

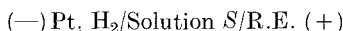
Complex Formation Between Glycine and Magnesium(II), Calcium(II), and Iron(II) at 25 °C in 3.00 M NaClO₄

Emilio Bottari* and Raffaella Porto

Chimica Analitica, Istituto Chimico, Università di Napoli, I-80134 Napoli, Italy

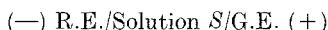
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Equilibria occurring between glycine (*L*) and magnesium(II) and calcium(II) were studied by measuring at 25 °C the electromotive force (e.m.f.) of the cell:



where R.E. is the reference electrode described in the text.

Equilibria taking place in solutions containing iron(II) and glycine were investigated by means of the cell:



where G.E. is the glass electrode. The general composition of solution *S* was in both cases the following:

B M in M^{2+} ; *H M* in H^+ ; *A M* in *L*; 3.00 *M* in ClO_4^- ; (3—*H*—2 *B*) *M* in Na^+ .

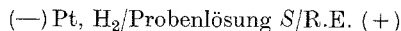
Experimental data were explained by assuming the existence of the species: $\text{Mg}L$ ($\log \beta_{1,0,1} = 1.53 \pm 0.05$); $\text{Mg}L_2$ ($\log \beta_{2,0,1} = 2.26 \pm 0.05$); $\text{Ca}L$ ($\log \beta_{1,0,1} = 0.75 \pm 0.03$); $\text{Fe}L$ ($\log \beta_{1,0,1} = 4.20 \pm 0.04$).

Protonation constants of aminoacetate, not known in the experimental conditions selected, were determined by means of e.m.f. measurements carried out with a H_2 electrode.

(Keywords: Complexes; Glycine, metal complexes; Electrochemistry)

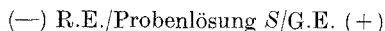
Komplexbildung zwischen Glycin und Magnesium(II), Calcium(II), bzw. Eisen(II) bei 25 °C in 3,00 M NaClO₄

Die Gleichgewichte zwischen Glycin (*L*) und Magnesium(II) bzw. Calcium(II) wurden bei 25 °C durch E.M.K. Messungen der folgenden Meßkette untersucht:



wobei R.E. Referenz-Elektrode bedeutet (siehe Text).

Zum Studium der Reaktion zwischen Eisen(II) und Glycin bei 25 °C wurde folgende Meßkette benutzt:



wobei G.E. Glas-Elektrode bedeutet.

Alle Meßproben hatten die folgende allgemeine Zusammensetzung: BM in M^{2-} ; HM in H^+ ; AM in L ; $3,00M$ in ClO_4^- ; $(3-H-2B)M$ in Na^+ .

Die experimentellen Daten konnten unter Annahme folgender Komplexe erklärt werden: MgL ($\log \beta_{1,0,1} = 1,53 \pm 0,05$); MgL_2 ($\log \beta_{2,0,1} = 2,26 \pm 0,05$); CaL ($\log \beta_{1,0,1} = 0,75 \pm 0,03$); FeL ($\log \beta_{1,0,1} = 4,20 \pm 0,04$). Die Protonierungskonstanten von Aminoacetat, die bei den gewählten experimentellen Bedingungen nicht bekannt sind, wurden mittels E.M.K. Messungen (mit Wasserstoff-Elektrode) bestimmt.

Introduction

This paper treats equilibria which take place in solutions where glycine and magnesium(II), or calcium(II), or iron(II) are present. Iron(II) was investigated in order to study in future the system iron(III)—glycine by means of e.m.f. measurements with a redox Fe^{3+}/Fe^{2+} electrode.

The three systems considered, were either not much studied or results of several investigations are often not complete or not in accord.

The system magnesium(II)—glycine has been studied by e.m.f. measurements carried out at 20 or 25 °C with a glass electrode and very low ionic strength $\mu \rightarrow 0^1$.

Two authors^{2,3} explain their experimental data by assuming the formation of MgL alone, but with different values of stability constants. Another author⁴ gives only approximate results; only one researcher⁵ finds two complexes MgL ($\log K = 3.45$) and MgL_2 ($\log K = 3.01$). The complex formation between calcium(II) and glycine was investigated by comparing the solubility of $Ca(IO_3)_2$ in the presence or in the absence of glycine¹. The increase of solubility in the presence of glycine was explained by assuming the formation of CaL with values of stability constant varying from $\log \beta = 1.35$ to $\log \beta = 1.43$.

The system iron(II)—glycine was investigated in all cases by e.m.f. methods carried out by means of a glass electrode. *Albert*⁶ (at 20 °C and $\mu = 0.01$) assumes the formation of FeL ($\log \beta_1 = 4.3$) and FeL_2 ($\log \beta_2 = 7.8$); *Perrin*⁷ finds (at 20 °C and in 1M KCl) the formation of FeL ($\log \beta = 3.83$) alone. More recently *Izatt, Johnson, and Christensen*⁸ find the complex FeL ($\log K = 4.31$) at 25 °C and $\mu \rightarrow 0$.

The aim of this work is to study predominant equilibria in solutions containing glycine, magnesium(II), calcium(II) and iron(II), in a wide concentration range, in order to decide if one or two complexes are present and to compare the obtained results. Thus it is necessary to use a concentrated ionic medium and to use e.m.f. measurements carried out with the hydrogen electrode, if possible. It was selected 3.00 NaClO₄ as ionic medium. In parallel with this work, the same equilibria were investigated in self medium 3.00 M NaClO₄ and 3.00 M glycine⁹.

A comparison will be presented in the conclusion of this paper between the results of the two works.

Symbols

B = total concentration of cations; b = free concentration of cations; H = analytical excess of H^+ ; h = free concentration of H^+ ; A = total concentration of ligand; a = free concentration of ligand; K_n = equilibrium constant of $H_{n-1}L + H^+ \rightleftharpoons H_nL$ defined by the relation:

$$[H_nL] = K_n [H_{n-1}L] h$$

where $n = 1, 2$.

$\beta_{r,p,q}$ = stability constant of the complex $M_qH_pL_r$ defined by the relation:

$$[M_qH_pL_r] = \beta_{r,p,q} b^q h^p a^r$$

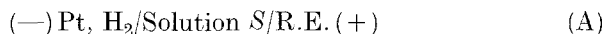
where $q \geq 1$; $p \geq 0$; $r \geq 1$.

M indicates one of the cations and L the ligand. Charges are omitted. \bar{n} = formation function, average number of bond L for central group, defined by:

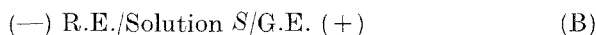
$$\bar{n} = \frac{\sum_q \sum_p \sum_r r \beta_{r,p,q} b^q h^p a^r}{B} = \frac{A - \sum_0^2 K_n h^n a}{B}$$

Method

Equilibria occurring between aminoacetate and the three cations under consideration were investigated at 25 °C and in 3.00 M $NaClO_4$ by e.m.f. measurements. For magnesium(II) and calcium(II), we have used the cell:



Whereas in the case of iron(II) it was necessary to use the following cell:



where G.E. is the glass electrode and R.E. $Ag, AgCl/0.01 M Cl^-; 2.99 M ClO_4^-; 3.00 M Na^+/3.00 M NaClO_4$.

The use of the H_2 electrode in the cell (A) was necessary because in the cases of $Mg(II)$ and $Ca(II)$ the complex formation takes place at high values of $-\log h$. In a previous work¹⁰ it was found that the behaviour of glass electrodes agrees with that of the H_2 electrode only until $-\log h \leq 8$ (in the same experimental conditions as here). All solutions S contained a remarkable excess of $NaClO_4$ with respect to the reagents. Thus the general composition of solution S was the following: $B M$ in M^{2+} ; $H M$ in H^+ ; $A M$ in L ; $3.00 M$ in ClO_4^- ; $(3-H-2B) M$ in

Na⁺. According to *Biedermann* and *Sillén*¹¹ it can be assumed that the activity coefficients of the reagents remain constant in spite of the variation of the concentrations. Concentrations can substitute activities in all the calculations.

The e.m.f. of the cell (A) and (B) at 25 °C and in mV units can be written as follows:

$$E_A = E_A^0 - 59.16 \log h - E_j \quad (1)$$

$$E_B = E_B^0 + 59.16 \log h + E_j \quad (2)$$

In (1) and (2) E_A^0 and E_B^0 are two constants, that together with E_j (liquid junction potential) were determined in the first part of each measurement in the absence of the ligand. E_j was a function only of h ; according to *Biedermann* and *Sillén*¹¹ we found $E_j = -17 h$.

Knowing E_A^0 , E_B^0 and E_j , in the second part of the measurements B and H were kept constant while A was gradually increased; h was determined for each point.

From B , H , A and the measured values of h the formation function \bar{n} could be calculated.

Experimental

Sodium perchlorate, perchloric acid, sodium hydroxide, glycine and iron(II) perchlorate were prepared and analysed as described before^{12,13}.

Calcium(II) perchlorate was obtained from both Merck "suprapur" CaCO₃ and HClO₄. The resulting solution boiled to free it from CO₂ was analysed for [Ca(II)]_{tot.}

Calcium(II) was precipitated as oxalate and titrated with KMnO₄ in acid solution. Alternatively the precipitate of CaC₂O₄ was ignited and weighed as CaCO₃. Results of several determinations agreed within $\pm 0.1\%$. In stock solution H was determined potentiometrically according to *Gran*¹⁴.

The stock solution of Mg(ClO₄)₂ was obtained by reaction of HClO₄ with basic carbonate of magnesium(II). This salt was obtained by solving the compound (MgCO₃)₄ · Mg(OH)₂ · 5 H₂O (C. Erba p.a.) in bidistilled water and by bubbling a strong stream of CO₂ pure. The magnesium(II) carbonate was obtained by boiling or by bubbling N₂. [Mg(II)]_{tot.} was estimated according to *Berg*¹⁵. Results of several determination agreed within $\pm 0.1\%$.

H was determined according to *Gran*¹⁴.

Differential pulse polarography carried out on concentrated samples of the reagents (by an Amel polarograph mod. 471) showed that electroreducible species at concentration $\geq 10^{-8} M$ were not detectable.

Nitrogen and hydrogen were purified as described previously⁹. A strong stream of N₂ was bubbled through all solutions containing iron(II) in order to avoid oxidation.

The details of the e.m.f. measurements are similar to that reported in Ref.¹⁶.

Results

Protonation Constants

The e.m.f. measurements of cell (A) provide h values, by means of eqn. (1). By combining h with the analytical data H and A the protonation function may be calculated:

$$\bar{n} = (H - h) A^{-1}$$

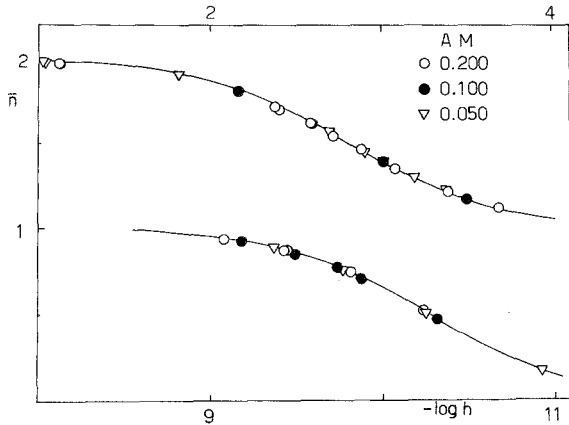


Fig. 1. Protonation function of aminoacetate; the curve is the normalised one in the position of the best fit

In Fig. 1, \bar{n} is plotted versus $-\log h$. Measurements at $A = 0.050$; 0.100 ; $0.200 M$ were performed. From Fig. 1, it can be seen that \bar{n} tends to 2 and that all points, independently of A , fall on the same curve. As expected, associated or polymeric species of glycine are not present in appreciable concentration in the studied range of concentrations. K_1 and K_2 values were obtained by means of the normalised curves method proposed by *Sillén*¹⁷. A family of theoretical curves of equation:

$$\bar{n} = \frac{Ru + 2u^2}{1 + Ru + u^2}$$

where $u = h\sqrt{K_1 K_2}$ and $R = K_1/\sqrt{K_1 K_2}$, was superimposed to the trend of the experimental points and plots were moved parallel to the abscissa in order to have best fit. In this way the following values were obtained:

$$\log K_1 = 10.27 \pm 0.03; \quad \log K_1 K_2 = 13.09 \pm 0.04;$$

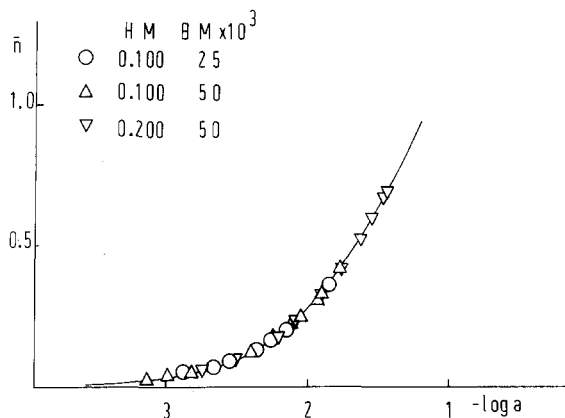


Fig. 2. Formation function of complexes between magnesium(II) and glycine; the curve is the normalised one in the position of the best fit

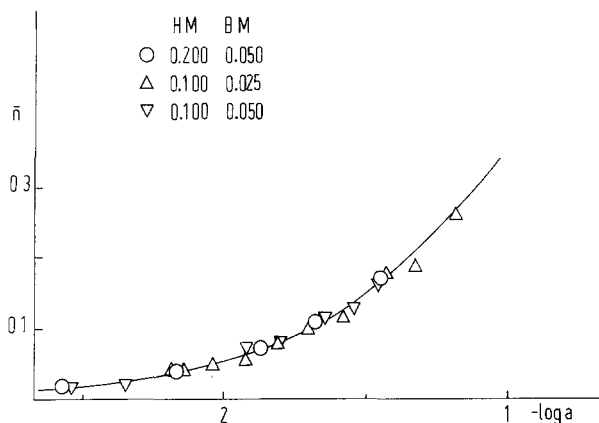


Fig. 3. Formation function of complexes between calcium(II) and glycine; the curve is the normalised one in the position of the best fit

The error limits were estimated from the maximum shift possible for the two plots for which agreement was still acceptable. Experimental points and theoretical selected curve in the position to best fit agree well as shown in Fig. 1.

Complex Formation Between Aminoacetate and Cations

The knowledge of K_1 and K_2 allows to calculate the free concentration of aminoacetate, a , from material balance relative to H , by taking into account the mass action law:

$$H = h + K_1 h a + 2 K_1 K_2 h^2 a + \sum_r \sum_p \sum_q p \beta_{r,p,q} b^q h^p a^r \quad (3)$$

In eqn. (3) hydrolytic species of the cations could be neglected in the used concentration range and on the basis of Refs.^{18,20}.

In order to calculate a from eqn. (3) it was supposed that no appreciable quantity of mixed complexes with participation of H^+ was formed, i.e. $p = 0$. It will be verified below. Eqn. (3) can be written:

$$a = (H - h) (K_1 h + 2 K_1 K_2 h^2)^{-1} \quad (4)$$

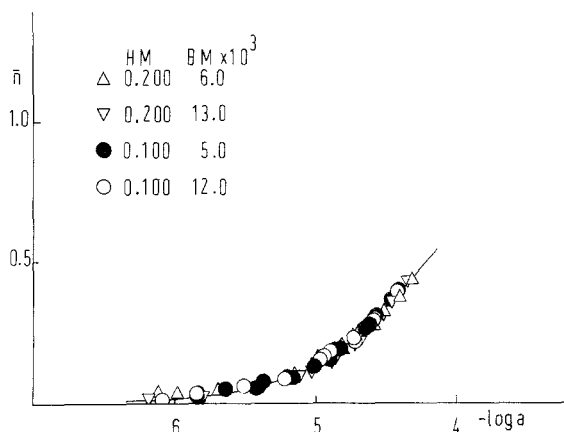


Fig. 4. Formation function of complexes between iron(II) and glycine; the curve is the normalised one in the position of the best fit

Figs. 2, 3 and 4 show the formation functions relative to the glycine complexes respectively with magnesium(II), calcium(II) and iron(II) in the form \bar{n} versus $-\log a$.

For all cases the experimental points fall on the same curve independently on B and H . Neither polynuclear nor complexes mixed with H^+ are formed. As soon as above formulated hypothesis is valid the a values obtained from (4) are accurate. The formed species and the relative stability constants $\beta_{r,0,1}$ were obtained with the normalised curve method proposed by *Sillén*¹⁷.

In the case of magnesium(II) the formation of MgL and MgL_2 explains the experimental data, whereas for calcium(II) and for iron(II) one complex CaL or FeL respectively explains well the experimental data. The following values of stability constants are found: MgL ($\log \beta_{1,0,1} = 1.53 \pm 0.05$); MgL_2 ($\log \beta_{2,0,1} = 2.26 \pm 0.05$); CaL ($\log \beta_{1,0,1} = 0.75 \pm 0.03$); $Fe(II)L$ ($\log \beta_{1,0,1} = 4.20 \pm 0.04$).

The error limits were estimated from the maximum shift possible for the plots for which agreement was still acceptable. The agreement between theoretical curves and experimental points as shown in Figs. 2, 3 and 4 is good.

Discussion and Conclusion

The measurements performed in 3.00 *M* NaClO₄ on the equilibria iron(II)—aminoacetate can be explained by assuming the existence of the complex FeL alone.

Unfortunately in the range $-\log h \geq 7$ precipitation takes place. From Ref.⁹ it results that in self medium two species are formed that should be FeL and FeL₂. However, in 3.00 *M* NaClO₄ we have determined only the stability constant relative to FeL.

The $\beta_{1,0,1}$ value proposed in this work for FeL seems to agree with that found by Albert⁶ by taking into account the different experimental conditions.

For magnesium(II) and calcium(II) in self medium⁹ and in this work the same complexes (CaL, MgL and MgL₂) are formed.

The values of the constants proposed here are lower than those reported in literature¹. The order of the stability for the complexes is the following: Ca < Mg < Fe(II).

Acknowledgment

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