Asian Journal of Chemistry Vol. 20, No. 7 (2008), 5621-5624

Stability Constants of Ternary Complexes of Cu(II) and Ni(II) With N-Substituted Anthranilic Acids with Some Amino Poly Carboxylic Acids

B. Krishna Rao†, K. Laxmi and Ch. Sarala Devi*
Department of Chemistry, Nizam College, Osmania University
Hyderabad-500 001, India
E-mail: dr_saraladevich@yahoo.com

Potentiometric titrations were carried out for the formation of binary and ternary complexes of the type MA, ML and MAL where M = Cu(II) and Ni(II), A = iminodiacetic acid (IMDA), hydroxyiminodiacetic acid (HIMDA) or nitrilotriacetic acid (NTA) and L = N-methyl anthranilic acid (N-Me.An.A.), N-butyl anthranilic acid (N-Bu.An.A.) or N-phenyl anthranilic acid (N-Ph.An.A.) at 303 K and 0.1 M ionic strength in 50 % (v/v) ethanol-water medium. The stabilities of the ternary metal complexes have been quantitatively compared with the stabilities of the corresponding binary metal complexes determined under identical experimental conditions and expressed in terms of Δ log K. The Δ log K values calculated for all the systems indicate the extent of stabilization and destabilization of ternary chelates compared to their binary chelates. The order of stability constants of ternary systems with respect to polyamino carboxylic acids is found to be IMDA > HIMDA > NTA. These were explained in the light of their basicities, charge neutralization and electrostatic interactions.

Key Words: Stability constant, Ternary complexes, N-Methyl anthranilic acid, N-Butyl anthranilic acid, N-Phenyl anthranilic acid.

INTRODUCTION

The stability constants of the ternary complexes of Cu(II) and Ni(II) with N-X-anthranilic acids (X = methyl, butyl and phenyl) and amino polycarboxylic acids *i.e.* IMDA, HIMDA and NTA are reported in this communication.

---

†Department of Chemistry, University College of Engineering, Kakatiya University, Warangal-506 009, India.

EXPERIMENTAL

All the chemicals used were of AR Grade. Iminodiacetic acid (IMDA), hydroxyiminodiacetic acid (HIMDA) or nitrilotriacetic acid (NTA) were obtained from Sigma Chemical Company. N-methyl, N-butyl and N-phenyl anthranilic acids were prepared by known methods[1,2] in laboratory. The solutions were prepared in doubly distilled water. The ligand solutions were prepared in ethyl alcohol. The metal ion solutions were standardized volumetrically by known methods[3]. Carbonate free potassium hydroxide was prepared and standardized with standard potassium hydrogen phthalate. The experimental method consisted of potentiometric titrations of N-substituted anthranilic acids with Cu(II) and Ni(II) in presence of other ligand *viz.*, IMDA, HIMDA and NTA at 303 K and 0.1 M ionic strength against standard KOH solution. The acid dissociation constants of ligands and stability constants of binary chelates were calculated by Irving Rossotti method[4], while stability constants of ternary chelates by Santhappa and Ramamurthy method[5] under the present experimental conditions. These values were further refined by using Best Computer Program[6].

RESULTS AND DISCUSSION

The stability constants have been determined potentiometrically in 50 % (v/v) ethanol-water medium at 303 K and 0.1 M ionic strength. The dissociation constant values and stability constant values of binary and ternary systems are presented in Table-1.

TABLE-1
STABILITY CONSTANTS OF BINARY AND TERNARY METAL COMPLEXES OF N-SUBSTITUTED ANTHRANILIC ACIDS AT 303 K AND 0.1 M IONIC STRENGTH IN 50 % (v/v) ETHANOL-WATER MEDIUM

System	Cu(II)		Ni(II)	
	log K	Δ log K	log K	Δ log K
N-Me.An.A	3.94	–	3.14	–
N-Bu.An.A	4.25	–	3.22	–
N-Ph.An.A	3.03	–	3.03	–
IMDA-N-Me.An.A	3.01	-0.93	2.48	-0.66
IMDA-N-Bu.An.A	3.11	-1.14	2.50	-0.72
IMDA-N-Ph.An.A	2.68	-0.35	2.37	-0.66
HIMDA-N-Me.An.A	2.92	-1.02	2.38	-0.76
HIMDA-N-Bu.An.A	3.02	-1.23	2.44	-0.78
HIMDA-N-Ph.An.A	2.40	-0.63	2.26	-0.73
NTA-N-Me.An.A	2.83	-1.11	2.19	-0.95
NTA-N-Bu.An.A	2.91	-1.34	2.30	-0.92
NTA-N-Ph.An.A	2.30	-0.73	2.17	-0.86

N-Me.An.A = N-methyl anthranilic acid, N-Bu.An.A = N-butyl anthranilic acid, N-Ph.An.A = N-phenyl anthranilic acid.

The ternary complex formation is inferred from the non-superimpossibility of theoretical composite curve on the experimental curve in the region of mixed ligand complex formation. This was further confirmed by the shift in the pH of precipitation in ternary system compared to corresponding binary system.

The ternary curve in all the systems studied closely follow the 1:1 M-IMDA/HIMDA/NTA binary curve in the lower pH region until the protons of ligand are neutralized. This implies that these ligands act as primary ligands (A) in the corresponding systems and form binary complexes in the first step. The divergence of the ternary curve (MAL) from the 1:1 binary curve (MA) after the formation of primary metal chelate (MA), reveals the interaction of secondary ligand (L) *viz.*, N-X-anthranilic acids (X = methyl/butyl/phenyl) in the second step to form corresponding ternary complex of the type (MAL), following step wise equilibria (eqns. 1 and 2). This was further confirmed by the pH ranges of complexation of M-L and M-A systems which vary considerably to favour the stepwise equilibrium.

$$M + A \rightleftharpoons MA \qquad \text{(Charges omitted)} \qquad (1)$$

$$MA + L \rightleftharpoons MAL \qquad (2)$$

It is found that the order of stabilities of ternary chelates with respect to primary ligands follows the order: IMDA (H_2A) > HIMDA (H_2A) > NTA(H_3A). This may be due to the role of electrostatic factors during the formation of ternary chelates[7-10]. In the case of IMDA and HIMDA systems, these ligands bind with metal ion (M^{2+}) by dissociation of two protons resulting in a neutral chelate in their respective systems, which in turn react with secondary ligand (HL) to form a mono negative ternary metal chelate $(MAL)^-$. Where as in the case of NTA, it being a ligand with three dissociable protons (H_3A) results in the formation of mono negative $(MA)^-$ primary chelate in the first step. The interaction of mononegatively charged primary chelate with secondary ligand (HL) in subsequent step would lead to the formation of doubly negatively charged ternary chelate $(MAL)^{2-}$. As charge repulsions are more for the formation of ternary chelates of NTA, the stabilities in these systems are relatively low as compared to other two systems studied. Such an observation would lead to the conclusion that the charge neutralization and charge repulsive forces influence the stability of ternary complexes.

The Δ log K values in ternary chelates with IMDA are less negative compared to other systems. These trends can be explained on the basis of steric factor[11-15]. The less bulky IMDA will have least steric hindrance compared to HIMDA and NTA resulting in the formation of more stable ternary complexes in solution.

The order of stability of ternary chelates with respect to N-substituted anthranilic acids were found to be N-butyl anthranilic acid > N-methyl anthranilic acid > N-phenyl anthranilic acid. This is in accordance with their basicity order, the higher the basicity of the ligand the greater is the stability of the metal complex. The substitution of methyl group by a more bulky group like phenyl on the nitrogen atom of the ligand not only causes more steric hindrance but also decrease the basicity of ligand because of mesomeric effect. The higher stabilities in N-butyl anthranilic acid systems than those in N-methyl anthranilic acid systems may be due to the inductive effect of butyl group, which increases the electron density on nitrogen atom.

The order of relative stability with respect to metal ion is Cu(II) > Ni(II). The higher order of stabilities of Cu(II) complexes may be ascribed to the orbital stabilization due to John-Teller distortion and the better π-donor capacity of Cu(II) as compared to other metal ions.

Stability constants of ternary chelates are lower than those of the binary systems, resulting in negative Δ log K values[16-19]. Such a lowering of stabilities of ternary complexes compared to that of binary chelates may be due to the greater destabilization effect, caused by the ligand repulsion in the ternary complexes than that in the binary systems, coupled with the availability of lesser number of coordination sites of metal in (M-A) than in the free metal ions.

REFERENCES

1. P.A. Petyunin, V.S. Shkiyaav and M.E. Konshin, *Zhur Priklad Khim*, **33**, 1428 (1960).
2. C.F.H. Allen and C.H.W. MacKee, *Org. Synth.*, **19**, 16 (1939).
3. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, Longman, London, edn. 3, p. 160 (1971).
4. H.M. Irving and H.S. Rossotti, *J. Chem. Soc.*, 2904 (1954).
5. S. Ramamoorthy and M. Santhappa, *J. Inorg. Nucl. Chem.*, **32**, 1623 (1970); *Indian J. Chem.*, **9**, 30 (1971).
6. R.I. Motekaitis and A.E. Mantell, *Can. J. Chem.*, **60**, 2403 (1982).
7. H. Sigel, *Angew Chem. Int. Ed.*, **14**, 394 (1975).
8. P.K. Bhattacharya, *J. Scient. Ind. Res.*, **40**, 382 (1981).
9. B. Pullman, Molecular Association in Biology, Academic, New York (1968).
10. E. Parkar et al., *Z. Naturforsch.*, **B34**, 208 (1979).
11. H.A. Scheraga, *Acc. Chem. Res.*, **12**, 7 (1979).
12. L.D. Petit and R.J.W. Helford, *Med. Ions Biol. Sys.*, **9**, 173 (1979).
13. C. Tanford, The Hydrophobic Effect, Wiley Inc., New York (1973).
14. E. Beda, B.F. Fischer and H. Sigel, *J. Am. Chem. Soc.*, **23**, 2998 (1980).
15. H. Sigel, *Acc. Chem. Res.*, **3**, 201 (1970).
16. Ch. S. Devi and M.G.R. Reddy, *Indian J. Chem.*, **25A**, 600 (1986).
17. B.K. Rao, S. Raj, Kashiram and M.G.R. Reddy, *Indian J. Chem.*, **26A**, 1076 (1987).
18. Ch. V.R. Reddy, Ch. S. Devi and M.G.R. Reddy, *Indian J. Chem.*, **30A**, 385 (1991).
19. C. Sita, V.K. Mohan, Ch. S. Devi and M.G.R. Reddy, *Indian J. Chem.*, **30A**, 526 (1991).

(*Received*: 31 October 2007; *Accepted*: 20 May 2008) AJC-6585