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Potentiometric Studies of Nickel (II), Copper (II) and Cobalt (II) Binary Complexes with Glycine Amino Acid in Aqueous Solution

Marzieh Sadat Neiband
Department of Chemistry, Payame Noor University (PNU),
19395-4697 Tehran, Islamic Republic of Iran

Abstract: The complexation equilibria of glycine with some transition metal ions such as Cu^{2+}, Co^{2+} and Ni^{2+} were studied by potentiometric method in aqueous solution. All of the titration steps were carried out at 25.0±0.1°C and ionic strength (μ) of 0.1 M supported by $NaNO_3$. The overall stability constants logβ's of respective species were evaluated by computer refinement of the corresponding potentiometric pH titration data using BEST computer program. The corresponding distribution diagrams were depicted as a function of pH by using SP and SPE programs. The most likely species were obtained from distribution diagrams. Complex stabilities follow the trend copper(II)>nickel(II)>cobalt(II) which is in agreement with the Irving-Williams series.

Key words: Potentiometric study, nickel (II), copper (II), cobalt (II), glycine, complexe formation

INTRODUCTION

The determining of thermodynamic parameters of complexes using potentiometric data to develop and propose new methods for selective and sensitized determination of trace amounts of ions is a challenging problem. For example, a high stability constant with fast complex formation which could be obtained from the stability constant led to development of a new analytical method. Their stability constants can be of significance in order to predict different chemical processes such as isolation, extraction or preconcentration methods (Gracia and Gomis, 1996; Cao and Zhang, 1999) since many elements present in trace amounts can be isolated by complexing reagents. The magnitude of the stability constant indicates the particular level of tolerance to the interference by other species. The stability constant is dependent on several parameters such as electronegativity, hardness or softness of the donor atoms in the ligand structure, topology of the ligand and the ionic radii, charge, hardness or softness of the metal ion and its atomic number (Dwyer and Mellor, 1964) Nowadays different programs such as the KINFIT (Dye and Nicely, 1971) and BEST (Motekaitis and Martell, 1982) programs have been used for evaluating the stability constant of complexes or dissociation constants of ligands, using potentiometric data (Shokrollahi *et al*., 2008; Machado *et al*., 2004; Derikvand *et al*., 2013; Shokrollahi and Haghighi, 2012). In the present research, the researchers decided to investigate the effect of the ligand structure on the stability constants of the complexation of the copper, nikel and cobalt ions, using this data we can focus on synthesizing new ligands with higher stability constants for its selective and sensitive determination. Many transition and heavy metal cations play an active role in a great number of biological processes being components of several vitamins and drugs.

On the other hand, it is well known that proton transfer plays an important role in the reactions in aqueous solution such as complex formation acid and base catalyses and enzymatic reaction (Ando *et al*., 1982). Thus, the accurate determination of acidity and stability constants values are fundamental to understanding the behavior of ligands and their interaction with metal ions in aqueous solution. It is well-known that the simplest electroanalytical technique for determination of stability constants is potentiometric titration system using glass electrode. The purpose of this work is to investigate the protonation constants of Glycine (Fig. 1) and stability constants of complex formation with some transition metal ions using the BEST program developed by Martell and his coworkers (Motekaitis and Martell, 1982) for potentiometric titration.

Glycine is one of the most common amino acids found within human proteins, it's not surprising that this simple compound has so many functions with the

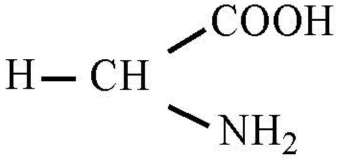

Fig. 1: Chemical structure of Glycine (Gly)

body. Glycine is particularly important in maintaining healthy digestive and central nervous systems. It's role in the production of human growth hormones and creatine have also seen glycine become a valuable amino acid for athletes wanting to build muscle mass and strength. Glycine also has positive applications for individuals suffering from neurobehavioral disorders diabetes, chronic fatigue and certain cancers. As more research and clinical trials are conducted, it's likely that this amino acid will continue to play an important role in the treatment of a range of medical conditions.

MATERIALS AND METHODS

Experimental

Apparatus and materials: All potentiometric pH measurements were made using a Model 686 Metrohm Titoprocessor equipped with a combined glass-calomel electrode. All common laboratory chemicals used were of reagent grade from Merck (Darmstadt, Germany). Analytical grade nitrate salts of metal ions and Glycine amino acids with the highest purity available are purchased from Merck Company and used without any further purification. Carbonate free NaOH solution was standardized with potassium hydrogen phethalate. The HNO3 solution was standardized with standard NaOH. All solution were prepared in doubly distilled deionized water.

Potentiometric measurments: The procedures employed for the potentiometric pH measurements have been described in detail (Shokrollahi *et al*., 2008). In general, an experimental run involves collecting equilibrium data points throughout the entire pH range, between 2.0 and 11.50 as a function of millimoles standard NaOH, added using the piston buret through a fine capillary tip immersed in the solution. In titration, after each addition, the required time was allowed to reach chemical equilibrium.

All potentiometric pH measurements were done on solution in a 75 mL double-walled glass vessel using a Model 686 Metrohm Titoprocessor equipped with a combined glass-calomel electrode and the temperature was controlled at 25.0±0.1°C by circulating water through the double-walled glass vessel from a constant-temperature bath (home made thermostat). The cell was armed with a magnetic stirrer and a tightly fitting cap, through which the electrode system and a 10 mL capacity piston burette were inserted and sealed with clamps and O-rings. Atmospheric CO_2 was excluded from the titration cell with a purging steam of purified nitrogen gas. The system was maintained at an ionic strength of $\mu = 0.10$ M with $NaNO_3$ as a supporting electrolyte.

The pH measurement method for investigating dependency of complex nature to pH and calculating protonation constant of Glycine. The required amount of $NaNO_3$ (from a 0.50M stock solution), HNO_3 (0.10 M) and 0.025 M of Cu^{2+}, Co^{2+} and Ni^{2+} metal ions and 0.02 M Glycine and doubly distilled deionized water were added. To the required amount of doubly distilled deionized water was added to the cell to a total volume of 40 mL. The potentiometric study operates at the metal: amino acid molar ratios of 1:2. The accuracy rapidly decreases for higher molar ratios due to the fact that the characters of the titration curve of the complexes and the titration curve of the amino acid without metal ion are similar. The mutual ratios cannot be used because of the metal hydrolysis. solution was titrated potentiometrically with a CO_2 free 0.09860 M solution NaOH.

In the systems studied, the titration were performed up to pH values at which the formation of precipitates began and unstable emf measurements were obtained. From the titration curve of the first solution the acidic protonation constant of the amino acid and from the second titration curve the formation constants of different form of complexes was evaluated using the BEST program described by Motekaitis and Martell (1982). The value of $K_w = [H^+][OH^-]$ used in the calculation was $10^{-13.78}$.

The protonation and formation constants of all species were obtained through the least-squares refinement of its $p[H^+]$ profiles. Throughout this investigation the function minimized was the weighted average of the sums of squares of deviation between calculated and observed $p[H^+]$ value (σ_{fit}).

RESULTS AND DISCUSSION

In this study, the protonation of glycine amino acid and their complexation equilibria with three metal ions Cu^{2+}, Co^{2+} and Ni^{2+} were investigated by a potentiometric method.

Protonation constants: It has been occurred to us that BEST program following potentiometric titration is an accurate and a powerful method for binary ligand-metal ions complexation. In preliminary experiments, the fully protonated form of glycine was titrated with a standard KOH aqueous solution in order to obtain some information about their protonation constants. The protonation constants ($K_n^H = [H_mL]/[H_{m-n}L][H_n]$, the charges are omitted for simplicity) were calculated by computer refinement of pH-volume data using the computer program BEST. The results are reported by Jing. As the results show for glycine two protonation constant values were calculated. In glycine structure, first protonation constant (9.71) is attributed to the oxygen proton of the carboxylic acid group while the second with the value of 2.98 belongs to the protonation constant of the hydrogen which is attached to the nitrogen of ammonium gruop. The protonation equilibrium is as seen in the following Eq. 1 and 2 (ligand and proton charges have been omitted for simplicity):

$$H+L \leftrightarrow HL$$
$$H+HL \leftrightarrow H_2L$$
$$H_{n-1}L+L \leftrightarrow H_nL$$

And the deprotonation constants (K_n; n = 1, 2) are given as:

$$K_n = \frac{[H_{n-1}L][H^+]}{[H_nL]}$$

The protonation constants of glycine at ionic strength of 0.1 M $NaNO_3$ and temperature of 25°C were calculated.

Binary complex formation equilibria: The formation constants of metal ions and their stoichiometry with glycine as binary complexes were determined according to experimental section following refinement of pH-volume data by BEST program. The cumulative stability constants (β_{mlh}) are defined by Eq. 3 (charges are omitted for simplicity):

$$mM + lL + hH \rightleftharpoons M_mL_lH_h$$

$$\beta_{mlh} = [M_mL_lH_h]/[M]^m[L]^l[H]^h$$

Where:

M = Metal ion
L = Ligand
H = Proton
m, l and h = The respective stoichiometric coefficients

Since, the ligand and complexes activity coefficients are unknown, the β_{mlh} values are defined in terms of concentrations. In the evaluation of the component experimental data, the binary complex models were considered as known. The errors are minimized by the use of a high constant ionic strength of 0.1 M $NaNO_3$ and low ligand concentrations. The titration curves are given in Fig. 2. As it is seen in Fig. 2, the divergences between the titration curves (in the absence and presence of metal ions) indicate the interaction between metal ions and glycine amino acid. The data of such titrations has been used to calculate the equilibrium constants of the respective reactions between the metal ions and ligands.

Titration progress was stopped when the precipitate was seen in solution. Due to the differences between the hydrolysis degrees of the metal ions in similar conditions their titration stopping points were different from each other.

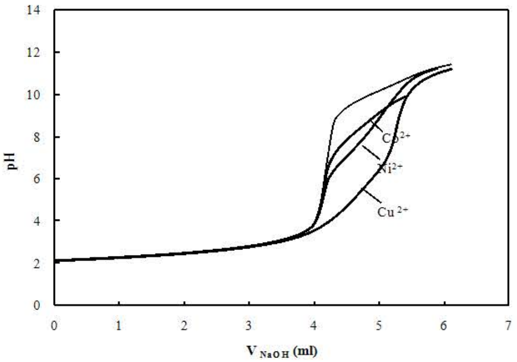

Fig. 2: Equilibrium pH titration curves of Glycine in absence and presence of metal ions at 25.0±0.1°C and ionic strength 0.1 M $NaNO_3$

Table 1: Overall stability constants for the interaction of H^+ (h) and Zn^{2+}(m) with Gly (l) their 1:2 mixture at 25±0.1°C and ionic strength 0.1 M $NaNO_3$

				Logβ		
System	m	l	h	PW	1	References
Cu^{2+}-Gly	1	1	0	8.54	8.37	Andreregg and Khileif
	1	1	2	17.44	14.96	Taha and Khalil
	1	2	0	16.79		
	1	2	1	23.20		
	1	2	2	27.75		
	1	1	-1	1.43	1.42	Sundberg and Martin
Ni^{2+}-Gly	1	1	0	6.59	5.64	Bribanti and colleagues
	1	1	2	16.86		
	1	2	0	11.25	10.39	Bribanti and colleagues
	1	2	1	19.58		
	1	2	2	27.00		
	1	1	-1	-8.47		
	1	1	-2	-19.55		
	1	2	-2	-15.82		
Co^{2+}-Gly	1	1	0	5.33		
	1	1	2	16.21		
	1	2	0	8.95	8.93	Bribanti and colleagues
	1	2	1	17.44		
	1	2	2	26.01		
	1	1	-1	-4.67		
	1	1	-2	-15.14		
	1	2	-1			

In the computer refinement of the titration data of M^{2+}-gly binary systems the detectable species are CuL, CuL_2, CuL_2H, CuL_2H_2, CuLOH, types are formed between Gly and Cu^{2+}. In the Ni^{2+}-Gly system the species NiL, $NiLH_2$, NiL_2, NiL_2H, NiL_2H_2, NiLOH, $NiL(OH)_2$ and $NiL_2(OH)_2$ are remained in the final refined model. CoL, CoLH, CoL_2, CoL_2H, CoL_2H_2, CoLOH, $CoL(OH)_2$, CoL_2OH and $CoL_2(OH)_2$ species for Co^{2+}-gly system were detected. The species distribution diagram are displayed in Fig. 3a-c and the respective obtained overall stability constants of these species which are presented in Table 1.

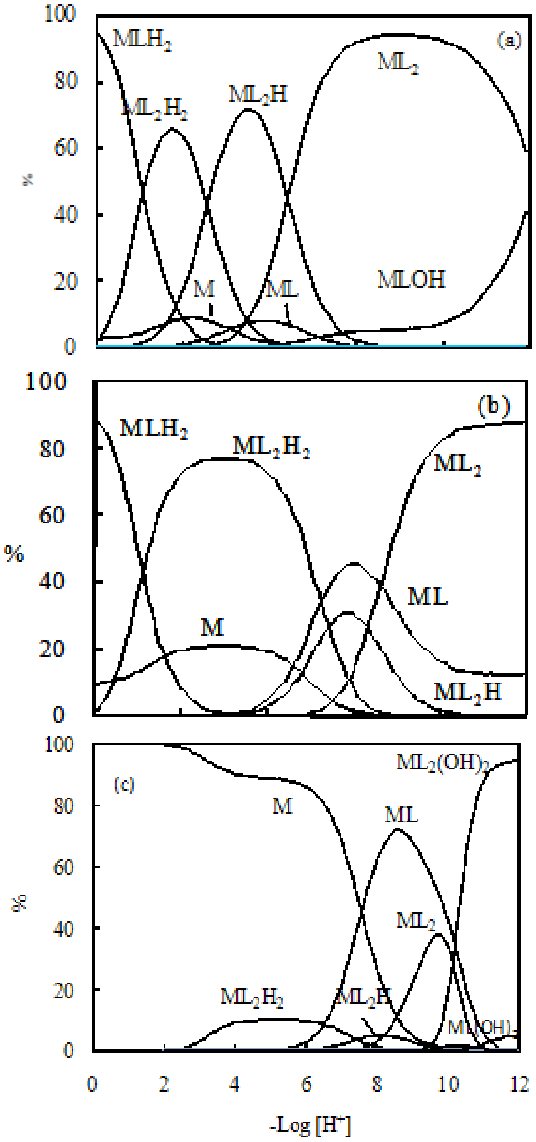

Fig. 3: Species distribution curves of binary systems of Glycine in presence of: a) Cu^{2+}; b) Ni^{2+} and c) Co^{2+} at 25±0.1°C and ionic strength 0.1 M $NaNO_3$

The show a decrease in these binary systems stability constants for the most metal copmlexes of this amino acid are in the order of Cu(II)>Ni(II)>Co(II). It is obvious that Cu^{2+} ion makes the most stable complexes with glycine in comparison with other cited metal ions. It should be noted that the stability constants result from a balance between the binding energy and the salvation energies of all charge species involved in complexation reaction.

CONCLUSION

The protonation constants of the ligands and formation constants of the resulting complexes were computed from pH-volume titration data using BEST program. The computer refinement of the titration data showed the presence of ML, MLH, MLH_2, ML(OH), $ML(OH)_2$, ML_2, ML_2H, ML_2H_2, ML_2OH and $ML_2(OH)_2$ species in binary systems. The distribution diagram of detectable species in absence and presence of metal ions as a function of pH was given by using SP and SPE program. The speciation studies indicate that there is a relatively strong interaction between Cu^{2+} and glycine in aquaues solution containing sodium nitrate as constant ionic medium rather than other metal ions considered in this study. The order of resulting stability constants for the cited M^{2+}-gly systems have relatively good compatibilities with Irving-Williams series.

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