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Studies On Formation Of Metal Complexes With Phenyl Glycine In The Presence Of Kojic Acid, Maltol, And Acetyl Acetone - Ph Metry

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ABSTRACT

Stability constant is defined as the metal-ligand interaction. It is also called formation constant indicating how strongly a metal binds with a ligand. Greater the formation strength between metal and ligand, greater is the stability constant of the particular metal-ligand complex. Stability constants associated with mixed ligand complexes of bivalent metal ions with Phenyl Glycine in presence of other O-O donors (viz., maltol, kojic acid, and acetylacetone) was evaluated potentiometrically at T=30 °C and I=0.1 M KNO_3 in aqueous medium. Stability trend is discussed in terms of nature of donor atoms and substituent groups present on ligands. Distributions of various species as a function of pH are also drawn using Microsoft Excel. The sequence of stability of ternary complexes with respect to their ligands decrease in the order: maltol > kojic acid > acetyl acetone.

KEY WORDS: Stability constant, Glycine, Phenyl Glycine, Kojic acid, Maltol, Acetyl acetone, binary and ternary metal complexes.

1. INTRODUCTION

Glycine, which is one of the most noted non-essential amino acids has been known for exhibiting its biological activity [1]. The Glycine betaine is also found to be very essential in plants as it aids in osmoregulation [2]. It is also known to show function as a neurotransmitter and also as an cyto-protective agent. The Glycine molecule has a side-chain, with one hydrogen atom attached [3]. A wide range of important molecules having low molecular weight including creatine, glutathione, purines, and porphyrins, are known to be the precursors of glycine [4].

In view of its catalytic activity, the present potentiometric work is undertaken to explore its binding tendency with different metal ions. The Glycine (Gly) and Phenyl Glycine (Phy Gly) was allowed to react with different metal ions in presence of other ligands viz., maltol (MA), kojic acid (KA), acetyl acetone (AA) The stabilities of the thus formed ternary complexes are evaluated and compared to check the factors by which they are governed. The simplest members of this class of compounds are malonaldehyde (MA) and acetylacetone (AA), well known both by experimental and theoretical studies to adopt an asymmetrical in their most stable conformation [5-11].

2 EXPERIMENTAL

2.1. Methods for the determination of the formation constants of metal complexes

Various physico-chemical methods such as pH-metry, spectrophotometry, polarography, ion exchange method etc. may be used to determine the formation constants. However, pH-method is most frequently used and accounts for most of the constants reported. A number of methods are available for most processing the pH-metric data to evaluate the acid dissociation constants of the ligands and formation constants of metal complexes (binary systems). Prominent among these are the classical Bjerrum's method [12]and its modified version such as Calvin & Wilson method [13],Rosetti&Rosetti method [14] and Irving & Rosetti method [15]. Marvell&coworker's have extensively used the algebraic method in which the constants are evaluated by setting up rigorous material balanced equations. Each of these methods has advantages and limitations depending upon the experimental conditions used. pH-metric methods have proved versatile and reliable in studying metal complexation in solution. So, pH-metric technique was selected to study the interaction of metal and ligands in solution. Thus, the pH- metric data obtained was used to calculate the formation constants of binary complexes formed in solution using algebraic method by setting up rigorous material balanced equations with PB-110 personnel computer. The formation constants of metal complexes were also calculated using sophisticated computer programme BEST [16]. In addition to this, distribution of various species present as a function of pH were computed from the computer program (SPE) [17].

2.2 pH-metric method:

The interaction of metal ion (M) with ligand which act as a weak acid (HL) leads to the formation of a metal complex (ML) by the replacement of the proton.

$$M + HL \rightleftharpoons ML + H^+ \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 1$$

The resulting changes in pH of the solution is used for calculating the stability constants pH-metry.

2.3. Apparatus and instruments

The burettes, pipettes and standard flasks employed were all calibrated [18].The apparatus used were made for Borosil glass and were cleaned with chromic acid, hydrochloric acid and double distilled water as a precaution against metal contamination. The weighing was done on a single pan electric balance.

2.3.1pH-meter

A control dynamic pH meter model APX 175 E/C (readable accuracy of 0.01 pH unit) equipped with gel filled combination electrode assembly was used for measurement of pH.

2.3.2Thermostat

Thermostat an INSREF high precision refrigerated thermostat provided with a pump arrangement for circulating the thermo stated water through the outer jacket of titration vessel (cell) was used for maintaining the temperature of the reaction system. The thermostat was capable of maintaining the temperature within ±0.10C of the required temperature by circulating the water through the outer jacket of the reaction cell.

2.3.3 Reagents

Distilled water

Distilled water was redistilled over alkaline $KMNO_4$, and the distillate was boiled to remove the dissolved CO_2 and O_2. Freshly prepared redistilled water was used for the preparation of the solutions.

2.3.4 Metal solutions

Approximately 0.05M solutions Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}-nitrates were prepared. The metal nitrates were of AnalaR grade quality. The concentrations of all the above metal ions in the stock solution were estimated volumetrically by titrating against standard solutions of disodium salt of ethylenediaminetetraacetic acid, using a suitable indicator as outlined by Schwarzenbach [19].

Sodium hydroxide as titrant

Carbonate free NaOH solution was prepared by the method of Schwarzenbach and Biderman [20] and stored in an automatic micro burette assembly (reservoir capacity 500ml) fitted with soda lime tube to protect against CO_2.The concentration of NaOH was determined by titrating with a standard potassium hydrogen phalate [21] using phenanthroline as indicator. The concentration was checked from time-to-time Micro burette (5ml with 0.02 graduations) was used.

Potassium nitrate as supporting electrolyte

A 1M stock solution of Potassium nitrate was prepared from AnalaR sample. Appropriate amount of this solution was used as a supporting electrolyte for adjusting the total ionic strength of the reaction mixture.

2.3.5 Calibration of electrode

Control dynamics pH meter fitted with a gel filled electrode was used to determine the hydrogen ion concentration (pH). The electrode system was calibrated using buffer solutions of 4,7 and 9.2 pH prepared from buffer tablets obtained from Glaxo India Limited. The observed pH meter reading was compared with the actual hydrogen ion concentration calculated from the data tabulated by Harmed and Owen [22].

2.3.6 Experimental details

The pH-titrations are carried out by taking 50 ml of the reaction mixture into a double walled glass titration cell with an inlet and outlet for the circulation of water (around the cell) at constant temperature from the thermostat around the cell. The reaction mixture is stirred continuously with the aid of a magnetic stirrer. Sufficient time is allowed for the establishment of equilibrium as indicated from the constancy of the pH- meter readings.

The ionic strengths of all the solutions have been adjusted to the desired value by adding calculated amount of 1 mol dm-3(KNO_3) solution as supporting electrolyte. A control dynamics pH meter with a gel filled, combination electrode was used to determine the hydrogen ion concentration (pH).

The acid dissociation constants and the stability constants for the binary complexes were determined by pH-metric titration of the ligands in the absence of and in the presence of metal ion respectively with standard NaOH. The pH meter readings were noted after addition of small increments of standard NaOH to the titration cell. From these readings, graphs of PH vs “a” or “m” were plotted. Where a= moles of base added per mole of the ligand and m=moles of base added per mole of the metal ion. The titration curve gives a qualitative indication of the composition of the metal complexes formed.

In all the titration involving metal ion pH readings were noted only for homogeneous solutions. Titration was stopped when a solid phase separated during the course of titration or if the pH meter readings showed a downward trend indicating metal ion hydrolysis. In this regard the use of pH-metric study is invaluable in detecting the onset of metal hydrolysis.

2.3.7 Free ligand titrations

The experimental method employed consisted of potentiometric titration of various ligands involved in this investigation with standard NaOH solution at 30^0C. The ionic strength was maintained constant at 0.1 mol dm-3(KNO_3) solution as supporting electrolyte and relatively low concentrations of the ligands (1.0×10^{-3}M) in aqueous medium. During the course of the titration a stream of nitrogen gas passed over the solution to eliminate the adverse effect of atmospheric carbon dioxide.

2.3.8 Binary metal titrations

Potentiometric titrations of ligands were carried out using standard NaOH solution in presence of selected metal ions such as Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}in an equimolar ratio at 30 ^{0}C, and I=0.1 mol dm-3 (KNO_3) in 500/0-dioxane and aqueous medium.

2.3.9 Calculations

(i) Acid dissociation constants of ligands

The acid dissociation constants of ligands Ka are calculated by framing material balanced equations and the final forms are given by equation 2.

$$Ka=\frac{[H]\{aT_L+[H]-[OH]\}}{T_L-\{aT_L+[H]-[OH]\}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..2$$

The calculations are done in the buffer region a = 0.3 to a =0.7 for Ka

$$T_L=\frac{(50\times\text{concentration of ligand})}{(50+\text{volume of base added})}$$

$$a=\frac{\text{volume of base}}{\text{Equivalent point}}$$

$$\text{Equivalent point}=\frac{\text{concentration of ligand}}{\text{Base concentratione}}$$

Calculations are done using the experimental data based on the trends in the titration curve on Microsoft word excel.

(ii) Stability constants of 1:1 binary metal complex

Monoprotonated ligands

The equilibrium involved in the formation of 1:1 metal-ligand complexes may be represented by equation2.3

The equilibrium involved in the formation of 1:1 metal-ligand complexes may be represented by equation2.3

$$M + HL \rightleftharpoons ML + H^+$$

$$K^{M}_{HL} = \frac{TM-[M]}{[M][L]} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

Where

$[L] = \beta.Ka/ [H]$

$\beta = (1\text{-}a)T_L\text{-}[H]+[OH]$

$[M]= [H/Ka+1]*[L]$

Ka= dissociation constant of the ligand

TL=Total concentration of the ligand

TM=Total concentration of the metal ion.

RESULTS AND DISCUSSION

Acid Dissociation Constants

(a) Phenyl glycine and Glycine; the free ligand titration curve (H2L+) of this ligand show inflection at a=1, followed by a buffer region in higher pH. The pKa values are calculated in the region a = 0 to a = 1.

(b) Maltol/Kojic acid/acetyl acetone: Free ligand titration curves of all these ligands show a single inflection at a = 1. The constants calculated in the buffer region a=0 to a=1 is presented in Table 1. The values are in good agreement with values found in literature [23-26]. The free ligand titration curves of MA, KA and AA and Phenyl glycine and Glycine are given in Fig.1 along with other curves.

Table 1: Logarithms of the stability constants of different systems at T: 30o; μ=

0.1 M (KNO3), aqueous medium.

Ligands	pKa	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Gly	9.34	4.90	5.59	8.20	5.25
Phy-Gly	8.76	3.77	4.95	7.27	4.54
KA	7.89	4.83	5.01	6.67	5.07
MA	8.5	5.36	5.51	7.17	5.61
AA	8.95	5.24	5.67	7.42	4.86

Binary Complexes

(a) Phenyl glycine and Glycine: Potentiometric titration curves of M $^{2+}$- Phenyl glycine and Glycine in 1:1 ratio shows a feeble inflection at m=1 followed by a buffer region. The separation of (M-L) curve from the free ligand curve is small for all metals, suggesting complex formation with low stability constants. The protonated constants are calculated in the buffer region of m=0 to m=1. The stability constants obtained and presented in Table I.

(b) M $^{2+}$-Maltol/Kojic acid/acetyl acetone: Potentiometric titration curves of M $^{2+}$-Maltol/Kojic acid/acetyl acetone/ in 1:1 ratio shows a single inflection at m = 1. The stability constants calculated in the buffer region m=0 to m=1 is presented in Table-1. The values have good matching with literature values.

Ternary Complexes

M $^{2+}$-Maltol / Kojic acid/acetylacetone: The potentiometric titration curves of the ternary complexes in 1:1:1 ratio shows an inflection at m = 3 indicating the simultaneous coordination. The constants are calculated in the buffer region m=1 to m=3, using the pKa of Phenyl glycine and Glycine and pKa of KA (or) MA (or) AA. The values then obtained are presented in Table 2.

A representative curve for (Cu $^{+2}$+Phenyl Glycine +MA) is shown in Fig.I.

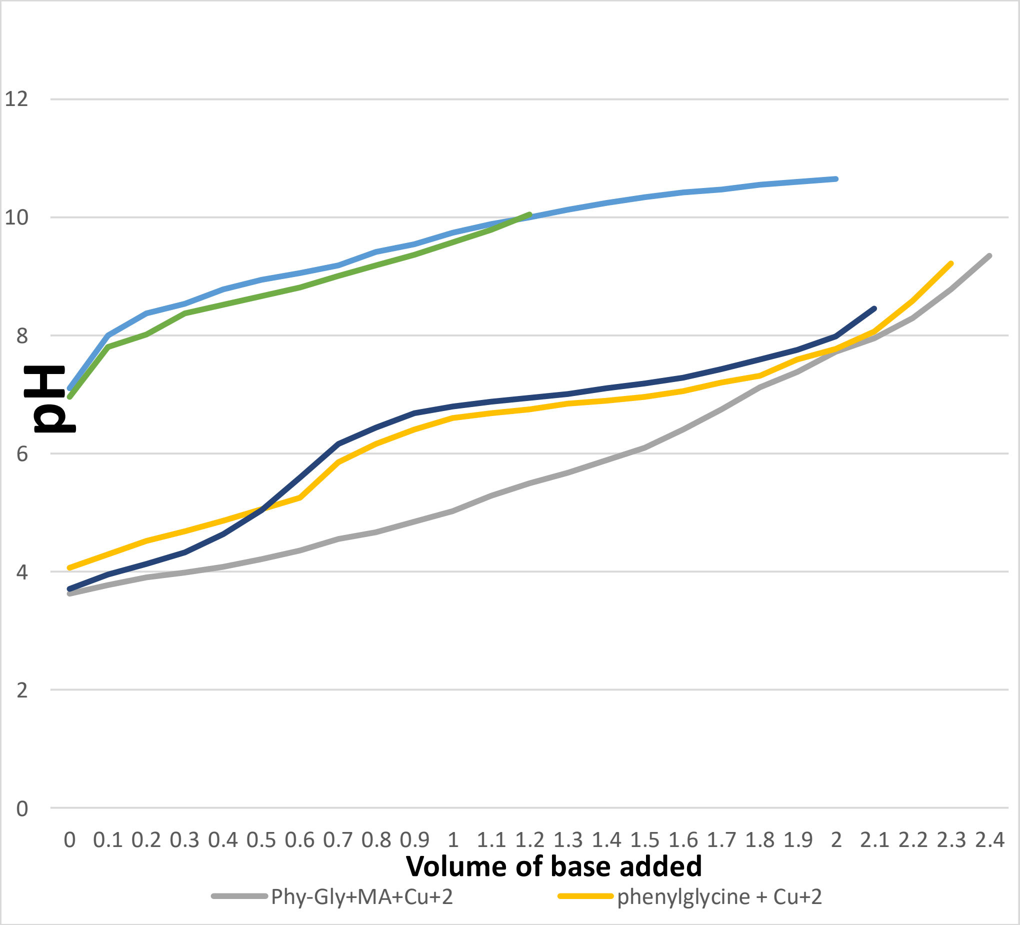

Table 2: Logarithms of the stability constants of ternary complexes of bivalent metal ion at T: 30°C; μ= 0.1 M (KNO_3), aqueous medium

Ligand combinations	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2}
Gly+KA	4.81	5.31	7.40	5.05
Gly+ MA	4.94	5.32	7.46	5.16
Gly+ AA	4.40	5.18	7.34	5.03
Phy-Gly+KA	4.08	4.75	6.37	4.3
PhyGly+MA	4.13	4.67	6.66	4.32
Phy-Gly+AA	3.87	4.67	6.38	4.43

The Concept of Δ log K

The relative stability of the ternary metal complexes (MLA) as compared to that of the corresponding binary complexes have been quantitatively expressed in terms of the parameter Δ log K, given by the Eq.4.

$\Delta \log K = [\log K^{MA}_{MLA} - (\log K^{M}_{MLA} + \log K^{M}_{MLA})]L_1$ …………4

In case of Phenyl glycine and Glycine complexes, Phy-Gly and Gly binds to the metal through oxygen and nitrogen. The statistically expected Δ log K value for the Interaction of two different bidentate ligands with square planar (or) distorted octahedral metal ion are -0.9 or 0.1 respectively.

The Δ log K values for ternary complexes containing maltol, kojic acid or acetylacetone are more positive (Table 3) than values expected on the statistical grounds, reflecting the extensive stabilization of these complexes. This stabilization may be due to (a) nature of donor atoms; O-O donors form better complexes with N-O donors, (b) formation of a neutral complex: the resultant ternary complex is neutral, (c) π-πinteractions: The ligand Phy-Gly and Gly, KA, MA and AA are capable of forming π-interactions, (d) the lowest stability of phenyl glycine is attributed to the electron withdrawing groups present on the ligand, which lowers the basicity and stability of metal complexes as is expected.

Table 3: Δ log K values of ternary complexes of bivalent metal ions

Ligand combinations	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2}
Gly+KA	0.09	0.28	0.8	0.2
Gly+ MA	0.04	0.27	0.24	0.09
Gly+ AA	0.5	0.41	0.96	0.6
Phy-Gly+KA	0.31	0.2	0.9	0.21
PhyGly+MA	0.36	0.28	0.61	0.22
Phy-Gly+AA	0.1	0.28	0.89	0.01

The sequence of stability of ternary complexes with respect to their ligands decrease in the order: maltol > kojic acid > acetyl acetone. The tentative structure of ternary complex is shown in Fig.2.

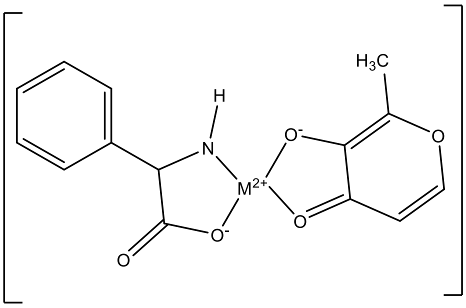

Fig.2: Tentative structure of ternary complex having Phy-Gly, M^{2+} and MA

The stability constants of ternary complexes of bivalent metal ions are in the order

$Cu^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+}$. This order is comparing with Irving-William's natural order of stabilities.

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