MIXED LIGAND COMPLEX FORMATION OF Cu (II) WITH PROPIOPHENONE DERIVATIVES AND AMINO ACIDS

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ABSTRACT

Equilibrium studies on the formation of binary M-L and ternary M-L-B complexes, where M = Cu and L = 5-Cl ,2-hydroxy propiophenone and 2-hydroxy propiophenone as primary ligand and amino acids as secondary ligands have been studied potentiometrically by Irving-Rossotti technique in 60% (v/v) ethanol. water medium at 25 ± 0.1ºC and at constant 0.1M $NaClO_4$ ionic strength. All the ligands forms 1 : 1 : 1 ternary complexes. The relative stability of ternary complexes expressed in terms of statistical parameter Δlog k and negative Δlog k values suggest that the formation of ternary complexes are favorable and variation of Δlog k has been explained in terms of metal-ligand-π interaction size of chelate ring and steric factors.

Key words : Potentiometric studies, Cu (II), Formation constant, Ternary complexes, Steric factors

INTRODUCTION

Mixed ligand complexes plays an important role in numerous chemical and biological systems[1,2] like water softening ion exchange resin, electroplating, dyeing, antioxidant, photosynthesis in plants, removal of undesirable and harmful metals from living organisms etc. Many of these mixed ligand complexes are suitable for mimicking the role of metal ions in active sites of metal enzymes, studying the toxic effects of metal ions, detoxification mechanism, drug designing[3, 4]. The formation of mixed ligand complexes is also important in understanding the behavior of pollutants in natural water[5].

Potentiometric study of (Cu–L–B) mixed-ligand system [5-chloro, 2-hydroxy-propiophenone (5-Cl-2HP)] and amino acids (B); L-phenylalanine (Phala), L-proline (Pro), L-threonine (Thr) and glycine (Gly)] was made by Irving-Rossotti titration technique in 60% (v/v) ($NaClO_4$) ionic strength, and the values obtained were found to be in good

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agreements with literature values reported[6, 7].

EXPERIMENTAL

Simple and halogen substituted phenols are starting materials for preparation of primary ligands and were prepared by Fries-migration reactions. Primary ligands are (i) 5-chloro, 2-hydroxy- propiophenone [L_2] and (ii) 2-hydroxy propiophenone [L_4]. All these ligands are characterized by I.R. spectra and their purity is checked by T.L.C., m.p. and usual organic tests.

Stability constant of these ligands were determined by Irving and Rossotti[8] techniques. For pH titration, the following six sets of the solution were prepared and titrated with 0.2 M NaOH solution.

(i)   2 mL of free $HClO_4$ (0.5 M)

(ii)   Mix. (a) + 10 mL 0.01M Pri. lig.

(iii)   Mix. (b) + 2 mL 0.01 M Cu (II).

(iv)   Mix. (a) + 10 mL 0.01 M Sec. lig.

(v)   Mix. (d) + 2 mL 0.01 M Cu (II)

(vi)   Mix. (b) + 10 mL 0.01M sec. lig + 2 mL 0.01M Cu (II)

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

RESULTS AND DISCUSSION

Determination of proton-ligand stability constant [pK]

The primary ligands used in the present investigation are mono basic acids having only one dissociable proton from hydroxyl group of the ligand. In general, ligands can be represented as HL and dissociated as –

$$HL \leftrightarrow H + L$$
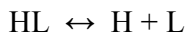
and hence, only one pK value was observed. The acid ligand curve deviated from acid curve and from this curve, the values of $\bar{n}_A$ for various pH curves were calculated and these were found to be 0.2-0.8 indicating formation of only one pK for each primary

ligand. pK values calculated by point-wise and half-integral methods were found to be in good agreement (Table 1).

Table 1. Proton-ligand stability constant [pK] of [5-Cl-2HP]

pH	$\bar{n}_A$	pK	pH	$\bar{n}_A$	pK	pH	$\bar{n}_A$	pH
7.50	0.7965	8.0926	7.80	0.6183	8.0098	8.3	0.4408	8.3896
7.55	0.7710	8.0773	7.85	0.5931	8.0135	8.4	0.4154	8.4851
7.60	0.7457	8.0672	7.90	0.5678	8.0638	8.5	0.3319	8.5696
7.65	0.7202	8.0608	8.00	0.5232	8.1183	8.6	0.2883	8.6607
7.70	0.6948	8.0574	8.10	0.5169	8.1294	8.7	0.2121	8.743
7.75	0.6440	8.0074	8.20	0.4916	8.2985			

Determination of metal-ligand stability constant [log K]

The deviation of [acid + ligand] curve from [acid + ligand + metal] curve along volume axis indicates the formation of complex species and it lies in the pH region, where hydrolysis is not expected. Metal-ligand stability constant of 5-Cl-2HP are given in Table 2. The stability constant of bivalent metal complexes derived from similar type of ligands generally follow the Irving-Rossotti[8] technique. The present complexes follow the order of stability as Co > Cu > Zn > Ni > Mn

Table 2. Metal-ligand stability constant of [5-Cl-2-HP] in 60% (v/v) ethanol-water medium at 25 ± 0.1ºC

	Co (II)	Ni (II)	Zn (II)	Cu (II)	Mn (II)
log K1	7.2527	7.2234	7.2529	7.2234	7.1599
log K2	6.5297	6.1831	6.2178	6.2753	6.2183
log Kβ	13.7824	13.4065	13.4705	13.4987	13.3782

[Cu-L-B]Complex formation equilibria

The formation equilibria of mixed ligand complexes with the ligands and Cu (II) are 1 : 1 : 1 ternary complexes and these are formed by simultaneous equilibrium.
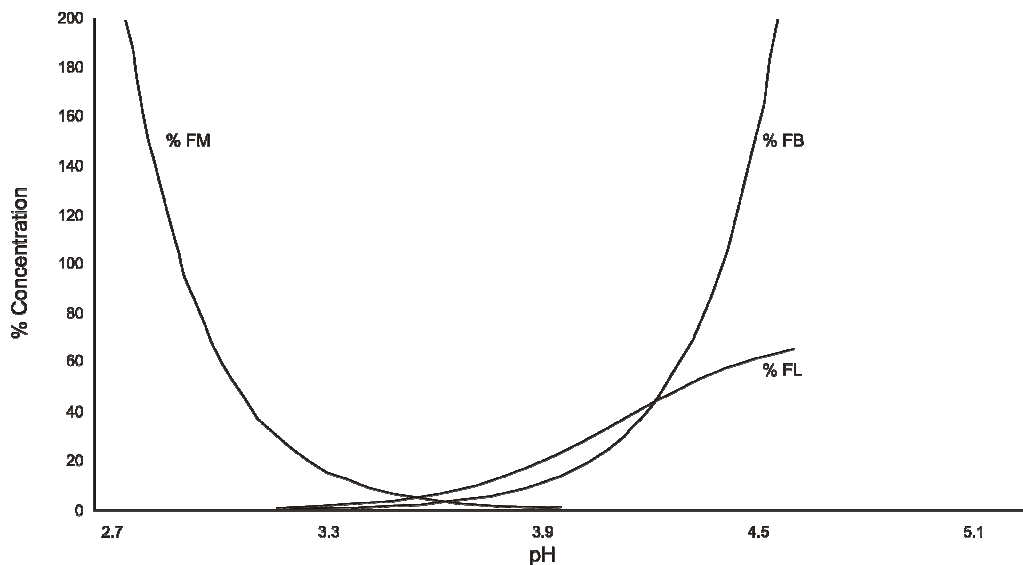

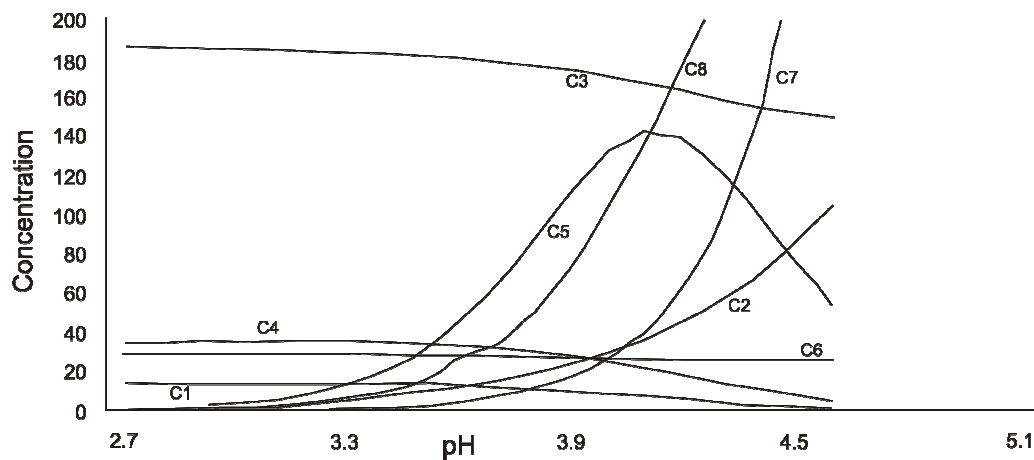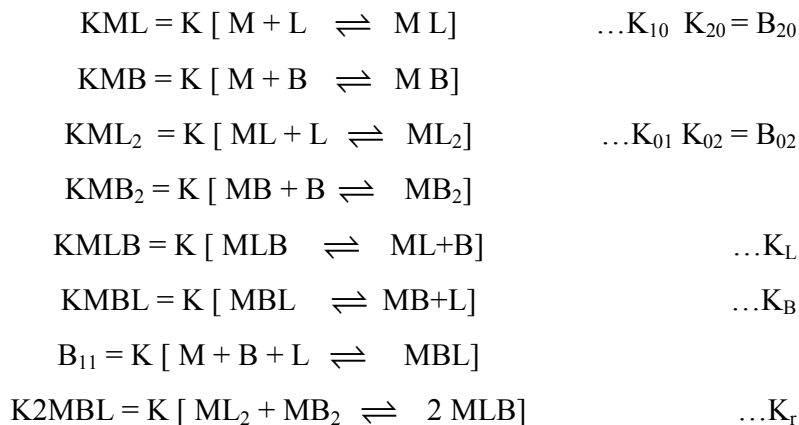**Fig. 1 : Percentage concentration of species of Cu (II)-L$_2$-B$_1$**

Fig. 2 : Concentration of species of Cu (II)-L$_2$-B$_1$

The preferential formation of ternary complexes over binary complexes has been discussed in terms of equilibrium constant and on the basis of speciation curves (Fig. 1), and percentage concentration species F_M, F_L and F_B, (Fig. 2). The complexation of mixed-ligand complex system of Cu (II) involve the following possible equilibria.

$$KML = K [M + L \rightleftharpoons M L] \qquad \dots K_{10} \ K_{20} = B_{20}$$

$$KMB = K [M + B \rightleftharpoons M B]$$

$$KML_2 = K [ML + L \rightleftharpoons ML_2] \qquad \dots K_{01} \ K_{02} = B_{02}$$

$$KMB_2 = K [MB + B \rightleftharpoons MB_2]$$

$$KMLB = K [MLB \rightleftharpoons ML+B] \qquad \dots K_L$$

$$KMBL = K [MBL \rightleftharpoons MB+L] \qquad \dots K_B$$

$$B_{11} = K [M + B + L \rightleftharpoons MBL]$$

$$K2MBL = K [ML_2 + MB_2 \rightleftharpoons 2 MLB] \qquad \dots K_r$$

The stability constant of ternary complexes are calculated by using 'SCOGS' computer programme and values are given in Table 3.

Table 3. Equilibrium constant values of Cu (II)–L–B

L –B	B_{11}	B_{20}	B_{02}	K_L	K_B	K_r	log k
L-Phala	13.4822	16.46	13.49	6.2588	5.0293	0.8186	2.246
L-Thr	13.6762	16.54	13.49	6.4528	5.3135	0.8382	1.9999
L – Pro	12.8471	14.14	13.49	5.622	4.3944	0.8652	1.9999
L- Gly	12.1217	14.16	13.49	4.8983	3.6690	0.7692	2.4999

The stability constant of ternary complexes are expressed in two ways (i) characterization of ternary complex by its disproportion constant of the reaction.

$$ML_2 + MB_2 \quad = \quad 2 MLB$$

The disproportion reaction is for the system containing ligands which forms 1 : 1 and 1 : 2 complexes individually with Cu (II) and (ii) The difference of stability constant between binary and ternary complexes can be given as –

$$\log k \;=\; \log \; KML_2 \; < \; \log KML_1$$

Generally $\log KML_1 > \log KML_2$; because more coordination positions are available for binding first ligand to metal ion than second ligand i.e. $\Delta \log k$ values are negative.

The negative values of $\Delta \log k$ obtained in the present investigation indicates that primary and secondary ligands forms ternary complexes rather than binary ones. The values of K_r 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].

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

$$L_2 \;=\; L - Pro > L - Phala > L - Thr > Gly$$

$$L_4 \;=\; L - Pro > L - Phala > Gly \; > L - Thr$$

Formation constant of the complexes were calculated by using the 'SCOGS' computer programme[11]. Estimates of some of the binary constant were obtained by the method of Irving and Rossotti[12]. Overall constant B_{02}, B_{20} and B_{11}, were obtained as computer outputs, from which the other constant were calculated using the appropriate reactions.

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