# Ionophoretic Study on Complexation of Manganese(II), Iron(II), Cobalt(II) and Nickel(II) with *m*-Chlorobenzoic Acid and Nitrilo-triacetic Acid

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Paper-electrophoretic technique has been employed for the study of complexes in solution. Here, binary complexes of Mn(II), Fe(II), Co(II) and Ni(II) formed with *m*-chlorobenzoic acid and nitrilo triacetic acid (NTA) have been studied along with their ternary complexes formed with the same ligands used as primary and secondary respectively at fixed pH 8.5 maintaining the temperature constant at 35°C and the ionic strength of $10^{-1}$ M throughout the investigation. The evidence for the formation of 1:1 complexes of the bivalent metals with *m*-chlorobenzoic acid was found. The stability constants of mixed ligand complexes of the above metals formed with *m*-chlorobenzoic acid and NTA have been found to be 7.68, 7.78, 7.86 and 7.93 respectively.

## INTRODUCTION

Stepwise complexation reaction has been studied by paper electrophoresis[1–3]. The device is well established in the field of mononuclear complexes, though it has also been extended for the study of ternary complexes[4, 5] as well. The present work studies the binary and ternary complexes of Mn(II), Fe(II), Co(II) and Ni(II) formed with *m*-chlorobenzoic acid and nitrilo triacetic acid (NTA). The stability constant of the complexes has also been determined.

## EXPERIMENTAL

The paper electrophoretic instrument is a system of mainly three units:
(1) Electrophoretic chamber.
(2) Voltage stabilizer.
(3) pH meter.

(1) *Electrophoretic Chamber*: It is a wooden box covered with a glass plate at the top, in order to prevent moisturous change causing the upset of equilibrium taking place inside. Two PVC moulded tanks are kept in it, in which electrolyte is taken. Two hollow metal plates covered with polythene plates have been used for maintaining the temperature by passing thermostated water. This assembly design minimises the disturbing effects of evaporation from the liquid flow in paper strips. Each tank is connected with a separate platinum wire throughout its length which serves as an electrode.

(2) *Voltage Stabilizer*: It is not only voltage stablizer but also D.C. converter. It may stabilize the voltage at different ranges *viz.* 0–100, 100–200 and 200–300 volts. It also converts A.C. into D.C. to carry out the electrophoresis at 200 volts.

(3) *pH Meter*:   It indicates the pH of the electrolyte. SICO-EMI Digital pH Meter M-EM 5 having a combined electrode and working on 230 volts/50 cycles stablized A.C. mains was employed for pH measurements.

Stock solutions of 5 M $HNO_3$ (B.D.H.), 2 M NaOH (B.D.H.) and $10^{-2}$ M *m*-chloro-benzoic acid (Kamphasol) were prepared from their AnalaR samples and 10 M NTA solution was prepared from a sample obtained from E. Merck (Darmstadt, G.F.R.). These solutions were standardised by usual methods. $10^{-1}$ M $HNO_3$ solution was used as background electrolyte with $10^{-3}$ M *m*-chloro-benzoic acid and $10^{-3}$ M NTA solutions for studying binary complexes. For ternary complexation $10^{-1}$ M $HNO_3$, $10^{-2}$ M NTA and $10^{-2}$ M *m*-chlorobenzoic acid solutions were used at fixed pH 8.5 by the addition of NaOH solution.

The strips were marked with metal cations in duplicate along with additional strips marked with glucose. After passing current for 15 minutes through strips, moistened with background electrolyte, a current of 200 volts was passed through the electrophoretic equipment for 1 h. The metal spots were detected by spraying 1-(2-pyridyl azo)-2-naphthol (PAN) indicator solution and their movements were measured. Again the pH of the background electrolyte was changed to measure movements for further observations.

## RESULTS AND DISCUSSION

(1) *M-m-Chlorobenzoic Acid Binary Systems:*   The overall ionophoretic mobility of four different cations, $Mn^{2+}$, $Fe^{2+}$, $Co^{2+}$ and $Ni^{2+}$, with the change of pH is represented graphically in Fig. 1.
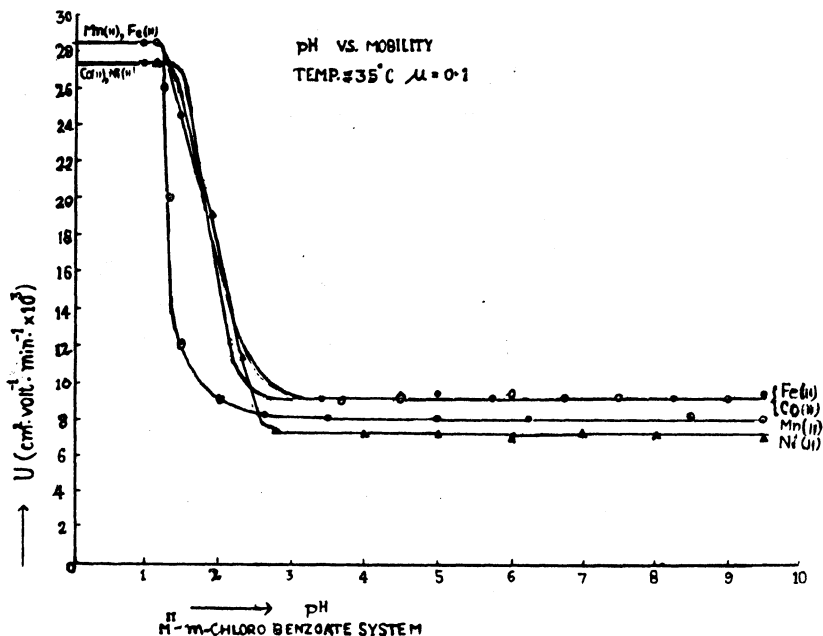


Fig. 1.   $M^{II}$-*m*-chlorobenzoate system

The figure shows the formation of two plateaus in each case. The first plateau represents the region of uncomplexed metal ion *i.e.* the region of low pH where the concentration of undissociated *m*-chlorobenzoic acid species is maximum. Beyond it, metallic cations show lower mobilities indicating their complexation with anionic species of *m*-chlorobenzoic acid. The second plateau represents the formation of 1 : 1 complex.

The region between these two plateaus corresponds to progressive conversion of uncomplexed metallic cation into binary complex with the ligands. Further increase in the pH of the background electrolyte has no effect as the mobility remains unaltered, ruling out the possibilities of formation of any higher mononuclear complex.

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

$$M^{2+} + L = (ML)^+$$
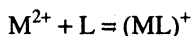
The metal spot on paper strip is thus a conglomeration of uncomplexed metal ion and 1 : 1 complex formed. The overall mobility is given by the equation

$$U = \frac{U_0 + U_1 K_1 L}{1 + K_1 L}$$

where $U_0$ and $U_1$ represent mobility of uncomplexed metal ion and 1 : 1 cationic complex. $K_1$ is the stability of 1 : 1 complex which can be expressed as:

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

By applying the principle of average mobility $K_1$ can be calculated with the help of mobilities of first and second plateaus. The pH's corresponding to these points are noted with the help of plot of pH *vs.* mobility. The knowledge of dissociation constant of *m*-chlorobenzoic acid and the value of pH helps in the 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 *m*-chlorobenzoic acid,
          $L$ = unprotonated *m*-chlorobenzoic 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 $K_s$ of 1 : 1 complex are depicted in Table-1 and may be compared with the findings of others.

(2) *Metal-NTA Binary Systems:*  It has been observed in the plot of overall mobility of metal spots in presence of NTA at different pH values that all the metal ions give two plateaus but the mobility of the last lies in the negative region which indicates the negatively charged nature of the complex. It is assumed that

only one NTA anion combines with metal ion which gave 1 : 1 M-NTA complex. Other works also report the same view. Table-1 shows the calculated values.

TABLE-1

STABILITY CONSTANTS OF BINARY AND TERNARY COMPLEXES

Temp. = 35°C, *m*-chlorobenzoic acid ionic strength = 0.1 M

| Metal ions | log $K_1$ | log $K_{M-NTA}$ | log $K_{M-NTA-m-chloro-benzoate}$ |
|---|---|---|---|
| Ni(II) | 4.733 | 10.65 | 7.93 |
| Co(II) | 4.635 | 10.60 | 7.86 |
| Fe(II) | 4.538 | 10.55 | 7.78 |
| Mn(II) | 4.441 | 10.45 | 7.68 |

(3) *Mixed Ligand Complexes of M-NTA-m-Chlorobenzoate Systems*: Electrophoresis was carried out at fixed pH 8.5 since all binary complexes of *m*-chlorobenzoate are formed below it. In order to aviod side interaction, the transformation of M-NTA into M-NTA-*m*-chlorobenzoate was studied purposely at 8.5. On plotting a graph between mobility and negative values of logarithm of concentration of added NTA, curves in Fig. 2 are obtained. The curves show two plateaus.
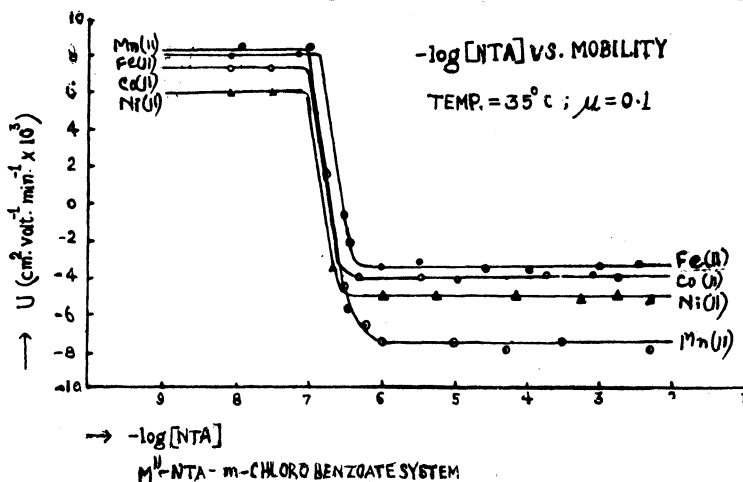


Fig. 2. $M^{II}$-NTA-*m*-chlorobenzoate system

The constant mobility in the first plateau corresponds to the mobility of 1 : 1 M-*m*-chlorobenzoate. The mobility at the second plateau becomes constant which corresponds to the mobility of a newly formed complex which may be a binary complex of M-NTA as:

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

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

$$M - L + NTA = M - L - NTA.$$
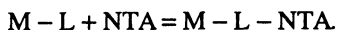
This mixed ligand complex is obtained by the addition of one species of NTA to the simple complex. The mobility of the second plateau is more negative than that of the first. It indicates the formation of more negatively charged complex. Since the mobility of the second plateau does not coincide with the mobility of 1 : 1 M-*m*-chlorobenzoate system, hence it is concluded that the mobility in the last plateau is due to the ligation of NTA anion to 1 : 1 M-*m*-chlorobenzoic acid complex. The stability constants of these complexes are calculated in the same manner as in case of binary complexes. 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[7-9]:

$$[NI-L-NTA] > [Co-L-NTA] > [Fe-L-NTA] > [Mn-L-NTA].$$
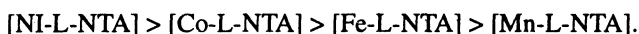
These findings are in accordance with the Irving-Williams order[10] for stability constants.

Thus ionophoretic technique is a good device for studying complexation reactions in solution and also to study mixed ligand complexes.

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