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COLOR REACTION OF HEAVIER RARE EARTHS WITH CHLOROPHOSPHONAZO III

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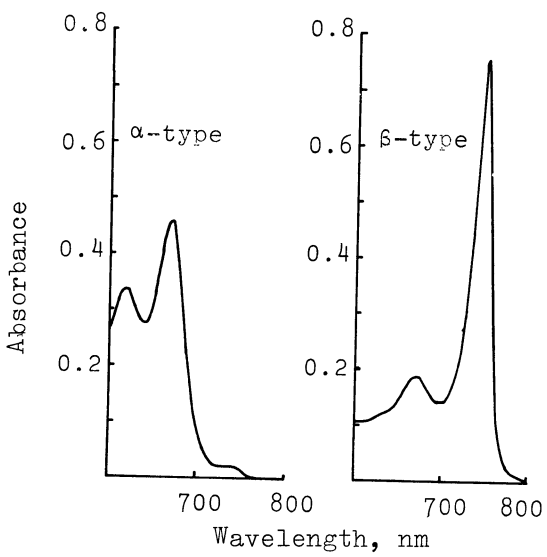
In absorption spectra of heavier rare earth (Gd to Lu) chelates of Chlorophosphonazo III, the absorption bands extend from 700 to 800 nm with a maximum at approximately 745 nm. The intensity of these bands increases with an increase in the mole ratio of the metal to the reagent and in the atomic number. Also it depends upon the pH value and the elapsing time. The corresponding chelates of lighter rare earths (La to Eu) do not exhibit a similar maximum under the same conditions.

The photometric reagent 2,7-bis-(4-chloro-2-phosphonobenzenazo)-1,8-dihydroxy-naphthalene-3,6-disulfonic acid (Chlorophosphonazo III), which is one of symmetrical derivatives of chromotropic acid was proposed by O'Laughlin and Jensen[1] as a sensitive reagent for rare earths and the determination was carried out by measurement of the absorbance at a maximum peak near 670 nm of the spectrum shown in Fig. 1. The pattern of the spectrum is defined as α-type. They observed that when lutetium concentration was increased up to approximately half the reagent concentration (6×10^{-6}M) at pH 3.0, a precipitate formed and the solution became colorless.

We found that the heavier rare earth (gadolinium to lutetium) chelates gave an absorption band, defined as β-type, as shown in Fig. 1, under a certain experimental condition. Tendency of the conversion of the α-type into the β-type increased with an increase in the mole ratio of the rare earth to the reagent and in the atomic number. Moreover, it depended upon the elapsing time as shown in Fig. 2.

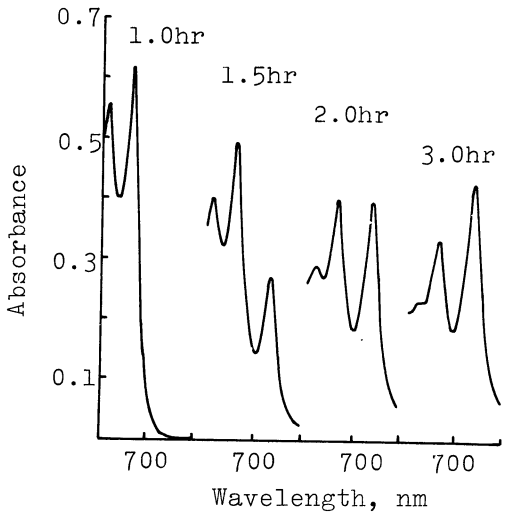
Fig. 3 shows the absorption spectra of the terbium chelate as a function of pH. Although the spectrum gave the typical α-type at pH 1.6, the pattern changed to the β-type, then again returned to the α-type with an increase in pH. In a series of

Fig. 1. Absorption spectra of rare earth chelates



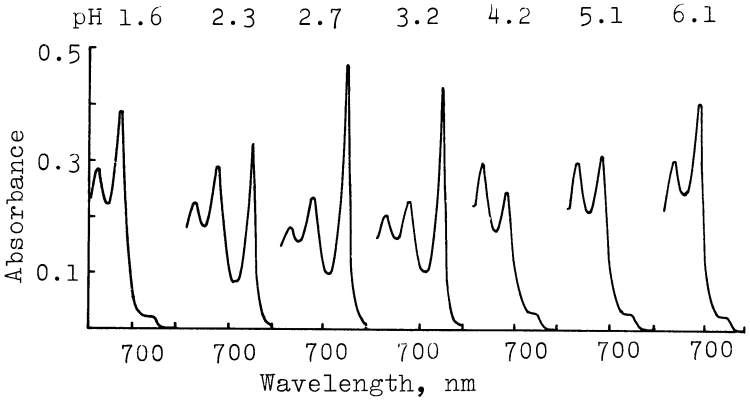
α-type : La/reagent=1/1
pH 1.7
β-type : Lu/reagent=1/1
pH 1.9
concentration of the reagent
$=6.25 \times 10^{-6}$M

Fig. 2. Absorption spectra of gadolinium chelates as a function of elapsing time



Gd/reagent=1.5/1
concentration of the reagent
$=1.25 \times 10^{-5}$M

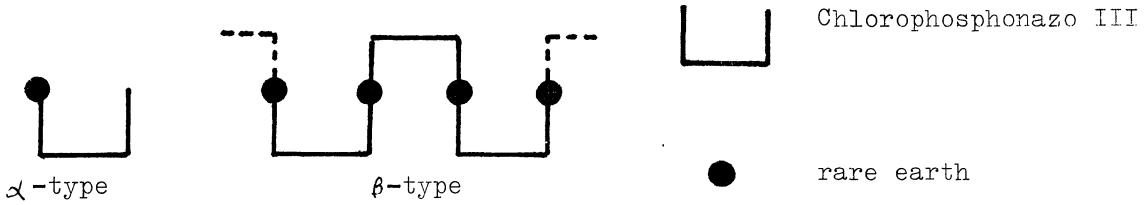
Fig. 3. Absorption spectra of terbium chelates as a function of pH



Tb/reagent=1/1
concentration of the reagent
$=6.25 \times 10^{-6}$M
The absorbance was measured 4 hrs. after preparation

the chelates of heavier rare earths, the pH values at which the β-type pattern dominated were as follows: Gd 3.3, Tb 2.8, Dy 2.0, Er 1.8, Tm 1.6, Yb 1.5, and Lu 1.4, and the height of the maximum at approximately 745 nm increased with an increase in the atomic number. No β-type spectrum for the lighter rare earth (lanthanum to europium) chelates was observed under the experimental conditions applied. The absorbance at 745 nm decreased with an increase in the concentration of coexisting metal ions and finally a dark violet precipitate was formed. The effect of the metal on the intensity of the absorbance was as follows in the decreasing order: magnesium, potassium, and sodium. However, it seemed anions did not contribute to the intensity. The analysis of the precipitated lutetium chelate gave the mole ratio of the metal to the reagent to be approximately 1.4 : 1.

Savvin reported[2] that only one functional group in the Arsenazo III, which is one of symmetrical derivatives of chromotropic acid, participates in the 1 : 1 chelate formation with rare earths. It is expected that the form of the α-type Chlorophosphonazo III chelate resembles that of the Arsenazo III chelate, because the ratio of the metal to the reagent in the α-type chelate is known[1] to be 1 : 1 and the spectrum of the α-type is similar to that of the Arsenazo III chelate. On the other hand, the β-type chelate is supposed to be chained-form, in which two functional groups of Chlorophosphonazo III interact with rare earths, and to be existing as a micelle. The simplified forms of these chelates may be represented as



The formation of the precipitate can be explained as the result of a coagulation of the micelle owing to the influence of the coexisting ions.

Recently, it has been reported that the chelate formed between a lighter rare earth and Carboxynitrazo[3] or Arsenazo-p-NO_2[4] which is an unsymmetrical bis-azo derivative of chromotropic acid gives a pattern similar to the β-type spectrum under a certain experimental condition.

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