed to the fact that only the 1:1 complex is deposited for lanthanum even when the nitrate is in excess.

The yields decreased for all the lanthanoids with an increase in the water content of the solution, as is shown in Fig. 4. The effect of water was greater for lanthanoid with a higher atomic number; and therefore, the difference in the yield among individual lanthanoids was enhanced by the addition of water. The yield was higher than 90% for elements from lanthanum to holmium in an anhydrous system, and ranged from 97.8% (for lanthanum) to 0.6% (for holmium) in a system containing 0.125 M H_2O. In a system of 0.5-M water content, the yield became 0% for europium and heavier lanthanoids, but was still higher than 80% for lanthanum, cerium, and praseodymium.

The above variation in the yield is consistent with the solubility data regarding complexes previously reported,[8] since the larger solubility of the complex results in the lower yield. The solubility generally decreases with an increase in the atomic number of the lanthanoid and with an increase in the water content of the solution. The anomalous behavior at cerium or the lower yield of the cerium complex (compared with the yield of praseodymium complex) reflects the larger solubility of the cerium complex. The yields shown in Fig. 4 are lower than those estimated from the solubility data assuming that equilibrium is attained. The lower yields are attributed to the fact that the equilibria are not entirely reached within two hours because the yields increased when they were determined after three days or longer.

The difference in the yield among individual

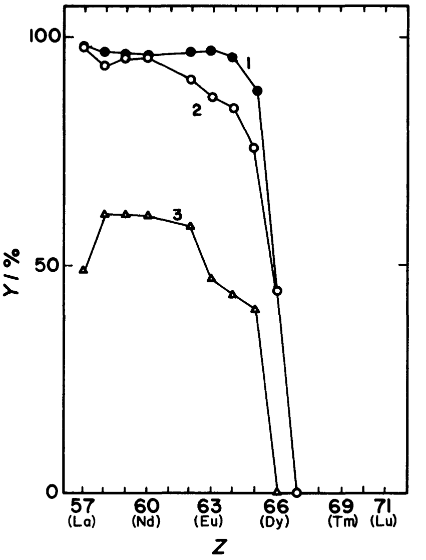

Fig. 3. Relationship between the yield (Y) of the solid EO5 complex and the atomic number (Z) of the lanthanoid.
Initial solution: $[Ln(NO_3)_3]=0.025$ M, $[H_2O]=0.125$ M.
1(●): EO5/Ln=2, 2(○): EO5/Ln=1, 3(△): EO5/Ln=1/2. Reaction time: 2 h.

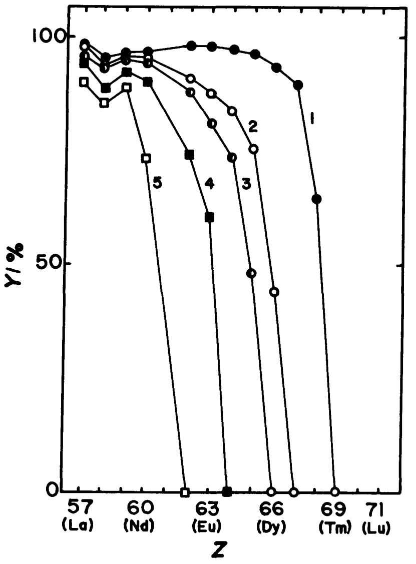

Fig. 4. Effect of the water content on the yield of the EO5 complex.
Initial solution; $[Ln(NO_3)_3]=[EO5]=0.025$ M.
1: $[H_2O]=0.0$ M, 2: $[H_2O]=0.125$ M, 3: $[H_2O]=0.25$ M, 4: $[H_2O]=0.375$ M, 5: $[H_2O]=0.5$ M. Reaction time: 2 h.

Table 1. Separation Factors($S_{Ln1,Ln2}$) for Several Couples of Lanthanoids

Reagent	$S_{Ln1,Ln2}$ for the pairs								
	La-Pr	Pr-Nd	Nd-Sm	Sm-Eu	Eu-Gd	Gd-Tb	Tb-Dy	Dy-Ho	Ho-Er
EO5[a]	1/1.53	1.34	2.48	1.72	1.70	1.71	1.75	1.76	1.74
EO5[b]	1/1.08	1.14	3.36	2.27	1.95	2.51	2.46	—	—
EO4[b]	4.71	1.99	5.50	2.94	2.05	—	—	—	—
EDTA[c]	10.81	2.0	3.1	1.4	1.02	4.8	2.25	3.6	1.8
D2EHPA[d]	6.72	1.7	5.0	2.2	1.6	3.2	2.0	2.1	2.1

a) Anhydrous system. b) System containing 0.0625 M H_2O. c) The values for EDTA were estimated from the stability constants of the complexes.[17] d) The values for D2EHPA were estimated from the distribution ratios.[18]

elements suggests the possibility of lanthanoid separation by fractional precipitation with EO5. The separation factors, $S_{\mathrm{Ln1,Ln2}}$, were determined for several two-lanthanoid systems to evaluate the ability of EO5 for the separation of lanthanoids. Table 1 lists the separation factors obtained in this study, together with those reported for systems using EO4,[9] ethylenediaminetetraacetic acid (EDTA)[17] and bis(2-ethylhexyl) hydrogenphosphate (D2EHPA).[18] The value of $S_{\mathrm{Ln1,Ln2}}$ were larger than unity except for the La–Pr, reflecting the trend of the yields that they were generally higher for lighter elements. The apparently anomalous value for a La–Pr pair is also reasonable considering that the yield of the lanthanum complex was lower than that of the praseodymium complex when EO5/Ln was 1/2. The separation factors observed for the systems containing water were higher than those for the anhydrous systems with two exceptions (La–Pr and Pr–Nd). The increase of the separation factors upon the addition of water is attributed to an enhancement of a difference in the yield among the individual elements described above. The separation factors obtained here were, like those for EO4, comparable to those for EDTA and D2EHPA which are the excellent reagents practically used for the separation of lanthanoids in ion-exchange and solvent-extraction processes, respectively. These results demonstrate that EO5 has an excellent separating ability.

The results also show that EO4 and EO5 are good precipitants for lanthanoid separation, though the loss of the solvent would be a serious problem regarding practical applications. A fractional precipitation may be favorable in some cases (for example, in the separation into two groups), since the procedure is simple and no special apparatus is required, though nowadays it is not popular because of the difficult procedures during multi-stage operation.

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