

Influence of Dielectric Constants of Methanol-Water Mixtures on Formation Constants of Cu(II)-Glycyl-Glycyl-Glycine Complexes

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Potentiometric investigation on Cu(II) complexes with glycyl-glycyl-glycine has shown 1 : 1 and 1 : 2 complex formation at 0.1 M ionic strength and different percentages of methanol-water mixtures. The data of pK and log k values increased with increasing the percentage of methanol-water mixture.

INTRODUCTION

The studies in metal-ligand complexes in solution of a number of metal ions with carboxylic acids, sulphonic acids, oximes, phenols etc. would be interesting which throw light on the mode of storage and transport of metal ions in the biological kingdom.

Banerjee *et al.*¹ have synthesised a number of mixed ligand alkaline earth metal complexes with a view to understand about the bio-inorganic chemistry of metal ions. The studies on metal ligand and mixed ligand have widely been reported². Proton-ligand stability constants of *o*-hydroxy acetophenone oxime and its substituted derivatives have been reported by Ingle and Khanolkar³. Narwade *et al.*⁴ have investigated metal-ligand stability constants of lanthanide ions with some substituted sulphonic acids spectrophotometrically. Chincholkar *et al.*⁵ have reported Fe(III) complexes with some substituted chalcones and isoxazolines in 70% dioxane-water mixture potentiometrically. Shelke *et al.*⁶ have studied equilibrium constants of UO₂(II) and Cu(II) ions with carboxylic acids in different percentages of dioxane-water mixtures. Raghuwanshi *et al.*⁷ have studied the conditional stability constants of Cu(II) complexes with some substituted isoxazolines in 70% dioxane-water mixture spectrophotometrically. Mandakmare *et al.*⁸ have investigated the interaction between UO₂(II) and substituted coumarines. Sondawale *et al.*⁹ have studied the influence of ionic strengths on complexes equilibria in aqueous medium.

The interaction between Cu(II) chelates with 2-hydroxy aromatic ketones is studied by Rabindranath¹⁰. Here an attempt has been made to study the complexing properties of Cu(II) with glycyl-glycyl-glycine peptide at 0.1 M ionic strength and different percentages of methanol-water mixtures potentiometrically.

EXPERIMENTAL

Chemicals: Glycyl-glycyl-glycine peptide ligand was obtained from

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Germany. Its solution was prepared in double distilled water (1.002×10^{-2} M), KNO_3 , HNO_3 and NaOH were used of AR grade reagents. $\text{Cu}(\text{NO}_3)_2$ was obtained from BDH and its solution was prepared in double distilled water and concentration was checked by EDTA.

pH-Meter: pH-meter Elico-LI-12 T was used in the present investigation for the pH measurement of solution. It was calibrated by standard buffer solution of pH 4.01, 7.00 and 9.20.

Calvin-Bjerrum Titration

The present work deals with the study of potentiometric titrations in different percentages of methanol-water mixtures at 0.1 M ionic strength. The titrations were carried out by using Calvin-Bjerrum technique in an inert atmosphere by bubbling oxygen free nitrogen gas in order to keep away CO_2 .

Experimental procedure involves potentiometric titrations in different percentages of methanol-water mixtures. Three sets of titrations are performed as follows:

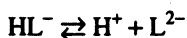
- (i) Free acid titration (nitric acid 1.00×10^{-2} M)
- (ii) Free acid (nitric acid 1.00×10^{-2} M) + peptide ligand (20.003×10^{-4}) and
- (iii) Free acid (HNO_3 1.00×10^{-2} M) + peptide ligand (20.003×10^{-4} M) + metal ions (4×10^{-4} M).

Three sets were titrated separately against standard solution of 0.2 M NaOH and 0.1 M ionic strength was maintained constant by adding an appropriate amount of 1 M KNO_3 solution. pH meter readings (B-values) are converted into actual pH values by making Van-Vitert and Hass correction¹¹

RESULTS AND DISCUSSION

Proton-ligand stability constants

Peptide of amino acid may be considered as a dibasic acid having two dissociable H^+ ions from $-\text{COOH}$ and $-\text{NH}_3$ groups. It can, therefore, be represented as H_2L



The proton-ligand formation numbers (\bar{n}_A) were calculated by Irving and Rossotti's expression¹². pK values (proton-ligand stability constants) were calculated from the formation curves between pH and \bar{n}_A by noting the pH at which $\bar{n}_A = 1.5$ and $\bar{n}_A = 0.5$ for different percentages of methanol-water mixtures. The accurate values of pK were determined by pointwise calculations which are presented in Table-1.

It is clear from Table-1 that pK₁ and pK₂ values increased with increasing the percentage of methanol-water mixture. Sondawale *et al.*¹³ have observed the same phenomenon in different percentages of ethanol/acetone-water mixtures.

Metal-Ligand Stability Constants

The stepwise formation constants of $\text{Cu}(\text{II})$ complexes with glycyl-glycyl-glycine peptide in different percentages of methanol-water mixtures were deter-

mined $\log k_1$ and $\log k_2$ values were directly computed from the formation curves (\bar{n} vs. pL) using half integral method. The most accurate values were calculated by pointwise calculations. These are presented in Table-2. It was observed that $\log k_1$ and $\log k_2$ values increased with increasing the percentages of methanol-water mixture. The change in colour during the titration showed the commencement of complex formation. The maximum value of \bar{n} at each percentage of methanol was around 2.0 which indicated the formations of 1:1 and 1:2 complexes.

TABLE-1
PROTON-LIGAND STABILITY CONSTANTS (pK_1 and pK_2) OF GLYCYL-GLYCYL-GLYCINE IN DIFFERENT PERCENTAGES OF METHANOL-WATER MIXTURES

% of methanol	Dielectric constant (D)	1/D	Mole fraction	pK_{COOH}	$pK_{NH_3^+}$
0	78.00	—	—	—	—
10	75.00	0.0133	0.010	6.50	9.80
20	70.10	0.0142	0.050	6.85	10.12
30	60.80	0.0162	0.160	7.00	10.45
40	57.20	0.0166	0.205	7.35	10.75
50	52.50	0.0190	0.435	7.72	11.00
60	50.20	0.0199	0.452	8.05	11.30
70	40.80	0.0245	0.490	8.31	11.62
80	40.10	0.0249	0.586	8.70	11.90

TABLE-2
METAL-LIGAND STABILITY CONSTANTS OF Cu(II)-GLYCYL-GLYCYL-GLYCINE COMPLEXES IN DIFFERENT PERCENTAGES OF METHANOL-WATER MIXTURE

% of Methanol	Dielectric constant (D)	1/D	Mole fraction	$\log k_1$	$\log k_2$	$\log k_1 - \log k_2$
0	78.00	—	—	7.85	3.92	3.93
10	75.00	0.0133	0.010	8.05	4.05	4.00
20	70.10	0.0142	0.050	8.25	4.15	4.10
30	60.80	0.0162	0.160	8.38	4.25	4.13
40	57.20	0.0172	0.205	8.50	4.38	4.12
50	52.50	0.0190	0.435	8.71	4.45	4.26
60	50.20	0.0199	0.450	8.85	4.62	4.23
70	40.80	0.0245	0.490	9.00	4.70	4.30
80	40.10	0.0249	0.586	9.20	4.81	4.39

One would expect a bigger difference between $\log k_1$ and $\log k_2$ values due to possible steric hindrance to the linking of the secondary ligand to the metal ion. The small difference may be due to *trans* structure.

The values of pK and $\log k$ increased may be due to the fact of the bulk solvent.

The data obtained in our present investigation were found to be in good agreement with the values obtained by Yasuda¹⁴ and Jahangirdar¹⁵.

Plots of $pK/\log k$ vs. $1/D$ (D = dielectric constant) and mole fraction

The plots between $pK/\log k$ vs. $1/D$ showed fairly linear relationship at low percentage of methanol-water mixture but nonlinear relationship for higher percentage of methanol. The plots between $pK/\log k$ vs. mole fraction showed linear relationship. The work of Harned and Owen¹⁶ has shown an approximate linear relationship for propionic acid in different percentages of dioxane-water mixtures. Water is recognised by all workers in solution field as being a unique structure ligand in the sense of having three-dimensional ice-like framework.

Franks and Ives¹⁷ have shown the addition of the first increment of other organic cosolvency to water. The dielectric constant of a medium is not solely responsible for the extent of dissociation; there is at least an additional factor of the chemical role of the solvent in most cases. Ohtaki¹⁸ showed the effect of solvent on the dissociation of ammonium and pyridinium ions.

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