Research Article

STUDY OF THE STABILITY CONSTANTS OF FEW BINARY METAL-EDTA COMPLEXES USING A NOVEL IONOPHORETIC TECHNIQUE

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ABSTRACT

Ionophoretic technique is used as a novel tool for the study of binary metal-EDTA complexes in the solution state. The specially designed simple Ionophoretic tube has been used for the investigation of the stability of metal-EDTA complexes. A graph of mobility against p^H is used to obtain the information of stepwise complexation of binary metal-EDTA complexes. The stability constants of Fe(III)-EDTA, Cu (II)-EDTA, Co (II)-EDTA and Ni(II)-EDTA complexes are found to be $10^{16.67}$, $10^{13.53}$, $1O^{13.16}$ and $10^{12.37}$ respectively at 25⁰C. The stability of complexes is in accordance with Irving William[4] natural order of stability

INTRODUCTION

Ethylene Diamine Tetra Acetic Acid (EDTA) is the first synthetic and abundant chelating ligand among all poly carboxylic Acids. The ligands like EDTA, DTPA, and NTA are used as laundry detergents or in the paper and textile industries .EDTA was patented by Munz1 and has wide spread applications . EDTA binds to catalytically active metal ions like Iron, Copper and Manganese. So the metals are not able to destroy bleaches. They are also used as water softeners. Other applications are in medical domain where chelators are applied as detoxificators to cure metal poisoning or as markers for special examinations. They are also used as tracers in groundwater studies. Hence the complexes must fulfill some requirement like water solubility thermodynamic stability and kinetic inertness. keeping this in view the investigation of stability of binary metal EDTA complexes viz.Fe(III)-EDTA Cu(II)-EDTA, Co(II)-EDTA and Ni(II)-EDTA is being done using simple and novel ionophoretic technique .

Experimental

Binary Fe(III-)EDTA,Cu(II)-EDTA,Co(II)-EDTA and Ni(II)-EDTA complexes.

A set of 15ml solution each containing $1×10-4$ M Fe (III) / $1×10-3$ M Cu(II),Co (II) and Ni(II)

0.1M HCLO4 and 0.2×10-3 M for Fe (III) and 0.2×10-2M EDTA for Cu (II), Co(II) and Ni(II) Were prepared at different P h values (by adding NAOH solution)

A set of 15 ml solution each containing $1x10^{-3}$ Co(II), 0.1M HClO$_4$ and $1x10^{-2}$ M ADP/ATP were prepared at different pH values (by adding NaOH solution). A 10 ml of the solution is taken in the electrophoretic tube and thermostated at 25°C. The tube (18 cm & 5 cm diameter) with a stopper in the middle was fused perpendicularly at the ends with short wider tubes of 1.2 mm diameter. 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 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 out in 15 ml flask the FE(III)content of the solution was converted In to Fe(III)thiocyanate Complex and Co(II) thiocyanate complexes and the absorbance was measured after making the volume to 15 ml. The Cu (II) content, Co(II) content of the anodic compartments Were converted to Cu(II) thiocyanate complex and Co(II) thiocyanate complexes and the Absorbance was measured at 420 nm and 625 nm

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The Ni(II) content of the solution was converted into nickel di methyl glyoximate complex And the absorbance at 445 nm was measured with spectrocolorimeter.

RESULTS AND DISCUSSION

Figure 1 shows the relationship between absorbance difference and the pH's and thus gives an idea of the change of overall mobility of metal ion species with change in hydrogen ion status of the systems containing *Fe(III-)EDTA,Cu(II)-EDTA,Co(II)-EDTA and Ni(II)-EDTA complexes.*
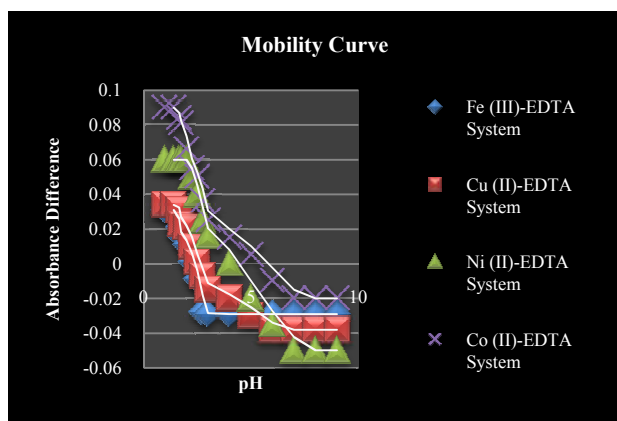
It is clear from the fig that all the four metal ions, two plateaus are obtained. The first plateauat low p^H shows the uncomplex metal ions were the concentration of highly protonated species of EDTA is maximum. Beyond this plateauthe mobility of the metal ion Decreases as the hydrogen ion concentration increases and EDTA exists as increasingly Deprotonated L^{4-} anionic species. In this region complexation of the metalion take place with this anionic species EDTA. The mobality in last plateau in each case lies in the negative region Showing negatively charged nature of the metal EDTA complexes hence it is inferred that only one anionic liganding species of EDTA combines with the metal ions, v_{iz}-Fe (III), Cu(II),Ni(II),Co(II) and to give 1:1(M-EDTA) Complex further increase of p^H beyond this plateau does not give any change in the mobility of the metal ions

Accordingly the pH corresponding to the average value of U_0 and U_1 is found from the figure. With the knowledge of the dissociation constants of EDTA the concentration of ligand at this pH are calculated. Its reciprocal gives the stability constants of the complexes. The calculated values are given in table - 1. The complexing capacity of the metal EDTA complexes is found to Be in the order i.e Fe(III) $\geq$ Cu (II)-EDTA $\geq$ Ni(II)-EDTA $\geq$ Co(II)-EDTA ,which is in accordance with the Irving Williams order**.** The overall, mobility (U) is a composite parameter contributed by different ionic species of the metal ion and is given by the following equation 1.

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

Where K' s are the stability constants of complexes and [L] is the concentration of ADP/ATP 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(1) is 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 graph with the knowledge of dissociation constant of EDTA, the concentration of EDTA at this pH is calculated. Its reciprocal gives the stability constants of the complexes. The calculated values are given in Table.1. The complexing capacity of the metal EDTA complexes is found to be in the order i.e., Fe(III) > Cu(II) > Ni(II) > Co(II), which is in accordance with the Irving- William's natural order of stability.

Table 1

Stability constants of 1:1 Metal –EDTA complexes ionic strength = 0.1M and temperature = 25^0c

Metal complexes	Calculated values	Literature values[3]
Fe(III) - EDTA	16.67	25
Cu (II) – EDTA	13.53	18.70
Co (II) – EDTA	13.16	18.52
Ni(II) – EDTA	12.37	16.26

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