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Haritma Chopra
Associate Professor,
Department of Chemistry,
Maitreyi College, University of
Delhi, Delhi-21, India

H.C. Malhotra
Professor (Retd.),
Department of Chemistry,
University of Delhi, Delhi-7,
India

Correspondence
Haritma Chopra
Associate Professor,
Department of Chemistry,
Maitreyi College, University of
Delhi, Delhi-21, India

Complexation of Co(II), Cu(II) and Ni(II) with 2-Amino ethanesulphonic Acid – Kinetic Studies

Haritma Chopra, H.C. Malhotra

Abstract

Kinetic study on the complexation of Co (II), Cu(II) and Ni(II) with 2-Amino ethanesulphonic acid, an essential prerequisite for absorption of fat in the body, has been carried out under first order conditions as a function of pH and temperature. A reaction scheme consistent with the kinetic data has been proposed. In case of complexation with Ni(II), deprotonated form of the ligand reacts in two ways (i) ring formation via oxygen (ii) ring formation via nitrogen.

The overall rate constant has been resolved into stepwise rate constants. The suggested mechanism is confirmed by the calculation of activation parameters and water exchange rate constant.

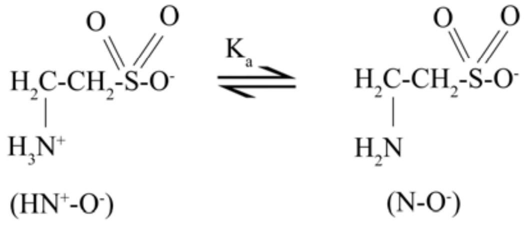
Keywords: Kinetics, complexation, metal ions, biochemical ligand, rate constant, activation parameters.

Introduction

2-Amino ethanesulphonic acid, commonly known as Taurine, is an essential prerequisite for absorption of fat in the body. Bile acids, which help in dissolving the fat molecules are synthesised by the liver and are conjugated to 2-Amino ethanesulphonic acid before being excreted into the intestine (Bremer, 1955) [1]. In case of heavy metal poisoning, 2-Amino ethanesulphonic can be trapped by the metal ions, thereby causing fat malabsorption. This results in bulky, foul smelling stools and finally weakening of the body.

Therefore, it was thought desirable to have a comparative knowledge of binding of metal ions by 2-Amino ethanesulphonic acid as model system.

The dissociation equilibrium of 2-Amino ethanesulphonic acid can be represented as:-



As the intra-molecular hydrogen bonding between the protonated amino group and the sulphonate group is quite weak, it is expected that the zwitterionic form should be reactive towards the metal ions. In order to check the reactivity of zwitterion, to know the various binding step, the rate determining step and the activation parameters corresponding to the interaction of protonated and deprotonated form of the ligand, kinetic investigations of the reaction of Co(II), Cu (II) and Ni (II) with 2-Amino ethanesulphonic acid were carried out.

Methodology

The kinetics of interaction of Co(II) and Ni(II) with 2-Amino ethanesulphonic acid was investigated in the pH range 6.19-7.41 and at ionic strength 0.1 M(KNO_3). In this pH range, no hydroxy species exist as hydrolysis occurs at higher pH. The studies were made at 620 nm using pH indicator method. The temperatures were maintained at 25, 30, 35 and 40 (±0.05) °C. The kinetics of interaction of Cu(II) with 2-Amino ethanesulphonic acid was carried out in the pH range 2.28-3.71, to avoid hydrolysis of Cu(II) to $Cu(OH)^+$ and at 0.1 M ionic strength. The temperatures of reaction mixture were maintained at 25, 30, 35 and 40(± 0.05) °C. The studies were made at 600 nm under first order conditions keeping [Cu(II)] [2-Amino ethanesulphonic acid]. No indicator was used as the transmittance changes were large enough to be monitored directly. From oscilloscope traces of change in concentration with time, values of k'_{obs} (first order rate constant) and k_{obs} (second order rate constants) were computed. These values are given in Table 1.

Result and Discussion

The overall differential equation for the interaction can be written as:-

$$\text{Rate} \quad \frac{-d[M(II)]}{dt} = \frac{-d\,[\text{2-Amino ethanesulphonic acid}]}{dt} \quad (1)$$

$$= k_{obs}[M(II)]\ [\text{2-Amino ethanesulphonic acid}] \quad (2)$$

$$= k'_{obs}\ [\text{2-Amino ethanesulphonic acid}] \quad (3)$$

Where, $k'_{obs} = k_{obs}\,[M(II)]$ (4)

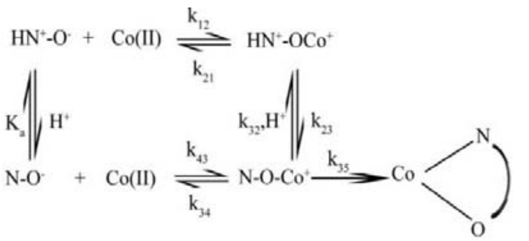
And M=Co(II), Cu(II) and Ni(II)

Equation (3), can also be written in terms of various forms of2-Amino ethanesulphonic acid that are expected to participate in complexation with M(Il).

$$\text{Rate} = k'_{obs}\{[HN^+\text{-}O^-] + [N\text{-}O^-]\} \quad (5)$$

$\{HN^+\text{-}O^-\}$ and $\{N\text{-}O^-\}$ are the monoprotonated and deprotonated forms respectively of the ligand.

Of the various plausible schemes, following scheme 1 was found to give the best fit with our kinetic data. According to this scheme, the monoprotonated and deprotonated forms react with Co(II) in a stepwise manner as shown below:-



Scheme 1

According to Scheme 1, rate of the reaction is written as:

$$\text{Rate} = k_{35}[N\text{-}O\text{-}Co^+] \quad (6)$$

Applying steady state approximation to unstable intermediates i.e. $(HN^+\text{-}O\text{-}Co^+)$ and $(N\text{-}O\text{-}Co^+)$

Rate of the reaction is expressed as:

$$k_{obs}\ \{1 + \frac{K_a}{[H^+]}\} = k_{12} + \frac{k_{43}K_a}{[H^+]} \quad (7)$$

This equation predicts a linear plot for $k_{obs}\{1 + K_a/[H^+]\}$ versus $[H^+]^{-1}$ and this was actually observed in the interaction of Co(II) with 2-Amino ethanesulphonic acid at 25, 30, 35 and 40 (±0.05) ºC (Fig. 1). These plots were used for the calculation of specific rate constants. The values of $k_{12}$and k_{43} were obtained from the intercept and slope respectively of these plots and are given in Table 1. The values of enthalpy and entropy of activation were obtained from the slope and intercept respectively of plots of log (k/T) versus 1/T. These values are reported in Table 1.

Table 1: Values of specific rate constants and their activation parameters for the interactions of Co(II) and Cu(II) with 2-Amino ethanesulphonic acid at effect different temperatures

Temperatures (± 0.05)ºC	**Co(II)- ligand**			**Cu(II) – ligand**		
	$k_{12} \times 10^{-3}$	$k_{43} \times 10^{-6}$	$k_o \times 10^{-5}$	$k_{12} \times 10^{-3}$	$k_{43} \times 10^{-9}$	$k_o \times 10^{-9}$
	$(M^{-1} s^{-1})$	$(M^{-1} s^{-1})$	(s^{-1})	$(M^{-1} s^{-1})$	$(M^{-1} s^{-1})$	(s^{-1})
25	1.0	0.85	0.43	1.75	0.98	0.79
30	2.0	0.95	0.48	3.50	1.25	0.63
40	5.5	1.26	0.65	9.00	1.64	0.83
$\Delta H^{\#}$	85.52	20.18	-	78.45	19.4	
$kJmol^{-1}$	± 0.2	± 1.43	-	± 3.57	± 2.11	
$\Delta S^{\#}$	83.68 +	-80.71		65.00	-24.18	
$JK^{-1}\ mol^{-1}$	3.01	± 4.18	-	± 4.99	± 2.06	

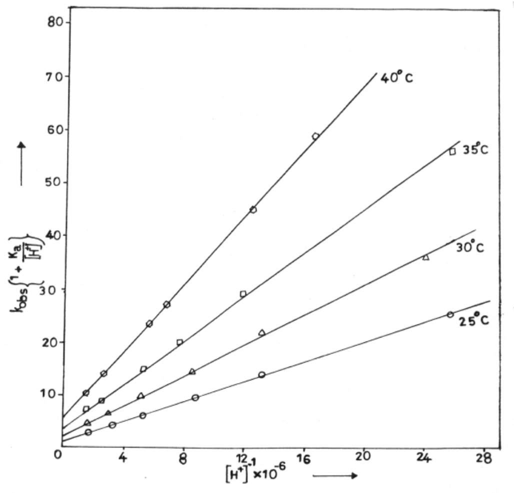


Fig. 14

Plots of k_{obs} {1 + K_a/ [H⁺]} versus [H⁺]⁻¹ for Co(II)-2-Amino ethanesulphonic acid complexation at different temperatures.

Fig 1: Plots of k_{obs} $\{1 + K_a/[H^+]\}$ versus $[H^+]^{-1}$ for Co(II)-2-Amino ethanesulphonic acid complexation at different temperatures.

Calculation of Water Exchange Rate Constant

According to Scheme 1, water exchange is taking place through the steps:-

$$HN^+ - O^- + Co(II) \xrightarrow{k_{12}} HN^+O\text{-}Co^+ \quad (8)$$

$$N\text{-}O^- + Co(II) \xrightarrow{k_{43}} N\text{-}O\text{-}Co^+ \quad (9)$$

Rate of complex formation is represented as:

$$k_f = k_{12}\ [HN^+\text{-}O^-]\ [Co(II)] + k_{43}[N\text{-}O^-]\ [Co(II)] \quad (10)$$

The Scheme 1 was correlated with general mechanism for substitution in terms of ion pair formation constant (K_{os}) and water exchange rate constant (k_o)(Fuoss, 1958; Eigen *et al*, 1962).

$$K_{os}k_o = k_{12} + k_{43} \quad (11)$$

From Table 1, we have, $k_{43} >> k_{12}$

The above equation is simplified to:

$$K_{os}k_o = k_{43} \quad (12)$$

Value of K_{os} was obtained from Fuoss equations. Knowing K_{os} and k_{43}, k_o was calculated. The value of k_o for Co(II)-2-Amino ethanesulphonic acid at 25 ºC was found to be $0.43 \times 10^5 s^{-1}$. The value of k_o at other temperatures is given in Table 1.

In both the cases, it is the sulphonate end of the ligand which is being attacked by the metal ion because of strong electrostatic force of attraction between oppositely charged ions. The value of specific rate constant k_{12} i.e. $1 .75 \times 10^3$ M^{-1} s^{-1} at 25 °C shows that the zwitterionic form is quite reactive. Also, Table 1 indicates that the reactivity of deprotonate form (k_{43}) is more than that of the zwitterionic form at all temperatures of our investigations. The reactivity of both the forms increase with rise in temperature. The obtained values of activation parameters further support the high reactivity of the deprotonated form of the ligand. The value of energy of activation for k_{12} step (involving zwitterionic form) is more than that for k_{43} step (involving deprotonated form). Negative value of entropy of activation corresponding to k_{43} step is suggestive of rapid ion pair formation followed by dissociative interchange.

The plots of $k_{obs}\{1+K_a/[H^+]\}$ versus $[H^+]^{-1}$ for the complexation of Cu(II) with 2-Amino ethanesulphonic acid were found to be linear. Linearity of these plots confirm that Scheme 1 is also applicable to this complexation reaction. The values of stepwise rate constants k_{12} and k_{43} were obtained from the intercept and slope respectively of these plots and are given in Table 1. The values of activation parameters were obtained, from the plots of log k and log k/T versus 1/T. These values are given in Table 1. The value of water exchange, rate constant was also computed using equation (12). The value of k_o at different temperatures is given in Table 1.

The reactivity of zwitterionic form of 2-Amino ethanesulphonic acid though significant, is found to be small in comparison to that of deprotonated form ligand (Table 1). Values of activation parameters (Table 1) also support this observation as $\Delta H^{\#}_{12}$ for the step involving zwitterionic form is more than that for $\Delta H^{\#}_{43}$, corresponding to deprotonated form. Negative value of entropy of activation corresponding to k_{43} step suggests that the reaction is between two oppositely charged ions. The proposed Scheme 1 was further confirmed by the calculated value of water exchange rate constant (Table 1). The value of k_0 at 25 °C was found to be $4.54 \times 10^9 s^{-1}$. This value compares well with these obtained from NMR studies (Swift *et al.*, 1962), in the absence of ligand.

Scheme 1 was applied to the complexation of Ni(II) with 2-Amino ethanesulphonic acid. Plots of k_{obs} $\{1+K_a/[H^+]\}$ versus $[H^+]^{-1}$ at different temperatures were found to be non-linear (Fig. 2).

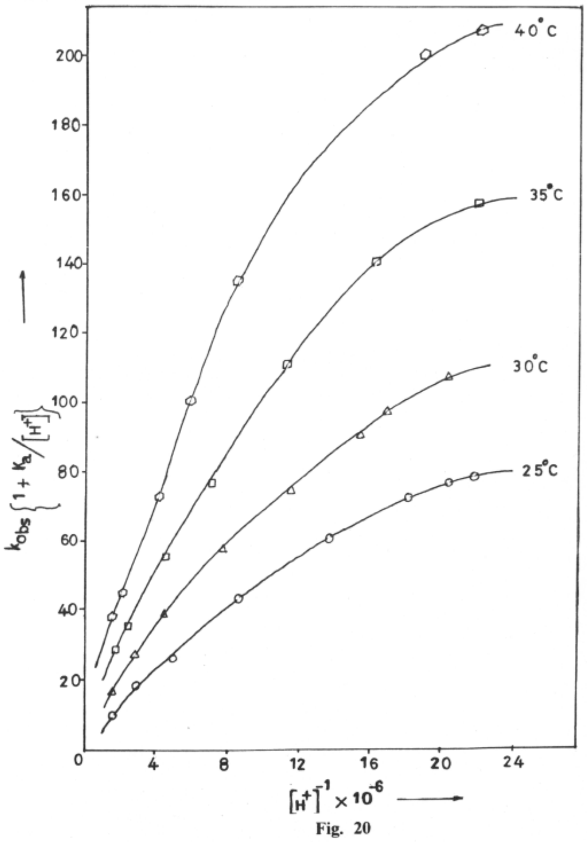


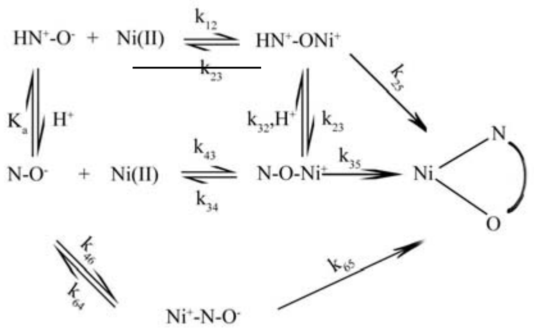
Fig. 20

Plots of k_{obs} $\{1 + K_a / [H^+]\}$ versus $[H^+]^{-1}$ for Ni(II)-

2-Amino ethanesulphonic acid complexation at different temperatures.

Fig 2: Plots of k_{obs} $\{1 + K_a / [H^+]\}$ versus $[H^+]^{-1}$ for Ni(II)-2-Amino ethanesulphonic acid complexation at different temperatures.

Therefore, Scheme 1 was modified to Scheme 2. In the modified scheme, various steps, such as chelate formation via k_{25} step and an attack of metal ion on amino end of the ligand were taken into consideration (Malhotra *et al.*, 2000).



Scheme 2

The overall rate of the reaction on the basis of the Scheme 2 is written as:

$$\text{Rate} = k_{35}[\text{N-O-Ni}^+] + k_{25}[\text{HN}^+\text{-O-Ni}^+] + k_{65}[\text{Ni}^+\text{-N-O}^-] \quad (13)$$

Applying steady state approximation for species (HN^+-O-Ni^+) and (N-O-Ni^+) and (Ni^+-N-O^-), rate equation is expressed as:

$$k_{obs} = \frac{A + B/[H^+]}{(C\,[H^+] + 1)} \times \frac{[H^+]}{(K_a + [H^+])} \quad (14)$$

Where $A = k_{12}$

$B = (k_{43}+k_{46})K_a$

$$C = \frac{(k_{21} + k_{25})K_a}{k_{35}}$$

The values of A, B and C were evaluated using a non- linear regression. The values of A, B and C at 25, 30, 35 and 40 (±0.05) °C are reported in Table 2. Using these values, specific rate constants k_{12}, ($k_{43}+k_{46}$) and ($k_{21}+k_{25}$)/$k_{35}\times K_a$ were calculated. These values are given in Table 2. From the Scheme 2, it is inferred that k_{43} is larger than k_{46} due to strong electrostatic interaction between negatively charged oxygen and positively charged nickel ion.

Activation parameters corresponding to specific rate constants were evaluated from the plots of log k and log k/T versus 1/T. These values are reported in Table 2.

The values of ($k_{43}+k_{46}$) and k_{12} (Table 2) indicate that deprotonated form will react more rapidly with Ni(II) as compared to zwitterionic form. Due to strong electrostatic interaction between the positive charge of Ni(II) ion and negative charge of sulphonate group, it is inferred that k_{43} is greater than k_{46}. The values of activation parameters corresponding to ($k_{43}+k_{46}$) and k_{12} (Table 2) further confirm that the deprotonated form is more reactive than the zwitterionic form of the ligand. The high negative value of entropy of activation is suggestive of associative mechanism being observed.

Table 2: Values of A, B, C specific rate constants and their activation parameters for the complexation of Ni(II) with 2-Amino ethanesulphonic acid at different temperatures

Temperatures (± 0.05) °C	**Ni(II)- ligand**					
	A	B × 10^6	C × 10^{-6}	k_{12} M^{-1} s^{-1}	($k_{43}+k_{46}$)× 10^{-3} M^{-1} s^{-1}	k_o × 10^{-3} s^{-1}
25	45	2.50	5.5	45	2.23	1.13
30	60	4.12	5.2	60	2.78	1.40
40	100	10.00	4.1	100	3.99	2.01
ΔH$^\#$ (kJmol^{-1})	-	-	-	45.74 ± 3.5	32.88 ± 0.11	-
ΔS$^\#$ (JK^{-1}mol^{-1})	-	-	-	-69.68 ± 11.8	-87.99 ± 3.7	-

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References

1. Bremer J. Act Chem Scand. 1955; 9:268.
2. Eigen M, Tamm K, Elektrochem Z. 1962, 66, 93, 107.
3. Fuoss RM. J Am ChemSoc., 1958; 80:5059.
4. Swift TI, Connick RF. J Chem Phig. 1962; 37:307.
5. Maitell E, Smith RM. Critical Stability Constants –Amino acid, Plenum Press, 1973, III.
6. Malhotra HC, Chopra H. J Indian Chem Soc. 2000, II.