Kinetics of the Complex Formation between Fe(III) and *o*-Hydroxybenzylamine-*N*,*N*,*O*-triacetic Acid (HBATA) and *o*-Aminophenyl-*N*,*N*,*O*-triacetic acid (APTA)

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Abstract

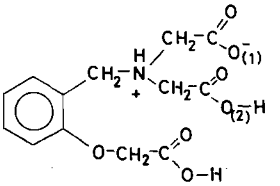
The kinetics of the complex-formation reactions of Fe(III) with the title ligands were investigated at 30 °C and ionic strength 0.2 mol dm^{-3} KNO_3. Each reaction is first order with respect to the metal ion and ligand. From the hydrogen ion concentration dependence of the reaction rates, it shows that complex formation occurs through two paths illustrated as follows

$$\begin{tikzcd}
\{Fe(H_2O)_5OH\}^{2+} + H_3L \arrow[r, shift left, "k_3"] \arrow[d, shift left] & \arrow[l, shift left, "k_{-3}"] \{Fe(H_2O)L\} + 2H_3O^+ + 3H_2O \\
\{Fe(H_2O)_5OH\}^{2+} + H_2L^- \arrow[u, shift left, "K_1"] \arrow[r, shift left, "k_4"] & \arrow[l, shift left, "k_{-4}"] \{Fe(H_2O)L\} + H_3O^+ + 4H_2O
\end{tikzcd}$$

for HBATA, $k_3 = (7.7 \pm 0.5) \times 10^3$ mol^{-1} dm^3 s^{-1}, $k_4 = (1.51 \pm 0.02) \times 10^5$ $mol^{-}1$ dm^3 s^{-1}; for APTA, $k_3 = (5.0 \pm 0.4) \times 10^3$ mol^{-1} dm^3 s^{-1}, $k_4 = (1.10 \pm 0.02) \times 10^5$ mol^{-1} dm^3 s^{-1}. The possible mechanisms of the reactions have been discussed.

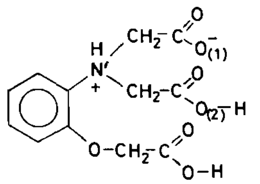
Introduction

HBATA and APTA are one kind of new ligands which contain a aminocarboxylic acid group as well as a phenoxyacetic acid group. Unlike the aminocarboxylic acids already studied extensively, both ligands have a rigid benzene frame which probably exerts an effect on the stabilities, structures, bonding and reactions of complexes possessing HBATA and APTA; furthermore, the derivatives of phenoxyacetic acids have special physiological actions [1, 2]. In view of these considerations, we have studied the stability constants of complexes of the title ligands with some metal ions in aqueous solutions, synthesized a series of complexes, characterized them with the usual physicochemical measurements and also with the X-ray crystal structure analysis over the past few years [3–8]. Yet we know little about the reaction kinetics of these ligands with metal ions. In the present paper, the kinetics of complex-formation reactions of Fe(III) with HBATA and APTA were investigated and the reaction mechanisms were discussed.



HBATA [3]

$K_1 = 4.27 \times 10^{-3}$
$K_2 = 2.57 \times 10^{-4}$
$K_3 = 1.66 \times 10^{-10}$



APTA [8]

$K_1 = 2.95 \times 10^{-3}$
$K_2 = 4.27 \times 10^{-4}$
$K_3 = 1.41 \times 10^{-6}$

Experimental

HBATA and the monopotassium salt of APTA were prepared by the following procedures [3, 8].

HBATA

o-Hydroxybenzylamine (0.1 mol) was dissolved in 100 ml hot benzene, then chloroacetic acid (0.6 mol) and NaOH (1.25 mol) were added to the above solution. The mixture was continuously stirred at 60 °C. After 6 h, the white precipitate was removed from the mixture and dissolved in hot water. The solution was acidified to pH 2 with 6 mol dm^{-3} HCl and left to stand overnight. The precipitate was recrystallized in deionized water and white needle crystals obtained, melting point (m.p.) 246 °C (dec.). *Anal.* Calc. for $C_{13}H_{15}NO_7$: C, 52.5; H, 5.08; N, 4.71. Found: C, 52.5; H, 4.93; N, 4.79%.

Monopotassium Salt of APTA

o-Aminophenol (0.25 mol) was added to an aqueous solution of $ClCH_2COOK$ (1 mol). The mix-

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ture was heated under N_2 with continuous stirring and the pH was maintained above 10 with 5 mol dm^{-3} KOH. After 1½ h $ClCH_2COOK$ (0.25 mol) was added to ensure the reaction was completed and the mixture was left to continue refluxing until the pH of the solution remained constant. The solution was acidified to pH 3.3 with 6 mol dm^{-3} HCl when it was cooled and left to stand overnight. The precipitate was recrystallized twice in deionized water and the white microcrystal monopotassium salt of APTA obtained, m.p. 208 °C (dec.). *Anal.* Calc. for $C_{12}H_{12}NO_7K$: C, 44.86; H, 3.76; N, 4.36. Found: C, 44.81; H, 3.77; N, 4.26.

Solutions of the ligands were prepared by dissolving weighed amounts of the solid ligands in water. $Fe(NO_3)_3{\cdot}9H_2O$, KNO_3, KOH and HNO_3 were analytical reagent grade. All solutions were made in deionized water.

All kinetic runs were performed under pseudo-first-order conditions with the ligands in excess $(2.00\text{–}5.00) \times 10^{-3}$ mol dm^{-3} for HBATA, $(2.50\text{–}10.0) \times 10^{-3}$ mol dm^{-3} for APTA) with respect to Fe(III) (2.00×10^{-4} mol dm^{-3} for HBATA, 2.50×10^{-4} mol dm^{-3} for APTA). The acidity of the solutions over the range 8×10^{-3} to 5×10^{-2} mol dm^{-3} was adjusted with nitric acid.

Kinetic measurements were carried out with a stopped-flow spectrophotometer (Union Giken RA401) at 30 °C and $I = 0.2$ mol dm^{-3} (KNO_3). The reaction kinetics were followed by monitoring the growth in absorbance due to complex formation at 390 nm for HBATA and 450 nm for APTA. The pseudo-first-order rate constants (k_{obs}) were evaluated with the curve-fitting method. Every k_{obs} given is the mean of at least ten kinetic runs with derivation within ±5%. The pH of the solutions was measured with a Radiometer pH M84 instrument equipped with a combined glass electrode (GK2401C). Microanalyses for C, H and N were performed by a Perkin-Elmer 2400C elementary analyzer.

Results and Discussion

Table 1 presents the observed pseudo-first-order rate constants as a function of total ligand concentration C_L and $[H^+]$. Figure 1 shows plots of k_{obs} against C_L at constant $[H^+]$. The straight lines suggest a first-order dependence on the ligand, i.e.

$$k_{obs} = b + a(H)C_L \qquad (1)$$

Taking account of the equilibria existing in solutions under the experimental conditions investigated,

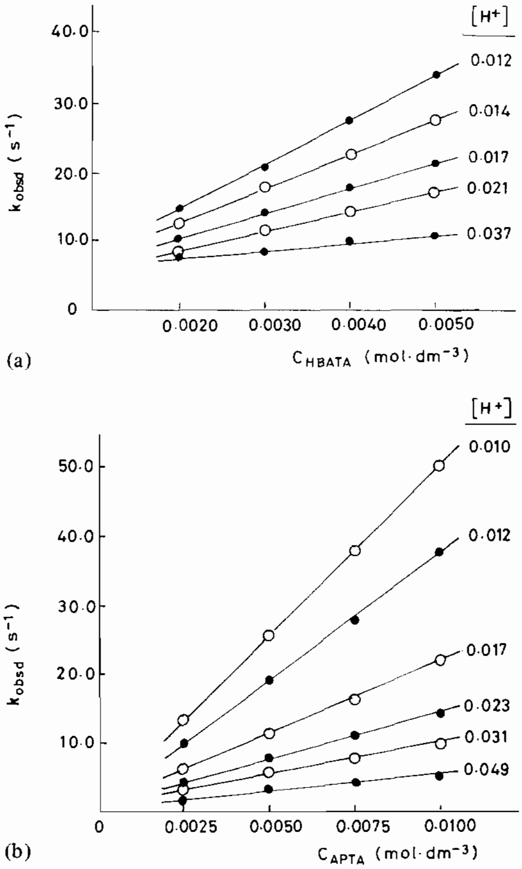
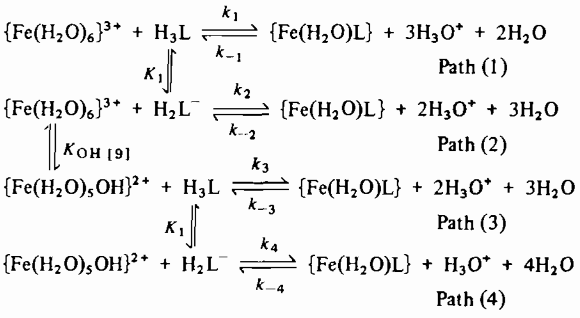


Fig. 1. Variation of k_{obs} as a function of (a) C_{HBATA} and (b) C_{APTA} at different acidities.

the following reaction schemes can be assumed on the basis of the experimental results:



$$\{Fe(H_2O)_6\}^{3+} + H_3L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \{Fe(H_2O)L\} + 3H_3O^+ + 2H_2O \qquad \text{Path (1)}$$

$$K_1$$

$$\{Fe(H_2O)_6\}^{3+} + H_2L^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \{Fe(H_2O)L\} + 2H_3O^+ + 3H_2O \qquad \text{Path (2)}$$

$$K_{OH}\,[9]$$

$$\{Fe(H_2O)_5OH\}^{2+} + H_3L \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \{Fe(H_2O)L\} + 2H_3O^+ + 3H_2O \qquad \text{Path (3)}$$

$$K_1$$

$$\{Fe(H_2O)_5OH\}^{2+} + H_2L^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \{Fe(H_2O)L\} + H_3O^+ + 4H_2O \qquad \text{Path (4)}$$

H_3L represents H_3hbata and H_3apta; H_2L^- represents H_2hbata$^-$ and H_2apta$^-$

For the present conditions, the integrated expression (2) can be derived from the scheme.

$$\ln \frac{[\{Fe(H_2O)L\}]eq.}{[\{Fe(H_2O)L\}]eq. - [\{Fe(H_2O)L\}]_t} = k_{obs}t \qquad (2)$$

where

TABLE 1. Kinetic data for formation^{a} of (a) Fe(III)–HBATA ($C_{\mathrm{Fe(III)}} = 2.00 \times 10^{-4}$ mol dm^{-3}) and (b) Fe(III)–APTA ($C_{\mathrm{Fe(III)}} = 2.50 \times 10^{-4}$ mol dm^{-3})

(a)								
$C_L = 2.00 \times 10^{-3}$ mol dm^{-3}								
$[H^+]$ (10^{-3} mol dm^{-3})	9.58	14.3	19.0	23.6	28.8	38.6		
k_{obs} (s^{-1})	18.6	12.1	9.3	8.0	7.4	7.3		
$C_L = 3.00 \times 10^{-3}$ mol dm^{-3}								
$[H^+]$ (10^{-3} mol dm^{-3})	11.5	14.6	18.7	23.9	29.1	40.1		
k_{obs} (s^{-1})	22.0	17.0	12.9	10.5	9.1	8.5		
$C_L = 4.00 \times 10^{-3}$ mol dm^{-3}								
$[H^+]$ (10^{-3} mol dm^{-3})	10.5	13.3	17.1	22.0	27.5	38.0		
k_{obs} (s^{-1})	32.6	24.5	17.9	13.7	11.3	9.5		
$C_L = 5.00 \times 10^{-3}$ mol dm^{-3}								
$[H^+]$ (10^{-3} mol dm^{-3})	9.61	13.0	15.9	21.0	27.1	31.1	37.4	
k_{obs} (s^{-1})	43.4	31.5	23.6	17.0	13.4	11.7	10.4	
(b)								
$C_L = 2.50 \times 10^{-3}$ mol dm^{-3}								
$[H^+]$ (10^{-3} mol dm^{-3})	8.08	10.5	13.6	16.3	20.2	30.2	38.8	48.6
k_{obs} (s^{-1})	16.9	12.7	8.0	6.1	4.7	3.0	2.0	1.5
$C_L = 5.00 \times 10^{-3}$ mol dm^{-3}								
$[H^+]$ (10^{-3} mol dm^{-3})	8.44	11.0	13.3	16.6	23.0	28.3	37.5	48.2
k_{obs} (s^{-1})	38.7	22.8	16.0	10.8	7.7	6.0	4.5	3.2
$C_L = 7.50 \times 10^{-3}$ mol dm^{-3}								
$[H^+]$ (10^{-3} mol dm^{-3})	8.63	11.0	14.3	19.1	23.0	33.0	41.8	51.4
k_{obs} (s^{-1})	46.7	32.2	21.7	15.1	9.9	7.3	5.2	3.7
$C_L = 10.0 \times 10^{-3}$ mol dm^{-3}								
$[H^+]$ (10^{-3} mol dm^{-3})	9.25	12.4	16.4	21.1	30.4	49.8		
k_{obs} (s^{-1})	56.3	35.7	23.2	15.9	9.6	5.2		

$^{a}t = 30$ °C, $I = 0.2$ mol dm^{-3} KNO$_3$.

$$k_{\mathrm{obs}} = \left(k_1 + k_2 \frac{K_1}{[H^+]} + k_3 \frac{K_{\mathrm{OH}}}{[H^+]} + k_4 \frac{K_1 K_{\mathrm{OH}}}{[H^+]^2}\right) \times \left(\frac{[H^+]^3}{K_{\mathrm{app}}} + \frac{\alpha(H_3L)[H^+]}{[H^+] + K_{\mathrm{OH}}} C_L\right) \qquad (3)$$

$$\alpha(H_3L) = \frac{[H^+]^3}{[H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+] + K_1K_2K_3}$$

$$K_{\mathrm{app}} = \frac{k_1}{k_{-1}} = \frac{[H^+]^3[\{Fe(H_2O)L\}]eq.}{[H_3L]eq.[\{Fe(H_2O)_6\}^{3+}]eq.}$$

K_1, K_2, K_3 are the successive acid dissociation constants of the ligands [3, 8].

By comparing eqn. (3) with eqn. (1), we can get

$$a(H) = \frac{\alpha(H_3L)[H^+]}{[H^+] + K_{\mathrm{OH}}} \left(k_1 + k_2 \frac{K_1}{[H^+]} + k_3 \frac{K_{\mathrm{OH}}}{[H^+]} \times k_4 \frac{K_1 K_{\mathrm{OH}}}{[H^+]^2}\right) \qquad (4)$$

On rearrangement eqn. (4) gives eqn. (5)

$$A(H) = \frac{a(H)([H^+] + K_{\mathrm{OH}})}{\alpha(H_3L)} = k_1[H^+] + (k_2K_1 + k_3K_{\mathrm{OH}}) + k_4 \frac{K_1K_{\mathrm{OH}}}{[H^+]} \qquad (5)$$

The plots of $A(H)$ versus $[H^+]^{-1}$ yield straight lines for both ligands (see Fig. 2), therefore, the contribution made by pathway (1) to the total reaction should be negligible. The values of k_4 and $k_2K_1 + k_3K_{\mathrm{OH}}$ were calculated with a linear least-squares regression analysis and are summarized in Table 2.

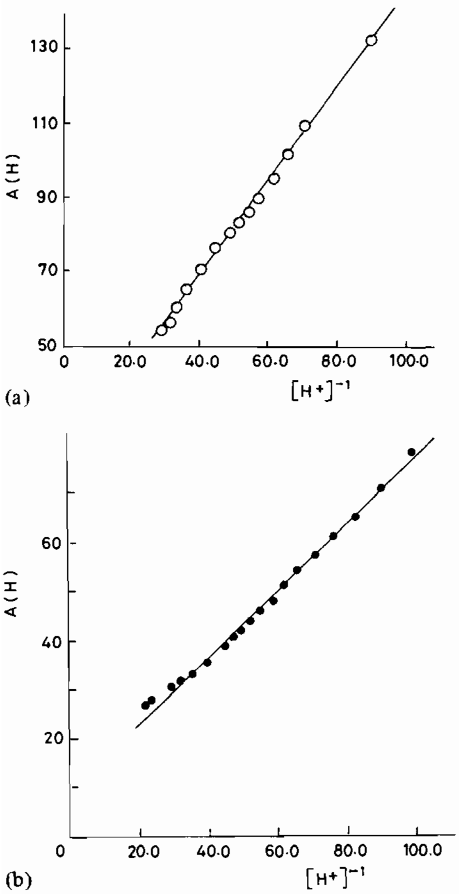


Fig. 2. Reciprocal hydrogen-ion concentration dependence of A(H) for (a) Fe(III)–HBATA and (b) Fe(III)–APTA complex formation.

According to the interchange mechanism [10] complex-formation reaction occurs through two successive steps:

$$\{Fe(III)aq.\} + L \overset{K_{os}}{\rightleftharpoons} \{Fe(III)aq.\}...L \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} \{Fe(III)Laq.\} + H_2O$$

where {Fe(III)aq.} represents $\{Fe(H_2O)_6\}^{3+}$ and $\{Fe(H_2O)_5OH\}^{2+}$, K_{os} is the equilibrium constant for the fast outer-sphere complex formation, k_i the interchange rate constant of L and H_2O between the second and first coordination spheres and k_{-i} the rate constant for the reverse process. Under the condition of ligand in excess, $k_f = K_{os}k_i$ (k_f stands for k_1, k_2, k_3 and k_4). Consequently, the rates of reactions, which take place with a rate-determining step involving the loss of H_2O from the inner-sphere of the metal ion in the outer-sphere complex (I_d), are insensitive to the nature of the ligands entering the reactions, when ligands having the same charge type react with an identical metal ion. It is seen (as shown in Table 2) that k_4(HBATA) is approximately the same as k_4(APTA). The closeness between the two rate constants suggests that the reaction rates at which $\{Fe(H_2O)_5OH\}^{2+}$ reacts with H_2hbata^- and H_2apta^- are independent of the entering ligands. So the corresponding reactions may occur through the I_d mode.

Since pathway (2) and pathway (3) have the same dependence on $[H^+]$, we cannot give the exact values of k_2 and k_3. However, it is possible to get some information about the complexation reactions in line with the reported results. If the intercepts were equal to k_2K_1, we should get k_2(HBATA) = (3.6 ± 0.2) X 10^3 mol^{-1} dm^3 s^{-1} and k_2(APTA) = (3.4 ± 0.2) X 10^3 mol^{-1} dm^3 s^{-1}, i.e. the rate of reaction between $\{Fe(H_2O)_6\}^{3+}$ with H_2L^- reaches as high as 10^3, which sounds unrealistically large for complex-formation reaction of $\{Fe(H_2O)_6\}^{3+}$, besides, the reactivity of $\{Fe(H_2O)_5OH\}^{2+}$ is almost 10^3 times greater than that of $\{Fe(H_2O)_6\}^{3+}$ due to the coordinated OH^- in $\{Fe(H_2O)_5OH\}^{2+}$ [11–14]. So it may be reasonable to assume that the k_3K_{OH} term nearly makes the whole contribution to the intercept. Thus we can obtain k_3(HBATA) = (7.7 ± 0.5) X 10^3 mol^{-1} dm^3 s^{-1} and k_3(APTA) = (5.0 ± 0.4) X 10^3 mol^{-1} dm^3 s^{-1} which fall within the normal range of reaction rates concerning $\{Fe(H_2O)_5OH\}^{2+}$. Again there is only a slight discrepancy between the values of k_3(HBATA) and k_3(APTA), thereby the reaction of $\{Fe(H_2O)_5OH\}^{2+}$ with H_3L also follows the I_d mechanism.

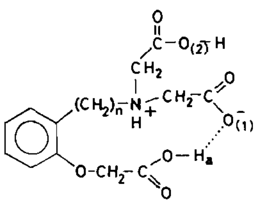
Further inspection of the experimental results indicates points worthy of discussion. First, the reaction rate of Fe(III) with HBATA is slightly larger than that with APTA. This fact may be ascribed to the difference in structure between HBATA and APTA. Owing to the higher electronic density on the N atom in HBATA, the interaction between N(HBATA) and H^+ is stronger

TABLE 2. Kinetic parameters for the reactions of Fe(III) with HBATA and APTA: t = 30 °C, I = 0.2 mol dm^{-3} KNO_3

Ligand	$k_2K_1 + k_3K_{OH}$ (intercept)	$k_4K_1K_{OH}$ (slope)	k_3 (10^3)[a] (mol^{-1} dm^3 s^{-1})	k_4 (10^5) (mol^{-1} dm^3 s^{-1})
HBATA	15.5 ± 1.0	1.30 ± 0.02	7.7 ± 0.5	1.51 ± 0.02
APTA	10.1 ± 0.7	0.65 ± 0.01	5.0 ± 0.4	1.10 ± 0.02

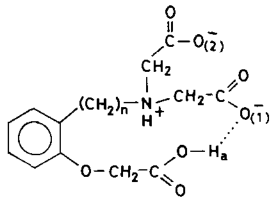
[a] Assuming k_3K_{OH} = intercept.

than that between N′(APTA) and H$^+$, which leads to the overall positive charge on [—NH]$^+$ being less than that on [—N′H]$^+$. As a consequence of the inductive effect, the less positive charge on [—NH]$^+$ results in higher electronic densities on the carboxylate oxygens ($O_{(1)}$ and $O_{(2)}$) of HBATA. Therefore, when {Fe(III)aq.} approaches ligands in the direction of the carboxylate oxygens, the resulting outer-sphere complex of {Fe(III)aq.} with HBATA is more stable than that of {Fe(III)aq.} with APTA. Since $k_f = K_{os}k_i$, the more stable the outer-sphere complex is, the faster the reaction is. Second, the ratio of k_4/k_3 is 20 for HBATA and 22 for APTA. There may be two factors contributing to the ratio. On the one hand, since k_3 refers to the process between the +2 ion and neutral H_3L, while k_4 refers to the process between +2 ion and −1 ion H_2L^-, the K_{os} of $\{Fe(H_2O)_5OH\}^{2+}...H_2L^-$ is larger than that of $\{Fe(H_2O)_5OH\}^{2+}...H_3L$. On the other hand, the numerous atoms inserted between $O_{(1)}$ and H_a makes it possible to form a hydrogen bond between $O_{(1)}$ and H_a with less tension. When $\{Fe(H_2O)_5OH\}^{2+}$ approaches a negative charged carboxylate oxygen $O_{(1)}$, the strong intra-ligand hydrogen bond hinders the interaction between $\{Fe(H_2O)_5OH\}^{2+}$ and H_3L due to the reduced negative charge on $O_{(1)}$ as well as the steric hinderance, which reduces k_3. However, when $\{Fe(H_2O)_5OH\}^{2+}$ reacts with H_2L^-, this is not the case. $\{Fe(H_2O)_5OH\}^{2+}$ can approach H_2L^- in the direction of $O_{(2)}$ without being influenced by the intra-ligand hydrogen bond in the rate-determining step.



H_3L

(n=0, APTA; n=1, HBATA)



H_2L^-

(n=0, APTA; n=1, HBATA)

Acknowledgement

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