Inorganica Chimica Acta, 24 (1977) 201–205

Polarographic Investigation of the Zinc–N,N-Dihydroxyethylglycine System

J. K. JAILWAL*, JAI KISHAN and R. C. KAPOOR
Department of Chemistry, University of Jodhpur, Jodhpur-342001, India
Received September 30, 1976

Complex formation of zinc with N,N-dihydroxyethylglycine (Bicine) has been studied polarographically at various pH values. The electrode processes were found to be irreversible, the degree of which depending on pH of the solution. At pH 5 the system was evaluated as quasi-reversible. Zinc formed 1:1 and 1:2 simple metal–ligand complexes. At higher pH values in alkaline range, mixed hydroxy complexes were found to form. The following complex species MX_1, MX_2, $M(OH)X$, $M(OH)X_2$ *and* $M(OH)_2X$ *were evaluated. The logarithmic values of overall stability constants were 7.27, 8.50, 11.52, 12.66 and 15.85 respectively.*

Introduction

N,N-Dihydroxyethylglycine (Bicine) has a tendency to form complexes with various metal ions which have been studied by a number of investigators [1–14]. Martell *et al.* [1–3] have investigated the complex formation of bicine with a number of metal ions such as Cu(II), Ni(II), Co(II), Fe(II), Mn(II), Zn(II), Cd(II), Mg(II), Fe(III), La(III), Cr(III) and Zr(IV) potentiometrically. Toren and Kolthoff [4] have studied the Fe(III,II)–bicine system polarographically. The fact that the Sr(II) complex of bicine is less stable than that of Ca(II) has been utilized by Takamoto [5] for the separation of Sr(II) and Ca(II). Roseff [6] has investigated the interaction of Y^{91}-labeled chelate of bicine with serum constituents. Wong [7] has reported by pH measurements that bicine combines with Pr(III) and Nd(III) to form 1:1 and 1:2 complexes. Codell *et al.* [8] have studied the Ti(III)–bicine system by EPR and spectrophotometric techniques.

Complex formation of bicine with rare-earths and a number of bi- and trivalent metal ions has been investigated by Jokl *et al.* [9, 10] using paper electrophoresis. Nozaki *et al.* [11] have reported polarographic studies of the complexation of Pb(II), Cd(II) and Cu(II) with bicine. Simple and mixed hydroxy complexes were evaluated. Kapoor and Jaiwal [12] have reported the existence of a very weak Tl(I)–bicine complex polarographically. Ce(III) and Ce(IV) form chelates with 1, 2 and 3 mol of ligand per metal ion, according to the porentiometric investigations of Kapoor and Aggarwal [13]. They have also reported the polarographic study of this system [14].

Bicine is less basic than glycine yet it has equal or higher affinity for metal ions. This is due to the participation of hydroxyethyl groups in complex formation. Jokl *et al.* [9] have shown on the basis of their investigations on electrophoretic mobility of bicine with a series of bi- and trivalent central ions, that bicine is potentially a 4-donor complex forming agent because alcoholic hydroxyl groups can participate as donor groups in formation of chelates.

A polarographic investigation of the Zn(II)–bicine system is reported in this paper. This system behaved irreversibly at the dropping mercury electrode. At pH 5 it was found to be quasi-reversible. Simple 1:1 and 1:2 metal–ligand complexes formed were treated by the methods of Deford–Hume [15] and Lingane [16]. Mixed hydroxy complexes formed at higher pH values were evaluated by the method of Schaap and McMasters [17].

Experimental

Polarographic study of the complex formation of Zn(II) with bicine was carried out at various pH values. The ionic strength of all experimental solutions was kept constant at 1.0 by adding appropriate amounts of potassium chloride.

Polarograms were recorded with an automatic Radelkis type OH 102 polarograph. The dropping mercury electrode (DME) used had the following characteristics: t = 3.36 sec, m = 2.37 mg/sec and h = 40 cm. All electrode potentials were measured against a saturated calomel electrode (SCE) which was connected to the experimental solutions through a potassium chloride salt bridge. A Radiometer pH meter (type TTT1d) was used for pH measurements.

All reagents used were of analytical grade. Bicine supplied by Sigma Chemical Company (USA) was used as such in these studies. Before recording polaro-

---

*Present address: Quality Control Laboratories, Indian Drugs and Pharmaceuticals Limited, Hyderabad-500037, India.

grams, the experimental solutions were deaerated by bubbling pure nitrogen through them. The studies were carried out at 30° ± 0.1 °C by keeping the polarographic cell assembly in an Ultrathermostat.

Results and Discussion

The reduction of Zn(II) in presence as well as in absence of bicine exhibited an irreversible nature at DME. The values of slopes of log-plot analyses of the waves for pure Zn(II) and complexed Zn(II) in the pH range of 8 to 11 were 0.040 ± 0.002V, giving the value of the transfer coefficient α as 0.75. The slope values differed at other pH values.

The $E_{1/2}$ values of the Zn(II)–bicine system were found to be pH dependent. Polarographic waves of the solutions containing 5×10^{-4} *M* Zn^{2+} and 2.5×10^{-2} *M* bicine were recorded at different pH values. The $E_{1/2}$ value remained unchanged in the pH range of 1 to 4 and then it became increasingly more negative with pH, up to pH 8. Again in the pH range of 8 to 9.5 no appreciable shift in $E_{1/2}$ could be observed. It gradually became more negative with further increase in pH (Figure 1). Since the dissociation of bicine is complete at about pH 10, the shift of $E_{1/2}$ above this pH shows the participation of hydroxyl ions in complexation.

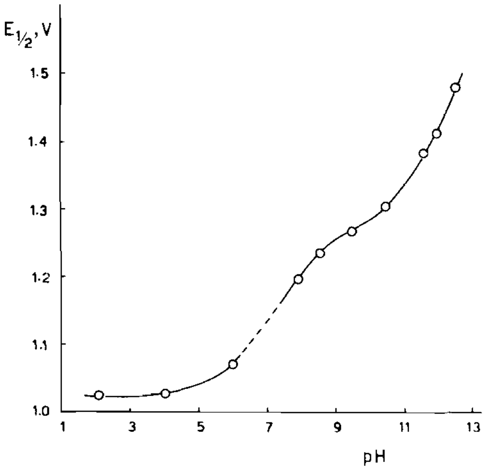

Fig. 1. Plot of $-E_{1/2}$ *vs.* pH. The dotted portion indicates the double wave region.

The concentration of free ligand in different sets of experiments was calculated by using pK_1 and pK_2 values of 2.5 and 8.11 respectively [4].

Simple Complexes

Simple Zn(II)–bicine complexes were investigated at pH values of 5 to 8. In all sets of experiments, the Zn^{2+} ion concentration was kept at 5×10^{-4} *M* while the bicine concentration was varied from 1.25×10^{-2} to 0.5 *M*. With increase in ligand concentration the $E_{1/2}$ values became more negative indicating complex formation. This variation of $E_{1/2}$ with ligand concentration (logarithmic) at different pH values is shown in Figure 2.

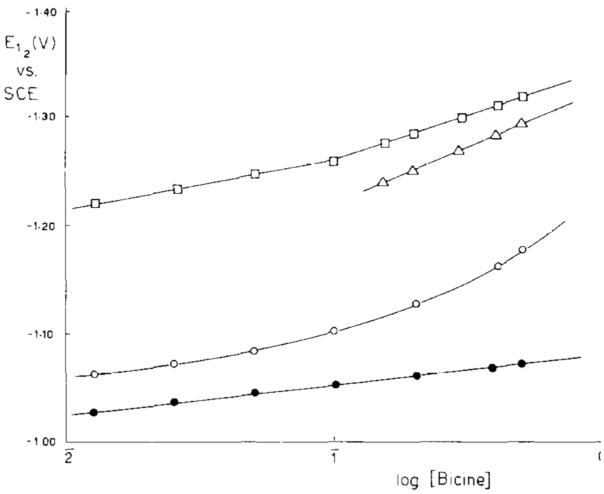

Fig. 2. Plot of $E_{1/2}$ *vs.* log[bicine] at pH values of 5 (●), 6 (○), 7 (△) and 8 (□).

The reduction of pure zinc as well as of the complex system at pH 8 and above was found to be purely diffusion controlled as the plot of $\sqrt{h}$ *vs.* i gave straight lines passing through the origin in all the cases. On the other hand, at pH values of 5, 6 and 7, small deviation was observed as $\sqrt{h}$ *vs.* i plots, although lying on a straight line, did not pass through the origin. Therefore, the values of the coordination number evaluated at these pH values were considered approximate. However, the values of the coordination number determined at these pH values were supported by the results obtained at pH 8 and above, where the electrode processes were purely diffusion controlled.

At pH 5 single well defined waves were obtained in the concentration range of 1.25×10^{-2} *M* to 0.1 *M* bicine whereas at higher concentration a second ill-defined wave appeared at the plateau of the first wave with comparatively small wave height. At this pH, the system appeared quasi-reversible since the log-plot analysis of the waves was not linear, instead a curvature was obtained at various bicine concentrations. The first wave was analysed when double waves were obtained for bicine concentration greater than 0.1 *M*. In the case of quasi-reversible systems, the asymptote drawn from sufficiently positive potentials in the log-plot analysis intersects the potential axis at the reversible half-wave potential, $E_{1/2(r)}$, which can be used for analysis purpose [18] (Figure 3). These $E_{1/2(r)}$ values were plotted against log[bicine] values which gave a straight line corresponding to the formation of a 1:1 complex.

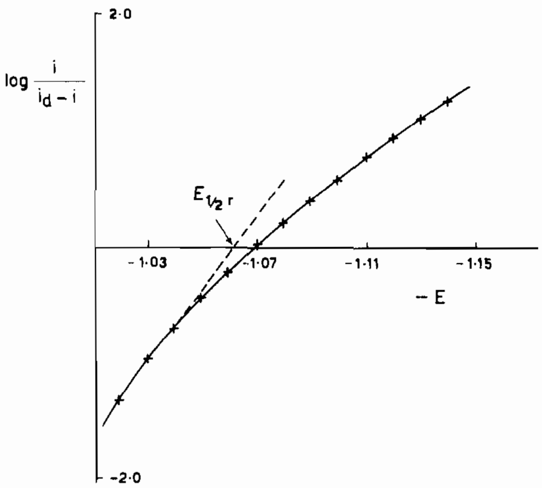

Fig. 3. Plot of E *vs.* log $i/(i_d - i)$ at pH 5.0.

At pH 6 double waves were obtained at all concentrations of bicine. The height of the first wave decreased whereas that of the second wave increased with ligand concentration, with the total height remaining constant. The $E_{1/2}$ of the first wave became more negative with increasing bicine concentration whereas the $E_{1/2}$ of the second wave remained unchanged at −1.255V. On plotting $E_{1/2}$ *vs.* log[bicine] for the first wave, a curvature was obtained, suggesting the formation of consecutive complexes. The log-plot slope values varied (0.044V and greater) with ligand concentration, especially at higher concentrations. Approximately, therefore, the lower concentrations of bicine gave the value of p as 1 whereas the higher concentrations corresponded to the value of p as 2.

At pH 7 in the lower concentration range of 1.25 X 10^{-2} *M* to 0.1 *M* bicine, ill-defined double waves in close proximity were obtained. On further increase in the ligand concentration, the double waves were reduced to single well defined waves with the log-plot slope values of 0.050 V. The shift of $E_{1/2}$ values with ligand concentration (0.15 to 0.5 *M*) corresponded approximately to the formation of a 1:2 complex.

The stability constants of the complexes could be evaluated quite conveniently at pH 8, since the value of the transfer coefficient, α, was found to be the same for zinc in absence as well as in the presence of bicine at this pH. When $E_{1/2}$ values were plotted against log[bicine], two straight lines resulted, suggesting the formation of two complex species in solution. The first line corresponding to the bicine concentration of 1.25 X 10^{-2} *M* to 0.1 *M* gave the value of p as 1.17 ≃ 1. The second line in the concentration range of 0.1 to 0.5 *M* bicine gave the value of p as 2.02 ≃ 2. Thus 1:1 and 1:2 simple metal–ligand complexes were formed. The logarithmic values of the overall stability constants of these complexes were obtained as 7.47 and 8,71 respectively, using the expression

$$E_{1/2c} = E_{1/2s} + \frac{0.06}{\alpha n} \log K_{diss}$$

at 1*M* ligand concentration. The value of coordination number, p, was determined by using the relation

$$\frac{dE_{1/2}}{d\log[x]} = -p\,\frac{0.06}{\alpha n}$$

The notations used have their usual significance. By applying the method of Deford and Hume [15], the corresponding values were obtained as 6.90 and 8.79, respectively, according to Figure 4.

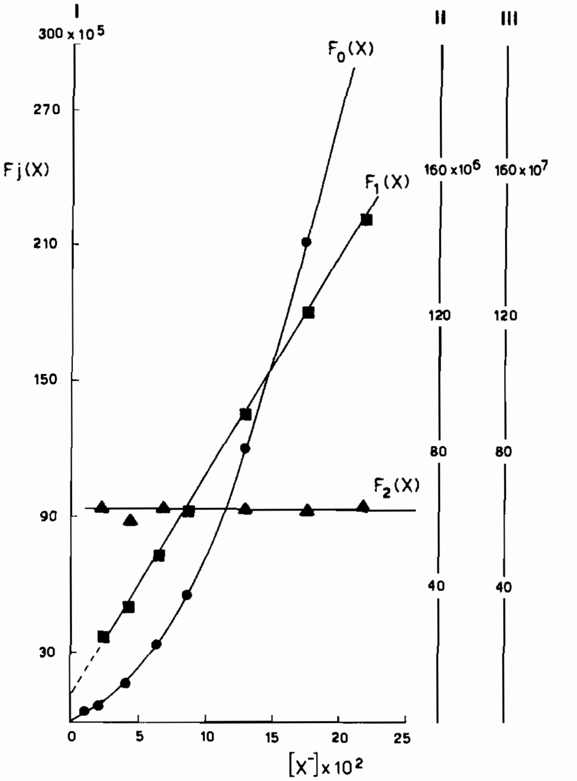

Fig. 4. Plot of $F_j(X)$ *vs.* $[\bar{X}]$ ligand concentration. Plot of $F_0(X)$ *vs.* $[\bar{X}]$ (● I). Plot of $F_1(X)$ *vs.* $[\bar{X}]$ (■ II). Plot of $F_2(X)$ *vs.* $[\bar{X}]$ (▲ III).

Mixed Hydroxy Complexes

The formation of mixed hydroxy complexes is evident from the dependence of $E_{1/2}$ on pH (Figure 1). Schaap and McMasters' method [17] of mixed ligand complexes, an extension of the original method of Deford and Hume [15] for the evaluation of successive complexes, was used for the evaluation of mixed hydroxy complexes of zinc. This procedure has been used for the study of mixed hydroxy complexes of Cd(II), Cu(II) and Pb(II) by Nozaki *et al.* [11]. Besides bicine anion (X^-), OH^- ion also acts as a ligand in the present case. The formation of mixed hydroxy complexes can be expressed as

$$M^{n+} + iOH^- + jX^- = M(OH)_iX_j^{n-(i+j)}$$

The following relationship for the overall stability constant β_{ij} and the shift in $E_{1/2}$ value due to complex formation holds, which can be identified with the function $F_{00}(OH, X)$, thus

$$F_{00}(OH, X) = \Sigma\beta_{ij}[OH]^i[X]^j = \text{antilog}[0.435\frac{\alpha nF}{RT}(E_{1/2s} - E_{1/2c}) + \log\frac{I_s}{I_c}] \qquad (1)$$

where α is the transfer coefficient of the electrode process, which was found to be a constant in the present case in the pH range of 8 to 11 (0.75). $E_{1/2(s)}$, $E_{1/2(c)}$, I_s and I_c are the half-wave potentials and diffusion current constants of simple and complexed metal ion respectively.

Since OH^- is monodentate and X^- is bidentate, the function $F_{00}(OH, X)$ can be represented as

$$\begin{aligned} F_{00}(OH, X) &= \{1 + \beta_{01}[X] + \beta_{02}[X]^2\} \\ &\quad + \{\beta_{11}[X] + \beta_{12}[X]^2\}[OH] \\ &\quad + \{\beta_{21}[X]\}[OH]^2 \\ &\quad + \ldots\ldots\ldots\ldots\ldots \\ &= A + B[OH] + C[OH]^2 \qquad (2) \end{aligned}$$

In the pH range where $[X^-]$ is constant, at constant concentration of bicine, A, B, C will also become constant. By obtaining the function F_{00} from equation (1) as a function of $[OH^-]$, F_{10} and F_{20} can be calculated succesively as

$$F_{10}(OH, X) = [F_{00} - A]/[OH] = B + C[OH]$$

$$F_{20}(OH, X) = [F_{10} - B]/[OH] = C$$

The extrapolation at $[OH^-] = 0$ of the plots of F_{i0} *vs.* $[OH^-]$ gives the values of A, B, and C. The F_{ij} functions can be calculated according to the following relationships:

$$F_{01}(OH, X) = \frac{[A - 1]}{[X]} = \beta_{01} + \beta_{02}[X]$$

$$F_{02}(OH, X) = \frac{[F_{01} - \beta_{01}]}{[X]} = \beta_{02}$$

$$F_{11}(OH, X) = \frac{B}{[X]} = \beta_{11} + \beta_{12}[X]$$

$$F_{12}(OH, X) = \frac{[F_{11} - \beta_{11}]}{[X]} = \beta_{12}$$

$$F_{21}(OH, X) = \frac{C}{[X]} = \beta_{21}$$

The dependence of half-wave potential on pH was investigated at ionic strength of 1.0, Zn^{2+} concentration of 2×10^{-4} *M* and bicine concentrations of 6×10^{-3} *M*, 1×10^{-2} *M* and 2×10^{-2} *M* in the pH range of 8 to 11 at each concentration of bicine, keeping $[X^-]$ constant and varying the OH^- concentration. The plots of F_{i0} *vs.* $[OH^-]$ were plotted by using $E_{1/2}$ *vs.* pH curves in the pH range of 10–11.

The values of A, B and C in equation (2) were calculated at three different concentrations of bicine, *viz.* 6×10^{-3}, 1×10^{-2} and 2×10^{-2} *M*. The plots of F_{i0} *vs.* $[OH^-]$ at $[X^-]$ of 6×10^{-3} *M* and 1×10^{-2} *M* are shown in Figure 5. From Figure 5, the values of A, B and C were derived and used to calculate β_{01}, β_{02}, β_{11}, β_{12} and β_{21} in the way mentioned above. The mean values of stability constants are given in Table I. The values of $\log\beta_{01}$ and $\log\beta_{02}$ were consistent with those obtained in the case of the simple system, as is evident from Table I. Thus at pH 8, no appreciable amount of mixed hydroxy complexes is formed.

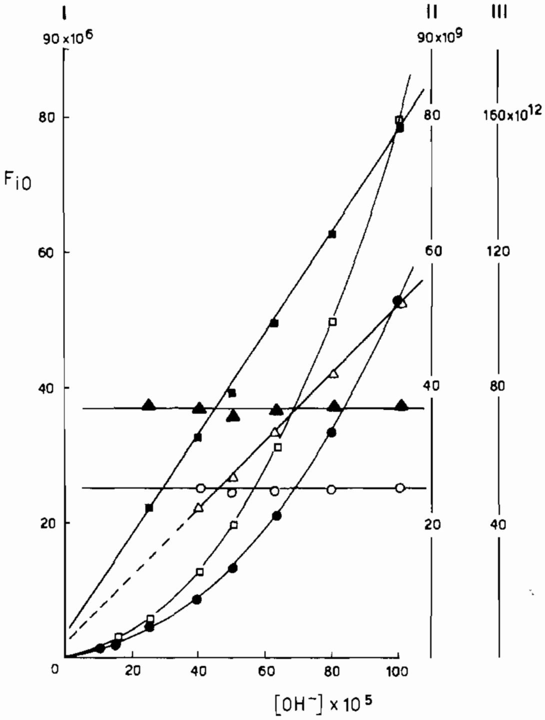

Fig. 5. Plot of F_{i0} *vs.* $[OH^-]$ at $[\bar{X}] = 6 \times 10^{-3}$ and 1×10^{-2} *M*. $F_{00}(OH,X)$ *vs.* $[OH^-]$ (● I). $F_{00}(OH,X)$ *vs.* $[OH^-]$(□). $F_{10}(OH,X)$ *vs.* $[OH^-]$ (△ II). $F_{10}(OH,X)$ *vs.* $[OH^-]$ (■). $F_{20}(OH,X]$ *vs.* $[OH^-]$ (○ III). $F_{20}(OH,X)$ *vs.* $[OH^-]$ (▲).

TABLE I. Logarithmic Values of Overall Stability Constants of Zinc Complexes.

Method	MX_1	MX_2	$M(OH)X$	$M(OH)X_2$	$M(OH)_2X$
Schaap–McMaster	7.27	8.50	11.52	12.66	15.85
Deford–Hume	6.90	8.79			
Kolthoff–Lingane	7.47	8.71			
Potentiometry [1]	5.36	8.64			

Acknowledgment

One of the authors (J.K.) is thankful to the CSIR, New Delhi, for the award of a Junior Research Fellowship.

References

1 S. Chaberek Jr., R. C. Courtney and A. E. Martell, *J. Am. Chem. Soc., 75,* 2185 (1953).
2 R. C. Courtney, R. L. Gustafson, S. Chaberek Jr. and A. E. Martell, *J. Am. Chem. Soc., 80,* 2121 (1958).
3 B. I. Intone and A. E. Martell, *J. Am. Chem. Soc., 82,* 358 (1960).
4 P. E. Toren and I. M. Kolthoff, *J. Am. Chem. Soc., 77,* 2061 (1955).
5 S. Takamoto, *Nippon Kagaku Zasshi, 81,* 915 (1960).
6 B. Roseff, *Ann. N.Y. Acad. Sci., 88,* 479 (1960).
7 P. Wong, *Hong Kong Bap. Coll. J.,* 82 (1962).
8 M. Codell, S. Fujiwara, K. Nagashima and T. Seki, *Bull. Chem. Soc. Japan, 38,* 21 (1965).
9 V. Jokl, J. Majer and M. Mazakova, *Chem. Zvesti., 18,* 584 (1964).
10 V. Jokl, J. Majer, H. Sharf and H. Kroll, *Mikrochim. Acta, 1–2,* 63 (1966).
11 T. Nozaki, A. Tanaka and T. Nishimoto, *Nippon Kagaku Zasshi, 92,* 159 (1971).
12 R. C. Kapoor and J. K. Jailwal, *Indian J. Chem., 10,* 554 (1972).
13 R. C. Kapoor and B. S. Aggarwal, *Indian J. Chem., 11,* 71 (1973).
14 R. C. Kapoor and B. S. Aggarwal, *J. Indian Chem. Soc., 51,* 137 (1974).
15 D. D. Deford and D. N. Hume, *J. Am. Chem. Soc., 73,* 5321 (1951).
16 J. J. Lingane, *Chem. Rev., 29,* 1 (1941).
17 W. B. Schaap and D. L. McMasters, *J. Am. Chem. Soc., 83,* 4699 (1961).
18 J. Heyrovsky and J. Kuta, "Principles of Polarography", Academic Press, New York (1965), p. 214.