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EQUILIBRIUM STUDIES OF TERNERY COMPLEXES OF SOME TRANSITION METAL (II) IONS WITH PENICILLAMINE

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ABSTRACT

The interaction of Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) metal ions with penicillamine (PEN) has been studied by pH-metric technique at 0.1 M (KNO_3) ionic strength at 302 ± 0.5 K in aqueous medium. The data obtained were used to evaluate the values of proton-ligand and metal-ligand stability constants using Irving-Rossotti titration technique. Mixed ligand complex studies of these metal ions using nitrilotriacetic acid (NTA), iminodiacetic acid (IMDA), aspartic acid (ASP) and glutamic acid (GLU) as primary ligands and PEN as secondary ligand have been carried out pH-metrically at the same conditions.

Keywords: Ternary complexes, Transition metal ions, penicillamine, nitrilotriacetic acid, iminodiacetic acid, aspartic acid and glutamic acid.

INTRODUCTION

Recently, there has been considerable interest in the study of binary, ternary and quaternary complexes by pH-metric method[1-3]. The ligand penicillamine (PEN) acts as a chelating agent useful in the treatment of Wilson's disease and biliary cirrhosis, and lead, gold or mercury poisoning [4-6].

Ternary complexes of Ni (II) and Cu (II) with nicotinic acid as primary ligand and imidazoles, benzimidazole, histamine and L-histidine as secondary ligands have been studied by Nair and Neekantan[7]. Patil and Mhaske have studied the stability constants of Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) with nitrilotriacetic acid and Iminodiacetic acid as primary ligands and penicillamine and cephalexin as secondary ligands potentiometrically[8]. Nigam and coworkers have studied the ternary complexes of Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) using ASP as primary ligand and thymine as secondary ligand potentiometrically[9]. Ternary complexes of Cu(II) using ASP and GLU as primary ligands have been reported potentiometrically by Pandeya and Patel[10].Kalshetti and coworkers have studies binary and ternary complexes of Co (II), Ni (II), Cu (II) and Zn(II) [11]. Mixed ligand complexes of transition metal(II) ions with N-(2-hydroxybenzylidene)-2,3-dimethylaniline as primary ligand and N-(2-hydroxy-1-naphthylidene)-4-chloroaniline as secondary ligand has been studied by Mapari and Mangaonkar[12]. Solution equilibria of ternary systems involving transition metal ions, hydroxamic acids, and bioligands have been studied by Khalil and Mahmoud[13]. Gazala Mohamed studied the ternary complexes of Co (II) involving nitrilotriacetic acid and some biologically active ligands[14].

In this paper the stability constants of ternary complexes of Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) ions with NTA, IMDA, ASP and GLU as primary ligands and PEN as secondary ligand at 302 ±0.5 K and at fixed ionic strength, μ = 0.1M KNO_3 using modified form of Irving-Rossotti pH-metric technique in aqueous medium have been studied[15].

EXPERIMENTAL

The ligand PEN was obtained from Sigma and was used as such. Carbonate free sodium hydroxide solution was prepared by standard method[16]. All other solutions were prepared in doubly distilled water.

The pH-metric measurements were carried out by using Elico digital pH-meter model L-120 with combined glass-calomel electrode with an accuracy of ± 0.01 of pH unit at 302 ± 0.5 K. The pH-meter was standardized against 0.05 M potassium hydrogen phthalate solution in acid medium and 0.01M borax solution in alkaline medium.

For determination of proton-ligand stability constant of the secondary ligand and the metal-ligand stability constants of ternary complexes, the following set of solutions were prepared and titrated against standard alkali solution.

Ternary Systems

i. 9.6 X 10^{-3}M HNO_3
ii. 9.6 X 10^{-3}M HNO_3 + 1.0 X 10^{-3}M secondary ligand
iii. 9.6 X 10^{-3}M HNO_3 + 1.0 X 10^{-3}M primary ligand +1.0 X 10^{-3}M metal ion
iv. 9.6 X 10^{-3}M HNO_3 + 1.0 X 10^{-3}M primary ligand +1.0 X 10^{-3}M metal ion + 1.0 X 10^{-3}M secondary ligand

The ionic strength was maintained constant (0.1M) by adding required volume of 1M KNO_3. The ratio of metal (M): primary ligand (A): secondary ligand (L) was maintained at 1: 1: 1 in each of the ternary system.

RESULTS AND DISCUSSION

Proton-Ligand Stability Constants

The plots of volume of alkali (NaOH) against pH-meter readings were used to evaluate the proton-ligand stability constants of PEN. The deviation between free acid titration curve and secondary ligand titration curve was used to evaluate the formation functions $\bar{\eta}_A$. The proton-ligand formation curves were then obtained by plotting the values of $\bar{\eta}_A$ versus pH-meter readings. From the graphs, the values of $\log K_1^H$ and $\log K_2^H$ were evaluated by half integral method (method A) and point wise calculation method (method B) and presented in Table 1.

$\log K_1^H$

Table-1: Proton-Ligand Stability Constants of PEN

Ligand	$\log K_1^H$		$\log K_2^H$		$\log \beta^H$	
	Method(A)	Method(B)	Method(A)	Method(B)	Method(A)	Method(B)
PEN	10.54	10.57	7.92	7.92	18.46	18.49

The formation curve for PEN was found to be extended between 0 to 2 in the $\overline{(A}$ scale at fixed ionic strength and temperature indicating that the dissociation of H_2PEN as follows:

$$H_2PEN \rightleftharpoons PEN^- + H^+ \rightleftharpoons PEN^{2-} + H^+$$

The values of $\log K_1^H$ and $\log K_2^H$ for the PEN are due to dissociation of - $^+NH_3$ and –SH groups.

Metal – Ligand Stability Constants of Ternary Complexes

The metal – ligand stability constants of the ternary complexes were evaluated assuming that the formation of hydrolyzed products, polynuclear complexes, hydrogen and hydrogen bearing complexes were absent. An examination of titration curves indicates that complex formation has taken place in the solution on the following grounds:

1. The ternary complex titration curves show the displacement with primary complex titration curves. The horizontal distance was measured between acid curve and the secondary ligand curve ($V_2 – V_1$) and subtracted through the horizontal distance between ternary complex curves and primary complex titration curves ($V_4 – V_3$) show the positive difference which proves the earlier released of protons in the formation of ternary complexes.
2. The hydrolysis of the metal ions was suppressed and precipitation did not result.

The values of $\bar{\eta}$ vary from 0 to 1.0, thus confirming the formation of 1:1:1 mixed ligand complexes. The values of $\log K_{MAL}^{ASP}$ and $\log K_{MAL}^{GLU}$ have been evaluated from the formation curves ($\bar{\eta}$ vs. pL). At $\bar{\eta}$= 0.5 in the formation curve, pL = log K. The metal- ligand stability constant of PEN as secondary ligands and NTA, IMDA, ASP and GLU as primary ligands are presented in Table-2.

Table-2: Metal – Ligand Stability Constants of Ternary Complexes

System	$\log K^{MA}_{MAL}$									
	Mn (II)		Co (II)		Ni (II)		Cu (II)		Zn (II)	
	A	B	A	B	A	B	A	B	A	B
[M(II)- (NTA) (PEN)]	6.22	6.24	6.52	6.55	7.08	7.10	7.13	7.16	6.30	6.32
[M(II)-(IMDA) (PEN]	6.37	6.35	7.68	7,68	10.70	10.71	7.77	7.80	9.10	8.98
[M(II) - (ASP) (PEN)]	4.38	4.40	4.78	4.80	6.60	6.64	7.52	7.50	5.52	5.51
[M(II)- (GLU) (PEN)]	4.60	4.62	5.80	5.82	8.02	8.05	8.50	8.52	7.07	7.09

The Irving-Williams order[17, 18]of stability constants was observed in ternary complexes which is -
Mn (II) < Co (II) <Ni (II) <Cu (II) > Zn (II)

This sequence of stability of complexes with respect to metal ion is due to deceasing atomic radius and increasing the second ionization potential.

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