Full Proceeding Paper

POTENTIOMETRIC STUDY OF MIXED LIGAND COMPLEXES OF PROPIOPHENONE DERIVATIVES WITH TRANSITION METAL AND AMINO ACIDS.

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ABSTRACT

Objective: Mixed ligand complexes plays an important role in numerous chemical and biological systems [1-2] Like water softening, ion exchange resins, electroplating, dyeing antioxidants, photosynthesis in plants, removal of undesirable and harmful metals from living organisms etc. mixed co-ordination by proteins and related substances has been subject of the investigation of many workers.

Material and Methods: Simple and Halogen substituted phenols are starting materials for preparation of primary ligands and were prepared by Fries-migration reactions. Primary ligands are i) 3-chloro, 2-hydroxy-propiophenone[L_1], 2) 2-Hydroxy propiophenone [L_4] all these ligands are 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) and its purity are checked by T.L.C., M.P. and organic tests.

The proton-ligand & metal-ligand stability constant of binary and ternary systems of Cu(II) with propiophenone derivatives and amino acids have been studied potentiometrically by Irving-Rossotti technique in 60% (v/v) Ethanol Water medium at 250c ± 0.10c and at constant 0.1M Tonic strength. The difference between the stability of ternary and their corresponding binary complexes has been expressed interms of parameter logk and negative logk values suggest that the formation of ternary complexes are favorable and variation of logK have been explained interms metal-ligand(pi) interaction, size of chelating ring and Steric factors.

Results: The stability constant of bivalent metal complexes derived from similar type of ligands generally follow the Irving Williams order. The present complexes follow the order of stability as

L_1 = Mn > Cu > Zn > Ni> Co. And L_2 = Cu > Ni > Co > Zn > Mn.

The order of stability of ternary complexes with respect to secondary ligands for respective primary ligands is.
L_1=L - Phala > L - pro > L - Thre > Gly.
L_2=L - Pro > L - phala > Gly > L - Thre

Conclusion: In the present investigation, all these complex systems contains five membered ring on the one side with amino-acids. And six member ring on other side with primary ligand.

Keywords: - Potentiometric studies, Stability Constant, Cu (II), Binary and Ternary Complexes, Steric factors

INTRODUCTION

Mixed ligand complexes of metal ions of biological importance with amino acids and their derivatives are of great significance, at low pH, peptide group under goes both protonation and metallation at the carbonyl oxygen atom. Metal atom coordinate with–NH_2 group of N-atom takes-place only upon substitution of the amide proton, for which primary ligating site at a chelating position is essential[3-4]Mixed ligand complexes are suitable for mimicking the role of metal ions in active sites of metallo enzymes, studying the toxic effect of metal ions, detoxification mechanism and drug designing[5-6] The formation of mixed ligand complexes is also important in understanding the behavior of pollutants in natural water. [7]

Mixed ligand complexes plays an important role in numerous chemical and biological systems[1-2] Like water softening, ion exchange resins, electroplating, dyeing antioxidants, photosynthesis in plants, removal of undesirable and harmful metals from living organisms etc. mixed co-ordination by proteins and related substances has been subject of the investigation of many workers.

The formation of mixed ligand complexes is also important in understanding the behavior of pollutants in natural water [8]

The PH metric study of [CULB] mixed-ligand system [3-chloro, 2-Hydroxy-propiophesone (3-Cl-2HP)] and Amino acids (B) L-Phenylalanine (phala), L-proline (pro), L-Threonine (Thr) and Glycine (gly)] determined by Irving-Rossotti titration technique in

60% (v/v) (NaClO4) ionic strength, in the present Investigation five/six membered rings are formed due to co-ordination of metal with ligands and value of log K shows the preferential formation of ternary complexes.

MATERIAL AND METHODS

Simple and Halogen substituted phenols are starting materials for preparation of primary ligands and were prepared by Fries-migration reactions. Primary ligands are 1) 3-chloro, 2-hydroxy-propiophenone [L_1], 2) 2-Hydroxy propiophenone [L_4]. All these ligands are 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) and its purity are checked by T.L.C., M.P. and organic tests.

Stability constant of these ligands are 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.

- 2ml of free $HClO_4$[0.5M]
- Mixt.(a)+10ml 0.01M pri.lig.
- Mixt.(b)+2ml0.01MCu(II).
- Mixt.(a)+10ml 0.01M Sec.lig.
- Mixt(d)+2ml 0.01M Cu(II)
- Mixt (b) + 10ml 0.01M sec. lig + 2ml 0.01M Cu(II)

The ionic strength of above solutions was maintained at 0.1M with the help of 1M NaClO4 solution and total volume of solution was made 50ml.

RESULT AND DISCUSSION

Proton-ligand and Metal ligand equilibria

The determination of proton-ligand stability constant was carried and verified by least-square method. Primary ligand contains only-one replaceable hydrogen atom hence only-one pK value is observed. The acid-ligand curve deviates from acid-curve Indicating the deprotonation or phenolic-OH group in this pH range. and from this curve the values of n_A for various pH curve calculated and found to be in the range 0.2 to 0.8 Indicating formation of only-one pk for each primary ligand. pK values calculated by point-wise and Half- integral method were founds to be in good agreement..

The displacement of metal titration curve along volume axis indicate the formation of complex species and lie in the pH region, where hydrolysis is not expected, the probability of formation of poly-nuclear complex was ruled out as the metal concentration were very

dilute. Proton ligand and Metal-ligand stability constant of 3-Cl-2HP are given in table (1).
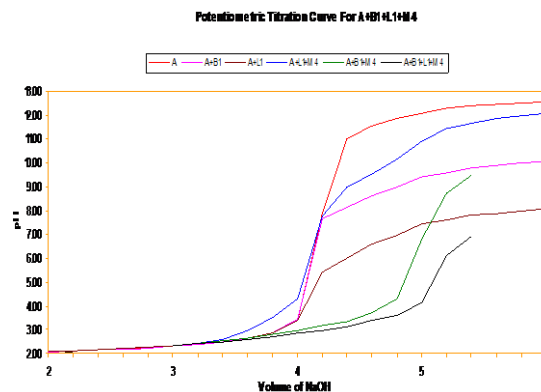

Fig.1:

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	L_1	Logk_1	Logk_2	7.2903	6.8166	6.9963	7.1222	7.1544
		Log B		5.8608	5.3957	5.3925	5.7171	5.6283
				13.1111	12.2123	12.3888	12.8394	12.7827
8.6969	L_2	LogK_1		8.0937	8.2227	8.1182	8.12	.8.1508
		LogK_2		7.3798	7.3205	7.4531	7.484	7.3705
		LogB		15.4735	15.5432	15.5713	15.604	15.5213

The stability constant of bivalent metal complexes derived from similar type of ligands generally follow the Irving Williams order. The present complexes follow the order of stability as

L_1 = Mn > Cu > Zn > Ni> Co.
L_2 = Cu > Ni > Co > Zn > Mn.

[Cu-L-B]Complex formation Equilibria

Complex formation equilibria of Cu(II) with the 3-Cl-2 HP and amino-acids [sec. ligand]starts at PH values much lower than the PH range of metal-ligand equilibria. Therefore the formation equilibria of mixed- ligand complexes with these ligands and 1:1:1 ternary complex is formed by simultanous equilibrium.

The preferential formation of ternary complexes over binary complexes has been discussed in terms of equilibrium constant. The complexation of mixed-ligand complex system of Cu (II) involves the following possible equilibia.
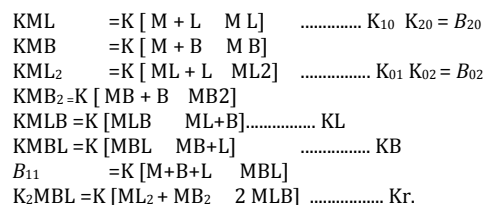
KML $= K [M + L \quad M L]$ .... $K_{10} \ K_{20} = B_{20}$
KMB $= K [M + B \quad M B]$
KML$_2$ $= K [ML + L \quad ML2]$ .... $K_{01} \ K_{02} = B_{02}$
KMB$_2 = K [MB + B \quad MB2]$
KMLB $= K [MLB \quad ML+B]$................ KL
KMBL $= K [MBL \quad MB+L]$ .... KB
B_{11} $= K [M+B+L \quad MBL]$
K$_2$MBL $= K [ML_2 + MB_2 \quad 2 MLB]$ .... Kr.

Table.2: Equilibrium Constant Values of Cu (II) – L1 - B

L –B	B11	B20	B02	KL	KB	Kr	log k
L-Phala	13.627	16.46	12.83	6.504	5.119	0.878	1.999
L-Thr	13.07	416.54	12.83	4.570	0.805	0.805	2.500
L – Pro	12.995	14.14	12.83	4.491	4.491	0.930	1.749
L- Gly	12.020	14.16	12.83	3.515	3.515	0.7934	2.499

The stability constant of ternary complexes are calculated by using 'SCOGS' computer programme and values are given in table (2)

The stability constant of ternary complexes are expressed in two ways (1) characterization of ternary complex by its disproportion constant of the reaction.

$$ML_2 + MB_2 = 2 MLB.$$
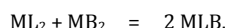
The disproportion reaction is for the system containing ligands which forms 1:1 and 1:2 complexes Individually with Cu(II) and (2) The difference of stability constant between binary and ternary complexes i.e. 10gk

$$logk = log KML_2 - log kML_1$$

Generally log KML$_1$> log KML$_2$; because more co-ordination positions are available for binding first ligand to metal ion. than second ligand i.e. Δ10gk values are negative.

The negative values of logk obtained in the present investigation indicate that primary and secondary ligands forms 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.]

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

L_1= L - Phala > L - pro > L - Thre > Gly.
L_2= L - Pro > L - phala > Gly > L - Thre

Complex formation equilibria have been elucidated on the basis of the concentration species curve fig- (1) of the complexes obtained as computer outputs.

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

CONCLUSION

In the present investigation, all these complex systems contains five membered ring on the one side with amino-acids. And six membered ring on other side with primary ligand.

REFERENCES

1. Bleck M.T. "The determination of complex equilibria," d-van Norstrand C. Inc. N.Y. Chapt- 8 (1969).
2. Aimarin I.P and Sheleksha K.I.Pure applied Chemistry, 21, 4461 (1970).
3. Lioyd L.E, Mc-Donald B.E and Grampton E.W fundamentals of nutrion 1978.
4. Lucassen M.and Sarkar B.J Toxical Envirn Health ,5,(1979)879.
5. Sigel H, Angew Chem. Int. Ed. Engl.1975, 14,394.
6. Mukhergee G.N.and Chakraborty P.K. J.Ind. Chem. Soc. Vol. 78, 2001,(565-571)
7. Ramamoorthy W and Manning P.N. J .Inorg. Chem. 9, 1259, (1970).
8. Irving H and Rossotti H.S. J.Chem.Soc 3397 (1953); 2904 (1954), Chidambaram M.V and Bhattacyarya M.V. J. Inorg. Nucl. Chem. 39, 2471 (1970).
9. Sigel H. IUPAC.Co-ordination chemistry 20, Banerjia, pergamon N.Y. (1980)
10.Martell A.E. Stability constants, special publications of chemical society.
11.Sayee I.G., Talanta, 1968, 15, 1397.
12.Irving H.M and Rossotti H.S. J. Chem. soc. 1954, 2904 (1977)