IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 9, Issue 4 Ver. I (Apr. 2016), PP 21-24
www.iosrjournals.org

Ionophoretic Technique in the Study of Complexes of Resorcinol and Tyrosine with Copper (II)

[1] Dr. SyedaSameena Aziz , [2]HafeezaShamoona
[1](Department of Chemistry,Anwar-ul-uloom College ,Mallepally, Hyderabad-500001, India)
[2](Department of Chemistry,Auroras Degree andPG College , Chikadpally , Hyderabad -500020,India)

Abstract: *Ionophoretic technique has been used to study the equilibria in simple and mixed ligand systems in solutions . For the study of ternary complexes the concentration of Resorcinol and tyrosine is kept constant , while that of the secondary ligand EDTA is varied. A graph of mobility against –log [EDTA] is used to obtained information on the formation of mixed ligand complexes and to calculate the stability constant. The stability constant of Cu(II)-Resorcinol, Cu(II)-Tyrosine, Cu(II)-Resorcinol-EDTA and Cu(II)-Tyrosine-EDTA complexes have been found to be* $10^{12.55}$,$10^{6.53}$,$10^{9.81}$*and* $10^{7.43}$ *respectively at = 0.1 (*$HClO_4$*) and* 25^0*c for ligand tyrosine and* 30^0*C for ligand Resorcinol .*

Keywords: *Ionophoretic technique, Ionophoretictube[1] , EDTA, ternary complexes.*

I. Introduction

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

Copper is essential for plants, animals and human health hence has a wider importance for research , therapeutic ,industrial , and toxicological consideration .Consequently , a variety of methods are available for its determination. During an investigation on the reactivity of copper (II) ions with differ plant phenolics ,the copper ion showed selective interaction with resorcinol ,in preference to other phenolics including its structural isomers viz., catechol and quinol, forming a colored complex with maximum absorbance at 450 nm.

The stability constant provides the information required to calculate the concentration of the complex in the solution .There are many areas of application in chemistry, biology and medicine.

II. Experimental

The technique consisted in carrying Ionophoresis in background electrolyte containing 0.lM perchloric acid and 0.01M Resorcinol / 0.01M Tyrosine with 0.001 Cu(II) and for ternary complexes the concentration of EDTA ranges from$2x10^{-2}$ with Cu(II) ions. The NaOH solution was added to produce the desired pH for the study the binary complexes.

In each Ionophoretic observations. Electrolysis was carried out for 45 minutes at 50 V and at 250C. For the study of ternary complexes the experimental procedure was slightly modified. Here the back ground electrolyte contained secondary ligand (EDTA) in addition to primary ligand (Resorcinol/Tyrosine). For the ternary complexes the pH was always maintained at 8 (by adding NaOH solution) and the concentration of secondary ligand (EDTA) ranged from 10^{-6} to 10^{-2} M.

Procedure for binary metal-tyrosine/resorcinol complexes:

A set of 15 ml solution containing $1x10^{-3}$ M Cu (II), 0.1M HClO4 and $1x10^{-2}$ Tyrosine /Resorcinol were prepared at different pH values. A 10 ml of the solution was taken in the ionophoretic tube and thermostat at 25^oC. The tube (18 cm & 5 cm diameter) 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 Cu (II) content of the solution was converted to Cu(II) – thiocyanate complex[7] . The volume was raised up to the mark and the absorbance was measured at 450 nm with Digisunspectrocolorimeter. The Cu (II) content at the anodic compartment was converted to Cu(II) – thiocyanate complex**[10]** and absorbance was measured at 420 nm after making up the volumes to 15 ml.

Procedure for the study of Metal –Tyrosine/Resorcinol –EDTA ternary complexes:

An appropriate reaction mixture containing metal ions and Tyrosine/Resorcinol and 0.1 M acid was adjusted to pH 8.0 and the secondary ligand (EDTA) was added progressively and the ionophoretic mobility was recorded. The mobility was plotted against – log [EDTA].

III. Results And Discussion

Cu-Tyrosinesystem and Cu-Resorcinol 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.

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

Where k's are the stability constants of complexes and [L] is the concentration of Tyrosinate anion and Resorcinol anion .u's are the ionic mobilities of different species of the metal ion 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 $(u_0+u_1 / 2)$ provided $k_1[L]=1$ Accordingly the pH corresponding to the average value of u_0 and u_1 is found from the figure 1. With the knowledge of the dissociation constants of Resorcinol(pk_2= 11.32, Pk_1,= 9.15)[2] and of Tyrosine (pk_2= 10.1, Pk_1,= 9.11)[3]. the concentration of Tyrosinate ion and Resorcinol 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 Cu(II) with Tyrosine ,Resorcinol and EDTAIonic Strength = 0.1 M, Temp. = 25°C , 30°C .

Stability constants	**Cu (II) value**	
	Calculated values	Literature values *
$\log k^{M}_{M-Tyrosine}$	6.53	7.80*
$\log k^{M}_{M-Resorcinol}$	12.55	-
$\log k^{M}_{M-EDTA}$	13.53*	18.70*
$\log k^{M}_{M-Tyroisne-EDTA}$	7.43	-
$\log k^{M}_{M-Resorcinol-EDTA}$	9.81	-

Reference no.(for column ii) – 4
Reference no.(for column iii) – 5 , 6

M- EDTA System:

The overall mobility's of the metal ion in solution in the presence of EDTA 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 EDTA anion is assumed to combine with one bivalent metal ion to give a 1:1 M-EDTA binary Complex, which is in conformity with finding of the other workers[7-9]. The stability constants of complexes with EDTA (K^{M}_{M-EDTA}) were calculated as described for the M-Tyrosine/Resorcinol system and are given in Table 1.

M-Tyrosine–EDTA System and M-Resorcinol-EDTA system

This system was studied at pH 8 with a specific purpose . It was observed from mobility curves, for M-Tyrosine/Resorcinol and M- EDTA binary System that binary complexes are formed much before pH 8 .To avoid any side interactions the transformation of the M-Tyrosine/Resorcinol complexes into M-Tyrosine/Resorcinol-EDTA complexes is investigated at Ph. 8.0 .

The plots of overall mobility (Absorbance difference)against -log [EDTA] 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-Tyrosine/Resorcinol 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 of 1:1 M- EDTA complex (fig -2) .It is therefore inferred that the species corresponding to the second plateau is due to the coordination of $EDTA^{4-}$ anion to a 1:1 M -Tyrosine/Resorcinol anion moiety resulting the formation of 1:1:1 $(M\text{- Tyrosine/Resorcinol-EDTA })^{3-}$ mixed complex . This can be shown as :

$(M\text{-Tyrosine})^{+}$ + $EDTA^{4-}$ __________ $(M\text{-Tyrosine-EDTA})^{3-}$ ……………….. (3)

$U = u_0\ f\,M\text{-Tyrosine} + u_1 f\,M\text{-Tyrosine-EDTA}$ …………………….. (4)

$(M\text{-Resorcinol})^{+}$ + $EDTA^{4-}$ __________ $(M\text{- Resorcinol-EDTA})^{3-}$ ……………….. (3)

$U = u_0\ f\,M\text{- Resorcinol} + u_1 f\,M\text{- Resorcinol-EDTA}$ …………………….. (4)

Where u_0 and u_1 are the mobilities and f M-Tyrosine/Resorcinol and f M-Tyrosine/Resorcinol-EDTA are the mole fractions of M-Tyrosine/Resorcinol and M-Tyrosine/Resorcinol-EDTA complexes respectively . From fig -3 the total concentration of EDTA at which the overall mobility is mean of the mobilities of the two plateaus was determined . For this the concentration of $EDTA^{4-}$ anion at pH 8.0 was calculated .$k^{M\text{-}}_{tyrosine/resorcinol}$ is obviously equal to 1/[L] . These calculated values of stability constants are also recorded in table 1.

Fig 1. Mobility Curve: Cu (II)-Tyrosine system and Cu (II)-Resorcinol system

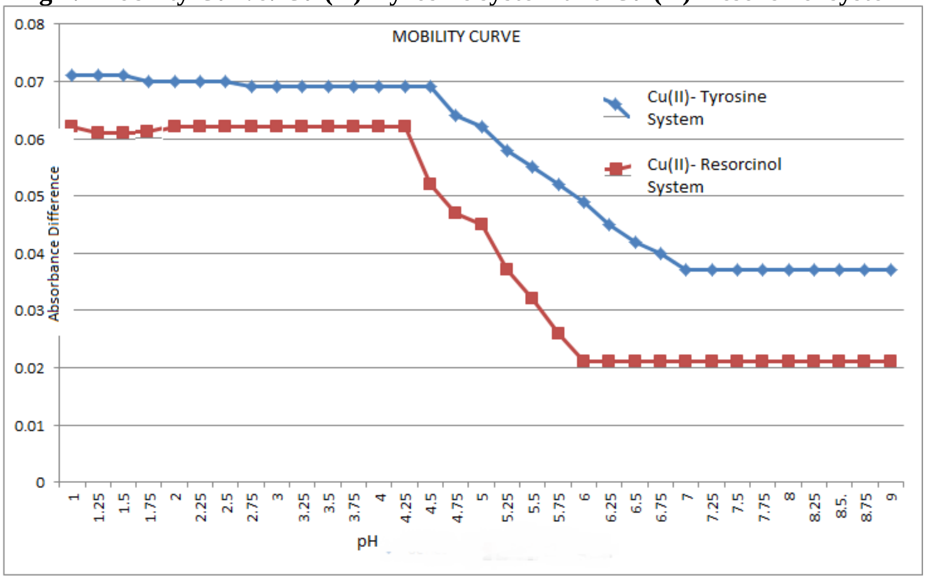


Fig 2. Mobility Curve: Cu (II) – EDTA system

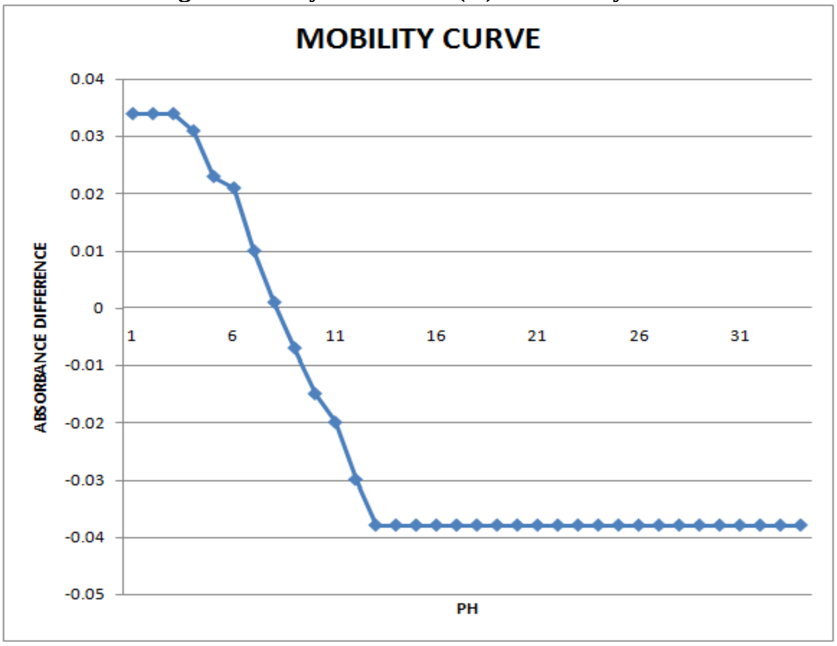
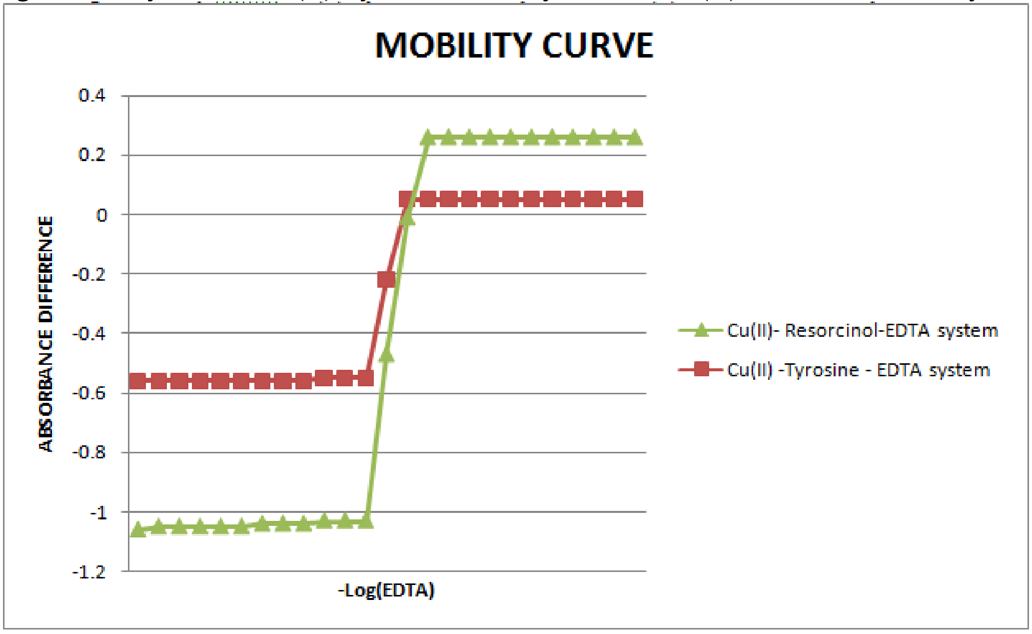


Fig 3 .Mobility Curve : Cu(II)-Tyrosine-EDTA system and Cu(II)-Resorcinol-EDTA system



References

[1]. JOURNAL-Singh,R.K.P.; and Yadav, K.L.;J.Electrochem.Soc.India (1986) 35,77.

[2]. PAPER-Dept. of general chemistry, Indian Institute of science, Bangalore(India) by C .J Abhichandani and S.K.K Jhatkar :1722-33,printed at the Banglore press.

[3]. JOURNAL -J .Biol .Chem . 1930,88:589-600 by John B . Dalton , Paul L . Kirk and Carl L.A Schmidt.(from the division of biochemistry , University of California Medical school,Berkeley)

[4]. Article- The apparent dissociation constant of diiodotyrosine , its heat of solution and its apparent heat of ionization . www.jbc.org by guest on march 8th ,2016 (page no .-592)

[5]. THESES-Doctoral thesis of SyedaSameenaAziz , 2002, University Of Allahbad. JOURNAL- DuyguInci – RahmiyeAydm ;J.SolutionChem (2014) 43:711-726 .

[6]. BOOK-Martell,A.E.,andSmith,R.M., (ed) Critical stability constants,vol – I ,aminoacids ,Plenum press , New York (London) , 11 ,35 ,139, 204 (1974)

[7]. JOURNAL-Joshi,R, Banerjee,S.P ,J.Ind.Chem.Soc .; 74 ,601-603 (1997) .

[8]. BOOK-Ayres ,H.;Gilbert; ¨Qualitative Chemical Analysis¨ , New York ,London ,John wea.BOOK CHAPTER-Norkers,E;Vaskelis , A; Zakaites I ; Talanta , 43(3) 465-470 (1996) .

[9]. BOOK-Text book of Quantitative Chemical Analysis , Vogel 5th edition (2001) 454-462 .