

Ionophoretic studies on mixed complexes : Metal-acetic acid-nitrilotriacetate

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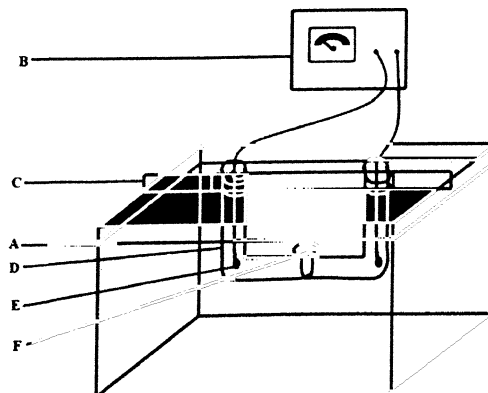
Manuscript received online 11 July 2012, revised 09 August 2012, accepted 10 August 2012

Abstract : Quantitative indication of a complex formation comes from the estimation of the stability or formation constants characterizing the equilibria corresponding to the successive addition of ligands. The binary equilibria of metal ions, viz. Fe^{III} , Cu^{II} , Ni^{II} and Co^{II} -acetic acid and also mixed equilibria $\text{Fe}^{\text{III}}/\text{Cu}^{\text{II}}/\text{Ni}^{\text{II}}/\text{Co}^{\text{II}}$ -acetic acid-NTA (nitrilotriacetic acid) have been studied using ionophoretic technique. The stability constants of metal-acetic acid binary complexes are found to be 4.42, 3.58, 3.42 and 3.37 that of metal-acetic acid-NTA mixed complexes have been found to be 6.34, 6.31, 6.14 and 6.11 for Fe^{III} , Cu^{II} , Ni^{II} and Co^{II} complexes, respectively at 25 °C and ionic strength $\mu = 0.1 \text{ mol dm}^{-3}$ (HClO_4).

Keywords : Binary complex, mixed complex, overall mobility, stability constants, ionophoretic technique.

Introduction

The stabilities of binary and mixed complexes are known to play an important role in a number of metabolic, biological and toxicological functions¹. Copper(II) acetate is used as a pigment and a fungicide whereas aluminium acetate and iron(II) acetate are used as mordants for dyes². It is a weak acid because at standard temperature and pressure the dissociated acid exists in equilibrium with the undissociated form in aqueous solution in contrast to strong acid, which are fully dissociated. Mixed metal complexes play an important role in various biological systems and in different fields of chemistry^{3,4}. Hence, the formation stability and reactivity of these complexes have been an active field of research⁵. The present work⁶ describes the ionophoretic technique for the determination of stability constants of the binary and ternary metal complexes. It has been observed that the ternary complexes of NTA are more stable than the binary metal-acetic acid complexes. The superiority of NTA over the other ligands lies in possession of additional coordination sites in a single moiety. Hence NTA chelated ternary complexes are more stable than other binary complexes⁷. A simple ionophoretic tube has been designed, which after standardization yields remarkable results⁸.



Ionophoresis set-up : (A) Water bath, (B) electrophoresis supply, (C) support, (D) ionophoretic tube, (E) Pt electrodes, (F) stopper.

Results and discussion

Metal-acetic acid binary system :

Fig. 1 illustrates the relationship between absorbance differences and the pH's and thus gives an idea of the change of overall mobility of the metal ion species with change in hydrogen ion status of the system containing Fe^{III} , Cu^{II} , Ni^{II} , Co^{II} and acetic acid. A curve with a number of plateaus indicates the formation of certain complex species. A plateau is obviously an indication of a pH range where mobility is practically constant. The first

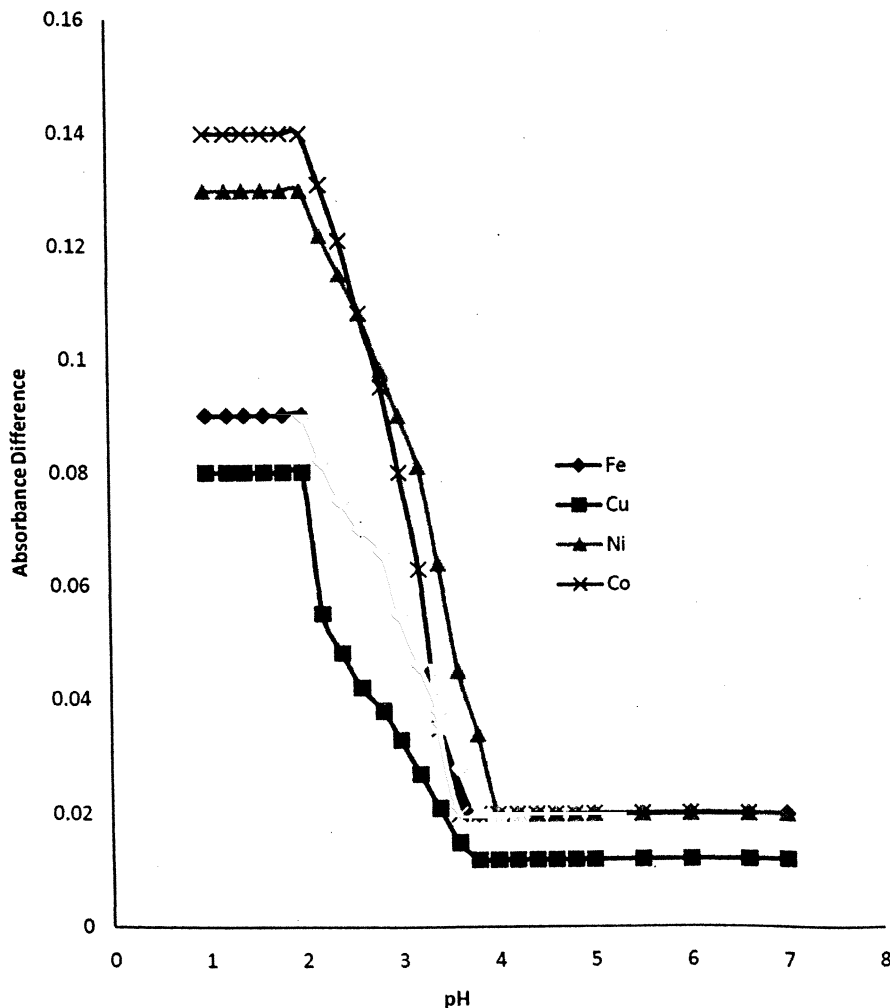


Fig. 1. Mobility curve : Metal-acetic acid systems.

plateau in each case corresponds to a region of pH where metal ions are uncomplexed. In this low pH region, the protonated form of acetic acid is maximum. Further increase in pH from this region onward which naturally leads to increase in ligating acetic acid anion concentration $[L^-]$ and brings about a progressive decrease in overall ionic mobility of the metal ion species. This decrease indicates formation of complex of the metal ion with the ligand. A point is reached beyond which mobility of the metal ion species remain constant regardless of the increase of pH of reaction mixture. This is the second plateau which corresponds to a pH region in which 1 : 1 complex is predominantly formed. One acetic acid anion combines with each metal ion to form $[Fe(CH_3COO)]^{2+}$, $[Cu(CH_3COO)]^+$, $[Ni(CH_3COO)]^+$ and $[Co(CH_3COO)]^+$

cationic complexes with Fe^{III} , Cu^{II} , Ni^{II} and Co^{II} respectively. Beyond this plateau increase of pH has no effect and mobility remain constant.

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

$$U = \frac{u_0 + u_1K_1[L] + u_2K_1K_2[L]^2 + \dots}{1 + K_1[L] + K_1K_2[L]^2 + \dots} \quad (1)$$

where K 's are the stability constant of complexes and $[L]$ is the concentration of acetic acid ion. u 's (u_0, u_1, u_2) are the ionic mobilities of different species of the metal ions which can be accessed from the plateaus of the figure. In the region between first and second plateau the system contains overwhelmingly a mixture of free metal ion and

1 : 1 complex. The existence of 1 : 2 complexes can be excluded and hence the third term in the numerator and the denominator of the above equation can be justifiably neglected. U would be equal to $(u_0 + u_1)/2$ provided $K_1[L] = 1$.

Accordingly the pH corresponding to the average value of u_0 and u_1 is found from the figure and with the knowledge of the dissociation constant of acetic acid ($pK_1 = 4.56$)⁹ the concentration of acetic acid ion at this pH is calculated. Its reciprocal gives the stability constant K of the 1 : 1 complex. The concentration of acetic acid anion $[L^-]$ is determined as :

$$[L^-] = \frac{[L_T]}{1 + k/[H^+]} \quad (2)$$

where $[L_T]$ is the total concentration of the ligand acetic acid and k is the dissociation constants of the acetic acid.

Metal-acetic acid-NTA ternary system :

Fig. 2 depicts the observation of studies carried out in M-acetic acid-NTA ternary complexes. These graphs clearly show the formation of two plateaus in each case. The first plateau corresponds to binary M-acetic acid complexes whereas the second plateau corresponds to the formation of new complex.

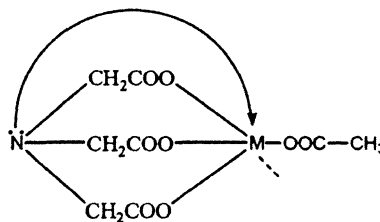
This new complex may be mixed complex of the type M-L-NTA or pure M-NTA complex. But with the help of related graphs of M-NTA complexes it was found that the absorbance difference in case of new complex is not identical to M-NTA pure complex. Further this ternary complex has greater mobility than that of binary M-acetic acid complex hence these observations confirm the formation of mixed M-L-NTA complex.

Thus it is inferred that the mobility in the last plateau is due to coordination of the NTA anion to a 1 : 1 metal-acetic acid moiety resulting in the formation of 1 : 1 : 1 mixed metal-acetic acid-NTA complex as



Regarding the coordination mode of the acetic acid anion, it forms a 1 : 1 binary complex. In this complex, the geometry may be octahedral (coordination number-6) in which one position is satisfied by the monodentate anion and others by the solvent molecule (aqua group). A chelat-

ing spin free six-fold octahedral structure for mixed-ligand complexes with metal ions (Fe^{3+} , Cu^{2+} , Ni^{2+} , Co^{2+}) is shown below in which the acetic acid anion and nitrilotriacetate act as monodentate and tetradentate ligands, respectively.



For M-L-NTA complexes the stability constant K' is calculated by using modified equation.

$$U = \frac{u_0 + u_1 K' [NTA]}{1 + K' [NTA]} \quad (4)$$

Here u_0 and u_1 are the mobilities of M-L and M-L-NTA complexes.

From the figures concentration of NTA at which overall mobility is the mean of the mobilities of the two plateaus is determined. The concentration of NTA anion at pH 7.0 for this NTA concentration is calculated. K is obviously equal to $1/[NTA]$. All these values are also reported in Table 1 and clearly indicate the superior coordinating power of NTA anion to other acids species.

Table 1. Stability constants of binary and ternary mixed complexes

Ionic strength $\mu = 0.1 M$, Temp. = 25 °C

Metal ion	Stability constant	
	$\log K_{ML}^M$	$\log K_{M-L-NTA}^{M-L}$
Calculated values (this work)		
Fe ^{III}	4.42	6.34
Cu ^{II}	3.58	6.31
Ni ^{II}	3.42	6.14
Co ^{II}	3.37	6.11

The stability constant values for binary and ternary complexes of Fe^{III}, Cu^{II}, Ni^{II} and Co^{II} are in the order : Fe^{III} > Cu^{II} > Ni^{II} > Co^{II} which follows the Irving-William's¹⁰ order for the stability constants of transition metals of the first transition series.

Experimental

Metal-acetic acid binary system :

One set of 15 mL solution each containing 1×10^{-3} M, Cu^{II}, Ni^{II}, Co^{II}, 0.1 M HClO₄ and 1×10^{-2} M acetic acid was prepared at different pH values (by adding NaOH solution). In case of Fe^{III}, 1×10^{-4} M Fe^{III}, 0.1 M HClO₄ and 1×10^{-3} M acetic acid was used. 10 mL of this solution is taken in an electrophoretic tube and then thermostated at 25 °C. The tube (18 cm long and 0.5 cm bore) with a stopper in the middle was fused perpendicularly at the ends with short wider tubes of 1.2 cm bore. The position of the tube 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 × 0.5 cm) platinum electrodes were dipped in each arm cup and a 50 V potential difference was applied between them.

Electrolysis of the solution was allowed for 45 min, after which the middle stopper of the tube is closed. The solution of the anodic compartment was taken out in a 15 mL flask. The copper content of the solution was converted into copper thiocyanate¹¹. The volume was raised to a mark in the flask and the absorbance at 408 nm was measured with CZ-specol spectrophotometer. The Co^{II} content of the anodic compartment was converted into cobalt thiocyanate¹¹ complex and absorbance at 625 nm was measured after making up the volume to 15 mL. The Ni^{II} content was converted to nickel dimethylglyoximate¹² and absorbance was taken at 445 nm. Similarly the Fe^{III}

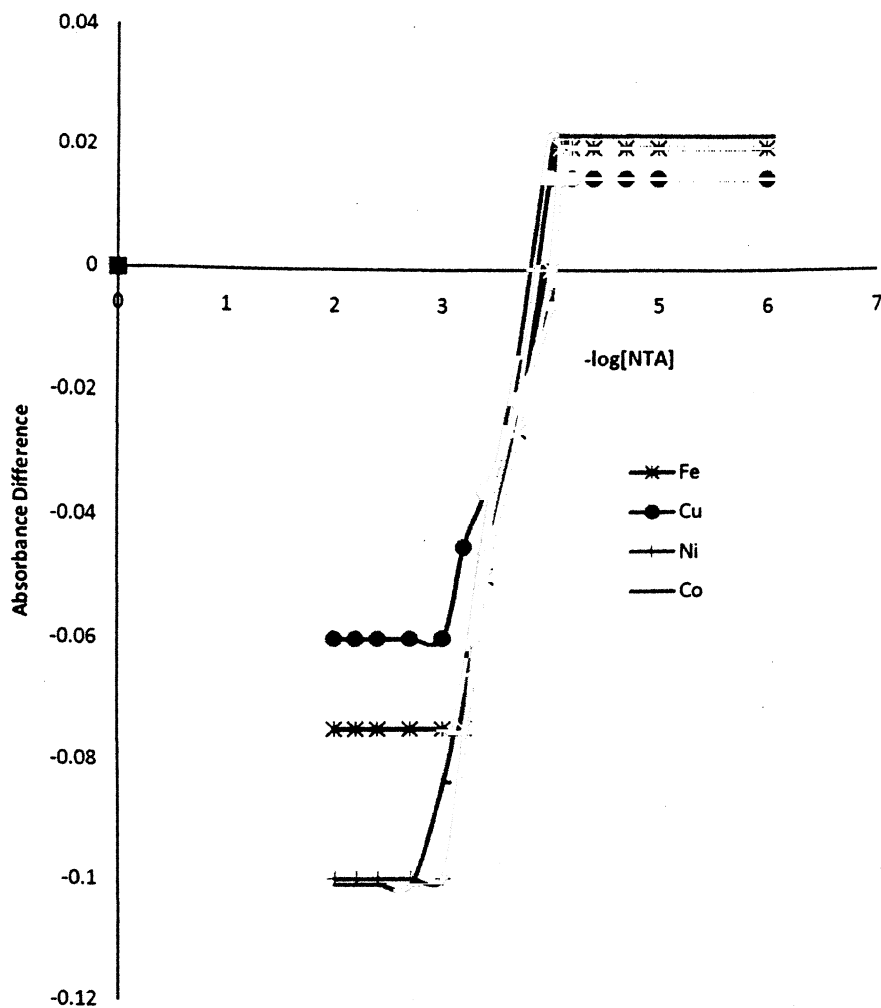


Fig. 2. Mobility curve : Metal-acetic acid-NTA systems.

content of the anodic compartment was converted to Fe thiocyanate¹² complex and absorbance was measured at 480 nm against a reagent blank. These observations are graphically represented in Fig. 1.

Metal-NTA binary system :

The experiments for binary complexes of the Fe^{III}, Cu^{II}, Ni^{II}, Co^{II}-NTA are prerequisite for the study of metal-acetic acid-NTA ternary complexes. These studies have been carried out by Aziz¹³ and Sarika Sachan¹⁴. In these studies it was observed that with each metal ion-NTA forms two plateaus, the first for uncomplexed metal ion and the last for 1 : 1 anionic complex species. Their observations have been taken for comparison with our observations found in case of ternary complexes.

Metal-acetic acid-NTA ternary system :

The study of ternary complexes was carried out by progressive addition of secondary ligand NTA from $1 \times 10^{-6} M$ to $1 \times 10^{-2} M$ at a fixed pH 7.0 to a mixture of metal ion (having same concentration as in binary systems), $1 \times 10^{-2} M$ acetic acid and 0.1 M perchloric acid. The reason behind keeping the reaction mixture at pH 7.0 is that much ahead of this pH the simple binary complexes of metal acetic acid and M-NTA are formed and remain intact even beyond this pH.

The amount of secondary ligand NTA was increased each time in the ionophoretic tube and the electrolysis of the solution and its observations were recorded each time as it was done in case of binary complexes. These observations are graphically represented in Fig. 2.

A number of factors¹⁵ (e.g. diffusion, ionic strength and temperature) obviously vitiate the ionophoretic mobility of a particular ion. The technique described here is almost free of these vitiating factors and the reliability may vary to $\pm 2\%$.

Conclusion :

In the last, it is concluded that this simple handy ionophoretic technique can be used as a strong tool for

the study of metal-ligand interactions in binary and mixed complexes in solution². Also this technique can be used to reduce the level of these metal ion in living system through complexation in solution.

Acknowledgement

Authors are thankful to Head, Department of Chemistry, University of Allahabad, Allahabad for providing research facilities. Authors are also thankful to UGC, New Delhi for financial assistance.

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