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Influence of Dielectric Constants of Dioxane-Water Mixture on Formation Constants of Cu(II)-Glycyl-Glycyl-Glycine Complexes

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The interaction between Cu(II) complexes with glycyl-glycyl-glycine in different percentages of dioxane-water mixture at 0.1 M ionic strength and at 27 ± 0.1°C has been studied potentiometrically. The method of Bjerrum and Calvin, as modified by Irving and Rossotti, has been used in the present work. The data obtained can be used to study the values of proton-ligand and metal-ligand stability constants for 1 : 1 and 1 : 2 complexes. It showed that proton-ligand and metal-ligand stability constants increase with increasing the percentage of dioxane-water mixtures.

INTRODUCTION

The studies in metal-ligand complexes in solutions 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. Metal ligand stability constants of dicarboxylic acids (succinic acid, itaconic acid, adipic acid, etc.) with transition metal ions have been determined in aqueous medium by many workers[1]. Banerjee *et al.*[2] have synthesised a number of mixed ligand alkaline earth metal complexes with a view to understand the bio-inorganic chemistry of metal ions. The studies on metal ligand and mixed ligand have widely been reported[3]. Narwade *et al.*[4] have investigated metal-ligand stability constants of lanthanide ions with some substituted sulphonic acids spectrophotometrically. Proton-ligand stability constants of *o*-hydroxy acetophenone oxime and its substituted derivatives have been reported by Ingle and Khanolkar[5]. Shelke *et al.*[6] have studied equilibrium constants of UO_2(II) and Cu(II) ions with carboxylic acids in different percentages of dioxane-water mixture. Chincholkar *et al.*[7] have reported Fe(III) complexes with some substituted chalcones and isoxazolines in 70% dioxane-water mixture potentiometrically. The conditional stability constants of Cu(II) complexes with some substituted isoxazolines in 70% dioxane-water mixture have been studied by Raghuwanshi *et al.*[8] Sondawale *et al.*[9] have studied the influence of dielectric constants of methanol-water mixtures on formation constants of Cu(II)-glycyl-glycyl-glycine complexes. The interaction between UO_2(II) and substituted

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coumarins have been investigated by Mandakmare *et al.*[10] Sawwalakhe *et al.*[11] have studied the metal-ligand stability constants with 1,3-diketone, substituted pyrazoles and pyrazolines spectrophotometrically.

The interaction between Cu(II) chelates with 2-hydroxy aromatic ketones is studied by Rabindranath[12]. 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 dioxane-water mixtures potentiometrically. Recently Kadu *et al.*[13] have investigated the transition metal ion complexes with some substituted pyrazolines and pyrazoles at 0.1 M ionic strength in 70% dioxane-water mixture.

EXPERIMENTAL

Glycyl-glycyl-glycine peptide was procured from 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. $Cu(NO_3)_2$ was obtained from BDH and its solution was prepared in double distilled water and concentration was checked by EDTA.

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.

The present work deals with the study of potentiometric titrations in different precentages of dioxane-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.

The experimental procedure involves potentiometric titrations in different percentages of dioxane-water mixtures. The sets of titrations are performed as follows:

(1) Free acid titration (nitric acid 1.00×10^{-2} M)

(2) Free acid (nitric acid 1.00×10^{-2} M) + peptide ligand (20.003×10^{-4} M) and

(3) Free acid (nitric acid 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 correction[14].

RESULTS AND DISCUSSION

Peptide of amino acid may be considered as a dibasic acid having two dissociable H^+ ions from —COOH and —NH_3 groups. It can, therefore, be reported as H_2L.

$$H_2L \rightleftharpoons H^+ + HL^-$$
$$HL^- \rightleftharpoons H^+ + L^{2-}.$$

The proton-ligand formation numbers ($\bar{n}_A$) were calculated by Irving and Rossotti's expression[15]. Proton-ligand stability constants (pK values) 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 dioxane-water mixtures. The accurate values of pK were determined by pointwise calculations which are presented in Table-1.

TABLE-1

% of dioxane	Dielectric constant (D)	1/D	Mole fraction	pK $COOH^-$ $\bar{n}_A = 1.5$	pK NH_3^+ $\bar{n}_A = 0.5$
0	76.0	0.0131	–	6.50	9.8
10	67.0	0.0148	0.0125	6.85	10.5
20	62.0	0.0161	0.0500	7.30	11.2
30	52.6	0.0190	0.0900	7.70	12.0
40	47.0	0.0212	0.1230	8.10	12.7
50	43.5	0.0230	0.2000	8.50	13.4
60	42.0	0.0238	0.2400	8.90	14.0
70	36.0	0.0227	0.3290	9.30	14.8

It is clear from Table-1 that pK_1 and pK_2 values increased with increasing the percentage of dioxane-water mixture. Sondawale *et al.*[16] have observed the same phenomenon in different percentages of ethanol/acetone-water mixtures.

Metal-ligand stability constants: The stepwise formation constants of Cu(II) complexes with glycyl-glycyl-glycine peptide in different percentages of dioxane-water mixtures were determined. 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 percentage of dioxane-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 dioxane was around 2.0 which indicated the formation of 1 : 1 and 1 : 2 complexes.

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

% of dioxane	Dielectric constant (D)	1/D	Mole fraction	log k_1	log k_2	log k_1 – log k_2
0	76.0	0.0131	–	7.84	3.85	3.99
10	67.0	0.0148	0.0125	8.22	3.83	4.39
20	62.0	0.0161	0.0500	8.54	4.15	4.39
30	52.6	0.0190	0.0900	9.14	4.36	4.78
40	47.0	0.0212	0.1230	9.45	4.50	4.95
50	43.5	0.0230	0.2000	9.85	4.65	5.20
60	42.0	0.0238	0.2400	10.25	4.85	5.40
70	36.0	0.0277	0.3290	10.65	5.00	5.65

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 Yasuda[17] and Jahangirdar[18]

Plot 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 dioxane-water mixture but nonlinear relationship for higher percentage of dioxane. The plots between pK/log K *vs.* mole fraction showed linear relationship. The work of Harned and Owen[19] 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 Iven[20] have shown the addition of the first increment of other organic covalency 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. Ohtaki[21] showed the effect of solvent on the dissociation of ammonium and pyridinium ions.

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