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Formation of Erbium and Holmium Mixed Complexes with Complexane and Carbonate Ion

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Synopsis. The formation of erbium and holmium mixed complexes with one species of complexanes and carbonate ion in alkaline solution (pH 10.5—10.7) was investigated spectrophotometrically. The results suggest that carbonate ion additionally combines with the EDTA and CyDTA chelates, while does not with the DTPA chelates.

In a previous paper[1)], the mechanism of formation and composition of erbium and holmium chelates with one of complexanes and 5-sulfosalicylic acid in alkaline solution were investigated. It is well known that tripositive rare earth salts, especially the heavier rare-earth salts are dissolved in a potassium carbonate solution because the carbonate complex forms.[2,3)] The formation of the erbium and holmium carbonate complexes causes a remarkable enhancement of the intensity in the hypersensitive bands of the metal ions.[4)] Though the rare earth–complexane chelates are very stable, the enhancement of the intensity is not remarkable.[1)] In the present paper, the formation of the mixed complexes has been studied by inquiring the enhancement of the intensity of a hypersensitive band with increasing concentration of carbonate ions added to the alkaline solutions of the rare earth–chelates of ethylenediaminetetraacetic acid (EDTA), *trans*-1,2-cyclohexanediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid (CyDTA), and diethylenetriamine-*N*,*N*,*N'*,*N''*,*N''*-pentaacetic acid(DTPA).

Experimental

All the absorption spectra were measured with a Hitachi EPS-3T automatic recording spectrophotometer.

The preparation of the reagents and the experimental procedure were carried out by the similar manner described in the previous paper.[1)] A potassium hydroxide solution for adjusting pH was stored in a reagent bottle with a soda lime tube.

Results and Discussion

The absorption spectra of the alkaline solution (pH 10.5—10.7) containing various combination of erbium and holmium (Ln), one species of the complexanes and the carbonate ion were recorded between 340 and 650 nm. As references the characteristic spectra in the region of 380 nm for erbium and 450 nm for holmium, obtained from these systems with the corresponding spectra of the rare earth–carbonate complexes (pH 10.5—10.7) and the rare earth chlorides (pH 2.0) are given in Figs. 1 and 2. From the results, the absorption spectra of the Ln–EDTA–CO_3^{2-} and Ln–CyDTA–CO_3^{2-} systems are quite different from that of the Ln–EDTA and Ln–CyDTA systems, respectively, and also from that of the Ln–CO_3^{2-} systems.

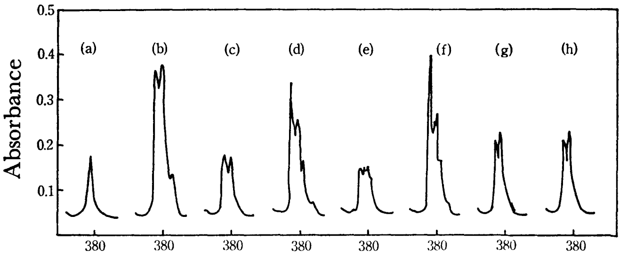

Fig. 1. Absorption spectra of aqueous solutions of erbium-complexane-CO_3^{2-} systems. (a) $ErCl_3$, (b) Er : CO_3^{2-} = 1 : 40.4, (c) Er : EDTA = 1 : 1.1, (d) Er : EDTA : CO_3^{2-} = 1 : 1.1 : 2.1, (e) Er : CyDTA = 1 : 1.3, (f) Er : CyDTA : CO_3^{2-} = 1 : 1.3 : 2.0, (g) Er : DTPA = 1 : 1.3, (h) Er : DTPA : CO_3^{2-} = 1 : 1.3 : 2.0. The ratio represents mole ratio (concentration of Er^{3+} is 0.02276 M).

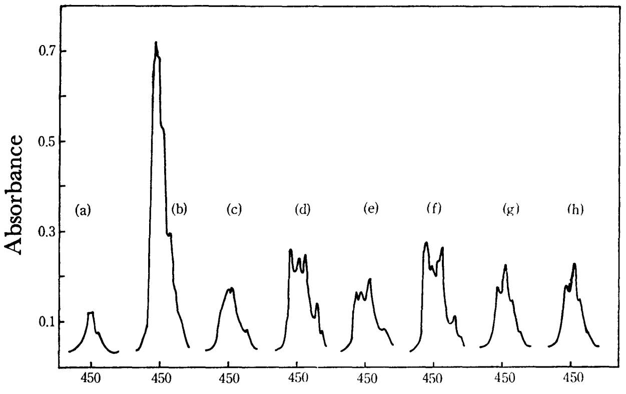

Fig. 2. Absorption spectra of aqueous solution of holmium-complexane-CO_3^{2-} systems. (a) $HoCl_3$, (b) Ho : CO_3^{2-} = 1 : 39.2, (c) Ho : EDTA = 1 : 1.3, (d) Ho : EDTA : CO_3^{2-} = 1 : 1.3 : 2.0, (e) Ho : CyDTA = 1 : 1.3, (f) Ho : CyDTA : CO_3^{2-} = 1 : 1.3 : 2.0, (g) Ho : DTPA = 1 : 1.3, (h) Ho : DTPA : CO_3^{2-} = 1 : 1.3 : 2.0. The ratio represents mole ratio (concentration of Ho^{3+} is 0.02348 M).

As Fig. 3 shows, the absorbance at the maximum of the absorption band in the Er–CyDTA system increases with increasing concentration of carbonate ions, and becomes almost constant in the region above one of $[CO_3^{2-}]/[Er^{3+}]$ mole ratio. Similar results were obtained from the Er–EDTA, Ho–EDTA, and Ho–CyDTA systems. Moreover, the continuous variation method was applied to study the mole ratio at which CO_3^{2-} combines with the chelates. The composition

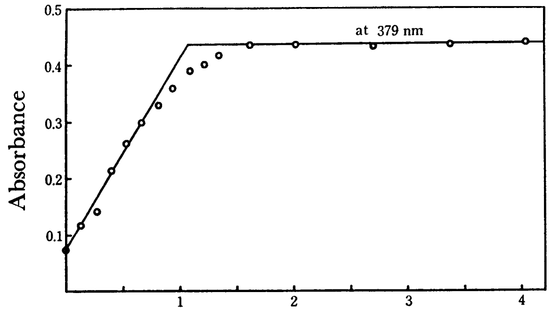

Fig. 3. Variation in absorbance as a function of mole ratio of [CO$_3^{2-}$]/[Er-CyDTA]. (concentration of Er^{3+} is 0.02276 M)

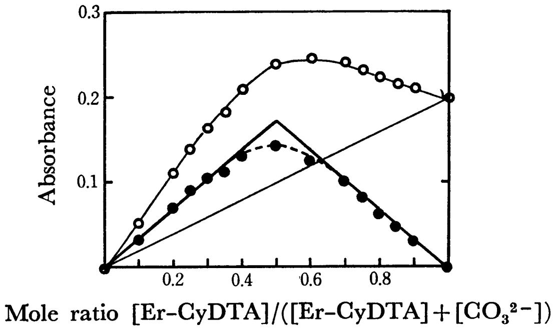

Fig. 4. Continuous variation plots in Er-CyDTA and CO$_3^{2-}$ system. (at 379 nm)

of the rare earth–EDTA and –CyDTA chelates is well known to be 1 : 1 mole ratio.[5,6] The result obtained, for instance, from the Er–CyDTA–CO$_3^{2-}$ system is shown in Fig. 4. The total concentration of Er–CyDTA and CO$_3^{2-}$ ion was maintained at 0.02276 M. The peak (at 379 nm) at mole fraction [Er–CyDTA]/([Er–CyDTA]+[CO$_3^{2-}$]) of 0.5 indicates combining ratio of 1 : 1. Similar results were obtained from all the other systems. Therefore, the combining ratio of these mixed complexes can be estimated to be Ln : complexane : CO$_3^{2-}$=1 : 1 : 1. The spectra obtained from the Ln–complexane–CO$_3^{2-}$ systems were affected neither by an addition of excess CO$_3^{2-}$ ion nor by that of excess EDTA and CyDTA. Accordingly, it is deduced that the formation of the mixed complexes is based on an addition reaction of the second ligand CO$_3^{2-}$ ion to the rare earth–complexane chelates. The difference in the absorption spectra between the Ln–DTPA and Ln–DTPA–CO$_3^{2-}$ systems is scarcely recognized as Figs. 1 and 2 show.

From these results, it is considered that the coordination sites of the rare earth ions are not completely occupied by the coordination center of hexadentate EDTA and CyDTA, while completely occupied by that of octadentate DTPA, that is, the preferred coordination number of the metal ions seems to be 8 than 6.

References

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