

THESIS APPROVED

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A POLAROGRAPHIC STUDY OF
ZINC(II)-GLYCINE
INTERACTIONS

By

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A THESIS

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INTRODUCTION

When a metal combines with an electron donor, the resulting substance is said to be a complex, or coordination compound. If the substance which combines with the metal ion contains two or more donor groups so that one or more rings are formed, the resulting structure is said to be a chelate.

The determination of equilibrium constants is of importance in the study of chelate compounds, since it is one promising approach to the accumulation of data which lead to a comprehensive understanding of chelates and the relationships which govern their formation and structure. There are several well known methods of calculating the equilibrium constant for complex formation: through pH measurements, described by Bjerrum¹; ion exchange, outlined by Schubert and Richter²; methods based on Beer's Law; oxidation potentials, described by Riley and Gallafent³; and polarographic measurements, described by Lingane⁴.

The formation constants of zinc(II)-glycine complexes have not been determined by the polarographic method, but have been determined from pH measurements at 25° C by Maley and Mellor^{5,6}, Bjerrum⁷, Albert⁸, and Monk⁹. Ley¹⁰ has determined the formation constant of the zinc(II)-glycine complex at 25° C from conductance measurements. It was of interest to extend the investigation of the zinc(II)-glycine system to higher glycine concentrations in order to determine whether the 1:3 complex exists and can

be detected polarographically. It was also desirable to extend the investigation to temperatures other than 25° C to evaluate the several thermodynamic quantities associated with the complex formation reactions.

EXPERIMENTAL

Materials- All chemicals were of analytical reagent grade products. Stock solutions of zinc(II) nitrate were analyzed gravimetrically as zinc oxalate using ethyl oxalate in the presence of zinc(II) nitrate solution at 80° C¹¹. Standard stock solutions of glycine were prepared directly from the vacuum-dried compound. The purity of glycine was determined by potentiometric titration with standard hydrochloric acid. Potassium nitrate was used as the supporting electrolyte.

Apparatus- The pH measurements were made with a Beckman model-G pH meter equipped with Beckman glass electrode number 40498 and Beckman calomel electrode number 39970. Buffer solutions of pH 4 and 7 were used to standardize the instrument. Polarographic current-voltage curves were obtained with a Fisher Elecdropode model 65, equipped with a Fisher recorder model F35-1PH560-51-T24-T46-T68. All potentials were measured against a saturated calomel electrode(S.C.E.). Characteristics of the capillary were: $m=1.95$ mg/sec, $t=3.8$ sec open circuit and out of water at a mercury column of 60 cm. The method was standardized by determining the

copper(II)-glycine formation constant at 25° C. A value of 15.5 was obtained. Li, White, and Yoest¹² reported a value of 15.1 at 25° C.

Determination of pK_2 values- The determination of pK_2 values of glycine were obtained from potentiometric titrations. A stock solution that was 0.1 Molar in glycine was prepared by protonating 9.99 meq. of glycine using 14.00 meq. of 0.100N hydrochloric acid. Titrations were carried out on 5 ml aliquots of protonated glycine solution at 25°, 30°, and 35° C with carbon dioxide free 0.100N potassium hydroxide. Sufficient potassium nitrate was added to keep the ionic strength constant (0.15). The titration vessel was fitted with four inlets. These inlets were used to admit the glass and calomel electrodes, micro-buret, and an inlet for nitrogen to insure an inert atmosphere. A magnetic stirrer was used for uniform mixing before each pH measurement was made.

CALCULATION OF FORMATION CONSTANTS

Solutions of 5×10^{-4} M zinc(II) nitrate were analyzed only and compared with analyses of identical solutions made with various concentrations of glycine from 0.01 to 0.16M. Sufficient standardized carbon dioxide free potassium hydroxide solution was added to keep the pH above 8. All solutions analyzed by the dropping mercury electrode were maintained constant at an ionic strength of 0.15 with potassium nitrate. Triton X-100 (Rohm and Haas Co.) was used as a maximum suppressor.

A standard H-cell was fitted with an inlet and outlet so that oxygen could be eliminated by passing nitrogen through the system. To insure complete removal of oxygen from the nitrogen, and to presaturate it the nitrogen was passed through a train of pyrogallic acid and through potassium nitrate solution before entering the system.

The reversibility of the electrode was tested by plotting $\log \frac{i}{i_d - i}$ against $E_{d.e.}$ ¹³ at each of the temperatures for the zinc(II) ion solutions. The slope of the lines indicated that two electrons were transferred, and that the reduction of the chelated zinc metal took place in one step. The equation for the electrode reaction in this case was assumed to be



that is chelation was assumed to take place between zinc ion and the anion of the amino acid¹⁴.

The number of glycine ligands coordinated to the central zinc(II) ion was calculated from the slope of plots of ΔE vs $\log(\text{gly})_f$ according to the following equation^{4,13}

$$\frac{\Delta E}{\log(\text{gly})_f} = -p(2.303RT/nF) \quad (1)$$

where p is the number of ligands coordinated and ΔE the change in half-wave potential of the zinc ion due to chelation. The concentration of unprotonated glycine, $(\text{gly})_f$, was calculated from the

pH of the solution, the pK_2 of glycine and the effective concentration of glycine, $(\text{gly})_e$, by means of the relation

$$pK_2 - \text{pH} = \log \left\{ \left[\frac{(\text{gly})_e}{(\text{gly})_f} \right] - 1 \right\} \quad (2)$$

The effective concentration of glycine was obtained by subtracting the concentration of glycine combined with zinc from the total molar concentration of glycine present. The stability constants were calculated by the relation¹¹

$$\left(\frac{E_{1/2}}{2} \right)_c - \left(\frac{E_{1/2}}{2} \right)_s = \left(\frac{2.303RT}{nF} \right) \log K_d \frac{f_c k_s}{f_s k_c} - p \left(\frac{2.303RT}{nF} \right) \log (\text{gly})_f \quad (3)$$

where $\left(\frac{E_{1/2}}{2} \right)_c$ and $\left(\frac{E_{1/2}}{2} \right)_s$ are potentials for complex and metal respectively. Activity coefficients are represented by f_c and f_s for complex and metal. The symbols k_c and k_s are constants which are proportional to the square root of the diffusion coefficients of the complex and metal ions respectively. Equation (3) was rearranged slightly to the following form which places emphasis upon $K_{st.}$, the over-all stability constant (formation constant), rather than the dissociation constant, K_d .

$$\left(\frac{E_{1/2}}{2} \right)_c - \left(\frac{E_{1/2}}{2} \right)_s = - \left(\frac{2.303RT}{nF} \right) \log (K_{st.} \frac{f_s k_c}{f_c k_s}) - p \left(\frac{2.303RT}{nF} \right) \log (\text{gly})_f \quad (4)$$

The ratio $f_s k_c / f_c k_s$ is assumed to be constant, because of the constant ionic strength (0.15).

RESULTS

In Plate 1 a plot of pH vs ml of base reveals the end-point for neutralization of the carboxyl group on the amino acid and the end-point for the titration of glycine from the zwitterion $\text{NH}_3^+\text{CH}_2\text{COO}^-$ to the anion $\text{NH}_2\text{CH}_2\text{COO}^-$. The half-equivalence points indicated pK_2 values of 9.70, 9.50 and 9.30 at 25°, 30° and 35° C respectively. A plot of $\frac{\text{dpH}}{\text{dml}}$ vs ml of base from original titration data reveal identical end-points. Li, White, and Yoest¹² have reported pK_2 values for glycine in an aqueous media at a ionic strength of 0.15 at 25°, 30° and 40° C as being 9.68, 9.52 and 9.21 respectively.

The existence of three distinct complexes at each of the three temperatures is shown in Plate 2. Equation (1) was used to obtain experimental and theoretical slopes for the number of ligands bound to the central metal-ion at the three temperatures. The slopes obtained from 0.1 to 0.16M glycinate ion at 25°, 30° and 35° C were 0.094, 0.094 and 0.099 respectively compared to theoretical values at 25°, 30° and 35° C of 0.089 for $p=3$, 0.090 for $p=3$, and 0.092 for $p=3$ respectively. The slopes obtained from 0.04 to 0.08M glycinate ion at 25°, 30° and 35° C were 0.057, 0.061 and 0.060 respectively compared to theoretical values at 25°, 30° and 35° C of 0.059 for $p=2$, 0.060 for $p=2$, and 0.061 for $p=2$ respectively.

PLATE 1

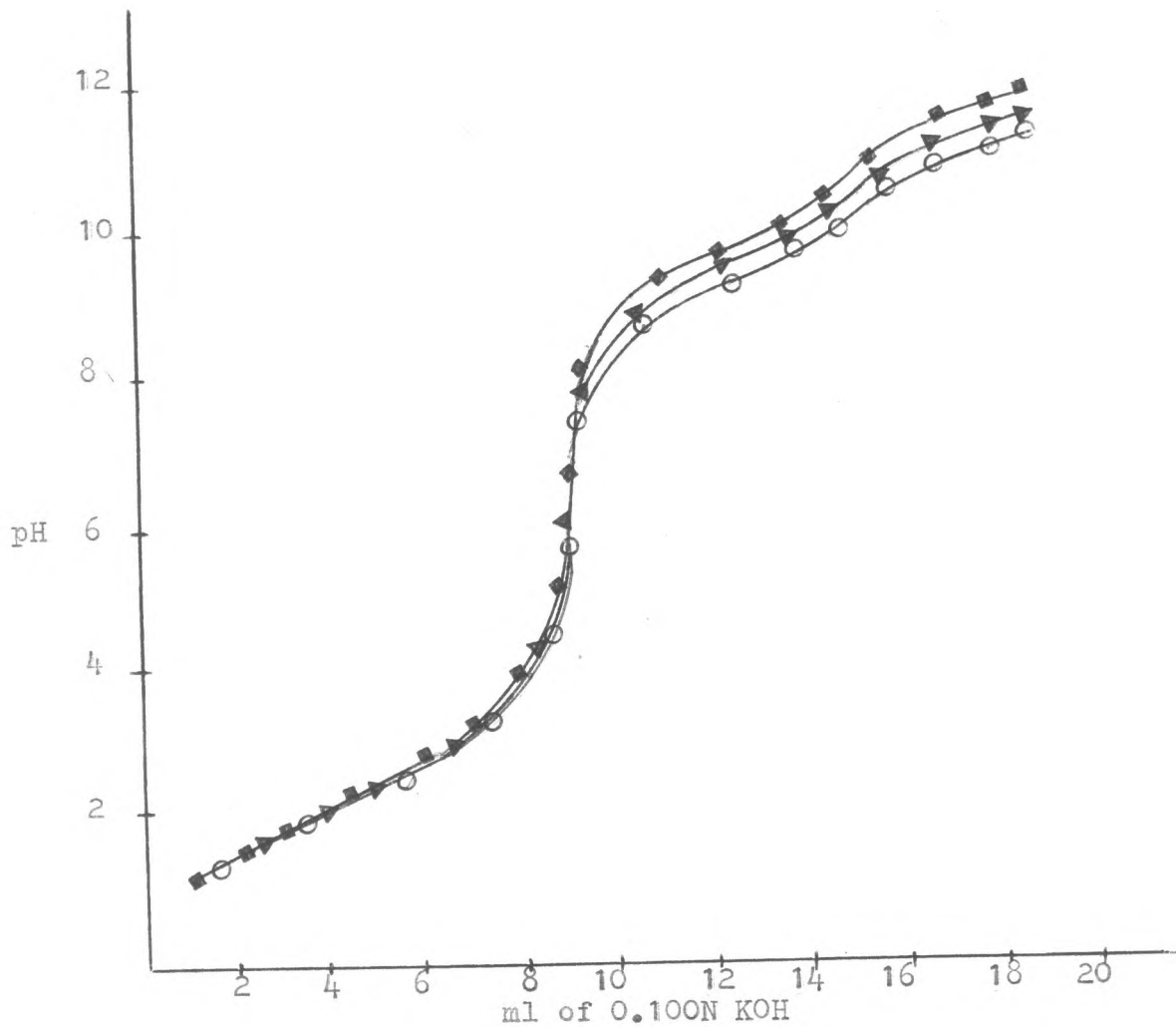


Plate 1. Potentiometric titration of protonated glycine.
■■■ 25°C; ▲▲▲ 30°C; ○○○ 35°C.

PLATE 2

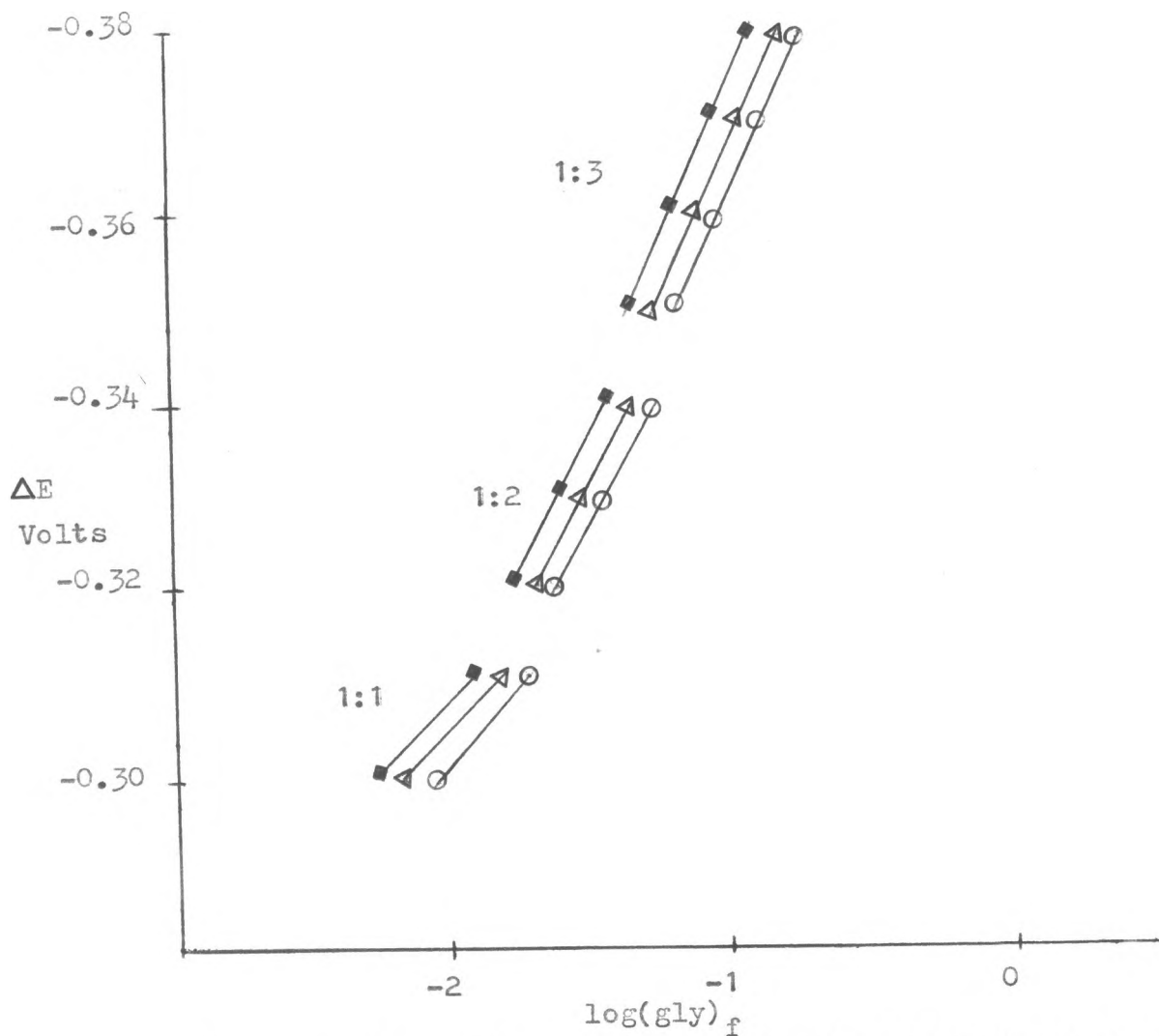


Plate 2. Half-Wave potential shift for zinc(II) complex of glycine, (gly). ■■■25°C; $\Delta\Delta\Delta$ 30°C; $\circ\circ\circ$ 35°C.

The 1:1 complex ($p=1$) is assumed to occur from a glycinate ion concentration of 0.02M to lower concentrations. The formation of such a complex is shown in Plate 2, but because of insufficient data no formation constant or thermodynamic values are reported.

Over-all stability constants and thermodynamic values are reported in Table 1. The enthalpy values were obtained from the best straight lines of $\log K_{st.}$ vs $1/T$. The entropy values were calculated by means of the Gibbs-Helmholtz equation. The thermodynamic values in Table 1 are uncertain by about ± 1.67 Kcal/mole.

DISCUSSION

The relative stabilities of the glycine chelates of the transition metals have been determined by Ley from conductance measurements to be $Cu > Ni > Co$, $Zn > Cd$. It is interesting to note that the formation constants for 1:2 copper, nickel, cobalt and cadmium glycine complexes are 15.10^{12} , 10.92^{12} , 8.94^{15} and 8.1^{16} respectively. Formation data in Table 1 is in agreement with Ley's order and is also in agreement with the order determined by Mellor and Maley¹⁵ who insert lead between nickel and cobalt.

Spike and Parry¹⁷ consider the enthalpy of formation ΔH^0 , a measure of the binding energy, and the entropy of formation ΔS^0 , a measure of all probability factors controlling the stability of the complex. The values in Table 1 for enthalpy and entropy changes for copper(II) and nickel(II) glycine complexes show that

Table 1. Thermodynamic Values and Formation Constants for
M(II)-Glycine Complexes.

Reaction	Temp., °C	log $K_{st.}$	$-\Delta H^{\circ}$, Kcal/mole	$-\Delta G^{\circ}$, Kcal/mole	ΔS° , (e.u.)
$Zn^{++} + 2 \text{gly}$ $Zn(\text{gly})_2$	25	8.37		11.4	16.0
	30	8.16	6.53	11.3	15.0
	35	8.10		11.5	16.0
$Zn^{++} + 3\text{gly}$ $Zn(\text{gly})_3$	25	9.10		12.3	13.0
	30	9.05	8.35	12.6	13.0
	35	8.86		12.5	13.0
$*Cd^{++} + 2\text{gly}$ $Cd(\text{gly})_2$	25	8.1			
$**Cu^{++} + 2\text{gly}$ $Cu(\text{gly})_2$	25	15.10	21.0		-1.0
$**Ni^{++} + 2\text{gly}$ $Ni(\text{gly})_2$	25	10.92	14.0		+2.5
$**Cd^{++} + 3\text{gly}$ $Cd(\text{gly})_3$	25	9.94			

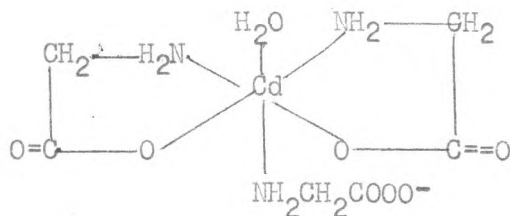
* A.E. Martell and Calvin, Chemistry of Metal Chelate Compounds,
Prentice Hall, Inc., New York, N. Y., 1952, p. 528.

** Li, White and Yoest¹².

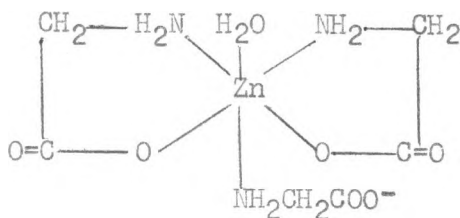
free-energy is due primarily to enthalpy. The ΔH° and ΔS° values for the zinc(II)-glycine complexes indicate that both enthalpy and entropy effects contribute to the free-energy change. Data in Table 1 indicate that at 25° C the enthalpy for copper(II) and nickel(II) glycine complexes are about three and two times greater respectively than the zinc(II)-glycine complex. This difference in heat of formation indicates the relative binding ability of zinc(II) compared to copper(II) and nickel(II).

Calvin and Melchior¹⁸ have suggested that a d orbital is involved in the binding of chelates of this type by these metals. It is interesting to note that copper and nickel have unfilled 3d orbitals and tend to favor the square-planar configuration while zinc and cadmium with filled d orbitals form tetrahedral structures.

The 1:3 zinc(II)-glycine complex was detected polarographically at high concentrations of glycine. The over-all formation constants and thermodynamic values are reported in Table 1. Li, White, and Yoest suggested that the tendency to form the 1:3 cadmium(II)-glycine complex is extremely weak and that $\log k_3 = 1.8$ (the difference between the over-all formation constants for the 1:3 and 1:2 cadmium(II)-glycine complexes reported in Table 1). This weak tendency to form the higher order complex was attributed to the tetrahedral structure cadmium tends to favor. The structure proposed by Li, White, and Yoest was



Data in Table 1 indicate similar chelation for the 1:3 zinc(II)-glycine complex. The chelation of a third molecule for zinc is extremely weak. This is indicated by $\log K_3=0.73$, and by the entropy of formation, $\Delta S^\circ=-3.0$ (e.u.). The entropy change for the first two ligands is large and positive. A possible structure for the complex is therefore



in which two glycinate ions are chelated and the third is not.

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