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Color and Precipitation Reactions of Lanthanoids with Chlorophosphonazo III

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Aqueous solutions of pH 1—3 containing Chlorophosphonazo III chelates of lanthanoids give an absorption spectrum of the α-type, the spectrum showing two maximum peaks at approximately 620 and 670 nm, in the presence of an excessive amount of the reagent. However, the chelates of heavier lanthanoids give an absorption band of the β-type, which extends from 700 to 800 nm with a maximum at 745 nm, with an increase in the mole ratio of the metal against the reagent. A dark-violet precipitate forms from the solution, giving the β-type spectrum under certain experimental conditions. The combining ratio of the metal against the reagent in the precipitate is estimated to be 1:1. Since a reaction rate from the α-type to the β-type corresponds to the second order, the combining form between the metal and the reagent in the β-type chelate is assumed to be 2 : 2, *i.e.*, a dimer. The chelates of lanthanum to samarium do not give the β-type spectrum under the same conditions.

The Chlorophosphonazo III [2,7-bis(4-chloro-2-phosphonophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid] reagent, which is one of the symmetrical bisazo derivatives of chromotropic acid, was used by O'Laughlin and Jensen to determine a micro-amount of the lanthanoids.[1] The determination was carried out by the measurement of the absorbance at a maximum peak near 670 nm of the absorption spectrum. The pattern of the spectrum was previously defined as α-type by the present author.[2] O'Laughlin *et al.* reported that, when the lutetium and ytterbium concentrations were increased to approximately half of the reagent concentration of 6×10^{-6}M at pH 3.0, a precipitate was formed and the solution became colorless.[1] The present author found the heavier lanthanoid chelates gave an absorption band, defined as of the β-type, which extends from 700 to 800 nm with a maximum at 745 nm, and a dark-violet precipitate is formed in the solution containing the β-type chelate under certain experimental conditions.[2]

In the present paper, the equilibrium relationship between the α-type and β-type chelates, the reaction rate of the change from the α-type to the β-type chelate, and the combining ratio of a metal against the reagent in the precipitate and the β-type chelate are investigated.

Experimental

Apparatus. All the absorption spectra were measured with a Hitachi EPS-3T automatic recording spectrophotometer. The hydrogen-ion concentration was determined by means of a Hitachi model M-4 pH meter.

Reagents. Standard aqueous solutions of lanthanoid chlorides were prepared from the respective oxides in a 99.9% purity.

Chlorophosphonazo III obtained from the Dojindo Co., Ltd., was used without further purification. The concentration was represented by multiplying the amount weighed by 0.76 because the purity of this reagent was 76%.[3]

Procedure. The absorption spectra were recorded after the prepared solutions had been allowed to stand for more than 50 h, unless otherwise indicated. Since the precipitate formed in the solution was readily dispersed by shaking, the measurement could be carried out by using the resulting solution.

The concentration of lanthanoid and phosphorus in the precipitate was estimated by the following procedure: the precipitate was obtained by adding 10 ml of a 2.4×10^{-4} M thulium, ytterbium, or lutetium chloride solution to 10 ml of a 2.4×10^{-4} M Chlorophosphonazo III solution at pH 1—2. The precipitate was then separated from the solution by centrifuging, and the supernatant was removed from the tube. An acidic solution of pH 1 containing a samll amount of magnesium chloride, used for preventing deflocculation of the precipitate, was added to the precipitate in the tube. The centrifuge tube was then shaked to disperse the precipitate into the solution. Again, the solution was removed from the precipitate by centrifuging. The dispersing and centrifuging was repeated 3—5 times. A part of the precipitate was then transferred into a conical beaker and decomposed by concentrated perchloric and nitric acids. After a clear solution had been obtained, the lanthanoid and phosphorus were determined spectrophotometrically by the O'Laughlin[1] and Lucena-Conde[4] methods respectively.

Results and Discussion

Absorption Spectra of the Lanthanoid Chelates. Figure 1 shows the absorption spectra of the aqueous

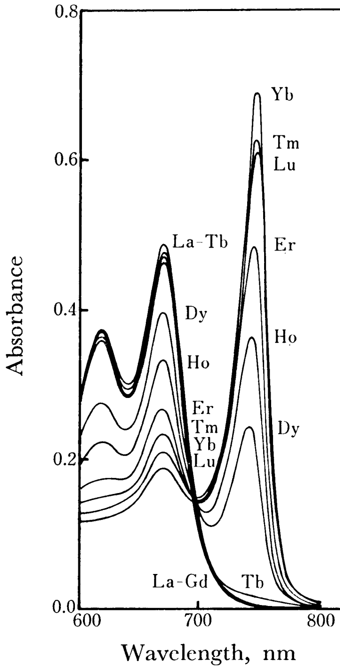

Fig. 1. Absorption spectra of lanthanoid Chlorophosphonazo III Chelates. Concentration of lanthanoids: 7.50×10^{-6}M. Concentration of reagent: 7.50×10^{-6} M. pH 1.6.

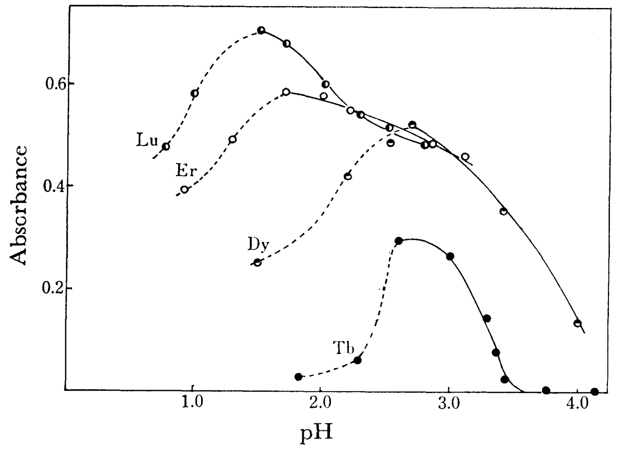

Fig. 2. Flariation of absorbance at 745 nm as a function of pH. Concentration of lanthanoids: 7.50×10^{-6}M. Concentration of reagent: 7.50×10^{-6}M.

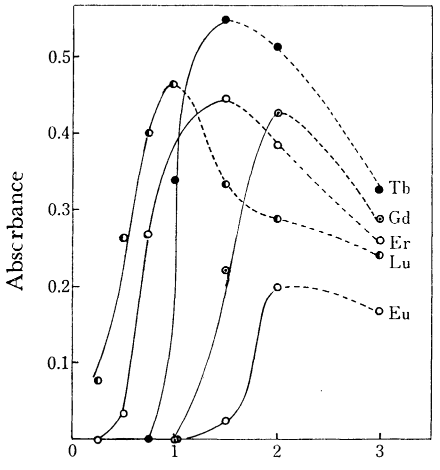

Fig. 3. Variation of absorbance at 745 nm as a function of mole ratio, $[Ln^{3+}]/[reagent]$. Concentration of lanthanoids: 7.50×10^{-6}M. pH 2.5.

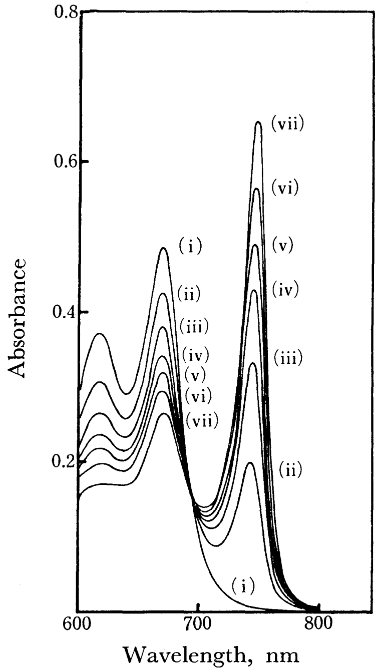

Fig. 4. Variation of absorption spectra of thulium chelate as a function of elapsing time.
Concentration of thulium: 7.50×10^{-6}M.
Concentration of reagent: 7.50×10^{-6}M. pH 2.0.
(i) 0.0, (ii) 0.25, (iii) 0.5, (iv) 1.0, (v) 2.0, (vi) 6.0, (vii) 72 h.

solution of pH 1.6 containing an equimole of each lanthanoid and Chlorophosphonazo III. The spectra of the chelates of lanthanum to terbium give an similar pattern and correspond to that of the α-type. On the other hand, the chelates of dysprosium to lutetium give a maximum absorption band at 745 nm, which is characteristic of the β-type. The tendency for the conversion from the α-type into the β-type increases with an increase in the atomic number, except in the case of lutetium.

Figure 2 shows the variation in the absorbance at 745 nm for the chelates of several lanthanoids as a function of the pH. The height of the maximum peaks and the degree of the transfer of the maximum position to the lower region increase with an increase in the atomic number. The precipitate was observed in a lower pH range than each maximum position; the dotted line indicates the range. The chelates of lanthanum to gadolinium do not give the β-type spectrum in the pH range between 1.0 and 4.0.

Figure 3 shows the variation in the absorbance at 745 nm as a function of the mole ratio of each lanthanoid to the reagent. The intensity of the absorption band first increases and then decreases with an increase in the mole ratio. The maximum values of the ratio for thulium to lutetium, for terbium to erbium, and for europium to gadolinium were observed at the mole ratios of approximately 1 : 1, 1.5 : 1, and 2 : 1 respectively. However, the absorption band of the β-type was not observed in the case of lanthanum to samarium even when the mole ratio of [metal]/[reagent] attained 15 : 1.

Reaction Rate of the Variation from the α-Type to the β-Type Chelate. Figure 4 shows the variation in the absorption spectrum of the thulium chelate from the α-type to the β-type as a function of the elapsed time. The spectrum gives the typical α-type at first, and then the pattern changes to the β-type with time. An isosbestic point is observed at approximately 700 nm. This fact suggests that an equilibrium relationship exists between the α-type and β-type chelates. The order of the reaction rate was investigated, and the following results were obtained; (i) the concentration of the β-type chelate follows Beer's law at 745 nm, and (ii) x and a, which represent the absorbance at 745 nm after t and 72 h respectively, are proportional to the reacting and initial concentration of the α-type chelate respectively. Figure 5 shows that the reaction rate for the thulium chelate is second-order, because the $1/(a-x)$ *vs.* t diagram gives a straight line.

Composition of the β-Type Chelate. Figure 6 shows the the continuous-variation plots at 745 nm for the holmium chelate. The peak at the mole fraction [Ho]/([Ho]+[reagent]) of 0.5 indicates that the combining ratio is 1 : 1. Moreover, the mole ratio of the lantha-

TABLE 1. ESTIMATION OF THE COMBINING RATIO OF LANTHANOID TO A REAGENT BY MEANS OF AN ANALYSIS OF THE LANTHANOID AND PHOSPHORUS IN THE PRECIPITATE

Lanthanoid used as precipitants	Phosphorus in the precipitate (mmol)	Lanthanoid in the precipitate (mmol)	Combining ratio, [lanthanoid]/[reagent]
Lu^{3+}	3.390×10^{-4}	1.686×10^{-4}	1.00
Lu^{3+}	2.658×10^{-4}	1.354×10^{-4}	1.02
Lu^{3+}	1.665×10^{-4}	0.920×10^{-4}	1.10
Lu^{3+}	1.795×10^{-4}	0.917×10^{-4}	1.02
Yb^{3+}	2.950×10^{-4}	1.518×10^{-4}	1.03
Yb^{3+}	5.525×10^{-4}	2.642×10^{-4}	0.96
Tm^{3+}	2.458×10^{-4}	1.180×10^{-4}	0.96
			Average 1.01

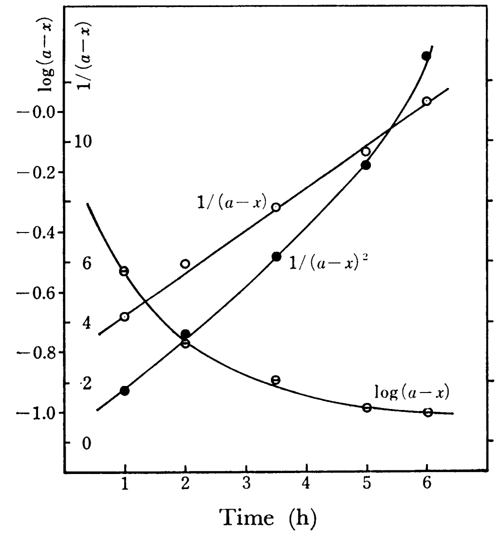

Fig. 5. Determination of order of reaction rate.

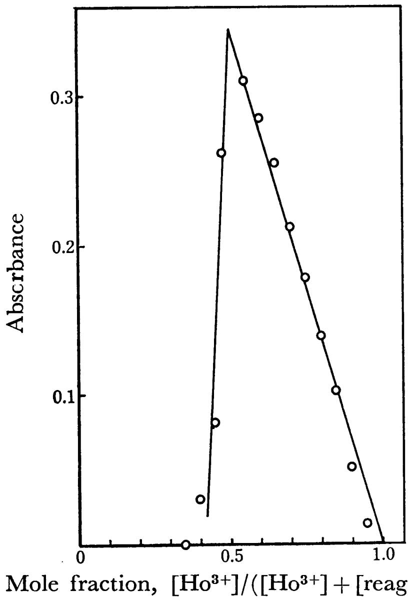

Fig. 6. Continuous variation plots at 745 nm for holmium chelate.
$[Ho^{3+}]+[reagent]=1.25\times10^{-5}M$. pH 2.2.

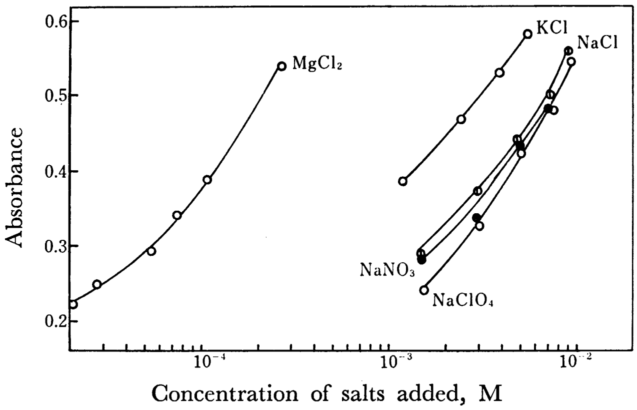

Fig. 7. Variation of absorbance of dysprosium chelate at 745 nm with increasing of coexisting salts. Concentration of Dy^{3+}: $6.25\times10^{-6}M$, Concentration of reagent: $6.25\times10^{-6}M$, pH 3.0.

noid to phosphorus in the precipitate obtained from the solution of the *β*-type chelate was estimated by the method described above. Table 1 shows that the mole ratio of lanthanoid against phosphorus is 1 : 2; *i.e.*, the combining ratio of lanthanoid against the reagent is 1 : 1. The impurities in the Chlorophosphonazo III used were presumed to be mono- and bisazo derivatives of chromotropic acid and unreacted chromotropic acid.[5] However, it is considered that these materials do not react to lanthanoids under the present experimental conditions.

Savvin reported[6] that only one functional group in Arsenazo III, which is one of the symmetrical derivatives of chromotropic acid, participates in the 1 : 1 chelate formation with lanthanoids. It is expected that the form of the *α*-type chelate of Chlorophosphonazo III resembles that of the Arsenazo III chelate, because the ratio of the metal against Chlorophosphonazo III is known[1] to be 1 : 1 and the spectrum of the *α*-type is similar to that of the Arsenazo III chelate. Thus, it may be concluded from the results of the reaction rate that the *β*-type chelate is a 2 : 2 dimer. The present author previously reported[2] that the *β*-type chelate may be supposed to be a chained-form in which two functional groups of Chlorophosphonazo III interact with the lanthanoids. However, the recent work shows that the β-type chelate is not the chained-form, but the 2 : 2 form.

Figure 7 shows the variation in the absorbance of the dysprosium chelate as 745 nm as a function of the concentration of the coexisting metal ions. The absorbance increases with an increase in the concentration of the coexisting metal ions, and finally the precipitate is formed. The effects of the metals on the intensity of the absorbance are in the following increasing order: sodium, potassium, and magnesium. However, it seems that anions do not contribute to the intensity. The formation of the precipitate may be explained by a coagulation of the anionic β-type chelate as a result of the influence of the coexisting cations.

The β-type spectrum was not observed in the Chlorophosphonazo III chelates of iron(III), aluminum, gallium, indium, scandium, zirconium, thorium, and uranium(VI), nor in the Arsenazo III chelates of these metals, including all of the lathanoids. On the other hand, it has been reported by several investigators that the chelate formed between a lighter lanthanoid and Carboxynitrazo[7] or Arsenazo-*p*-NO_2,[8,9] which is an unsymmetrical bisazo derivative of chromotropic acid, gives an absorption spectrum which is similar to the β-type. It is interesting to study the reason why the β-type spectrum appears considering the relationship between the positions or sorts of functional groups in the reagent and the ionic radius or coordination number of the metals.

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