

Kinetics of the complexation of Ni(II) and Co(II) with L-2,6-diaminocaproic acid

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Kinetics of complexation of Ni(II) and Co(II) by L-2,6-diaminocaproic acid has been investigated as a function of pH and temperature at 0.1 M KNO₃ using stopped flow technique. The overall rate constants have been resolved into stepwise rate constants. The activation parameters corresponding to each step have been evaluated. A reaction scheme on the basis of the comprehensive kinetic study consistent with our kinetic data has been proposed.

The metal-amino acid chelates¹⁻⁷ are of immense significance both chemically and biologically. L-2,6-diaminocaproic acid (lysine) is one of the major constituents of enzymes like trypsinogen and metallothionien, human serum albumin⁸ and of peptides that mediate in transportation of metal ions from blood to tissues. Its excessive retention in the tissues causes mental retardation.⁹ A defect in the renal absorptive mechanism leads to increased excretion of lysine in urine.

To understand these biological processes a comprehensive kinetic and mechanistic study of the complexation reaction of Ni(II) and Co(II) with L-2,6-diaminocaproic acid has been carried out. These investigations would serve as model systems for complex biological and biochemical processes.¹⁰

Materials and Methods

L-2,6-diaminocaproic acid and bromothymol blue (B D H, England), KNO₃ (Sarabhai, G R), 2,6-lutidine (Merck-Schuchardt), HCl (Glaxo, A R), Ni(NO₃)₂·6H₂O and Co(NO₃)₂·6H₂O were used as such.

The kinetics of the interaction of Ni(II) and Co(II) with L-2,6-diaminocaproic acid was investigated in the pH range 6.37-7.07 and 6.06-7.25 respectively at 25, 30, 35 and 40 ± 0.05°C and at ionic strength 0.1 M KNO₃. The pH of the solution was adjusted using 2,6-lutidine and HCl. The pH of mixing was taken on a Radiometer pH-meter (pH M26). The driving syringes and reaction chamber were thermostated with the circulatory type thermostat (German, model NBE).

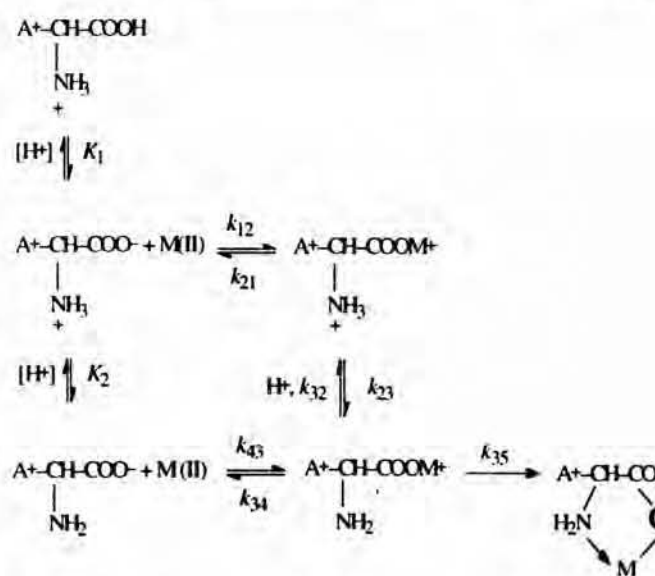
The reactions were studied under first order conditions by taking M(II) in excess. The kinetic runs were made on an Aminco Morrow stopped flow spectrophotometer. The absorbance changes were monitored at 620 nm.

Oscilloscope traces of log ΔV versus time (where ΔV were directly proportional to concentration changes) were used to evaluate first order rate constants.

Results and Discussion

k_{obs} (second order rate constant) is found to increase linearly with pH and temperature (Table 1).

Lysine is a tridentate ligand but as four methylene groups separate the two amino functional groups, it behaves as a bidentate ligand only. The monoprotonated form of the ligand (H₃N⁺-(CH₂)₄-CH(NH₂)-COO⁻) is found to be the predominant¹¹ one. This is verified by



where, M(II) = Ni(II) and Co(II); A⁺ = -(CH₂)₄-NH₃⁺

Scheme I

Table 1 - Values of second order rate constants for the interaction of Ni(II) and Co(II) with L-2,6-diaminocaproic acid at different pH's and temperatures

$\mu = 0.1 \text{ M KNO}_3$, [L-2,6-diaminocaproic acid] = $8.00 \times 10^{-3} \text{ M}$,
 [Ni(II)] = $8.01 \times 10^{-3} \text{ M}$ and [Co(II)] = $8.06 \times 10^{-3} \text{ M}$.

Ni(II)-L-2,6-diaminocaproic acid		Co(II)-L-2,6-diaminocaproic acid	
pH	$k_{\text{obs}} \times 10^3$ $\text{M}^{-1}\text{s}^{-1}$	pH	$k_{\text{obs}} \times 10^3$ $\text{M}^{-1}\text{s}^{-1}$
Temp = $25 \pm 0.05^\circ\text{C}$			
6.37	6.5	6.06	11.0
6.75	15.0	6.22	11.3
7.07	26.5	6.44	11.7
7.13	31.5	6.65	12.5
7.25	40.1	6.78	13.0
7.27	42.5	6.94	14.2
		7.11	15.8
Temp = $30 \pm 0.05^\circ\text{C}$			
6.24	13.5	6.39	17.0
6.29	18.5	6.41	17.2
6.67	27.7	6.52	17.6
6.77	34.5	6.75	19.3
7.04	57.5	6.77	19.4
7.30	105.0	6.99	22.0
		7.15	25.0
Temp = $35 \pm 0.05^\circ\text{C}$			
6.18	39.6	6.22	24.5
6.21	42.9	6.43	26.1
6.65	67.6	6.63	27.2
6.92	102.1	6.74	28.3
7.21	174.5	6.88	30.9
7.29	206.4	7.02	33.2
		7.13	37.0
Temp = $40 \pm 0.05^\circ\text{C}$			
6.33	146.6	6.24	43.2
6.66	192.3	6.37	44.3
6.90	258.5	6.63	48.6
6.97	282.9	6.87	54.8
7.07	332.5	6.93	56.6
		6.99	60.2
		7.25	76.1

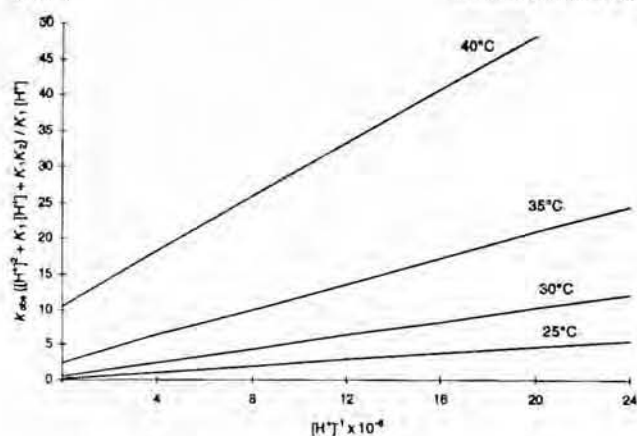


Fig. 1 - Plot of $k_{\text{obs}} \{[H^+]^2 + K_1 [H^+] + K_1 K_2 / K_3 [H^+]\}$ versus $[H^+]^{-1}$ for Ni(II) - L-2,6-diaminocaproic acid interaction.

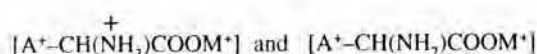
the higher value of the specific rate constant (k_{43}) corresponding to the monoprotonated form of lysine.

To understand the interaction of the various reactive forms of lysine with metal ions, Scheme 1 is found to give the best fit with our kinetic data :

Rate from Scheme 1 is given by Eq. (1)

$$\text{Rate} = k_{35} [A^+-CH(NH_3^+)-COOM^+] \quad \dots(1)$$

Applying steady-state approximation to intermediates



$$d/dt [A^+-CH(NH_3^+)COOM^+] = 0$$

$$= k_{12} [A^+-CH(NH_3^+)COO^-] [M(II)]$$

$$- k_{21} [A^+-CH(NH_3^+)COOM^+]$$

$$- k_{23} [A^+-CH(NH_2)COOM^+]$$

$$+ k_{32} [H^+] [A^+-CH(NH_2)COOM^+] \quad \dots(2)$$

$$d/dt [A^+-CH(NH_2)COOM^+] = 0$$

$$= k_{43} [A^+-CH(NH_2)COO^-] [M(II)]$$

$$- k_{34} [A^+-CH(NH_2)COOM^+] - k_{35} [A^+-CH(NH_2)COOM^+]$$

$$+ k_{23} [A^+-CH(NH_3^+)COOM^+] - k_{32} [H^+] [A^+-CH(NH_2)COOM^+]$$

...

Rearranging, we get :

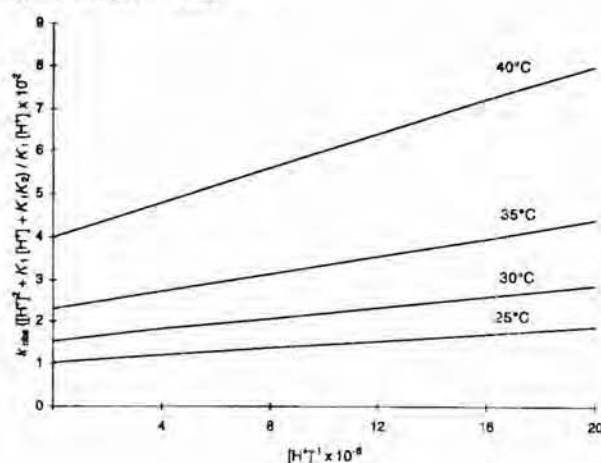
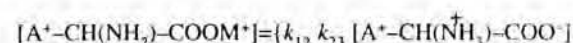


Fig. 2 - Plot of $k_{\text{obs}} \{[H^+]^2 + K_1 [H^+] + K_1 K_2 / K_3 [H^+]\}$ versus $[H^+]^{-1}$ for Co(II) - L-2,6-diaminocaproic acid interaction.



$$+ k_{23} k_{43} [A^+-CH(NH_2)COO^-] [M(II)]\} /$$

$$k_{21} k_{32} [H^+] + k_{23} (k_{34} + k_{35}) \quad \dots(4)$$

Substituting $[A^+-CH(NH_2)COOM^+]$ in Eq.(1), we get:

$$\text{Rate} = \frac{k_{12} k_{23} k_{35} [A^+-CH(NH_3^+)COO^-] + k_{23} k_{35} k_{43} [A^+-CH(NH_2)COO^-] [M(II)]}{k_{21} k_{32} [H^+] + k_{23} (k_{34} + k_{35})} \quad \dots(5)$$

From the dissociation equilibria of L-2,6-diaminocaproic acid

$$[A^+-CH(NH_3^+)COO^-] = \frac{K_1 [A^+-CH(NH_3^+)COOH]}{[H^+]} \quad \dots(6)$$

$$[A^+-CH(NH_2)COO^-] = \frac{K_1 K_2 [A^+-CH(NH_3^+)COOH]}{[H^+]^2} \quad \dots(7)$$

Substituting in Eq. (5) and on rearranging, we get :

$$\text{Rate} = \frac{k_{12} k_{23} k_{35} K_1 [H^+] + k_{23} k_{35} k_{43} K_1 K_2}{k_{21} k_{32} [H^+] + k_{23} (k_{34} + k_{35})} \times \frac{[A^+-CH(NH_3^+)COOH] [M(II)]}{[H^+]^2} \quad \dots(8)$$

Also, the overall rate equation for M(II) - L-2,6-diaminocaproic acid interaction can be written as :

Table 2 -Values of stepwise rate constants and rate constant for water exchange for the interaction of Ni(II) and Co(II) with L-2,6-diaminocaproic acid

Temp. ($\pm 0.05^\circ\text{C}$)	Ni(II)-L-2,6-diamino- caproic acid				Co(II)-L-2,6-diamino- caproic acid			
	$k_{12} \times 10^1$	$k_{43} \times 10^{-2}$	$k_0 \times 10^{-2}$	$k'_0 \times 10^{-1}$	$k_{12} \times 10^{-2}$	$k_{43} \times 10^{-3}$	$k_0 \times 10^{-3}$	$k'_0 \times 10^{-2}$
25	1.3	2.8	1.4	0.1	1.1	5.6	2.8	15.7
30	5.0	4.8	2.4	0.7	1.6	6.5	3.3	22.8
35	27.5	7.1	3.6	3.8	2.3	8.2	4.1	32.8
40	105.0	10.6	5.4	15.0	4.0	11.5	5.8	57.1

$$\text{Rate} = k_{\text{obs}} \{ [A^+-\text{CH}(\text{NH}_3^+)-\text{COOH}] + [A^+-\text{CH}(\text{NH}_3^+)-\text{COO}^-] + [A^+-\text{CH}(\text{NH}_2)-\text{COO}^-] \} [M(\text{II})] \quad \dots(9)$$

$$= k'_{\text{obs}} \{ [A^+-\text{CH}(\text{NH}_3^+)-\text{COOH}] + [A^+-\text{CH}(\text{NH}_3^+)-\text{COO}^-] + [A^+-\text{CH}(\text{NH}_2)-\text{COO}^-] \} \quad \dots(10)$$

$$\text{where, } k'_{\text{obs}} = k_{\text{obs}} [M(\text{II})] \quad \dots(11)$$

Substituting for $[A^+-\text{CH}(\text{NH}_3^+)-\text{COO}^-]$ and $[A^+-\text{CH}(\text{NH}_2)-\text{COO}^-]$ in Eq. (9) and rearranging we get:

$$\text{Rate} = k_{\text{obs}} \{ [H^+]^2 + K_1 [H^+] + K_1 K_2 \} \times \frac{[A^+-\text{CH}(\text{NH}_3^+)-\text{COOH}] [M(\text{II})]}{[H^+]^2} \quad \dots(12)$$

Comparing Eqs (8) and (12), we get :

$$k_{\text{obs}} \{ [H^+]^2 + K_1 [H^+] + K_1 K_2 \} = \frac{k_{12} k_{23} k_{35} K_1 [H^+] + k_{23} k_{35} k_{43} K_1 K_2}{k_{21} k_{32} [H^+] + k_{23} (k_{34} + k_{35})} \quad \dots(13)$$

Applying approximations that $k_{35} \gg k_{34}$ (as the reaction goes to completion) and at high pH's, $k_{23} (k_{34} + k_{35}) \gg k_{21} k_{32} [H^+]$, we get :

$$\begin{aligned} k_{\text{obs}} \{ [H^+]^2 + K_1 [H^+] + K_1 K_2 \} / K_1 [H^+] \\ = k_{12} + k_{43} K_2 / [H^+] \end{aligned} \quad \dots(14)$$

The value of K_2 at 25°C is taken from the literature¹² and corrected for temperatures of our investigations.⁴

The validity of the suggested Scheme is confirmed by linear plots of

$$k_{\text{obs}} \frac{[H^+]^2 + K_1 [H^+] + K_1 K_2}{K_1 [H^+]}$$

versus $[H^+]^{-1}$ (Figs 1 and 2). The values of k_{12} and k_{43} obtained from these linear plots are presented in Table 2. The corresponding activation parameters are evaluated from the plots of $\log k$ and $\log k/T$ versus $1/T$. For Ni(II) the enthalpies of activation $\Delta H^\ddagger_{12}$ and $\Delta H^\ddagger_{43}$ are found to be 222 and 58 kJmol^{-1} and the entropies of activation $\Delta S^\ddagger_{12}$ and $\Delta S^\ddagger_{43}$ to be 467 and -16 $\text{JK}^{-1}\text{mol}^{-1}$ respectively. Whereas for Co(II), $\Delta H^\ddagger_{12}$ and $\Delta H^\ddagger_{43}$ are evaluated to be 59 and 35 kJmol^{-1} and $\Delta S^\ddagger_{12}$ and $\Delta S^\ddagger_{43}$ to be -22 and -70 $\text{JK}^{-1}\text{mol}^{-1}$. The high value of $\Delta H^\ddagger$ corresponding to step k_{12} for Ni(II)-L-2,6-diaminocaproic acid, confirms the non-reactivity of the diprotonated form of the ligand. Whereas the high value of $\Delta S^\ddagger_{12}$ suggests a reaction between two similarly charged ions.

Finally, the rate law in terms of outersphere complex formation constant (K_{os}) and rate constant of water loss (k_0) is given by

$$\text{Rate} = d/dt [ML^+] = K_{\text{os}} k_0 [M^{2+}] [L^-] \quad \dots(15)$$

Taking k_{12} and k_{43} steps in Scheme 1, it can be written that

$$\text{Rate} = \{ k_{12} [A^+-\text{CH}(\text{NH}_3^+)-\text{COO}^-] + k_{43} [A^+-\text{CH}(\text{NH}_2)-\text{COO}^-] \} [M(\text{II})] \quad \dots(16)$$

Because $k_{12} \ll k_{43}$, Eq. (16) reduces to

$$\text{Rate} = k_{43} [\text{M(II)}] [\text{A}^+ - \text{CH}(\text{NH}_2) - \text{COO}^-] \quad \dots(17)$$

Comparing Eqs (15) and (17), we get

$$K_{os} k_0 = k_{43} \quad \dots(18)$$

The value of k_0 ($= k_{43} / K_{os}$) and k'_0 ($= k_{12} / K'_{os}$) are calculated by substituting the value of K_{os} which is determined using Fuoss equation¹³ (Table 2).

The water exchange constants¹⁴ for Ni(II) ion and Co(II) ion at 298K are $2.7 \times 10^4 \text{ sec}^{-1}$ and $1.13 \times 10^6 \text{ sec}^{-1}$ respectively. The values of k_0 reported in our study are $\sim 10^2$ times lower than the values reported earlier, because of the formation of more stable outer sphere complexes in our studies.

The difference in the value of k_0 for the two cations can be explained on the basis of crystal field stabilisation energy. The loss of water molecule from inner coordination sphere of the metal ion changes its geometry from octahedral to square pyramidal, which being unstable changes to trigonal bipyramidal (TBP) immediately. The difference in CFSE (O_h -TBP) values¹⁵ for Ni(II) and Co(II) is 5.73 and 2.55 Dq respectively. This difference in CFSE values is responsible for raising the energy barrier to a higher level in case of Ni(II). This fact is further confirmed from the values of energies of activation which is higher in case of Ni(II). It is, therefore, inferred that CFSE in a way is responsible for decreasing values of water exchange rate constants in the order Ni(II) < Co(II).

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