# Ionophoretic Study of Complexation Reactions of Mixed Ligand Complexes in Copper(II), Nickel(II), Zinc(II) and Cobalt(II)-Nitrilo-tri-Acetate-Benzoate Systems

C.S. PANDEY*, R.S. TRIVEDY, C.K. SINHA* and NEELAM KUMARI
*Department of Chemistry*
*S. Sinha College, Aurangabad-824 101, India*

Paper-electrophoresis is adopted for the study of the equilibria in mixed ligand complex system in solution. Here in addition to a constant concentration of a primary ligand, the background electrolyte (0.1M $HNO_3$) also contains nitrilo-tri-acetic acid (NTA) as a secondary ligand at fixed pH 8.5. The increasing amount of NTA is added to the background electrolyte and the movement of spot of the metal ions are measured under an influence of electric field. The graphs were plotted in log [benzoic acid] versus mobility, which furnish information of the formation of mixed ligand complex and to calculate its stability constant. The metal(II)-benzoate and metal(II)-nitrilo-tri-acetate binary systems have also been studied since they are a pre-requisite for the study of mixed ligand complexes.

## INTRODUCTION

Paper-electrophoresis has been devised[1–4] as a technique for the study of stepwise complexation reaction. The method seems to be well established in case of mono-nuclear complex as this technique has also been extended for the study of mixed complexes[5, 6] as well. In the present work we have studied the mixed ligand complexes in system of [Cu(II), Zn(II), Ni(II), Co(II)]-nitrilo-tri-acetic acid (NTA)-benzoate systems.

## EXPERIMENTAL

The paper-electrophoresis equipment consists of two PVC moulded tanks in which electrolyte is taken and two hollow metal plates covered with polythene plates have been used for maintaining the temperature by passing thermostated water. The whole assembly is placed in a wooden box covered with a glass plate at the top in order to prevent moisture change which upsets the equilbrium in the paper. This assembly design thus keeps to a minimum the disturbing effects of evaporation from the undesired liquid-flow in the paper.

Each electrode chamber contains a platinum wire throughout its length which serves as an electrode. The auxiliary unit is a specially designed one, which can be operated upon either voltage mode or on current mode. The voltage can be varied at different ranges, *viz.*, 0–100, 100–200 and 200–300 volts.

Sico-EMI Digital pH Meter M-EM5, having glass and calomel electrodes assembly and working on 220 volts/50 cycles stabilized A.C. mains, was employed for pH measurements.

Stock solutions of 5 M $HNO_3$, 2.0 M NaOH, 0.01 M benzoic acid were prepared from AnalaR samples (B.D.H.) and 0.01 NTA solution was prepared from a sample obtained from E. Merck (Darmstadt G.F.R.). The solutions were standardised by usual methods. 0.1 M $HNO_3$ was used as background electrolyte for studying binary systems and 0.01 M benzoic acid or 0.01 M NTA acid. In the study of ternary complexes 0.1M $HNO_3$ was used as background electrolyte and $10^{-2}$ M NTA or $10^{-2}$ M benzoic acid was used at pH 8.5 by the addition of NaOH solution.

The strips are marked with metal ions in duplicate along with additional strips marked with glucose. After passing current for 15 minutes to a moistened strip with background electrolyte, a current of 200 volts is passed through electrophoretic equipment for 1 h. The metal spots are detected by spraying 1-(2-pyridyl azo)-2-naphthol (PAN) indicator and their movements are measured. Again the pH of background electrolyte is varied and the movements of the ions are recorded for subsequent observations.

## RESULTS AND DISCUSSION

### (A) M-Benzoic acid binary systems

The graphical representation of over-all ionophoretic mobility with the change of pH is given in the Fig. 1. It is evident from the figures that two plateaus are

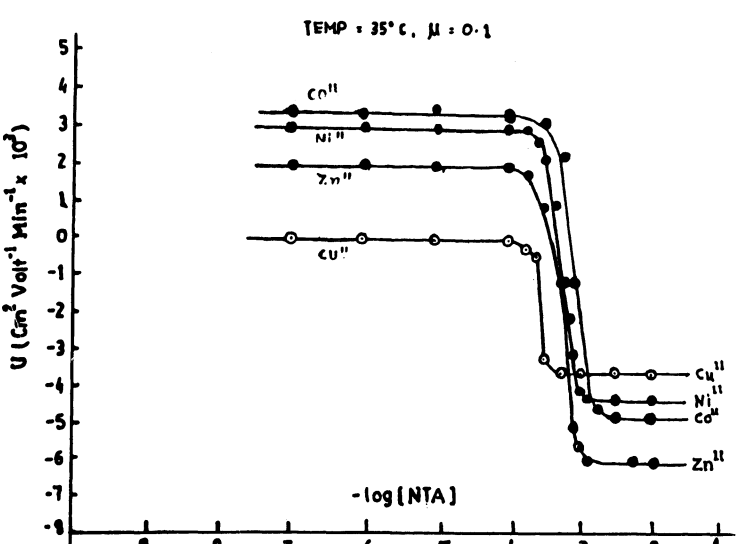


Fig. 1. $M^{II}$-NTA-BENZOATE SYSTEM, -log [NTA] vs. MOBILITY

formed in case of Zn(II), Co(II), Ni(II), whereas in case of Cu(II) three plateaus are obtained. The first plateau represents the region of uncomplexed metal ion *i.e.* a region of low pH, where the concentrations of undissociated benzoic acid species are maximum. Beyond the first plateau metal ions have gradually decreasing mobilities and hence it indicates the complexation of metal ions with anionic species of benzoic acid, whose concentration increases with increase of pH. The second plateau in case of Ni(II), Co(II) and Zn(II) represents the formation of 1:2 complex whereas in case of Cu(II) 1:1 complex. The region between first and second plateaus corresponds to progressive conversion of uncomplexed metal ion into binary complex with the ligands. Further increase in the pH of the background electrolyte has no effect in case of Ni(II), Co(II) and Zn(II) but Cu(II) gives rise to a third plateau with zero mobility, which indicates the formation of 1:2 complex of metal ion with the unprotonated species. On further increase in pH, the mobility remains appreciably unaltered ruling out the possibilities of formation of any higher mononuclear complex.

As we have started our studies from pH one due to experimental binding, it may be possible that 1:1 complex has been missed in case of Ni(II), Zn(II) and Co(II).

In view of the above observations the complex of metal ions with benzoate anion (L) may be represented as:

$$M^{2+} + L \rightleftarrows (ML)^{+}$$

$$(ML)^{+} + L \rightleftarrows ML_2$$

The metal spot on paper strip is thus a conglomeration of uncomplexed metal ion, 1:1 complexes and 1:2 complexes formed. The overall mobility is given by the equation:

$$U = \frac{U_0 + U_1K_1L + U_2K_2L^2}{1 + K_1L + K_1K_2L^2}$$

where $U_0$, $U_1$ and $U_2$ represent mobility of uncomplexed metal ion, 1:1 cationic complex and 1:2 complex respectively. $K_1$ and $K_2$ are stabilities of 1:1 and 1:2 complexes, which can be expressed as:

$$K_1 = \frac{ML}{M-L}$$

$$K_2 = \frac{ML_2}{ML-L}$$

By applying the principle of average mobility $K_1$ can be calculated with the help of mobilities of first and second plateaus; similarly $K_2$ can be calculated with the help of mobilities of second and third plateaus. The pH corresponding to these points are noted with the help of plot of pH versus mobility. The knowledge of dissociation constant of benzoic acid (4.21) and the value of pH helps in assessment of the unprotonated species at any pH with the relevant equation.

$$[L] = \frac{A_T}{1 + K[H^+]}$$

where, $A_T$ = total ligand concentration, K = dissociation constant of the benzoic acid, L = unprotonated benzoic acid.

The reciprocal of unprotonated ligand concentration gives the value of stability constant ($K_S$) *i.e.*

$$K_S = \frac{1}{[L]}$$

The calculated values of stability constant log $K_S$ of 1:1 and 1:2 complexes are depicted in Table 1 and may be compared with findings of others[8].

TABLE-1

Temp. 35°C Benzoic acid Ionic strength = 0.1M

| Metal ions | log $K_1$ | log $K_2$ | log $K_{M-NTA}$ | log $K_{M-NTA-Benzoate}$ |
|---|---|---|---|---|
| Cu(II) | 2.626 | 2.190 | 10.900 | 4.67 |
| Ni(II) | 2.359 | — | 10.575 | 4.47 |
| Zn(II) | 2.190 | — | 10.500 | 4.37 |
| Co(II) | 2.029 | — | 10.350 | 4.27 |

**(B) Metal-NTA binary systems**

It has been observed from the plot of overall mobility of metal spots in presence of NTA at different pH values that all metal ions gave two plateaus but the mobility of the last plateau lies in the negative region, indicating negatively charged nature of the complexes. It is assumed that only one NTA anion combines with metal ion which gave 1:1 M-NTA complex which is in accordance with the reported views of others[9]. Calculated values are depicted in Table 1.

**(C) Mixed ligand complexes of M-NTA-benzoate system**

The experiments were performed at fixed pH 8.5 since all binary complexes M-benzoate are formed below this pH. In order to avoid side interactions, the transformations of M-NTA complex into M-NTA-benzoate systems were studied purposely at pH 8.5.

On plotting a graph between mobility against negative value of logarithm of concentration of added benzoic acid, curves in Fig. 2 are obtained. The curves show two plateaus. The constant mobility in the first plateau corresponds to the mobilities of 1:1 M-NTA complexes. The mobility at second plateau becomes constant, which corresponds to the mobility of a newly formed complex which may be a binary complex of M-NTA as:

$$ML + NTA = M - NTA + L$$

where the one ligand of the complex has been completely replaced by one NTA. The newly formed complex may also be a mixed complex in accordance with the reaction:

$$M - L + NTA = M - L - NTA$$

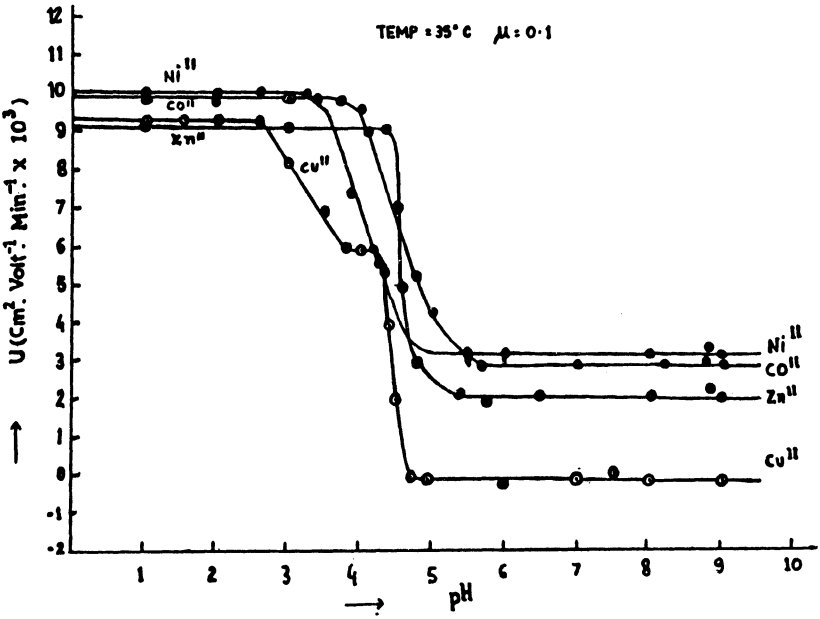


Fig. 2. $M^{II}$-BENZOATE SYSTEM, pH vs. MOBILITY

Here one NTA species is attached to the simple complex, resulting in a mixed ligand complex. The mobility of the second plateau is more negative than that of first indicating the formation of more negatively charged complex. Since the mobility of the second plateau does not coincide with the mobility of 1 : 1 and 1 : 2 M-benzoate system, hence it is concluded that the mobility in the last plateau is due to the ligation of benzoic acid anion to 1 : 1 M-NTA complex. The stability constants of these mixed complexes are calculated in the same manner as in the case of binary complex. These values are depicted in Table 1.

It is evident from the table that the stability constants of mixed ligand complexes show the following order with respect to metal ions.

[Cu-L-NTA] > [Ni-L-NTA] > [Zn-L-NTA] > [Co-L-NTA]

These findings are in accordance with the Irving-Williams order[10] for stability constants.

Thus ionophoretic technique is a good device for studying complexation reactions in solutions and also to study mixed-ligand complexes as well and to determine their stabilities.

## REFERENCES

1. P.C. Yadava, A.K. Ghosh, K.L. Yadava and A.K. Dey, *J. Chromatographia*, **9**, 416 (1976).

2. R.K.P. Singh, J.K. Sircar, R. Khelawan and K.L. Yadava, *J. Chromatographia*, **13,** 709 (1980).
3. R.K.P. Singh, J.K. Sircar, J.R. Yadava, P.C. Yadava and K.L. Yadava, *J. Electrochim. Acta*, **26,** 395 (1981).
4. R.K.P. Singh, J.R. Yadava, P.C. Yadava and K.L. Yadava, *Z. Phys. Chem.*, **264,** 464 (1983).
5. V. Czakis-Sulkowska, *Zesz Nauk Politech Lodz. Chem.*, **23,** 1746 (1965).
6. R.K.P. Singh and K.L. Yadava, *Trans. SAEST*, **16,** 163 (1981).
7. G.P. Sengupta and N.N. Ghosh, *J. Indian Chem. Soc.*, **66,** 438 (1989).
8. M. Yasuda, K. Yamaski and H. Ohtake, *Bull. Chem. Soc., Japan*, **33,** 1067 (1960).
9. A.E. Martell and R.M. Smith, Critical Stability Constants, Plenum Press, New York and London, Vol. 3, pp. 141 and 142 (1974).
10. H. Irving and R.J.P. Williams, *J. Chem. Soc.*, 3192 (1953).

(*Received*: 3 December 1993; *Accepted*: 28 May 1994) AJC-819

**CONTEMPORARY INORGANIC CHEMISTRY**
**(A Symposium in honour of Prof F.A. Cotton)**

**COLLEGE STATION, TX, U.S.A.**

**March 12–15, 1995**

*Contact Address:*

PROFESSOR CARLOS A. MURILLO / JOHN P. FACKLER (Jr)
Department of Chemistry
Texas A. & M. University
College Station, Tx-77843-3255, U.S.A.
*Tel.*: (409) 845-3646
*Fax:* (409) 845-9351

**1995 INTERNATIONAL CHEMICAL CONGRESS OF PACIFIC BASIN SOCIETIES**

**HONOLULU HI, U.S.A.**

**December 17–22, 1995**

*Contact Address:*

Congress Manager, Pacifichem-95
Suite 420
1155, 16th Street, N.W.
Washington DC-20036, U.S.A.
*Tel.:* +1(202) 872-4396
[illegible]