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pH metric study of binary and ternary complexes of Cu (II) with propiophenone derivatives and amino acids

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ABSTRACT

Proton ligand and Metal ligand formation constant of ternary complexes of the type MLB [Where L = i) L_1= 3-chloro,2-hydroxypropiophenone (3-Cl-2HP) ii) L_2 = 2-hydroxypropiophenone (2-HP)] and B = [B_1= Hippuric(hip) acid, B_2 = Glutamic acid (glu) B_3 =Histidine (hist), B_4= Aspartic acid (Asp)] And M = Cu (II) have been determined by potentiometrically in biologically relevant conditions at ionic strength μ = 0.1M $NaClO_4$ the overall stability constant have been evaluated using SCOGS computer program. The complexation equilibria have been derived on the basis of concentration species distribution curve and percentage distribution curve. In all cases primary ligands and secondary ligands are found to be compatible ligands. And there by proving greater stability of ternary complexes as compared to binary ones. The stability of ternary complexes expressed in terms of thermodynamic parameter Δlog k. and Negative values of Δlog k suggest that, the formations of ternary complexes are favorable. And the order of stability constant of ternary system with amino acids for respective primary ligands is. $L_1 = B_3 > B_4 > B_2 > B_1$ and $L_2 = B_3 > B_4 > B_2 > B_1$.

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KEYWORDS

pH - metric study;
Stability constant;
Binary and ternary complexes;
Cu-metal.

INTRODUCTION

The Cu metal complexes of hydroxyl and thio compound have been reported to be biologically active.[1] In trace amount copper is essential for life, about 98% of the Cu in normal human blood plasma is present as ceruloplasmin, a blue colored copper containing enzymes. The deficiency of Ceruloplasmin is associated with Wilson's disease caused by accumulation of Cu in brain and liver. Mixed ligand complexes play an important role in numerous chemical and biological system[2]. And such complexes are significance in the study of bio-fluids particularly when hyper accumulated metal ions are presents for physiological and pathological nature[3] mixed coordination by protein and related substances has been subject of investigation of many workers[5-7]. in the present paper, the formation has been studied potentiometrically by Irving-Rossotti techniques[6] in 60 % (v/v) ethanol-water medium.

EXPERIMENTAL

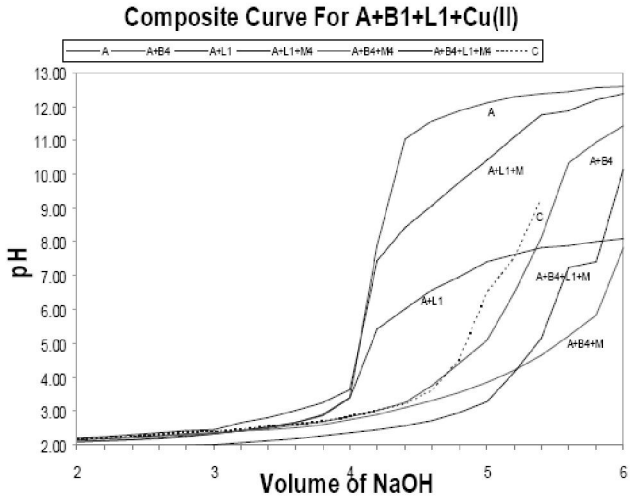
Primary ligands (2-HP and 3Cl-2HP) prepared by Fries-migration reactions. By using simple and halogen

substituted phenol and characterized by I.R. spectra. I .R bands of the ligands in KBr phase, [>C=O and -OH groups were identified] due to >C=O group at (1650-1670). And -OH group at (3650-3531). All the other chemicals are A.R. grade and were obtained from S.D. Fine chemicals ltd. An Elico model LI-120 digital pH meter with combined glass electrode was used for measurement of pH value and experimental procedure involves potentiometric titration of (1) 2ml of free HClO4 [0.5M]; (2)Mixt(i)+10ml0.01M.(L) ; (3)Mixt.(ii)+2ml-0.01MCu(II); (4) Mixt. (i) + 10 ml 0.01 M Sec.lig.(ii); (5)Mixt(iv)+2ml0.01MCu(II); (6) Mixt (ii) + 10 ml 0.01M sec. lig + 2 ml 0.01M

$Cu^{(II)}$ against standard 0.2M NaOH solution the initial volume of each solution was taken as 50 ml. The ionic strength of above solutions was maintained 0.1M with the help of 1M [$NaClO_4$] solution.

RESULT AND DISCUSSION

Stability constant of these ligands are determined by Irving-Rossotti techniques[8] at constant temperature 25 ± 0.1^{0}C in 60 % (v/v) ethanol-water medium.



1]

Primary ligands contain one hydroxyl group and one carbonyl group. Only-one replaceable proton is available, there fore only-one pK value (i.e. proton ligand stability constant) is obtained .and Amino-acids are bidentate ligand having carboxylic group and amino group, two replaceable protons are available, therefore two pK values are obtained.

Proton-ligand and metal-ligand stability constants of primary ligands with $Cu^{(II)}$ are calculated by Irving-Rossotti titration method.[8] And represented in TABLE 1. Primary ligands form 1:1and 1:2 complexes with $Cu^{(II)}$ in the pH range. Stability constant of bivalent metal complexes derived from similar type of ligands, generally follow the order of stability as. L_1 = Mn > Cu > Zn > Ni > Co. L_2 = Cu > Ni > Co > Zn > Mn.

TABLE 1 : Proton ligand and metal ligand stability constant of 2-HP and 3-Cl, 2-HP in 60% (v/v) ethanol-water medium at 25^0c+ 0.1^0c

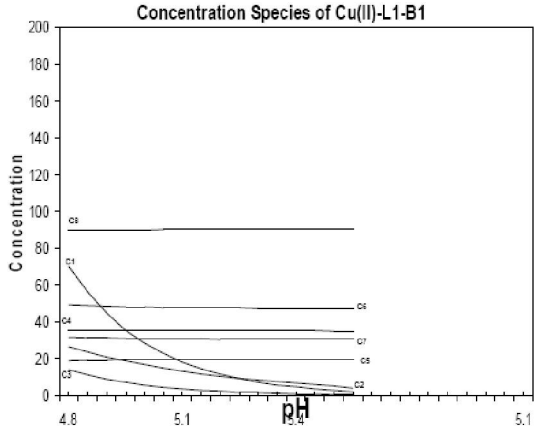
(pK) Ligands	Stability constant	Mn	Co	Ni	Cu	Zn
8.3838	$Logk_1$	7.2903	6.8166	6.9963	7.1222	7.1544
L1	$Logk_2$	5.8608	5.3957	5.3925	5.7171	5.6283
	Log β	13.1111	12.2123	12.3888	12.8394	12.7827
8.6969	$LogK_1$	8.0937	8.2227	8.1182	8.1200	.8.1508
L2	$LogK_2$	7.3798	7.3205	7.4531	7.4840	7.3705
	Log β	15.4735	15.5432	15.5713	15.6040	15.5213

2] Ternary complexes

(A) Cu^{II} - L^1-B^1 system

The formation equilibria of mixed ligand complexes with the ligands and Cu^{II} are 1:1:1 ternary complexes and formed by simultaneous equilibrium.

The preferential formation of ternary complexes over binary complexes has been discussed in terms of equilibrium constant .and on the basis of speciation curves as in Figure 2.



The percentage distribution curve free metal (F_M) decreases with increasing pH. Percentage concentration of free ligands F_L and F_B increases and particularly negligible as compared with that of F_M. all system investigated in the present paper shows similar behavior. The plots of concentration of various species Vs pH in

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this system are shown in figure 2 and 3 . from figure 2 it is clear that the equilibrium curves C_1 and C_2 for the formation of B and L shows continuous decreases in the concentration of B and L indicating the formation of CuBL in this pH range by equilibria Cu + B + L ↔ CuBL

The concentration of CuB and CuL decreases continuously with increasing pH

Which indicating the formation of CuBL is favorable by equilibria 8. and there is negligible conc. Of CuB and CuL the possibility of formation of CuBL by the equilibria CuB + CuL ↔ CuBL + Cu. --- (8). The conc. Of B and L are very low, where as conc. Of CuBL in this pH range is maximum which indicate the formation of CuBL in this pH range.

And Cu (II) - L_2-B_1 investigated in the present paper shows similar behavior.

The stability constant of ternary complexes are calculated by using 'SCOGS'[8] computer programme and

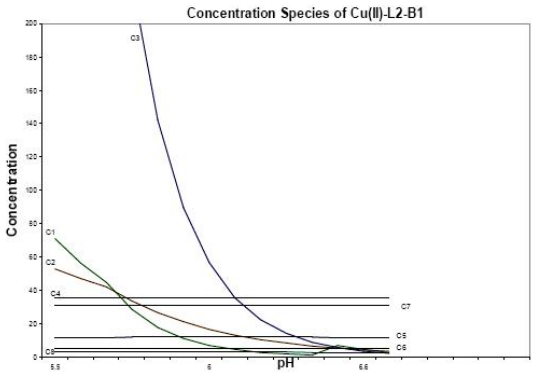

TABLE 2 : Stability constant values of Cu (II) - L_1 - B

L_1 -B	B_{11}	B_{20}	B_{02}	K_L	K_B	K_r	-Δlog k
L-Hip	8.2806	5.8755	12.839	1.0582	5.1222	0.9097	2.0000
L-Glu	8.7375	5.2725	12.839	1.6151	6.6223	1.0737	0.4999
L - Hist	18.2335	24.114	12.839	11.111	5.6222	1.0737	1.5000
L- Asp	15.5662	20.979	12.839	8.3338	6.6200	0.8995	2.5000

TABLE 3 : Stability constant values of Cu (II) - L_2 - B

L_1 -B	B_{11}	B_{20}	B_{02}	K_L	K_B	K_r	-Δlog k
L-Hip	8.7784	5.8755	15.604	0.6384	4.6200	0.8405	2.500
L-Glu	9.4852	5.2378	15.604	1.3652	7.3700	1.1029	0.7500
L - Hist	18.4810	24.114	15.604	10.361	5.7697	091585	1.2503
L- Asp	17.5640	20.979	15.604	9.444	6.6200	0.9423	1.5000

values obtained are represented in TABLE 2 and 3.

The stability constant of ternary complexes are conveniently characterized by two ways based on (1) Disproportion constant K_{DBR}.

$$K_{DBR = K}[ML_2 + MB_{2]} = 2\,MLB$$

The disproportion reaction is for the system containing ligands which forms 1:1 and 1:2 complexes Individually with Cu (II) and (2) The difference of stability constant between binary and ternary complexes i.e. Δlog k

$$\Delta 1\log k = \log KML_2 - \log KML_1$$

Generally $\log K_{ML1} > \log K_{ML2,}$ because more co-ordination positions are available for binding first ligand to metal ion. Than second ligand i.e. Δlog k values are negative .The negative values of Δ10gk obtained in the present investigation indicate that primary and secondary ligands form ternary complexes rather than binary ones.

The values of Kr are positive and about 1.0 for all ternary complexes indicates extra stabilization over binary ones, similarly the values of K_L and K_B are also positive, which also support that the ternary complexes are more stable than corresponding binary complexes.[9,10] overall constant B_{02}, B_{20}, B_{11}, were obtained as computer outputs, from which the other constant were calculated using the appropriate reactions.

The formation of mixed ligand chelate was confirmed by comparing mixed ligand curve and composite curve.[11] Mixed ligand curve did not coincide with either of the individual metal complex curve, and there fore 1:1:1 ternary complex is formed[11]

The order of stability of ternary complexes with respect to secondary ligands for respective primary ligands is.

$$L_1 = B_3 > B_4 > B_2 > B_1.$$

$$L_2 = B_3 > B_4 > B_2 > B_{1.}$$

The stability of metal chelates depends upon the total ring in the complex and the number of atoms in each ring. it also observed that the higher the number of chelate rings greater is the stability of complexes.[12]

In the present investigation all these complexes produces five membered ring on the one side with amino acids and six membered ring with primary ligands It was observed by some workers that, there is decrease in ligand stability with the increasing ring size.[13]

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