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Kinetics of complexation of Fe (III) with DL-2-Amino butanoic acid and L-2-Amino 3-methyl n-valeric acid

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Abstract

The kinetic study of Fe (III) with Butyrine and Isoleucine has been studied as a function of pH and temperature under first order conditions. A scheme consistent with the observations has also been proposed. The overall rate constant has been resolved into stepwise rate constants. The activation parameters corresponding to stepwise rate constants also support the proposed mechanism. The mechanism has been further confirmed by the calculation of water exchange rate constant.

Keywords: Kinetics, Complexation, Mechanism, Rate constant

1. Introduction

DL-2-Amino butanoic acid (Butyrine) and L-2-Amino-3-methyl n-valeric acid (Isoleucine) are constituents of normal urine. High concentration of L-2-Amino-3-methyl n-valeric acid appears in the urine of the patients suffering from muscular dystrophy. This excessive excretion can be avoided by the retention of Isoleucine in the body in the form of metal-isoleucine complex. Whereas, high concentration of L-2-Amino-3-methyl n-valeric acid during maple syrup urine disease causes brain damage (Dancis et al, 1966) ^[1]. This ligand must be removed from the body in the form of metal-isoleucine complex. DL-2-Amino butanoic acid is excreted in large quantities in the urine of patients suffering from defective reabsorption of amino acids by kidney. Therefore, the rate studies of binding of these ligands with metal ions can be used as models for checking the above mentioned metabolic disorders.

Review of the literature (Cavasino et al 1982; Gouger et al, 1974; Elezaby et al, 1986, Khan et al, 1976) ^[2, 3, 4, 5] reveals that not even a single kinetic study has been reported on the complexation of Fe(III) with protonated and deprotonated forms of amino acid. In order to establish the sequence of binding of Fe (III) with DL-2-Amino butanoic acid and L-2-Amino 3-methyl n-valeric acid a comprehensive kinetic study was carried out.

The observed kinetic data has been explained in terms of overall rate constant and step wise rate constants. The mechanism consistent with the kinetic data has also been suggested. The validity of the proposed mechanism has been confirmed by the calculation of activation parameters and water exchange rate constant.

Methodology

The kinetics of formation of complex of Fe (III) with DL-2-Amino butanoic acid was studied at 460 nm in the pH range 1.80-2.31, while that with L-2-Amino 3-methyl n-valeric acid in the pH range 1.59-2.26 using Aminco-Morrow stopped flow assembly. No indicator was used to carry out the investigations at 25, 30, 35 and 40(\pm 0.05) °C. All studies were done under first order conditions by taking excess of metal in comparison to the ligand. Oscilloscope traces of concentration change versus time were utilized to evaluate first order rate constants (k'_{obs}). The overall rate constant (k_{obs}) was calculated using the relation:

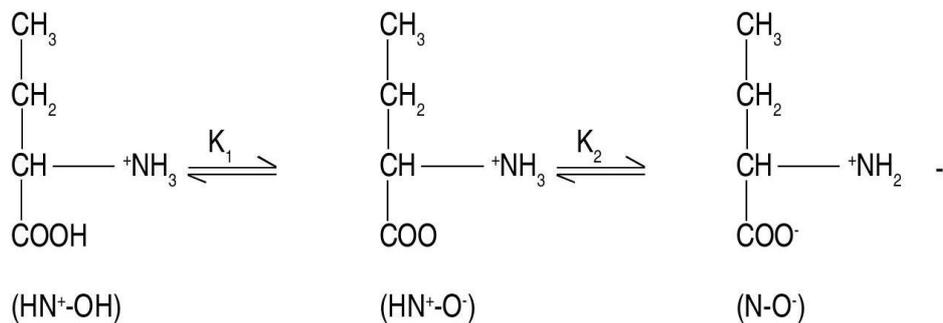
$$k_{obs} = \frac{k'_{obs}}{[(Fe(III))]} \quad - (1)$$

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RESULTS AND DISCUSSION

The dissociation equilibria of DL-2-Amino butanoic is represented as :



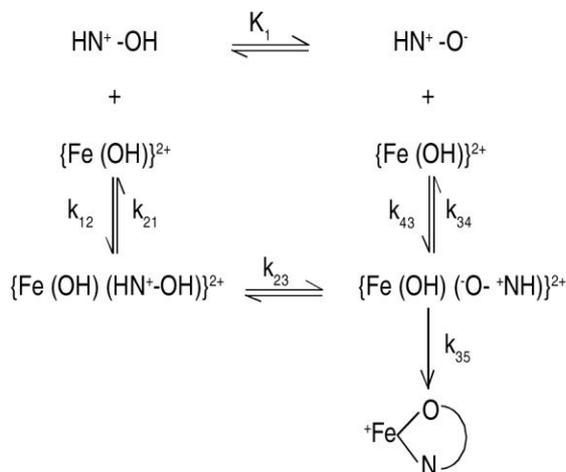
(HN⁺ -OH), (HN⁺ -O⁻) and (N-O⁻) represent the diprotonated, monoprotated and deprotonated forms respectively of DL-2-Amino butanoic acid.

$$K_1 = \frac{[\text{HN}^+ \text{-O}^-] [\text{H}^+]}{[\text{HN}^+ \text{-OH}]} \quad - (2)$$

$$K_2 = \frac{[\text{N-O}^-] [\text{H}^+]}{[\text{HN}^+ \text{-O}^-]} \quad - (3)$$

These forms of the ligand are expected to undergo complexation with metal ion. In case of trivalent metal ions, the higher positive charge and low ionic radii increase metal coordinated water interactions leading to hydrolysis. Therefore, the number of active species i.e. M³⁺ and M(OH)²⁺ increase. Hydrated ferric ion is appreciably hydrolysed in solution of pH 1.5. From previous studies (Khan et al,1976), it has been proved that the rate for the reaction of hydrolyzed ferric ion is higher than that of hydrated ferric ion. This is explained on the basis that the electron donation from hydrolyzed ferric ion is faster than from the aqua ferric ion.

The following Scheme1 was found to give the best fit with our kinetic data. In the proposed scheme, interaction with diprotonated and monoprotated forms of the ligand were taken into consideration. The reaction with deprotonated form was not considered as the concentration of latter was small in the pH range used.



Scheme 1

where {Fe(OH)}²⁺ represents hydrolyzed ferric species

The differential form of the rate equation is written as :

$$\text{Rate} = \frac{-d [\text{Fe}(\text{OH})^{2+}]}{dt} = k_{\text{obs}} [\text{Fe}(\text{OH})^{2+}] [\text{DL-2-Amino butanoic acid}]_T \quad - (4)$$

$$\text{Rate} = k_{\text{obs}} [\text{Fe}(\text{OH})^{2+}] \{ [\text{HN}^+ - \text{OH}] + [\text{HN}^+ - \text{O}^-] \} \quad - (5)$$

Using equation (3), we have

$$\text{Rate} = k_{\text{obs}} [\text{Fe}(\text{OH})^{2+}] \left\{ 1 + \frac{K_1}{[\text{H}^+]} \right\} [\text{HN}^+ - \text{OH}] \quad - (6)$$

According to Scheme1, rate is also written as :

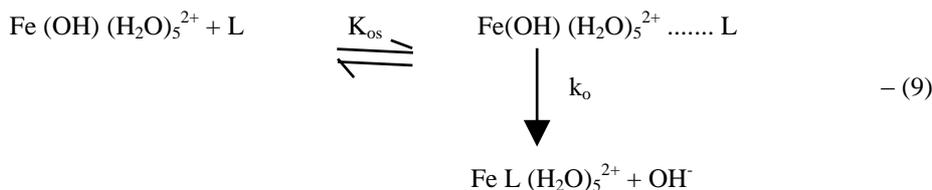
$$\text{Rate} = k_{35} [\{\text{Fe}(\text{OH})(\text{O}^- \text{NH})\}^{2+}] \quad - (7)$$

Applying steady state approximations, the above equation reduces to the form :

$$k_{\text{obs}} \left\{ 1 + \frac{K_1}{[\text{H}^+]} \right\} = k_{12} + k_{43} \frac{K_1}{[\text{H}^+]} \quad - (8)$$

The equation predicts a linear plot for $k_{\text{obs}} \left\{ 1 + \frac{K_1}{[\text{H}^+]} \right\}$ versus $[\text{H}^+]^{-1}$. This plot for Fe(III) –DL-2-Amino butanoic acid is shown in Fig.1. The slope and intercept of these plots were utilized for the calculation of stepwise rate constants and are reported in Table1. The values of activation parameters corresponding to stepwise rate constants k_{12} and k_{43} were calculated from the linear plots of $\log k$ and k/T vs $1/T$. These values are given in Table1

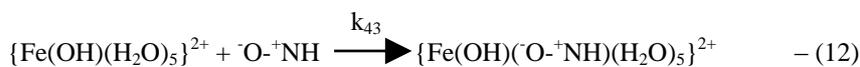
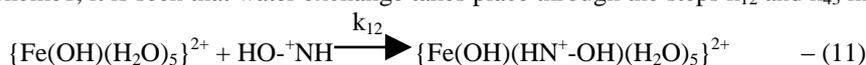
The kinetic behaviour of the reaction in this study was compared with the behaviour predicted by general mechanism for metal ligand complex formation as formulated by Eigen. (Eigen etal,1962)^[7] According to Eigen mechanism, the complex formation reaction involves the fast formation of an outer sphere complex followed by the substitution of water molecule coordinated to metal ion. Therefore, the Iron (III) complex formation can be depicted as :-



where L denotes the deprotonated and monoprotonated form of DL-2-Amino butanoic acid. Rate of such a reaction is expressed as :

$$\begin{aligned} \text{Rate} &= k_o [\text{Fe}(\text{OH})(\text{H}_2\text{O})_5^{2+} \cdots \cdots \text{L}] \\ &= K_{\text{os}} k_o [\text{Fe}(\text{OH})(\text{H}_2\text{O})_5^{2+}] [\text{L}] \end{aligned} \quad - (10)$$

From Scheme1, it is seen that water exchange takes place through the steps k_{12} and k_{43} in the following manner :



Using these equations, rate of water exchange is written as :

$$\text{Rate} = k_{12} [\text{Fe}(\text{OH})(\text{H}_2\text{O})_5^{2+}] [\text{HO}^- \text{NH}] + k_{43} [\text{Fe}(\text{OH})(\text{H}_2\text{O})_5^{2+}] [\text{O}^- \text{NH}] \quad - (13)$$

$\therefore k_{12} \ll k_{43}$ (Table1), therefore, equation (13) reduces to:

$$\text{Rate} = k_{43} [\text{Fe}(\text{OH})(\text{H}_2\text{O})_5^{2+}] [\text{O}^- \text{NH}] \quad - (14)$$

Comparing equation (10) and (13) we get :

$$k_{43} = K_{\text{os}} k_o \quad - (15)$$

Knowing k_{43} and K_{os} , value of k_o (water exchange rate constant) at different temperatures was calculated (Fuoss,1958)^[8]. These values are given in Table1. The values of k_{12} and k_{43} (Table 1) suggest that the extent of interaction with deprotonated form of the ligand is less than that of the monoprotonated form. However, the reactivity of both the forms increases with rise in temperature. This observation is larger in comparison to that for the monoprotonated form. High negative value of entropy of activation for k_{43} indicates that the reaction is between oppositely charged ions and follows associatively activated mechanism. This proposed mechanism is further supported by the calculation of water exchange rate constant (k_o) for iron

(III). The calculated value compares well with that obtained from NMR studies (Swift et al, 1962)^[6] for Fe(III), in the absence of ligand.

The same scheme 1 is found to be applicable for the complexation of Fe(III) with L-2-Amino-3-methyl n-valeric acid. The value of k_0 was calculated using equation (15). These values are reported in Table 1. The average values of activation parameters corresponding to k_{12} and k_{43} were calculated from the linear plots of $\log k$ and $\log k/T$ versus $1/T$. These values are reported in Table 1.

The values of specific rate constants k_{12} and k_{43} (Table 1) show that the reactivity of both diprotonated and monoprotonated forms of the ligand increase with increasing temperatures. Also, Table 1 shows that the monoprotonated form is more reactive than the diprotonated form. On the basis of activation parameter values (Table 1), it is concluded that the reaction via step k_{43} is faster than via step k_{12} . High negative value of entropy of activation corresponding to step k_{43} supports a rapid ion pair formation. The value for k_{43} step is found to be more for Fe(III) –L-2-Amino 3-methyl n-valeric acid ($1.51 \times 10^2 \text{ M}^{-1}\text{s}^{-1}$ at 25 °C) as compared to Fe(III) –DL-2-Amino butanoic acid system ($0.85 \times 10^2 \text{ M}^{-1}\text{s}^{-1}$ at 25 °C). This is explained on the basis that the –COOH group of former has greater electron density owing to increased number of methyl groups.

Table 1: Values of specific rate constant and their activation parameters for the interaction of Fe(III) with DL-2 Amino butanoic acid and L-2 Amino 3- methyl n- valeric acid at different temperature

Temp	Fe (III)-DL-2 Amino Butanoic Acid			Fe (III)-DL-2 Amino 3-methyl n-valeric acid		
°C	k_{12} ($\text{M}^{-1}\text{s}^{-1}$)	$k_{43} \cdot 10^{-2}$ ($\text{M}^{-1}\text{s}^{-1}$)	$k_0 \cdot 10^{-2}$ (s^{-1})	$k_{12} \cdot 10^{-1}$ ($\text{M}^{-1}\text{s}^{-1}$)	$k_{43} \cdot 10^{-2}$ ($\text{M}^{-1}\text{s}^{-1}$)	$k_0 \cdot 10^{-2}$ (s^{-1})
25	0.60	0.85	0.44	0.80	1.51	0.77
30	1.30	1.06	0.54	1.37	2.07	1.06
35	4.00	1.32	0.68	2.30	2.77	1.42
40	5.90	1.74	0.89	3.25	3.44	1.76
ΔH^\ddagger	116.69	36.71		71.77	34.44	
kJ mol^{-1}						
ΔS^\ddagger	125.5	-103.15		10.96	-103.76	
$\text{JK}^{-1} \text{mol}^{-1}$						

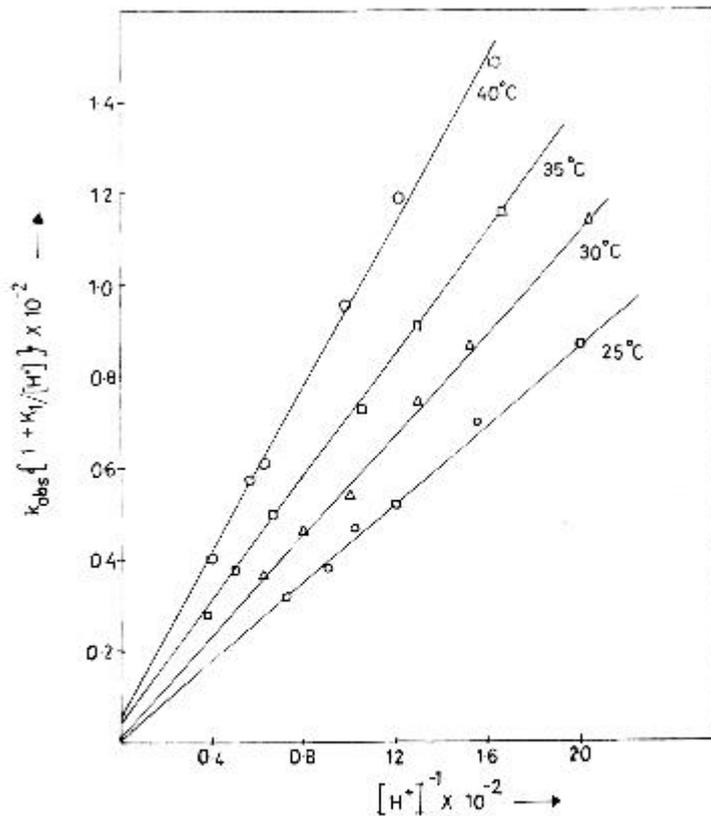


Fig. 1

Plots of $k_{obs} \{1 + K_1/[H^+]\}$ versus $[H^+]^{-1}$ for Fe(III)-

DL-2-Amino butanoic acid complexation at different temperatures.

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