Int. J. Chem. Sci.: 5(2), 2007, 785-790

EQUILIBRIUM STUDIES ON MIXED LIGAND COMPLEXES OF Cu (II) AND Fe (III) WITH SULPHUR CONTAINING LIGANDS AND AMINO ACIDS – A POTENTIOMETRIC STUDY

A. M. ZINE and H. B. NAGRE[a]

Department of Chemistry, R. B. Attal College, GEORAI, Dist Beed - 431127 (M. S.) INDIA
[a]Department of Chemistry, Vivekanand College, AURANGABAD – 431001 (M.S.) INDIA

ABSTRACT

The stability constants of mixed ligand complexes of sulphur containing ligands and amino acids with Cu (II) and Fe (III) have been studied by pH titration method at 26 ± 0.5°C and ionic strength 0.1M ($NaClO_4$). The sulphur containing ligand was thiomalic acid (TMA) and amino acids were glycine (gly), alanine (ala), and valine (val). The preferential formation of ternary complexes over binary complexes has been discussed in terms of the equilibrium constants.

Key words: Copper (II), Iron (II), Thiomalic acid, Amino acid, Complex

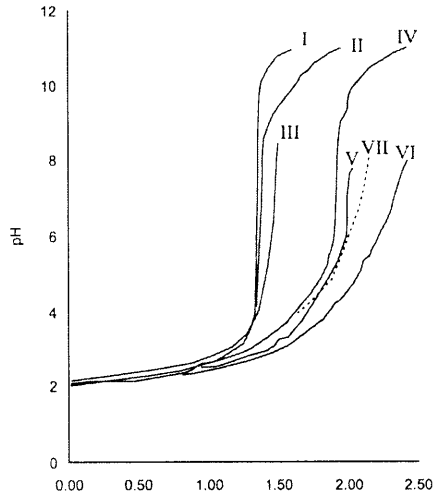
INTRODUCTION

The Cu (II) complexes of thiocompounds have been reported to be biologically active[1]. In trace amounts, copper is essential for life but even in moderate low concentration, it causes emesis and gastrointestinal irritation. The action of copper is due to its affinity for sulphydryl group[2]. About 98 % of the copper in normal human blood plasma is present as ceruloplasmin, a blue colored copper containing enzyme. Ceruloplasmin has direct effect on the availability of iron for synthesis of hemoglobin and other essential iron proteins[3]. The deficiency of ceruloplasmin is associated with Wilson's disease caused by accumulation of copper in brain and liver. The copper requiring enzyme tyrosinase catalyses the conversion of amino acid tyrosine to melanin pigments. This pigment shields the body from damaging ultraviolet radiation[4].

The chlorosis is caused by iron deficiency. Iron proteins are of different types and perform various functions like reversible oxygen binding for its transportation (by hemoglobin), its storage (by myoglobin), and reduction of H_2 to H_2O (by cytochrome C) and decomposition of H_2O_2 (by peroxidase). It is interesting to study the ternary complexes

of biologically active elements like Cu (II) and Fe (III) with sulphydryl group containing ligands like TMA and amino acids. In the present investigation, the same study is carried out. In sulphydryl compounds, the chemical equilibria is determined by soft character[5] of mercaptosulphur atom. Through the sulphdryl group, these compounds can participate in both acid-base and redox reactions[6].

EXPERIMENTAL



I	Acid
II	Acid + Glycine + Cu (II)
III	Acid + TMA + Cu (II)
IV	Acid + Glycine + TMA + Cu (II)
V	Acid + Glycine
VI	Acid + TMA
VII	Composite curve

Fig. 1. Cu (II) – TMA – glycine system

The ligands TMA, (Sigma), gly, ala, val (Sd fine) were used (AR grade). The ligands were purified by crystallization and their purity was checked by their melting points. The solutions of these were prepared in double distilled water. The copper ion solution was prepared by dissolving requisite amount of AR grade copper nitrate in glass distilled water and standardized using EDTA[7]. Details regarding other chemicals are described in earlier paper[8].

The measurements were carried out at 26 ± 0.5°C and ionic strength was maintained to 0.1 M with the help of sodium perchlorate. The pH measurements were carried out with ELICO digital pH meter model LI 120 with combined glass electrode having pH range 0 – 14. The experiments were carried out in an inert atmosphere by bubbling oxygen free nitrogen gas through out the course of titration. The stability constants were determined by Bjerrum's pH titration technique as modified by Irving and Rossotti[9]. Experimental titrations are graphically shown in Fig. 1

RESULTS AND DISCUSSION

The TMA is terdentate ligand. The TMA contains two carboxylic groups and a sulphydryl group. There are three proton ligand stability constants for thiomalic acid. The amino acids are bidentate ligands having carboxylic and amino groups. The proton ligand and metal ligand stability constants of Cu (II) and Fe (III) chelate are calculated by Irving and Rossotti method[10] and are presented in Table 1. The TMA forms 1 : 1 and 1 : 2 complexes with Cu (II) and Fe (III) in the pH range 2.00 to 6.25 and 2.50 to 6.50, respectively, while gly, ala, and val forms the 1 : 1 and 1 : 2 complexes with copper ion in the pH range 3.80 to 6.10 and with iron ion in the pH range 2.20 to 6.25. The glycine like binding mode[11] results in the five membered rings. In all these complexes, the copper and iron forms five membered chelate rings which are more stable because such rings cause less strain to molecules[12]. In metal chelate, TMA coordinates the metal ion through sulphur of sulphydryl and oxygen of carboxylate group while amino acid coordinates through oxygen of carboxylate group and nitrogen of amino group[13].

Table 1. Proton ligand stability constants and metal ligand stability constants

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

Ligand	$LogK_1^H$	$LogK_2^H$	$LogK_3^H$	$LogK_1^{Cu(II)}$	$LogK_2^{Cu(II)}$	$LogK_1^{Fe(III)}$	$LogK_2^{Fe(III)}$
TMA	10.50	4.0	3.20	13.48	7.41	12.18	7.08
Gly	9.56	2.40	-	8.18	6.65	10.22	9.34
Ala	9.63	2.4	-	8.09	6.78	10.24	9.59
Val	9.50	2.36	-	8.41	6.77	10.18	9.36

In the titrations of mixed ligand system against standard sodium hydroxide, the following equilibria are possible.

REFERENCES

1. H. Sigel, "Metal Ions in Biological Systems", Marcel Dekker Inc., New York, (1973) 2nd Ed. (1976) p. 25, 250.
2. D. Banerjea, "Coordination Chemistry", Tata McGraw Hill Publishing Company Ltd., New Delhi (1994) p.397.
3. D. Banerjea, "Coordination Chemistry", Tata McGraw Hill Publishing Company Ltd., New Delhi (1994) p.363.
4. D. Banerjea, "Coordination Chemistry", Tata McGraw Hill Publishing Company Ltd., New Delhi (1994) p.391.
5. R. G. Pearson, "Coordination Chemistry Review", **103**,403 (1990)
6. J. E. Huhee, E. A. Kaifer and R. L. Kaifer, "Advanced Inorganic Chemistry" Collins, New York (1993).
7. H. A. Flascha, "EDTA Titrations" Pergamon Press, Oxford (1965).
8. A. M. Zine, Int. J. Chem. Sci., **3(2)**, 295 (2005).
9. H. Irving and H. S. Rossotti, J. Chem. Soc., 3397 (1953); M. V. Chidambaram and P. K. Bhattacharya, J. Inorg. Nucl. Chem., **39**, 2471 (1970).
10. H. M. Irving and H. S. Rossotti, J. Chem. Soc., 2904 (1954).
11. M. S. Nair and M. A. Neelkantan, Indian J. Chem., **38A**,194 (1999).
12. Kamlesh Bansal, "Coordination Chemistry", Campus Book International New Delhi (2000) p.122.
13. Yoshuko Funae, Nobuo Toshioka, Itaru Mita, Teruo Sugihara, Tetsuya, Yukio Nakamura and Shinichi Kawaguchi, Chem. Pharm. Bull., **18(8)**, 1618 (1971).
14. A. E. Martell, "Stability Constants" Special Publication of Chemical Society.
15. M. S. Balkrishnan and M. Santappa, J. Inog. Nucl. Chem., **36**, 3813 (1974).
16. M.S. Balkrishnan and M Santappa, J. Inog. Nucl. Chem., **37**, 1229 (1975).
17. Y. Marcus, I. Eliezer and M. Zangen, Pro. Symp. Coord. Chem., Tihany, Hungary 409 (1964). Budapest (1965).
18. Y. Marcus and I. Eliezer, J. Phy. Chem., **66**, 1661 (1962).

Accepted : 10.01.2007