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KINETIC STUDY OF RARE EARTH-EDTA-TIRON MIXED COMPLEX FORMATION REACTION IN AQUEOUS SOLUTION

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Mixed complex formation reactions of the EDTA-rare earth complex with tiron were studied by the temperature jump method. The two step mechanism involving the intermediate complexes of EDTA-rare earth-protonated tiron ion agreed reasonably with the concentration dependency of observed relaxation times. The values of the formation rate constants were the order of $10^5 M^{-1} sec^{-1}$, which are two or three order less than the values in hydrated rare earth ions-murexide, -oxalic acid and -anthranic acid systems.

The ligand-ligand interaction, electrostatic and steric repulsion, acts as the retarding effects in these mixed comlex formation reactions.

Introduction

Rare earth-EDTA complexes react with the second ligand such as tiron (4, 5-dihydroxybenzene-1, 3-disulfonic acid) and form mixed complexes1). From the study of stability constants of various mixed complexes, rare earth ions are considered to have coordination number larger than six1,2). Crystallographic studies indicate that the coordination number of rare earth ions is eight or nine3). EDTA has six binding sites, while tiron has two. Therefore, in mixed complexes, the whole binding sites of two ligands may coordinate to the rare earth ion. The rate constants of complexation reactions of rare earth ions with murexide, oxalic acid and anthranic acid are very large ($10^7 \sim 10^8 M^{-1} sec^{-1}$)4,6). In the mixed complex formation reaction, ligand-ligand interactions, for example, steric hindrance and electrostatic repulsion, may influence the reaction rate. Using the temperature jump method, the rare earth-EDTA-tiron systems were treated kinetically in this investigation.

Experimental

The stock solutions of rare earth ions were prepared by adding oxides to known quantities of dilute

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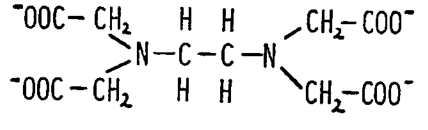
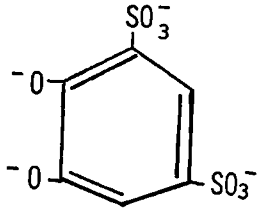
perchloric acid. The concentrations of rare earth ions in stock solutions were checked by the standard gravimetric method. The solutions containing the rare earth ion, EDTA, tiron and indicator (phenol red) were prepared and made up to ionic strength 0.1 with the concentrated sodium perchlorate solution. The rare earth ion and EDTA were always in the ratio 1 : 1. Therefore, in the sample solutions free EDTA ions and the rare earth ions uncoordinate with EDTA were negligible1).



EDTA



Tiron

The experimental procedures and instrumentation are described in a previous paper7). A representative relaxation spectrum for the Dy^{3+}-EDTA-tiron-indicator solution is shown in Fig. 1. No relaxation was observed for Dy^{3+}-EDTA-indicator solutions. The relaxation was seen when Dy^{3+}-tiron-indicator solutions were used. But the direction of the relaxation signal was opposite to Fig. 1. This relaxation may be due to the complexation reactions between Dy^{3+}, DyOH^{2+} and tiron ions8).

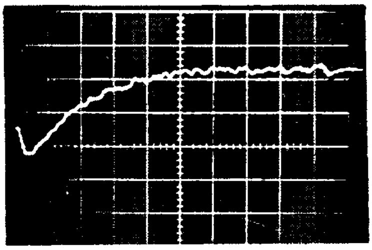


Fig. 1 Relaxation curve of EDTA-Dy^{3+}-tiron system at 25°C $(\mathrm{EDTA})_0=(\mathrm{Dy}^{3+})_0=2.50\times10^{-3}$M, $(\mathrm{tiron})_0=1.00\times10^{-3}$M, pH 7.65, indicator is phenol red
The sweep rate is 200 μsec/div.
Vertical scale is arbitrary units of absorbance at 560 nm.

Results and Disscussion

The initial concentrations of rare earth ions (and EDTA) and tiron, the pH values and the observed relaxation times, are shown in Table 1. Each relaxation time listed in Table 1 is an average of at least three photographic determinations. Dy^{3+}, Ho^{3+}, Er^{3+}, Yb^{3+} and Y^{3+} were used in this investigation. Gd^{3+}-EDTA-tiron-indicator solutions were tested but relaxation signals were too small to treat quantitatively (the relaxation times were in the range of 100 μsec). No relaxation was observed when La^{3+} was used as the metal ion. If M^{3+} is the rare earth ions, and E^{4-} and T^{4-} are the completely dissociated forms of EDTA and tiron respectively, the ions contributing to relaxations in pH 7~8 are EM^{-}, T^{4-}, HT^{3-}, H$_2$T^{2-} and EMT^{5-}1).

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The following one-step reactions were considered to test the concentration dependency of relaxation times:

$$EM^- + T^{4-} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} EMT^{5-}, \tag{1}$$

$$EM^- + HT^{3-} \underset{k'_{-1}}{\overset{k'_1}{\rightleftarrows}} EM^{5-} + H^+. \tag{2}$$

Table 1 Experimental conditions and relaxation times for rare earth ions-EDTA-tiron solutions

$(M^{3+})_0$	$(EDTA)_0$ 10^{-3}M	$(tiron)_0$ 10^{-3}M	pH	τ m sec
$(Dy^{3+})_0$	0.300	0.300	7.60	0.77
	0.500	0.500	7.60	0.57
	0.500	1.00	7.63	0.81
	0.800	0.800	7.70	0.55
	1.00	1.00	7.44	0.41
	2.00	1.00	7.68	0.36
	2.00	1.00	7.62	0.31
	2.50	1.00	7.65	0.29
$(Ho^{3+})_0$	0.500	0.500	7.58	1.02
	1.00	1.00	7.49	0.68
	2.00	2.01	7.58	0.47
	3.00	3.01	7.60	0.41
	4.00	4.01	7.53	0.30
$(Er^{3+})_0$	0.500	0.500	7.49	1.7
	0.700	0.700	7.47	1.2
	1.00	1.00	7.47	1.2
	2.00	2.00	7.70	0.78
	3.00	3.00	7.48	0.58
$(Y^{3+})_0$	0.500	0.500	7.47	1.06
	1.00	1.00	7.72	0.88
	2.00	2.00	7.51	0.58
	3.00	1.01	7.68	0.46
	4.00	4.00	7.46	0.33
$(Yb^{3+})_0$	0.500	0.500	7.63	7.0
	0.500	0.500	7.60	5.7
	0.700	0.700	7.91	5.3
	1.00	1.00	7.54	2.7
	2.00	2.00	7.67	2.3
	2.89	2.89	7.61	1.8
	3.00	3.00	7.48	1.2

$(M^{3+})_0$, $(EDTA)_0$ and $(tiron)_0$ represent the initial concentrations of the rare earth ion, EDTA and tiron, respectively.
Phenol red was used as indicator (initial concentration 1.5×10^{-5}M).

where k_1, k_{-1}, k'_1 and k'_{-1} are the rate constants.

The relaxation time as a function of equilibrium concentrations was derived from reactions (1), (2) and acid-base equilibria of tiron and the indicator[9]. But the observed relaxation times did not fit to the derived equation. Next, the following two-step reaction was considered.

$$\mathrm{EM^- + HT^{3-}} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{EMHT^{4-}} \overset{K_d}{\rightleftarrows} \mathrm{EMT^{5-} + H^+}. \tag{3}$$

K_d is the proton dissociation constant of $\mathrm{EMHT^{4-}}$. $\mathrm{EMHT^{4-}}$ in equation (3) is the intermediate ion which was not detected by the study of potentiometric titrations. But such an intermediate was treated in $\mathrm{Ni^{2+}}$-, $\mathrm{Co^{2+}}$- and $\mathrm{Zn^{2+}}$-tiron systems by Kustin *et al.*[10]. It is possible that in the rare earth-EDTA-tiron systems $\mathrm{EMHT^{4-}}$ exists though the concentration may be very low compared with $\mathrm{EMT^{5-}}$. To derive the relaxation time, the following protolytic reactions must be involved in the reaction mechanism.

$$\mathrm{H_2T^{2-}} \rightleftarrows \mathrm{HT^{3-} + H^+}, \qquad \mathrm{p}K_1 = 7.54, \tag{4}$$

$$\mathrm{HT^{3-}} \rightleftarrows \mathrm{T^{4-} + H^+}, \qquad \mathrm{p}K_2 = 12.38, \tag{5}$$

$$\mathrm{HIn} \rightleftarrows \mathrm{In^- + H^+}, \qquad \mathrm{p}K_1' = 7.9, \tag{6}$$

where $\mathrm{In^-}$ represents the dissociated species of the indicator.

The reciprocal relaxation time is deduced by Eqs. (3)~(6) assuming protolytic reactions are very fast compared with the complexation reaction between $\mathrm{EM^-}$ and $\mathrm{HT^{3-}}$. The result is

$$\frac{1}{\tau} = k_1 \cdot AA, \tag{7}$$

$$AA = (\mathrm{EM^-})\frac{\alpha}{(1+\alpha)} + (\mathrm{HT^{3-}}) + \frac{K_d}{(1+\beta)K_m K_1}, \tag{8}$$

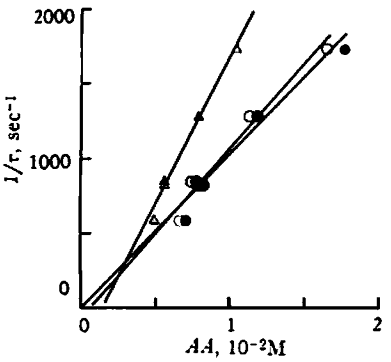

Fig. 2 Plot of $1/\tau$ *vs.* AA for $\mathrm{Er^{3+}}$
△: $K_d = 10^{-7}$
○: $K_d = 10^{-6}$
●: $K_d = 10^{-5}$

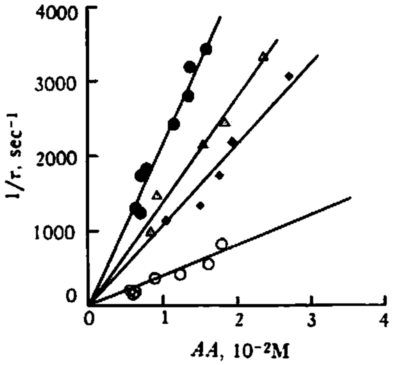

Fig. 3 Plot of $1/\tau$ *vs.* AA for $\mathrm{Dy^{3+}}$, $\mathrm{Ho^{3+}}$, $\mathrm{Y^{3+}}$, $\mathrm{Yb^{3+}}$ at $K_d \geq 10^{-5}$
●: $\mathrm{Dy^{3+}}$, △: $\mathrm{Ho^{3+}}$
◆: $\mathrm{Y^{3+}}$, ○: $\mathrm{Yb^{3+}}$

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$$\alpha=\frac{\delta(\mathrm{EMT^{5-}})}{\delta(\mathrm{EMHT^{4-}})},\qquad \beta=-\frac{\delta(\mathrm{EM^{-}})}{\delta(\mathrm{HT^{3-}})},$$

$$K_{\mathrm{m}}=\frac{(\mathrm{EMT^{5-}})}{(\mathrm{EM^{-}})(\mathrm{T^{4-}})}.$$

$(\mathrm{EM^-})$, *etc.*, are the equilibrium concentrations and δ shows the small deviation from the equilibrium concentration. α and β are calculated numerically using equilibrium concentrations and equilibrium constants. The values of K_1, K_2 and K_{m} were used from literature values[1]. As the value of K_{d} was not known, the trial values of K_{d} were used and the numerical values of AA in Eq. (8) were calculeted. If the reaction mechanism (3) and the value of K_{d} were suitable, the plot of $1/\tau$ *vs.* AA should be a straight line through the original point. The plot for $\mathrm{Er^{3+}}$ is shown in Fig. 2. It is clear that the plot is a straight line through the original point at $K_{\mathrm{d}}\geq10^{-5}$. The plot is nearly independent of the values of K_{d} over 10^{-5}. The concentrations of $\mathrm{EMHT^{4-}}$ are very low compared with those of $\mathrm{EMT^{5-}}$ within these values of K_{d}. The plot for $\mathrm{Dy^{3+}}$, $\mathrm{Ho^{3+}}$, $\mathrm{Y^{3+}}$ and $\mathrm{Yb^{3+}}$ at $K_{\mathrm{d}}\geq10^{-5}$ is shown in Fig. 3. The rate constant k_1 was obtained from the slope for each rare earth ion. The values of k_1 are listed in table 2.

Table 2 Rate constants of the complexation reaction of the type

$$\mathrm{EM^{-}+HT^{3-}}\xrightleftharpoons{k_1}\mathrm{EMHT^{4-}}\xrightleftharpoons{K_{\mathrm{d}}}\mathrm{EMT^{5-}+H^{+}}$$

$\mathrm{M^{3+}}$	$k_1\,(\mathrm{M^{-1}\,sec^{-1}})$
$\mathrm{Dy^{3+}}$	2.2×10^{5}
$\mathrm{Ho^{3+}}$	1.4×10^{5}
$\mathrm{Er^{3+}}$	1.0×10^{5}
$\mathrm{Y^{3+}}$	1.1×10^{5}
$\mathrm{Yb^{3+}}$	4.0×10^{4}

25°C, ionic strength 0.1, and $K_{\mathrm{d}}\geq10^{-5}$

The rate constants of complexation reactions between rare earth ions and murexide, oxalic acid and anthranic acid were $10^{7}\sim10^{8}\,\mathrm{M^{-1}sec^{-1}}$, nearly independent of the incomming ligands. The values of k_1 which show the rate constants of complexation reactions between EDTA coordinated rare earth ions $(\mathrm{EM^-})$ and $\mathrm{HT^{3-}}$ are about $2\sim3$ order less than those of aquo complexes $(\mathrm{M^{3+}})$ with murexide, *etc.*

Generally, complexation reactions proceed *via* the diffusion-controlled ion-pair formation. The rate-determining step is considered to be the release of water molecule from the inner coordinated sphere of rare earth ions[11]. On the complexation reaction of $\mathrm{EM^-}$ with $\mathrm{HT^{3-}}$, coordinated EDTA prevents the ion-pair formation with $\mathrm{HT^{3-}}$ by steric hindrance and electrostatic repulsion. The decreased rate constant of rare earth-EDTA-tiron mixed complex formation reactions may be understood by these ligand-ligand repulsions.

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