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Potentiometric Study of Mixed Ligand Complexes of Sulphur Containing Ligands and Amino Acids with Zn(II)

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The pH-metric study of ZnAB mixed ligand system [A = mercaptosuccinic acid (MSA), 2-mercaptopropionylglycine (2-MPG) and B = glycine (gly), alanine (ala), valine (val), cysteine (cys) and penicillamine (pen)] in aqueous solution at 26 ± 0.5°C and 0.1 M ($NaClO_4$) ionic strength shows the presence of mixed ligand complexes. In ZnAB complexes five-membered rings are formed due to the coordination of ligands with metal. The value of Δ log K shows the preferential formation of ternary complexes.

Key Words: Potentiometric, Zn(II), Mixed ligand complexes, Sulphur, Amino acids.

INTRODUCTION

Zinc is one of the 40 naturally occurring elements that has been detected in living bodies which is essential for healthy human life[1]. The hormone insulin, a zinc protein, is a very important drug. Insulin lowers blood glucose and hence is used for administering to diabetic patients[1]. Zinc is present in carboxypeptidase-A, a pancreatic enzyme which catalyses the hydrolysis of terminal peptide bond at the carboxylate end in proteins and peptides. In trace amounts zinc is essential for life due to its role in metalloenzymes, but even in moderate low concentration it causes emesis and gastro intestinal irritation[1]. It is interestin, therefore, to study the complexes of Zn(II) and sulphydryl compounds. The complexation of sulphur containing ligand depends upon the soft character of mercaptosulphur[2] of sulphydryl group.

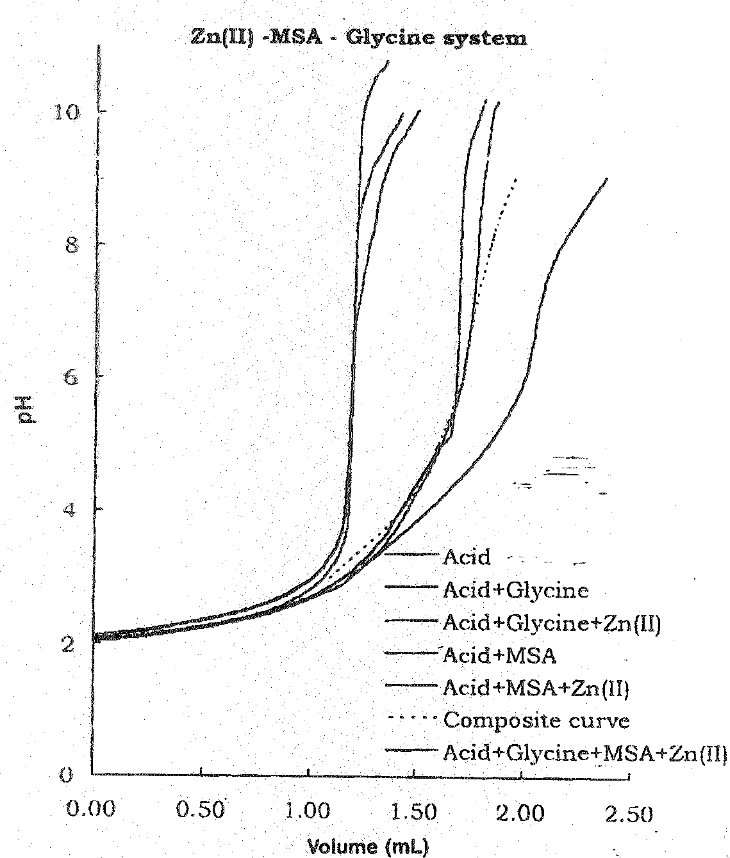
EXPERIMENTAL

The ligands used were of AnalaR quality. They were purified by crystallization and purity was checked by the melting point. The solutions of the ligands were prepared in glass-distilled water. The Zn(II) solution was prepared by dissolving requisite amount of AR grade zinc nitrate in doubly distilled water and standardized against EDTA[3] solution. The solution of sodium hydroxide was prepared[4] in carbonate-free distilled water and standardized against potassium hydrogen phthalate potentiometrically[5]. The sodium perchlorate and perchloric acid solution was prepared by taking requisite amount of the AnalaR sample in double distilled water. The aqueous solutions of ligands like 2-mercaptopropionylglycine (2-MPG) have a tendency to undergo oxidation by atmospheric oxygen; therefore freshly prepared solution was used in each titration. Elico digital pH-meter model LI-120 and combined glass electrode (CL-51) was used to measure pH at 26 ± 0.5°C. An inert atmosphere was maintained throughout the experiment by bubbling oxygen-free nitrogen gas. The stability constant was determined by using Calvin-Bjerrum titration technique as modified by Irving and Rossotti[6].

For pH titration the following thermo stated mixtures were titrated with carbonate-free 0.21 M NaOH solution:

(a) 2 mL of 0.24 M $HClO_4$,
(b) Mixture (a) + 10 mL 0.01 M mercaptosuccinic acid (MSA),
(c) Mixture (b) + 2 mL 0.01 M Zn(II),
(d) Mixture (a) + 10 mL 0.01 M amino acid,
(e) Mixture (d) + 2 mL 0.01 M Zn(II),
(f) Mixture (b) + 10 mL 0.01 M amino acid + 10 mL 0.01 M Zn(II).

The ionic strength of above solutions was maintained at 0.1 M with the help of 1 M $NaClO_4$ solution and total volume of solution was made 50 mL. The titrations are presented graphically in Fig. 1.



RESULTS AND DISCUSSION

The proton ligand and metal ligand stability constants of zinc chelates were calculated by Irving and Rossotti[6] method and are set out in Table-1. In acid solution the titration curves of amino acid lie before acid curve indicating association of proton to ligand molecule through lone pair of nitrogen of amino group[6].

TABLE-1
PROTON-LIGAND AND METAL-LIGAND STABILITY CONSTANTS OF Zn(II) BINARY COMPLEXES

Temp. = 26 ± 0.5°C; $\mu = 0.1$ M ($NaClO_4$)

Parameter	MSA	2-MPG	Gly	Ala	Val	Cys	Pen
$\log K^{1}H$	10.50	8.40	9.56	9.63	9.50	10.40	10.50
$\log K^{2}H$	4.70	3.60	2.40	2.40	2.36	8.20	7.80
$\log K^{3}H$	3.20	—	—	—	—	—	—
$\log \beta_{ML1}$	7.62	5.41	5.14	4.93	4.99	9.77	9.93
$\log \beta_{ML2}$	14.03	9.95	9.33	9.03	9.05	18.56	18.93

The MSA and 2-MPG are novel type of ligands. The MSA contains two —COOH and one —SH group while 2-MPG contains —COOH, —CONH and —SH groups. In Zn(II) chelates the binding sites of MSA are —SH and α-COOH groups, in 2-MPG the sites are —SH and —CONH. The amino acids, *e.g.*, gly, ala and val bind through —COOH and —NH_2 groups while cys and pen bind through —SH and —NH_2 groups[1]. All the ligands form 1 : 1 and 1 : 2 complexes with Zn(II). The gly, ala and val form 1 : 1 and 1 : 2 complexes in the pH range 6.00–8.50; cys and pen form complexes in the pH range 5.00–6.50 while 2-MPG and MSA form complexes in the pH range 5.00–7.50. From Table-1 it is observed that the values of metal ligand stability constants of the ligands MSA, 2-MPG, cys and pen are higher since these ligands are terdentate ligands.

The complexation of mixed ligand complex systems of Zn(II) involve the following possible equilibria:

$$K_{MX} = K(M + X \rightleftharpoons MX)$$
$$K_{MX1} = K(M + Y \rightleftharpoons MY)$$
$$K_{MX2} = K(MX + X \rightleftharpoons MX_2)$$
$$K_{MY2} = K(MY + Y \rightleftharpoons MY_2)$$
$$K_{2XY} = K(MX + Y \rightleftharpoons MXY)$$
$$K_{2YX} = K(MY + X \rightleftharpoons MXY)$$

and

$$\beta_{XY} = K(M + X + Y \rightleftharpoons MXY)$$

must be involved.

The mixed ligand titration curve does not coincide with either of the individual titration curves; therefore 1 : 1 : 1 ternary complex is formed by simultaneous equilibrium. The preferential formation of ternary complexes over binary complexes has been discussed in terms of equilibrium constant. The difference in stability between binary and ternary complexes is a way of measuring the tendency of formation of ternary complexes. The stability of ternary complexes can be expressed in two ways:

(1) The magnitude of Δ log K:

$$\Delta \log K = \log \beta XY - (\log K_{MX1} + \log K_{MY1})$$

or

$$\Delta \log K = \log K_{2XY} - \log K_{MY1}$$

or

$$\Delta \log K = \log K_{2YX} - \log K_{MX1}.$$

(2) The characterization of ternary complex by its disproportionation constant of the reaction

$$MX_2 + MY_2 \rightleftharpoons 2MXY$$

The disproportionation reaction is for the systems containing ligands which form 1 : 1 and 1 : 2 complexes individually with Zn(II). The stability constants of mixed ligand complexes of Zn(II) with MSA, 2-MPG and amino acids are presented in Table-2. The negative values of Δ log K obtained in the present investigation indicate that the primary and secondary ligand form ternary complexes rather than binary ones. The comparison of K_{2XY} and K_{MX1} shows that ternary complexes are more stable as compared to binary. The more positive values of disproportionation constant obtained in all the present mixed ligand systems compared to statistical values[7] show higher stability of mixed ligand complexes compared to binary complexes[8].

TABLE-2
STABILITY CONSTANTS OF MIXED LIGAND COMPLEXES OF Zn(II) WITH MSA, 2-MPG AND AMINO ACIDS

Temp. = 26 ± 0.5°C; μ = 0.1 M ($NaClO_4$)

System	β_{XY}	K_{DXY}	K_{2XY}	K_{2YX}	Δ log K
MSA-gly	11.10	1.66	3.48	5.96	–1.66
MSA-ala	11.13	1.42	3.51	6.20	–1.42
MSA-val	10.55	2.00	2.93	5362	–2.00
MSA-cys	16.00	1.39	8.38	6.23	–1.39
MSA-pen	15.88	1.67	8.26	5.95	–1.67
2-MPG-gly	8.49	1.86	3.08	3.55	–1.86
2-MPG-ala	8.57	1.77	3.16	3.64	–1.77
2-MPG-val	8.52	1.88	3.11	3.53	–1.88
2-MPG-cys	9.99	5.63	4.58	0.22	–5.63
2-MPG-pen	9.94	5.39	4.53	0.01	–5.39

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In the present investigation the amino acid binds the Zn(II) in the same way as in their binary species. The glycine like binding mode results in five-membered rings, which are very stable. In ternary complexes of Zn(II) all these complex systems contain five-membered rings on both sides of the metal. These rings contain oxygen atoms of carboxylic group of amino acid on one side and oxygen atom of MSA/2-MPG on the other side.

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