Asian Journal of Chemistry Vol. 18, No. 4 (2006), 3114–3116

NOTE

Potentiometric Studies of Some Ternary System of Cu(II) Complexes-with-Picolinic Acid and Some Amino Acids

AYESHA DURRANI*, MAZHAR FAROOQUI,
SIDDHARTHA PAKHARE, SIDDIQUI NAUSHEEN and AHMED ZAHEER†
Aurangabad College for Women, Aurangabad-431 001, India.

The proton-ligand stability constants and stability constants of binary and ternary system of Cu(II) with picolinic acid, L-serine, tyrosine, threonine and phenylalanine have been studied potentiometrically at 25 ± 0.5°C and μ = 1.0 M ($NaClO_4$) in aqueous medium. The mixed ligand chelates are shown to have formed in simultaneous equilibria. Cu(II) forms 1 : 5 : 5 complexes with all chelating agents.

Key Words: Cu(II), Ternary, Complexes, Picolinic Acid, Amino Acids.

The determination of stability constant is a paramount important in the knowledge of chelate as it enables to calculate the equilibrium concentration. The value of the stability constant facilitates the formation condition for complete formation of given metal-chelates. The stability of the metal-complex increases with increase in basicity of ligands substituted group may purely due to its steric affect[1–3] prevents the ligand ion from acquiring the orientation about the central metal ion[4, 5] most favourable to chelation. Metal ions play important role in the formation of stable complexes is of interest to the analytical chemists[6] and to bio-inorganic researchers[7].

The ligand picolinic acid, L-serine, tyrosine, threonine and phenylalanine were of analytical grade and obtained from Sd-fine chemicals. The Cu(II) metal of sigma chemical company USA. Sodium hydroxide, sodium perchlorate and perchloric acid of AnalaR quality were of Sd-fine Chemicals Ltd. All solutions were prepared in doubly distilled water.

The pH-metric measurements were carried out by using LI-612 ELICO India (accuracy ± 0.01pH unit). All the titrations were carried out in an insert atmosphere which was obtained by bubbling oxygen free nitrogen gas through the solution. The ionic strength was maintained at μ = 1.0 M ($NaClO_4$) at 25 ± 0.5°C.

Calculations : The stability constants and protonation and metal-ligand stability constants were calculated. The accurate values of log k_1^H were determined

†Maulana Azad College, Aurangabad-431 001, India.

by the point-wise calculations. For present work the determination of stability constant the concentration of the total (first and second) free ligand and the value of metals were calculated by the following expression obtained by the modification of Thompson and Loraas method[8].

$$X = 1 + \frac{2[H^+]^2}{K_1K_2 + K_1'K_2'} \cdot \frac{[H^+]}{K_2 + K_2'}$$

$$A = \frac{\{2T_X^o + 2T_Y^o + P - T_{OH} - [H]\}}{4[H]^2 2[H]}$$

$$\frac{(K_1K_2) + (K_1'K_2')(K_2 + K_2')}{}$$

$$K_{MXY} = \frac{(1/2)T_X^o + 2T_Y^o) - \{[A] - X\}}{T_M^o - [(1/2)(T_X^o + 2T_Y^o) - \{[A] - X\}\{(1/4)(A)^2 \cdot X\}}$$

$$\Delta \log K_{MXY} = \log K_{MXY} + \log K_{MXY}/2$$

For the present trend Cu(II) forms 1 : 5 complexes with all the ligand. The mixed-ligand complexation of Cu(II) with Picolinic acid as a primary ligand and other amino acids as the secondary ligand studied in the 1 : 5 : 5 ratio. When a metal forms a series of step-complexes with the ligand step-stability constant is found, as one possess from lowest to the highest Co-ordination number. The stability constants lies in the range of 5.00–7.00. Malhotra *et al.*[9] and Kumar[10] have investigated the kinetic and mechanism of complexation of Cu(II) with a number of amino acid and related biologically important ligands. The protonation constant and stability constant given in Table 1.

TABLE-1
PROTONATION CONSTANTS

Ligands	Log k_1^H	Log k_2^H	Cu(II)
Picolinic acid	5.0443	–	5.0220
Phenylalanine	10.9584	8.8356	3.0879
Threonine	10.9575	8.5451	3.9707
Tyrosine	10.5961	8.8453	2.6899
L-Serine	10.8805	8.3450	3.4291, 3.8136

The ternary complexes serve as useful models for many biological reactions. A connection between metal-chelation and at least types of cancer was suggest by Furst[11] and Schubert observed that metal-chelation apparently play a definite role in the case and treatment of malignancy[12]. A considerable number of metal-complex compound are now known to possess anti-tumour activity[13–17], the mixed-ligand complexes are generally more stable than the corresponding binary system. In present study we observed an increasing trend in the log K_{MXY} value of metal-ligand chelation.

TABLE-2
STABILITY CONSTANT OF MIXED LIGAND COMPLEXES

Metal ion	Mixed-ligand system	Log K_{MXY}	Δ logK
Cu(II)	P. A- Phenylalanine	3.6092	–4.5009
	P. A- Threonine	5.3859	–3.6069
	P. A- Tyrosine	5.6466	–2.0653
	P. A- L-Serine	5.1593	–3.2918

The titration curves were carefully analyzed for the possibility of protonation of NH group. All the chelates formed in simultaneous equilibria by taking M : X : Y in the ratio of 1 : 5 : 5 (M≠X = Y). the log K_{MXY} of all the ternary and chelates were determined by Loraas and Thomson method in the pH region where there was a maximum difference between composite curve and mixed-ligand titration curve. For the ternary system log K value are negative indicating that the primary ligand anions and the secondary ligand anions preferentially form mixed-ligand complexes.

REFERENCES

1. W.D. Johnson and Freiser, *Anal. Chim. Acta,* **11**, 201 (1954).
2. L. Merrit and Walker, *Ind. Eng. Anal. Edn.*, **18**, 387 (1944).
3. Irving, Butler and M.F. Ring, *J. Chem. Soc.*, 1489 (1948).
4. J.G. Breckenridge, R.W.J. Lewis and L.A. Quick, *Con. J. Res.*, **B-17**, 258 (1939).
5. C.F. Smith and W.M. Mecurdy, *Anal. Chem.*, **24**, 371 (1952).
6. I.P. Alimarin and V.I. Sheleskaya, *Pure. Appl. Chem.*, **21**, 461 (1970).
7. M.T. Beck-"The Determination of Complex Equilibria" D. Van Nostrand Co, Inc, NY, (1969).
8. L.C. Thompson and Loraas, *Inorg. Chem.*, **2**, 89 (1963).
9. H.C. Malhotra and J. Parkash, *Proc. India. Natl. Acad.*, **50**, 38, 46 (1984).
10. A. Kumar, *Indian J. Chem.*, **35A**, 999 (1994).
11. A Furst, Chemistry of Chelation in Cancer, Spring Field, 111 ions (1963).
12. J. Schubert, *Sci. Am.*, **214**, 40 (1966).
13. B. Rosenberg, *Platinum Metals Rev.*, **15**, 42 (1971).
14. D.R. Williams, *Chem. Rev.*, **72**, 203 (1972).
15. M.J. Cleare, *Coord. Chem. Rev.*, **12**, 349 (1974).
16. A. Khan, *J. Clin. Haemotolog. Oncol,* **7**, 1 (1977).
17. B. Rosenberg, *Biochim.*, **60**, 859 (1978).

(*Received*: 18 January 2005; *Accepted*: 2 May 2006) AJC-4852