

**NOTE****Mixed-Ligand Complexes of Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup> with 2,2'-Bipyridine as a Primary Ligand and DL-2-Aminobutanedioic Acid as Secondary Ligand**SHARDA SONI<sup>\*</sup>, MANU SIKARWAR<sup>†</sup> and AVNISH SHARMA<sup>‡</sup>

Department of Chemistry, Swami Keshvanand Institute of Technology, Jaipur-302 025, India

E-mail: sonidn9@yahoo.co.in

Modified form of Irving-Rossotti titration technique has been applied to study the formation constants of mixed ligand complexes of the type MAL where M = Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup> or Zn<sup>2+</sup>; A = bipyridyl and L = DL-2-aminobutanedioic acid at 30 °C ( $\mu = 0.1$  M). The values of the formation constants obtained in the mixed ligand system are little less than first formation constant of M-L simple systems.

**Key Words:** Mixed-Ligand complexes, 2,2'-Bipyridine, DL-2-Aminobutanedioic acid.

The study of mixed ligand complexes is receiving considerable attention for about past two decades<sup>1-8</sup>. Systems where two ligands successively combine in steps at different pH ranges have also been investigated in the last twenty years<sup>9-12</sup>. The work describe here relates to the study of mixed-ligand complex formation of some bipoisitive metal ions *viz.* Cu, Ni, Co and Zn with 2,2'-bipyridyl as primary ligand and DL-2-aminobutanedioic acid as secondary ligand by pH metric titration techniques<sup>13-15</sup>. The necessary condition for such mixed ligand system is that M (Bipy), 1:1 complex formed at low pH should be stable at higher pH where the secondary ligand gets coordinated.

DL-2-aminobutanedioic acid (ABDA) was supplied by BDH Poole, England. Other reagents used were also of AnalaR BDH grade. All solutions were prepared in double distilled water. The pH measurements were carried out on an EC digital pH meter. The titrations were carried out at 30 °C using a constant temperature bath ( $\pm 0.1$  °C).

The following solutions were prepared (total volume 25 mL) for titration in case of mixed ligand system.

- (A) = 0.004 M HClO<sub>4</sub> + 0.1 M NaClO<sub>4</sub>; (B) = (A) + 0.001 M Bipy  
(C) = (B) + 0.001 M M<sup>2+</sup> (metal salt solution); (D) = (A) + 0.001 M ABDA  
(E) = (C) + 0.001 M ABDA

<sup>†</sup>Department of Chemistry, Government Post Graduate College, Tonk-304 001, India.

<sup>‡</sup>Department of Chemistry, M.L.V. Government Post Graduate College, Bhilwara-311 001, India.

Each of the above samples were titrated against 0.1 M NaOH. A typical graph of pH against volume of alkali has been plotted for Cu-Bipy-ABDA (1:1:1) system and is given in Fig. 1. Other systems for Ni<sup>2+</sup>, Co<sup>2+</sup> and Zn<sup>2+</sup> gave similar type of graph. The formation curves of M<sup>n+</sup>-Bipy-ABDA system are given in Fig. 2.

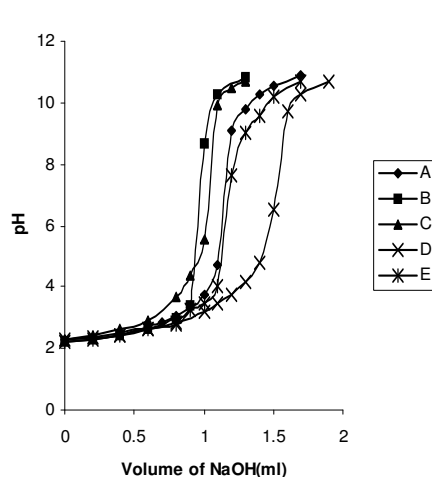


Fig. 1. Titration curves at 30 °C ( $\mu = 0.1$  M NaClO<sub>4</sub>) Cu<sup>2+</sup>-Bipy-ABDA system

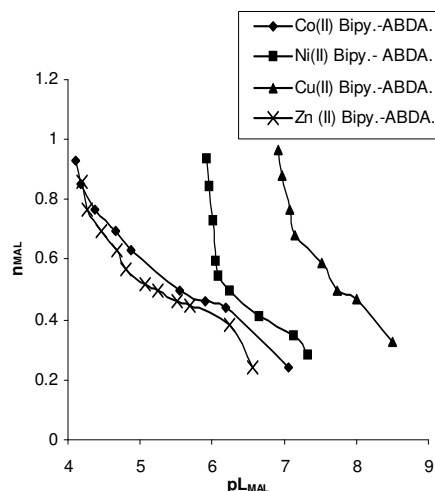


Fig. 2. Formation curves of M<sup>2+</sup>-Bipy-ABDA system

It has been observed that primary complex curve C diverges from the Bipy Curve B in the pH range at about 2 and onwards. The metal-Bipy 1:1 complex formation is complete at pH 4.0 and it forms hydroxo complex at pH about 8.0. Primary complex curve C and ternary complex curve E however overlap at lower pH which indicates that ABDA does not combine with metal ion where primary complexation takes place. However, curve E diverges from curve C after pH 3-4 suggesting the coordination of ABDA with primary complex, since the dissociation of primary complex does not take place in the pH range 4-8. It can be considered that ABDA combines with species [M(Bipy)]<sup>2+</sup> just as it does with [M(aq.)]<sup>2+</sup> in simple system. As such the horizontal distance between the curve D and E can be used for the calculation of  $\bar{n}_{MAL}$ . The average number of ABDA molecules associated with one [M(Bipy)]<sup>2+</sup>, using the equation as derived by Irving-Rossotti.  $\bar{n}_{MAL}$  and PL<sub>MAL</sub> values were calculated at different points in the pH range 4-8 and at  $\bar{n}_{MAL} = 0.5$  in the formation curves PL<sub>MAL</sub> = log K<sub>MAL</sub>.

The log K values of different systems have been presented in Table-1.

It is interesting to observe that the value of K<sub>MAL</sub> is nearly equal to K<sub>ML1</sub> and greater than the K<sub>ML2</sub>. In case of ternary complexes, Bipy is a neutral molecule so concentration of electrons around the metal ion in (M-Bipy)<sup>2+</sup> is more than the concentration of electrons around the metal ion in [M(H<sub>2</sub>O)<sub>n</sub>]<sup>2+</sup>. Thus from the consideration of statistical factor K<sub>MAL</sub> should be significantly lower than the K<sub>ML1</sub>. The

TABLE-1  
STABILITY CONSTANTS OF BINARY AND TERNARY  
CHELATES AT  $30 \pm 0.1$  °C ( $\mu = 0.1$  M) IN AQUEOUS MEDIA

Cation	log $K_1$	log $K_2$	log $K_{MAL}$
Co <sup>2+</sup>	6.0532	4.4188	5.5415
Ni <sup>2+</sup>	7.0914	5.1677	6.2427
Cu <sup>2+</sup>	8.6833	6.7891	7.7364
Zn <sup>2+</sup>	5.9002	4.4905	5.2416

values of  $K_{MAL}$  is, however, expected to be higher than the  $K_{ML2}$ . This because Bipy being a neutral molecule, the incoming secondary ligand  $[L^-]$  has not to face any electrostatic repulsion while reacting with  $[MA]^{2+}$  however the incoming ligand has to face an electrostatic repulsion while reacting with  $[ML]^+$  due to already existing  $L^-$ . The extent of steric hindrance exerted by the Bipy molecule may, however, be more than that exerted by  $L^-$  ion. In the system studied log  $K_{MAL}$  is less than the log  $K_{ML1}$  but the difference is small, which can be attributed to the fact that in the Bipy molecule, two nitrogen atom forms  $\sigma$  bond with the metal ion, also the existence of a strong M-L  $\pi$  interactions due to the back donation of electrons from the metal 'd' orbitals to the vacant delocalized  $\pi$  orbitals over the Bipy molecule which does not allow concentration of electrons on the metal ion to increase significantly and the electronegativity of the metal ion in  $[M-Bipy]^{2+}$ . Therefore the values of  $K_{MAL} = K_{ML}$ . The order of stabilities of the complexes with respect to metal ion is  $Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$  which is the same as that in the corresponding binary ML system.

## REFERENCES

1. J. Ambwani and A. Taneja, *Asian J. Chem.*, **11**, 609 (1999).
2. R.L. De and K. Samanta, *Indian J. Chem.*, **39**, 1098 (2000).
3. A. Mohan, K. Radha and M.S. Mohan, *Asian J. Chem.*, **10**, 50 (1998).
4. S. Sharma, K.K. Saxena and R.S. Saxena, *J. Electrochem. Soc. (India)*, **37**, 3 (1988).
5. V. Agarwal and K.K. Saxena, *Acta Cien. Ind.*, **20C**, 4 (1994).
6. K.D. Gupta, S.C. Bahel and J.N. Gaur, *Monatshfte Fur. Chem.*, **110**, 657 (1979).
7. K.D. Gupta, S.C. Baghel, K.K. Choudhary and J.N. Gaur, *J. Indian Chem. Soc.*, **54**, 863 (1977).
8. R.M. Sathe, N. Mahadevan and S.Y. Shetty, *Indian, J. Chem.*, **6**, 755 (1968).
9. D.D. Parrin and V.S. Sharma, *J. Chem. Soc.*, 1755 (1967).
10. G.H. Carvey, R.F. Boucki and A.E. Martell, *Inorg. Chem.*, **3**, 12, 88 (1964).
11. T.A. Boligan Jr. and A.E. Martell, *J. Inorg. Nucl. Chem.*, **29**, 453 (1967).
12. G.A. L'Heureux and A.E. Martell, *J. Inorg. Nucl. Chem.*, **28**, 481 (1966).
13. M.V. Chidambaram and P.K. Bhattacharya, *J. Inorg. Nucl. Chem.*, **32**, 3271 (1970).
14. H.M. Irving and H.S. Rossotti, *J. Chem. Soc.*, 3397 (1953); 2904 (1954).
15. T. Wagner-Janregg, B.E. Hackley Jr., T.A. Lies, O.O. Owens and R. Proper, *J. Am. Chem. Soc.*, **77**, 929 (1955).