

Polarographic study of the irreversible system of zinc(II) with L-histidine/1,2-diaminopropane

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Abstract. Binary complexes of zinc(II) with L-histidine/1,2-diaminopropane have been studied by using amalgam polarography. The characteristic of the composite polarograms show the irreversible nature of the electrode reaction process. The kinetic parameters such as standard rate constant, k_s , and transfer coefficient α , have been determined by Randles' method. Standard rate constants are of the order of 10^{-5} cm sec⁻¹. There is evidence for the presence of Zn (histidine)₃ species. Stability constants have also been determined.

Keywords. Zinc; L-histidine; 1,2-diaminopropane; standard rate constant; transfer coefficient; stability constant.

1. Introduction

Studies on the complexes of cadmium (Islam and Bhat 1981; Ramaiah *et al* 1982; Islam *et al* 1983) with different amino acids and diamines in our laboratory have been continued along with those of zinc(II), using L-histidine and 1,2-diaminopropane as ligands, by polarographic methods. The reduction of binary complexes of Zn(II) with L-histidine/1,2-diaminopropane at the dropping mercury electrode (DME) was found to be irreversible. Hence, amalgam polarography was used to study them and their stability constants were determined. In the presence of both the ligands, it was not possible to determine the satisfactory reversible potentials (or formal potentials). This paper deals with the studies on the irreversible nature of the electrode reaction process, determination of the kinetic parameters and the stability constants of the binary complexes of Zn(II) with L-histidine (his) and 1,2-diaminopropane (pn).

2. Experimental

A manual set-up of the polarograph, with a dropping mercury electrode in connection with a saturated calomel electrode (SCE) as the reference electrode, was used for obtaining current-potential curves. Measurements were carried out in the deaerated solution at $30 \pm 0.1^\circ\text{C}$ in the presence of a supporting electrolyte, KCl. The ionic strength was maintained at 0.5 M.

The capillary characteristics were: $m = 1.50$ mg sec⁻¹ and $t = 3.85$ sec (open circuit). Zinc sulphate (BDH, Analar) solution was standardised (Vogel 1968) by the oxinate

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method. L-histidine (Puriss, Fluka, AG) and 1,2-diaminopropane (E Merck) were used without further purification. 1,2-diaminopropane solution was standardised with standard hydrochloric acid using methyl red as indicator. 0.006% gelatin was used to suppress the pronounced maximum. Double distilled water was used for the preparation of the solution.

The dropping amalgam electrode was prepared according to Sundaresan *et al* (1967). A Radiometer pH meter was used for measuring the pH of the solution.

3. Results and discussion

3.1 Zinc-L-histidine system

A well-defined wave was obtained for zinc(II) with the half-wave potential at -1.003 V vs SCE. The composite polarograms of the solution were taken at 0.3 mM concentration of zinc(II) at different pL ($= -\log[\text{his}]$) values. It is found from the nature of the curves that the irreversibility increases with the increase of concentration of L-histidine. A few composite polarograms are presented in figure 1. The reversible potentials, E_r , were calculated from zero current potential by using Randles' (Randles 1962) method. The reversible potentials were used to calculate the formal potentials, E_f^0 , from the Nernst equation substituting the cathodic and anodic diffusion currents for the concentrations of oxidant and reductant, respectively. E_f^0 values at different pL values are tabulated in table 1.

Formal potentials were used for the calculation of over potential, η . The standard rate constant, k_s , and transfer coefficient, α , were evaluated from the cathodic waves using the method described by Chandrasekharan *et al* (1968). The values were obtained from a plot of $\log \{h/[1 + \exp(nF/RT)\eta]\}$ vs η (eqn (1)).

$$\log h/[1 + \exp(nF/RT)\eta] = \log (3/7D)^{1/2} k_s - \alpha nF/(2.303 RT)\eta, \quad (1)$$

k_s and α values are presented in table 1.

It is observed that the standard rate constants are of the order of 10^{-5} cm sec $^{-1}$ which shows the irreversible nature of the electrode reaction. Using the values of k_s and α , the current, i at different potentials were calculated with the help of (2) (Chandrasekharan *et al* 1968) and plotted to obtain

$$[(i_d) - i]/i = (1.13/k_s)(D/t)^{1/2} \exp(\alpha nF/RT)\eta + \exp(nF/RT)\eta \quad (2)$$

current-potential curves. These curves fitted well with the experimental curves. As the plot of E_f^0 vs pL gave a curve indicating the presence of a mixture of complexes, DeFord and Hume's (1951) method was applied for the determination of stability constants.

The $F_0(L)$ function for the second and third species can be written as

$$F_0(L) = 1 + \beta_2(L)^2 + \beta_3(L)^3 \quad (3)$$

$F_0(L)$ can be calculated from the measurable quantities as

$$F_0(L) = \text{antilog} \left[\left\{ 0.4343 \frac{nF}{RT} \Delta E_f^0 \right\} + \log \frac{(i_d)_s}{(i_d)_c} \right] \quad (4)$$

where the symbols have their usual significance. $F_0(L)$ values are given in table 1. The overall stability constants were evaluated by the graphical method. The values are:

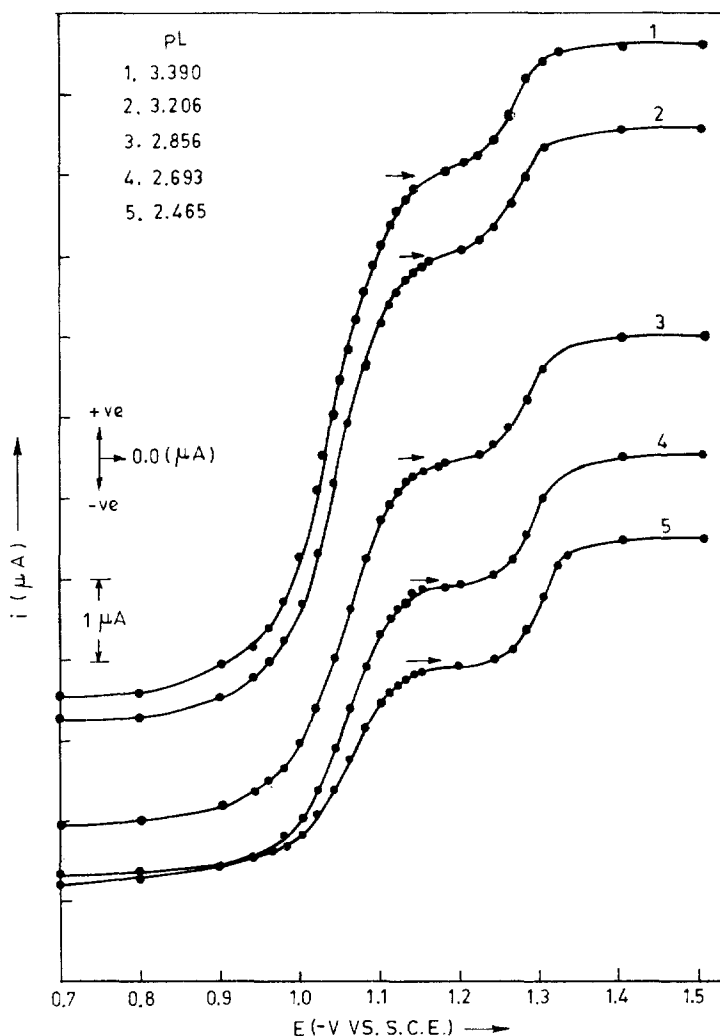


Figure 1. Composite polarograms; zinc-L-histidine system.

$\log \beta_2 = 11.75$ and $\log \beta_3 = 14.09$. The $\log \beta_2$ value agrees well with the literature value (Leberman and Rabin 1959). The calculated value of $\log \beta_1 = 6.55$.

An important feature of this investigation is the presence of $\text{Zn}(\text{his})_3$ as one of the complex species; this has not been reported earlier. Histidine is a potential terdentate ligand (Beech 1969), coordination being possible from the imidazole nitrogen atom, the amino group and the carboxyl group. Thus histidine may act as unidentate, bidentate or terdentate ligand. Williams (1970) and Perrin and Sharma (1967) have suggested that zinc coordinates tetrahedrally in the $\text{Zn}(\text{his})_2$ complex and the two carboxylic groups are only loosely bound. Chakravarty and Cotton (1963) have also found in their x-ray crystallographic studies of the zinc-histidine complex that coordination occurs through the tertiary imidazole nitrogen and α -amino nitrogen. The carboxyl oxygens are at larger distances from the coordination centre than the nitrogens and hence there will be

no bond formation possible. Comparing the $\log K$ values for copper and zinc of histidine and histamine complexes, Perrin and Sharma (1967) have concluded that histidine is bidentate in nature rather than terdentate in zinc-histidine complex. On the basis of this assumption it may be possible to form an octahedral $Zn(hist)_3$ species at higher concentration of histidine.

3.2 Zinc-1,2-diaminopropane system

Under same experimental conditions as described in the previous section, the composite polarograms of zinc (0.3 mM) in the presence of 1,2-diaminopropane of different concentrations were obtained. The characteristics of the composite polarograms show the irreversible nature of the electrode reaction. The reversible potentials and the formal potentials were calculated by using the same method as in the case of zinc-histidine system. k_s , α and $F_0(L)$ values are given in table 2, $\log \beta_2 = 10.23$ and

Table 1. Zinc-L-histidine system.

pL	α	$-\log k_s$	E_f^0 (-V vs SCE)	$F_0 \times 10^{-5}$	$F_1 \times 10^{-8}$	$F_2 \times 10^{-11}$	$F_3 \times 10^{-14}$
5.000	—	—	1.054	0.0005	—	—	—
4.598	—	—	1.078	0.003	—	—	—
4.215	—	—	1.104	0.026	—	—	—
3.807	—	—	1.126	0.120	—	—	—
3.390	—	—	1.154	1.123	—	—	—
3.206	0.55	4.58	1.166	2.648	—	—	—
3.066	0.56	4.64	1.174	4.741	5.570	6.540	1.045
2.856	0.65	4.99	1.188	14.070	10.196	7.388	1.250
2.693	0.69	4.99	1.200	35.825	17.544	8.591	1.440
2.465	0.68	4.79	1.216	121.110	34.932	10.075	1.270
2.310	0.68	4.70	1.227	274.898	56.136	11.463	1.186

$\log \beta_2 = 11.75$; $\log \beta_3 = 14.09$

Zn = 0.3 mM; $\mu = 0.5$ M (KCl); $(E_{1/2})_S = -1.003$ V (vs SCE).

Table 2. Zinc-1,2-diaminopropane system.

pL	α	$-\log k_s$	E_f^0 (-V vs SCE)	$F_0 \times 10^{-4}$	$F_1 \times 10^{-7}$	$F_2 \times 10^{-10}$	$F_3 \times 10^{-13}$
4.040	—	—	1.070	0.016	—	—	—
3.166	—	—	1.236	1.029	—	—	—
3.054	0.57	4.28	1.131	1.800	—	—	—
2.941	—	—	1.135	2.540	2.217	1.934	0.200
2.817	0.62	4.46	1.144	4.762	3.124	2.050	0.229
2.718	—	—	1.153	9.416	4.919	2.570	0.454
2.558	0.67	4.62	1.162	19.199	6.938	2.507	0.291
2.362	0.68	4.54	1.177	61.988	14.267	3.283	0.364
2.228	—	—	1.187	132.337	22.373	3.782	0.354
2.188	0.65	4.44	1.190	162.745	25.092	3.869	0.334

$\log \beta_2 = 10.23$; $\log \beta_3 = 12.54$

Zn = 0.3 mM; $\mu = 0.50$ M (KCl); $(E_{1/2})_S = -1.003$ V (vs SCE).

$\log \beta_3 = 12.54$, obtained graphically, agree well with literature values (Carlson *et al* 1945). Calculated value of $\log \beta_1 = 6.21$.

The values ($\log \beta_{10} = 12.60$ and $\log \beta_{20} = 15.00$) reported by Gupta *et al* (1980) appear to be high compared to those obtained in the present study and others (Sillen and Martell 1971). The high values may be due to the fact that Gelling's formulation (1962, 1963) is not applicable for an irreversible system. Tanaka and Tamamushi (1963) have successfully used Gelling's formulation for studying systems having $k_s > 10^{-3} \text{ cm sec}^{-1}$ only.

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References

- Beech G 1969 *Quart. Rev.* **23** 410
Carlson G A, McReynolds J P and Verhoek F H 1945 *J. Am. Chem. Soc.* **67** 1334
Chakravarty A and Cotton F A 1963 *J. Phys. Chem.* **67** 2878
Chandrasekharan V R, Sundaresan R, Saraiya S C and Radhakrishnan T P 1968 *Study of irreversible process by polarography*, BARC—370, Bhabha Atomic Research Centre, Bombay, India
DeFord D D and Hume D N 1951 *J. Am. Chem. Soc.* **73** 5321
Gellings P J 1962 *Z. Elektrochem., Ber. Bunsenger Phys. Chem.* **66** 477, 481, 799
Gellings P J 1963 *Z. Electrochem., Ber. Bunsenger Phys. Chem.* **67** 167
Gupta K D, Choudhary K K and Gaur J N 1980 *J. Indian Chem. Soc.* **57** 382
Islam M M and Bhat B G 1981 *Trans. Soc. Adv. Electrochem. Sci. Technol.* **16** 215
Islam M M, Singh R S and Bhat B G 1983 *Indian J. Chem.* (in press)
Leberman R and Rabin B R 1959 *Trans. Faraday Soc.* **55** 1660
Perrin D D and Sharma V S 1967 *J. Chem. Soc.* **A724**
Ramaiah M, Bhat B G and Sundaresan R 1982 *Proc. Indian Acad. Sci. (Chem. Sci.)* **91** 151
Randles J E B 1962 *Progress in polarography* (eds) P Zuman and I M Kolthoff (New York: Interscience) p. 123
Sillen L G and Martell A E 1971 *Stability constants of metal ion complexes* (London: The Chemical Society)
Sundaresan R, Saraiya S C and Sundaram A K 1967 *Proc. Indian Acad. Sci.* **66** 120
Tanaka N and Tamamushi R 1963 *Z. Phys. Chem.* **39** 117
Vogel A I 1968 *A text book of quantitative inorganic analysis* (3rd ed.) (London: The English Language Book Society)
Williams D R 1970 *J. Chem. Soc. (A)* 1550