Complex Formation Equilibria of Glycinehydroxamic Acid with Proton, Cu(II) and Ni(II) in Aqueous-Dioxan

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Glycinehydroxamic acid has been used in the design of metal chelates to supplement trace elements essential in animal nutrition [1]. The complex equilibria of glycinehydroxamic acid with proton and some metal ions has been reported in aqueous solution only [1,2]. No information is available in literature reagarding complex equilibria study of this ligand with proton and metal ions in mixed aqueous-organic solvents. The present study reports the protonation constants of this ligand and stability constants of its metal complexes in different compositions of water-dioxan mixtures.

EXPERIMENTAL

Glycinehydroxamate (or 2-amino-N-hydroxy-acetamide) of Sigma grade was used for this study. All other chemicals were of analytical grade. Glass distilled water was used for preparing solutions. The pH titration technique of Irving and Rossotti [3] was used to determine protonation constants of the ligand and stability constants of metal-ligand complexes. An EC digital pH meter with combined glass and calomel electrode assembly (of accuracy of $\pm$ 0.01 pH units) was used for pH measurements in potentiometric titrations. The pH values in water-dioxan mixtures were corrected using the method of Van Uitert and Hass [4]. 20 ml of the following water-dioxan solutions were prepared at ionic strength of 0.15 M NaCl in 0, 10, 20, 30, 40, 50 and 60% (V/V) dioxan:

(A) 5×10^{-3} M HCl;

(B) A + 2×10^{-3} M ligand and

(C) B + 4×10^{-4} M metal ion.

These mixtures were separately titrated potentiometrically against 0.1 N NaOH solution. The titration curves for acid, acid + ligand and acid + ligand + metal ion were drawn. A typical plot (for 10% dioxan) is shown in Fig.1. The values of $\bar{n}_A$, $\bar{n}$ and pL were calculated from the equations reported earlier [3].

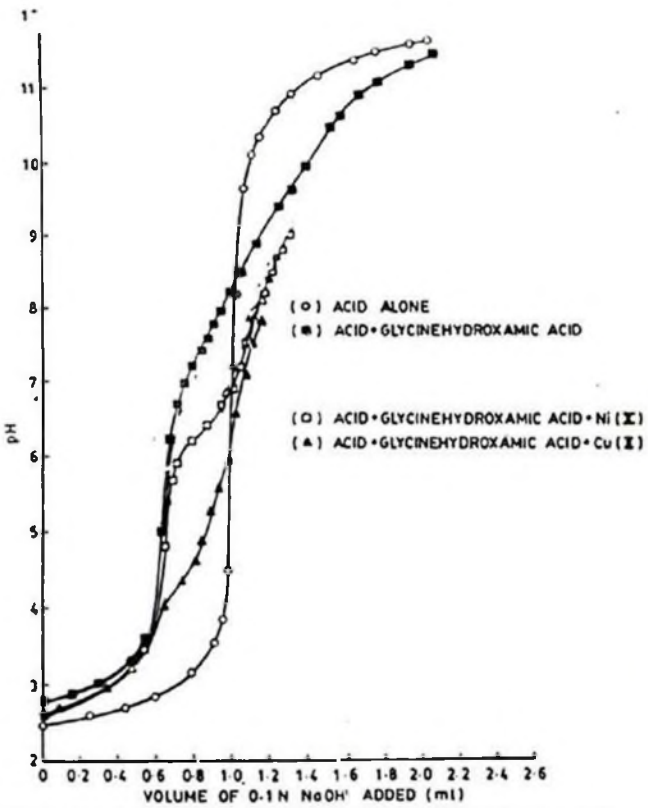


FIG.1 TITRATION CURVES FOR GLYCINEHYDROXAMIC ACID AND METAL-GLYCINEHYDROXAMIC ACID IN 10% (V/V) DIOXANE CONCENTRATION.

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Table I

Proton-ligand and metal-ligand stability constants of glycinehydroxamic acid in different compositions of water-dioxan mixtures.
I = 0.15 M NaCl; T = 30° C.

Dioxan % v/v	H^+		Cu^{2+}		Ni^{2+}	
	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$
0	9.25	7.35	10.75	8.86	7.04	6.49
10%	9.41	7.35	11.19	9.62	7.44	6.61
20%	9.55	7.36	11.47	9.87	7.76	6.96
30%	9.76	7.35	11.86	10.32	8.05	7.07
40%	10.01	7.40	12.37	10.43	8.36	7.31
50%	10.15	7.35	12.53	11.16	8.63	7.57
60%	10.36	7.36	13.01	11.41	9.07	7.94

The proton ligand stability constants have been determined from the first two titrations using the relationships:

$$\log K_1^H = pH + \log \frac{\bar{n}_A}{1 - \bar{n}_A}$$

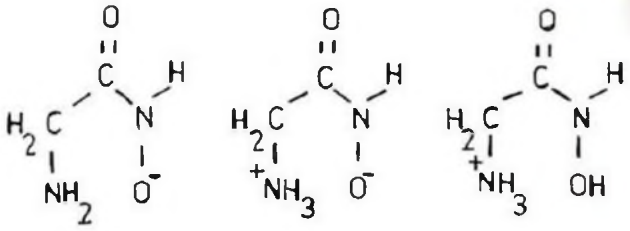
$$\log K_2^H = pH + \log \frac{\bar{n}_A - 1}{2 - \bar{n}_A}$$

Values of metal-ligand stability constants ($\log K_1$ and $\log K_2$) were obtained from the plots of n and pL, using the following equation reported earlier [3]:

$$\frac{\bar{n}}{(\bar{n} - 1)\,L} = \frac{(2 - \bar{n})\,L}{(\bar{n} - 1)} K_1K_2 - K_1$$

RESULTS AND DISCUSSION

The protonated ligand (I) has two ionizable protons: one from $-NH_3^+$ and the other from -NHOH group. The first protonation constant ($\log K_1^H$) corresponding to protonation of glycinehydroxamate ion (III) to zwitter ion (II) is found to be 9.25 and the second protonation constant ($\log K_2^H$) corresponding to protonation of zwitter ion to protonated species (I), is found to be 7.35 in aqeuous medium (Table I) and are in close agreement with those reported in literature [1].



Glycine hydroxamate	Zwitter ion	protonated ligand
III	II	I

It is worth mentioning that pK_1^H of protonated glyoxamic acid = $\log K_2^H$; pK_1^H of glyoxamic acid = $\log K_1^H$

The present results on protonation constants (Table I) showed that $\log K_1^H$ increased with increasing concentration of dioxan in water-dioxan mixtures. Born equation [5] predicts that creation of charge in media of low dielectric constant is an

unfavourable process and thus the equilibrium constant between glycinehydroximate ⟷ zwitterion, increases with increase in dioxan content. In the equilibria between zwitterion ⟷ protonated ligand, there is a decrease in the total charge; therefore, the values of log K_2^H are almost similar in water-dioxan mixtures.

From metal-ligand titration curves, values of n were calculated. This is found to lie between 0 and 2 in the pH range 3.3 - 5.5 for Cu^{2+} and 4.7-6.6 for Ni^{2+} in all compositions of water-dioxan mixtures. The trend in the variation of metal-ligand stability constants increased with increase in the concentration of dioxan in water-dioxan mixtures for each metal ion. The sequence Cu^{2+} > Ni^{2+} was followed for complexity constants in all cases which is in accordance with Irving-William's stability order of metal complexes [6]. Comparing the present log K values of Ni^{2+} - glycinehydroxamic acid in water-dioxan mixtures, with those of Ni^{2+} - glycine complexes (log K_1 5.83 and log K_2 4.7) [7] indicate that CONHOH group in glycinehydroxamic acid has greater affinity than the -COOH group in glycine for Ni^{2+} ion.

REFERENCES

1. D.A. Brown, M.V. Chidambaram and J.D. Glennon, *Inorg. Chem.*, **19** (1980) 3260.

2. E.B. Paniago and S. Carvalho. *Inorg. Chim. Acta.*, **136** (1987) 159.

3. H.M. Irving and H.S. Rossotti, *J. Chem. Soc.*, **(1954)** 2904; **(1953)** 3397.

4. L.G. Van Uitert and C.G. Hass, *J. Amer. Chem. Soc.*, **75** (1953) 451.

5. M. Bron, *Z. Physik.*, **1** (1920) 45.

6. H.M. Irving and R.J.P. Williams, *Nature*, **162** (1948) 746.

7. K. Mui, W.A.E. McBryde and E. Nieboer, *Canadian J. Chem.*, **52** (1974) 1821.