

# A Novel Ionophoretic Technique in the Study of Binary Serinate and Ternary Serinate NTA Complexes of Iron III and Copper II

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**Abstract:** Ionophoretic technique has been used to study the Fe(III) Cu(II) Serine binary and Fe(III) / Cu(II) Serinate – NTA ternary complexes. The stability constants of metal serinate binary complexes are found to be  $10^{9.29}$  and  $10^{7.95}$  and the stability constants of metal-serinate- NTA ternary complexes have been found to be  $10^{6.14}$  and  $10^{6.05}$  for Fe(III) and Cu (II) complexes respectively at = 0.1 (NaClO<sub>4</sub>) and 25<sup>o</sup>c.

**Keywords:** Ionophoretic technique, Ionophoretic tube stability constants, ternary complexes.

## I. INTRODUCTION

In the present communication, we have made an effort to assess the stability constants of metal complexes with a single ligand along with the systematic study of ternary complexes formed in a system containing various electrolyte ingredients. A simple ionophoretic tube<sup>1</sup> has been designed for this work, which yields remarkable results after standardization.

## II. EXPERIMENTAL

The technique consisted in carrying Ionopheresis in background electrolyte containing 0.1M perchloric acid and  $1 \times 10^{-3}$  serine with Fe(III) ( $1 \times 10^{-4}$ M) In case of Cu(II) ( $1 \times 10^{-3}$ ), serine /  $0.2 \times 10^{-2}$  M NTA was used. The NaOH solution was added to produce the desired pH for the study of binary complexes in each Ionophoretic observations. Electrolysis was carried out for 45 minutes at 50 V and at 25°C. For the study of ternary complexes the experimental procedure was slightly modified. Here the back ground electrolyte contained secondary ligand (NTA) in addition to primary ligand (Serine). For the ternary complexes the pH was always maintained at 7 (by adding NaoH solution) and the concentration of secondary ligand (NTA) ranged from  $10^{-6}$  to  $10^{-2}$  M.

## III. PROCEDURE FOR BINARY METAL SERINE COMPLEXES

A set of 15 ml solution containing  $1 \times 10^{-4}$  M Fe(III) /  $1 \times 10^{-3}$  M Cu(II), 0.1M HClO<sub>4</sub> and  $1 \times 10^{-3}$  Serine for Fe(III) /  $1 \times 10^{-2}$  Serine for Cu(II) were prepared at different pH values. A 10 ml of the solution was taken in the ionophoretic tube and thermostated at 25°C. The tube (18 cm & 5 cm dia) was adjusted in such a way that the level of the solution in one wide end arm reached a circular mark on it. This adjustment fixed the volume of

the solution on both sides of the middle stopper. Two (0.5 cm x 0.5Cm) platinum electrodes were dipped in each arm cup and 50V potential difference was applied between them. Electrolysis of the solution was allowed for 45 minutes after which the middle stopper of the tube was closed. The solution of the anodic compartment was taken in a 15 ml flask the Fe (III) content of the solution was converted to Fe (III) – thiocyanate complex<sup>2</sup>. The volume was raised up to the mark and the absorbance was measured at 480 nm with C2 – specolspectro colorimeter. The Cu (II) content at the anodic compartment was converted to Cu (II) – thiocyanate complex<sup>2</sup> and absorbance was measured at 408 nm after making up the volumes to 15 ml.

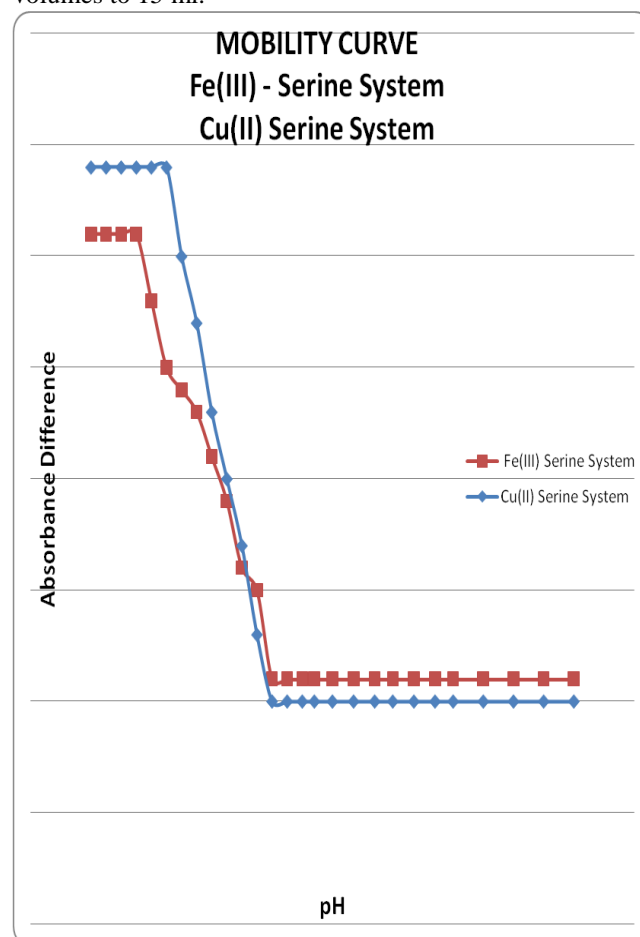


Fig. 1: Graph between Absorbance difference and PH Value.

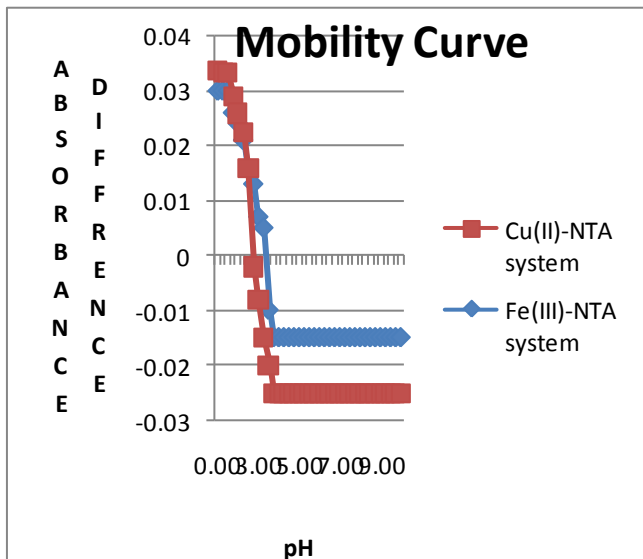


Fig. 2: Graph between Absorbance difference and PH Value.

### III. PROCEDURE FOR THE STUDY OF METAL – SERINE – NTA TERNARY COMPLEXES

An appropriate reaction mixture containing metal ions and serine and 0.1 M acid was adjusted to pH 7 and the secondary ligand (NTA) was added progressively and the ionophoretic mobility was recorded. The mobility was plotted against – log [NTA].

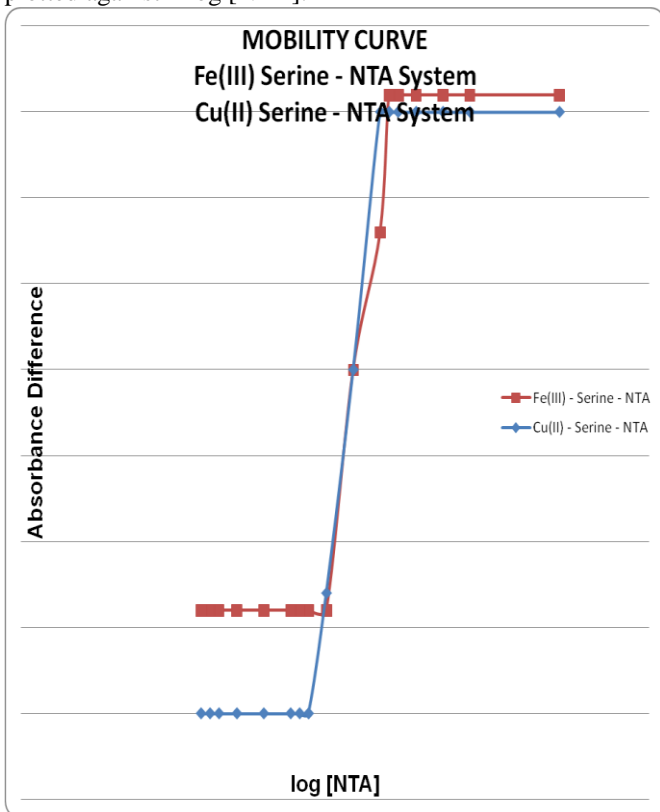


Fig. 3: Graph between Absorbance difference and Log (NTA) Value.

### IV. RESULTS AND DISCUSSION

#### M-Serine system

The overall, mobility (U) is a composite parameter contributed by different ionic species of the metal ion and is given by the following equation.

$$U = \frac{u_0 + u_1 k_1 [L] + u_2 k_1 k_2 [L]^2 + \dots}{1 + k_1 [L] + k_1 k_2 [L]^2 + \dots}$$

Where K' s are the stability constants of complexes and [L] is the concentration of serinate anion : u's are the ionic motilities of the different species of the metal ions which can be assessed from the plateaus of the figure(1) In the region between first and second plateau the system contains overwhelmingly a mixture of free metal ion 1:1 complex. From Figure 1 it is evident that there is no formation of 1:2 complex, hence the third term in the numerator and the denominator of the above equation can be justifiably neglected U would be equal to (U0+U1 / 2) provided k1[L]=1 Accordingly the pH corresponding to the average value of U0 and U1 is found from the figure. With the knowledge of the dissociation constants of serine (pk2= 9.06, Pk1,= 2.13)3. The concentration of serinate ion at this pH is calculated. Its reciprocal gives the stability constants K of the 1:1 complex. The calculated values are given in table - 1.

Table 1: Stability constants of some binary and ternary complexes of Fe(III) and Cu(II) with serine and NTA. Ionic Strength = 0.1 M, Temp. = 25°C.

	Fe <sup>III</sup> value		Cu <sup>II</sup> value	
	Calculated values	Literature values <sup>4</sup>	Calculated values.	Literature values <sup>4</sup>
log K <sub>M-serine</sub> <sup>M</sup>	9.29	9.2	7.95	7.88
log K <sub>M-NTA</sub> <sup>M</sup>				
log K <sub>M-serine NTA</sub> <sup>M</sup>	11.1	15.9	10.02	12.94
	6.14	-	6.05	-

#### M- NTA System

The overall mobility's of the metal ions in solution in the presence of NTA at different PH values are represented in Fig 2. It is evident from the figure that with each metal ion two plateaus are formed the mobility of the second plateau lies in the negative region, which shows the negatively charged nature of the complex. Hence only one NTA anion is assumed to combine with one bivalent or trivalent metal ion to give a 1:1 M-NTA binary Complex, which is in conformity with finding of the other workers<sup>4</sup>The stability constants of complexes with NTA (K<sub>MM-NTA</sub>) were calculated as described for the M-Serine system and are given in Table 1.

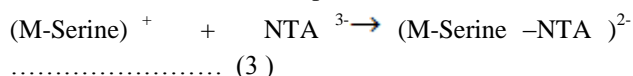
#### M-Serine –NTA System

This system was studied at pH 7 with a specific purpose. It was observed from mobility curves, for M-Serine and M- NTA binary System that binary

complexes( M-Serine ) and ( M- NTA ) are formed much before pH 7 .To avoid any side interactions the transformation of the M-Serine complexes into M-Serine - M- NTA complexes is investigated at Ph. 7.0 .

The plots of overall mobility (Absorbance difference) against -log [NTA] are given in fig -3 which shows two plateaus. The positive mobility in the region of first plateau is obviously due to 1:1 M-Serine complexes (  $ML^+$  ) ( see fig -1) .

The mobility corresponding to the second plateau lies in the negative region which shows the negatively charged nature of the complex. However the mobility of the last plateau is not in agreement with the mobility of 1:1 M- NTA complex (fig -2 ) .It is therefore inferred that the species corresponding to the second plateau is due to the coordination of  $NTA^{3-}$  anion to a 1:1 M-Serinate moiety resulting the formation of 1:1:1 (M-Serine -NTA )<sup>2-</sup> mixed complex . This can be shown as:



$$U = u_0 f M-serine + u_1 f M-serine - NTA \dots\dots\dots (4)$$

Where  $u_0$  and  $u_1$  are the mobilities and  $f M-serine$  and  $f M-serine - NTA$  are the mole fractions of M-serine and M-serine - NTA complexes respectively . From fig -3 the total concentration of NTA at which the overall mobility is mean of the mobilities of the two plateaus was determined. For this the concentration of  $NTA^{3-}$  anion at pH 7.0 was calculated .  $K^{M-Serine}$  is obviously equal to  $1/[L]$  . These calculated values of stability constants are also recorded in table 1.

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