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Complex Formation Reactions of Heavier Rare Earths with *meta*-Acetylchlorophosphonazo (CPAmA)*

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Abstract

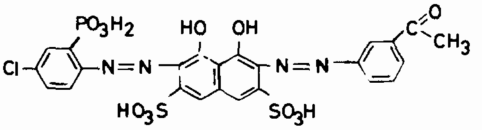
In acidic medium, heavier rare earths (RE) form 1:3 α-type complexes with CPAmA in excess of reagent. Under certain conditions, each of the α-type complexes is transformed to a β-type complex with an absorption peak at about 713 nm. The transformation reaction is a fist-order reaction which depends on the concentrations of reactants, mole ratio of RE/CPAmA, acidity and the standing time of the solution.

The stability constants and molar absorptivities of α-type complexes of RE–CPAmA decrease with the increase of the atomic numbers of heavier rare earths. The rate constants and half-life periods of their β-complex formation reactions are also dependent on their atomic numbers.

Introduction

The application of rare earths in various fields of science and technology is increasing because of their outstanding properties. Extensive research on analytical chemistry of rare earths has been made by Chinese analysts in the past decade [1].

The unsymmetric bisazo derivatives of chromotropic acid with one *o*-phosphono-*o*′-hydroxyazo functional group were found to be useful spectrophotometric reagents for total rare earths, sub-group and individual rare earths [2–7]. Among these reagents, *m*-acetylchlorophosphonazo (CPAmA), having a structural formula as follows:



has been employed successfully for the determination of rare earths [7], but few data have appeared on the study of the complex-formation reaction. In this paper, the reactions of heavier rare earths with CPAmA were studied in detail. The compositions, stabilities of the α-complexes, as well as the characteristics of the kinetics of their β-type complexes, were investigated and some regularities have been found.

Experimental

Reagents and Apparatus

m-Acetylchlorophosphonazo (CPAmA) was synthesized and purified as described previously [8]. Aqueous solutions 3.48×10^{-4} M and 7.20×10^{-5} M of CPAmA were prepared with the pure product.

The standard stock solution of holmium was prepared by dissolving holmium oxide (spec. pure) in hydrochloric acid and standardized by EDTA titration. The working standard solution was prepared by diluting with (1 + 200) hydrochloric acid to 3.00×10^{-4} M and 7.20×10^{-4} M. Standard solutions of gadolinium, terbium, dysprosium, erbium, thulium, ytterbium, lutetium and yttrium were prepared by the same procedure. The other chemicals were of analytical reagent grade; doubly distilled water was used throughout.

Absorption spectra and absorbances were recorded and measured on a Beckman DU-7HS spectrophotometer and a Model 751 spectrophotometer (Shanghai Analytical Instruments). A Model pHS-2 pH meter (Shanghai Second Analytical Instruments) was used to measure the pH of the solutions. A constant temperature was maintained by using an ultrathermostat.

General Procedures

Preparation of complex solution

In a 25-ml calibrated flask, reagents were added in the following order: rare earth, hydrochloric acid, distilled water, CPAmA. They were mixed well, diluted to the mark and the absorbance was measured at denoted wavelengths in a 1 cm cell against reagent blank (or as otherwise specified). The acidity of the

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solution was adjusted with hydrochloric acid and measured with a pH meter.

Measurements of Reaction Rates of β-type Complex

Under a constant temperature of 25 °C in a 25 ml calibrated flask, the complex solution was prepared as described above. The absorbance at the wavelength of maximum absorption was recorded on Beckman DU-7HS spectrophotometer assembled with a kinetic accessory.

Results and Discussion

Dissociation and Protonation Constants of CPAmA

CPAmA is a hexaprotic acid; its absorption spectra in different acidities are shown in Fig. 1. In media ranging from pH 1.20 up to 2.00 M hydrochloric acid, it is purplish-red in color with an absorption peak at 546 nm; the peak shifts to longer wavelength when the acidity is decreased. In strongly alkaline medium, the maximum absorption is at 591 nm with the formation of bluish-purple species. The protonation reaction is carried out in strongly acidic solution; the bright green protonated species gives a maximum absorption at 662 nm.

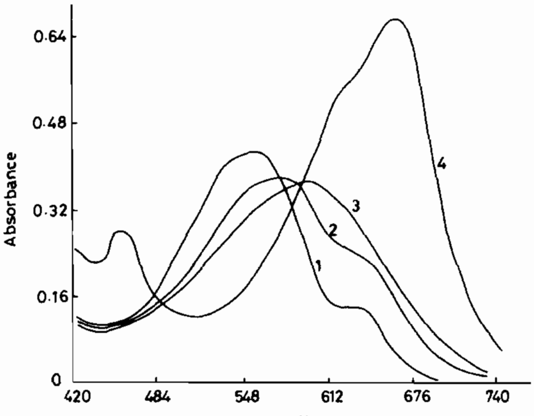


Fig. 1. Absorption spectra of CPAmA: (1) pH 1.30; (2) pH 9.00; (3) pH 11.78; (4) 9.17 M H_2SO_4. [CPAmA] = 2.02 × 10^{-5} M.

The stepwise dissociation and protonation constants were determined as described previously [8, 9]: pK_1, 0.39; pK_2, 1.12; pK_3, 2.74; pK_4, 6.79; pK_5, 9.73; pK_6, 11.46; and pK_p, −2.45.

Absorption Spectra of the Holmium–CPAmA Complex

The absorbance of the Ho–CPAmA complex is almost constant in the pH range of 1.35–3.30 in excess of CPAmA. The absorption spectra with various mole ratios of Ho:CPAmA at pH 1.50 ± 0.10 are shown in Fig. 2. It was found that the second absorption peak of the complex (the more sensitive peak) shifted to the longer wavelength with the increase in the concentration of CPAmA. The maximum absorption was at 656 nm, as the mole ratio was 1:1 and it would be 662 nm under the ratio of 1:3; a further increase in the concentration of CPAmA did not change the wavelength of the absorption peak. Obviously, complexes of various compositions exist under different conditions.

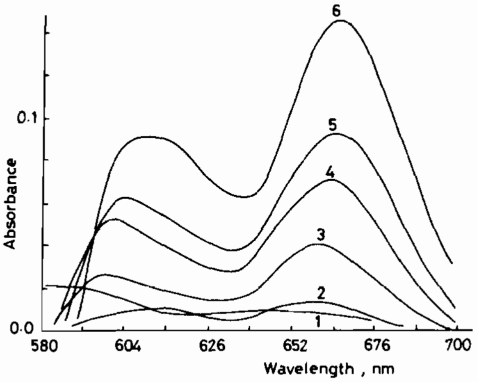


Fig. 2. Absorption spectra of the Ho–CPAmA complex: (1) [Ho] = 5.76 × 10^{-6} M; [CPAmA] = 2.88 × 10^{-6} M; reference = water. C_{Ho}/C_{CPAmA} = (2) 1:1; (3) 1:2; (4) 1:3 (5) 1:4; (6) 1:8; [Ho] = 2.88 × 10^{-6} M; reference = reagent blank; pH = 1.50 ± 0.10.

At pH 2.00 or higher, an increase in the concentrations of Ho and CPAmA to 10^{-5} M magnitude with the mole ratio from 1:1 to 1:5 would lead to the formation of a β-type complex (as defined by Taketatsu [10, 11]) after a short period of standing. As shown in Fig. 3, after standing, the absorbance of the second peak of the complex (α-type complex) is diminished gradually and that of the peak at 715 nm (β-type complex) is increased correspondingly; *i.e.* the longer the standing time, the more of α-type complex will transfer to β-type complex. An isosbestic point is located at 674 nm.

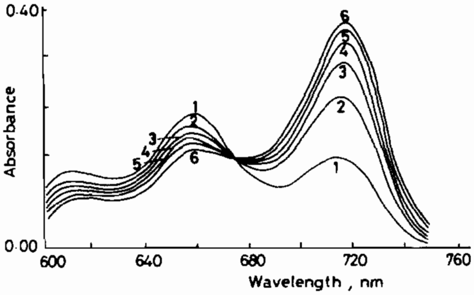


Fig. 3. Absorption spectra of the β-type complex of Ho–CPAmA: after (1) 5.0; (2) 10.0; (3) 15.0; (4) 20.0; (5) 25.0; (6) 30.0 min. [Ho] = 3.00 × 10^{-5} M; [CPAmA] = 1.20 × 10^{-5} M; pH = 2.00 ± 0.10.

TABLE I. Some Properties of Heavier RE–CPAmA Complexes

RE	λ^{α}_{max} (nm)	log β_s	$\epsilon \times 10^4$ ($l\ mol^{-1}\ cm^{-1}$)	λ^{β}_{max} (nm)	k (min^{-1})	$t_{1/2}$ (min)
Gd	661	47.85	6.49	711	1.24×10^{-1}	5.6
Tb	661	47.45	6.42	711	1.18×10^{-1}	5.9
Dy	660	47.22	6.39	711	1.11×10^{-1}	6.2
Ho	662	46.96	6.37	715	1.03×10^{-1}	6.7
Er	659	46.87	6.34	715	8.88×10^{-2}	7.8
Tm	659	46.71	6.30	715	7.54×10^{-2}	9.2
Yb	660	46.54	6.25	712	6.45×10^{-2}	10.7
Lu	659	46.36	5.48	714	6.19×10^{-2}	11.2
Y	659	47.03	5.95	713	9.26×10^{-2}	7.5

Kinetic Study on the β-Type Complex of Ho–CPAmA

Taketatsu [10, 11] classified the complex into α-type and β-type according to the wavelength of maximum absorption: shorter or longer than 700 nm. It was reported that the bisazo derivatives of chromotropic acid, having auxochromes such as –Cl, $-NO_2$ and $-COCH_3$, were reacted easily with rare earths to form β-type complexes [12]. As described previously, *p*-nitrochlorophosphonazo formed a β-type complex with yttrium [13] and CPAmA reacted with lanthanum to form a β-type complex [9]. However, the reaction rate of the La–CPAmA complex formation is slow, with a half-life period of 76.5 min.

The β-type complex of Ho–CPAmA was formed under the conditions described above. Complex formation proceeded after 5 min and was complete after about 40 min. On prolonging the standing time, the absorbance of the complex decreased and precipitation occurred. Experiments showed that relatively higher concentrations of the reactants and the mole ratio of Ho:CPAmA, slightly lower acidity and a longer standing time would favor β-complex formation.

As compared to the α-type complex, the β-type complex is more different from CPAmA, with a Δλ value (the difference in wavelengths between the complex and CPAmA) of 169 nm, whereas the Δλ of the α-type complex is 116 nm.

Under the following conditions; pH 2.00 ± 0.10, mole ratio of Ho:CPAmA 2.5:1 and temperature 298 K, $\log(A_{max} - A_t)$ and $1/(A_{max} - A_t)$ were plotted respectively *versus* t, where A_{max} is the maximum absorbance and A_t is the absorbance at denoted time. As shown in Fig. 4, the linear relation between $\log(A_{max} - A_t)$ and t indicates that the transformation reaction of α-complex to β-complex is a first-order reaction. The results obtained by a least-squares treatment are: rate constant, 1.03×10^{-1} min^{-1}; correlation coefficient, –0.9995; half-life period, 6.7 min.

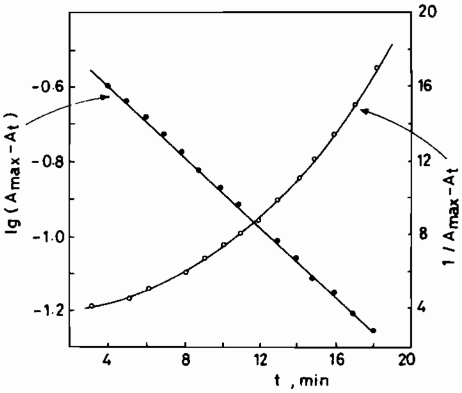


Fig. 4. Determination of reaction order of the β-type complex of Ho–CPAmA: [Ho] = 3.00×10^{-5} M; [CPAmA] = 1.20×10^{-5} M; pH = 2.00 ± 0.10; wavelength = 715 nm; T = 298 K.

The reactions of CPAmA with other heavier rare earths were similarly studied. They all gave relatively rapid β-type reactions and their characteristics are listed in Table I.

Composition of Complex

The molar composition of the holmium–CPAmA complex (α-type) formed at pH 1.50 was ascertained by Job's method of continuous variations, slope-ratio and equilibrium shift method. All three methods indicated that the metal-to-ligand ratio was 1:3, and the latter method also showed the existence of 1:1 and 1:2 complexes.

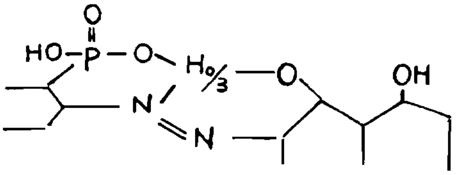
Stability Constants of Complex

Stability constants can be determined by the pH-dependent absorbances [14, 15]. The conditional stability constants of the 1:3 α-complex of holmium–CPAmA at various acidities are calculated by the following equation:

$$\log \beta_s' = \log \frac{A/\epsilon}{(C_{Ho} - A/\epsilon)(C_{CPAmA} - 3(A/\epsilon))^3}$$

where β_s' and ϵ are the conditional stability constant and molar absorptivity of the complex, and A is the absorbance at the denoted acidity.

CPAmA forms a stable α-complex with holmium, similar to that with lanthanum, with two six-membered rings having the following structure:



Hence in pH *ca.* 1.50, the dissociation of first –OH on the naphthalene ring (pK_5) and that of first proton dissociated from the $-PO_3H_2$ group (pK_3) should be considered for the estimation of the overall stability constant. According to the following equation:

$$\log \beta_s = \log \beta_s' + 3pK_3 + 3pK_5 - 6pH$$

experimental data and results are listed in Table II, the stability constant ($\log \beta_s$) of the Ho–CPAmA complex was calculated to be 46.96 ± 0.27 at a 95% confidence level.

TABLE II. Conditional Stability Constants and Overall Stability Constants of the α-Type Complex of Ho–CPAmA[a]

pH	A	$\log \beta_s'$	$\log \beta_s$
1.04	0.129	15.22	46.38
0.97	0.118	15.02	46.63
0.92	0.098	14.75	46.64
0.81	0.078	14.47	47.02
0.72	0.066	14.30	47.39
0.64	0.037	13.83	47.69

Mean $\log \beta_s = 46.92 \pm 0.27$

[a] $\epsilon = 6.37 \times 10^4$, $C_{Ho} = 2.88 \times 10^6$ M, $C_{CPAmA} = 1.73 \times 10^{-5}$ M, λ = 662 nm.

Properties of CPAmA Complexes of Other Heavier Rare Earths

The metal-to-ligand ratios of the CPAmA complexes (α-type) of Gd, Tb, Dy, Er, Tm, Yb, Lu and Y were determined to be all 1:3 by using the same methods. Their overall stability constants were estimated in a similar way and are listed in Table I. As shown in Fig. 5, the stabilities of the complexes of heavier rare earths with CPAmA decrease with increase of their atomic numbers (except Y), which is due probably to the steric hindrance. The stability constant of the yttrium complex is close to that of holmium but is less than that of lanthanum ($\log \beta_s$ = 50.07) [9].

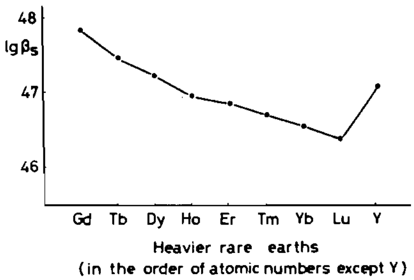


Fig. 5. Plot of $\log \beta_s$ of α-type complexes of RE–CPAmA *versus* the atomic numbers of heavier rare earths.

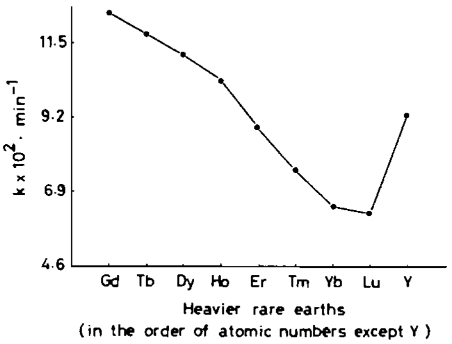


Fig. 6. Plot of rate constants of β-type complexes of RE–CPAmA *versus* the atomic numbers of heavier rare earths.

At pH 2.00 ± 0.10, all the heavier rare earths beside holmium give β-type reactions with CPAmA under the mole ratio of RE:CPAmA = 2:1. Their transformation reaction from α-type to β-type complexes are all first-order reactions, but the reaction rates are different. The absorption peaks of their β-complexes are all around 713 nm and the half-life periods are all shorter than that of the lanthanum complex ($t_{1/2}$ = 76.5 min). Their rate constants decrease with the increase of their atomic numbers, except for Y (Fig. 6).

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