NEW IONOPHORETIC TECHNIQUE FOR THE STUDY OF METAL COMPLEXES PART 1-GLYCINATE COMPLEXES

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Inophoretic technique has been used for the study of glycinate complexes of Cu(II) and Fe(III). Two complexes are formed with each metal ion. The stability constant of different species [CuL (log K = 8.15) CuL_2 (log K = 6.95) FeL^{2+} (log K = 9.72) and FeL_2^+ (log K = 8.45)] have been determined at 25°C and, μ = 0.1.

Migration of ions of pure electrolyte solutions has been widely studied but the migration in mixed electrolyte solution has not as yet been much investigated. This paper deals with later aspect. A successful effort has been made to assess the stability constants of mononuclear complexes formed in a system containing various electrolyte ingradients. A simple electrophoreic tube has been designed which yields good results after standardisation.

EXPERIMENTAL

Two sets of solutions each containing 2.0×10^{-5} M Cu(II), and 0.1 M $HClO_4$ with either 1.0×10^{-2} M or 1.0×10^{-3} M glycine were prepared. The pH of these solutions were adjusted to different values (by adding NaOH solution). 10 ml of each aliquot was taken in an electrophoretic tube and then thermostated at 25°C. The tube is 18.0 cm long and of 5 mm bore with a stopper in the middle and is fused perpendicularly at the ends with short wider tubes of 1.2 cm. bore. The position of the tube is adjusted in such a way that the level of the solution in one wide end arm reaches a circular mark on it. This adjustment fixes the volumes of the solution on both sides of the middle stopper. Two 0.5x 0.5 cm^2 platinum electrodes were dipped in each arm cup and a potential difference at 30 V was applied between them. Electrolysis of the solution was allowed for 30 minutes after which the middle stopper of the tube was closed. The solution of the anodic compartment was taken out in a 10 ml flask. The copper content of the solution was converted into Cu-Salicylic acid - nitrite complex [1]. The volume was made up to the mark in the flask and then absorbance at λ= 420 nm was measured with spekol Spectro-Colorimeter.

For the study of Fe (III) - glycine system, stock solution of M/100 Fe (III) was prepared by oxidizing standard ferrous ammonium sulphate solution with HNO_3 (1 ml). The excess of the acid was bolied off. Here again like Cu (II) - glycine system two sets of 50 ml solutions each containing 5.0×10^{-4} Fe (III) 0.1 $HClO_4$ with either 5.0×10^{-2} M or 2.5×10^{-2} M glycine at different pH'S were prepared. Each aliquot was electrolysed as in case of copper. The Fe (III) content of the anodic compartment was converted into Fe (III) - thiocyanate coplex [2] and absorbance at λ= 480 nm was measured after making up the volume to 10 ml.

It was found that absorbance by the Cu (II) - Salicylic acid-nitrite complex and Fe (III)- thiocyanate complex obeys Beer's Law in the relevant concentration ranges of the metal ions used in the ionophoretic studies and the presence of the glycine does not interfere in the absorbance measurements.

THEORETICAL

Under a potential gradient, a metal ion will move in the field, the speed and its direction depending upon the charge and size of the ion. Assuming the metal ion to have ligated with a ligand to give complexes as:

$$M^{n+} + L^- \underset{}{\overset{K_1}{\rightleftharpoons}} ML^{(n-1)+}$$

$$ML^{(n-1)+} + L \underset{}{\overset{K_2}{\rightleftharpoons}} ML_2^{(n-2)+}$$

It is obvious that free metal ion, $ML^{(n-1)+}$ and $ML_2^{(n-2)}$ complexes constitute

$$\frac{1}{1+K_1[L]+K_1K_2[L]^2} \qquad \frac{K_1[L]}{1+K_1[L]+K_1K_2[L]^2}$$

and $$\frac{K_1K_2[L]^2}{1+K_1[L]+K_1K_2[L]^2}$$

fractions respectively of the total metal in reaction mixture. During the process of electrolysis, different ions move in swarm in one direction or the other direction. Hence the environment of any ionic entity remains unchanged in bulk during migration. As such the composition of the metal ion (in free as well as in ligated states) remains intact during the migration. No doubt the speed of various ionic species of metal ion should be different, but the condition of fixed

composition at all time during the migration rules out separtion of the species in the bulk. Overall effect of this over-riding condition is that metal ion will move with a speed which is composite of weighted speeds of free and coplexed metal ions. The weighting factors should be actual fraction of the total metal ion constituted by a particular species. Hence the overall, mobility,U,should be given by the following expression as used by different workers [3,4].

$$U = f_1 u_1 + f_2 u_2 + f_3 u_3 + \ldots\ldots\ldots$$

where u_1 , u_2 , u_3 and f_1 , f_2 , f_3 are mobility and mole fraction of M^{n+} , $ML^{(n-1)+}$ and $ML_2^{(n-2)+}$ respectively.

if the tube is not uniform, the potential gradient will be different at different places. The resistance of the reaction mixture present in narrower zones of the tube will be greater than an overall resistance which should be constituted of several varying resistances put in series. Obviously the potential gradient in the norrower zone will be more than that in the broader zones. It would certainly be inversely proportional to the cross sectional area of the bore at that particular zone and hence the mobility of a particular ion in this zone will also be inversely proportional to the cross sectional area of the bore at that zone. This will lead to the necessary conclusion that the number of ions passing out through any cross sectional area per unit time would be the same regardless of the non uniformity of the tube.

A number of factors (e.g diffusion, ionic strength, temperature) obviously vitiate the electropohretic mobility of a particular ion. Diffusion should be significant in the vicinity of the electrodes. A perusal of the literature reveals that the diffusion coefficients to the ions are $\sim 10^{-5}$ cm^2 sec units which is negligible in comparision to the ionic mobilites ($\sim 10^{-3}$ cm). Thus diffusion cannot affect the electrophoretic mobilities. For assessment of the effect of other factors, electrolysis of metal ions Cu^{2+} and Fe^{3+} at two concentrations and in presence of the medium of identical acidity and the ionic strength was carried in the electrophoretic tube. The loss in concentration of the metal ion in anodic compartment from (absorbance measurements), should obviously be proportional to mobility of positively charged metal ion leaving that compartment. Table 1 records our observation. It is seen that the ratio of the loss in concentration in the anodic compartment and the concentration before electrolysis is constant regardless of the initial concentration of the metal ions. This fact amply justifies the view point that in the electrolysis process in the tube the mobility of the metal ion is not at all changed by its dilution or nonuniformity of the tube. In the literature ionic mobility of Cu (II) and Fe (III) is reported as 2x56.6/96500 and 3x68/96500 [5]. The ratio of

TABLE 1

μ = 0.1 TEMPERATURE = 25°C

IONOPHORETIC MOBILITIES IN THE IONOPHORETIC TUBE

Metal ion	Conc. x 10^4 M/L	Absorbance* A_0	Absorbance* A_t	ΔA^{**} / A_0	ΔA.R (Fe III) / A.R (Cu (II))
Fe(III)	5.0	1.00	0.41	0.59	1.78
Cu(II)	0.2	0.80	0.53	0.33	
Fe(III)	2.5	0.50	0.21	0.58	1.78
Cu(II)	0.1	0.40	0.27	0.325	

* A_o is absorbance before electrolysis; A_t is absorbance after 30 mts electrolysis

** Absorbance ratio (A.R) is $(A_0 - A_t)/A_0$

these two mobilities is 1.80. The ratio as determined electrophoretically comes out to be 1.78 which is quite in agreement with the literature value.

Thus ionophoretic measurements obtained with electrophoretic tube is reliable to ± 1% error.

RESULTS AND DISCUSSION

Figure 1a and 1b illustrate relation between absorbance differences and pH's and thus give an idea of the change of overall mobility of the metal ion species with change in hydrogen ion status of the system containing metal ion and glycine. In each figure three plateaus are discernible. The first plateau corresponds to a region

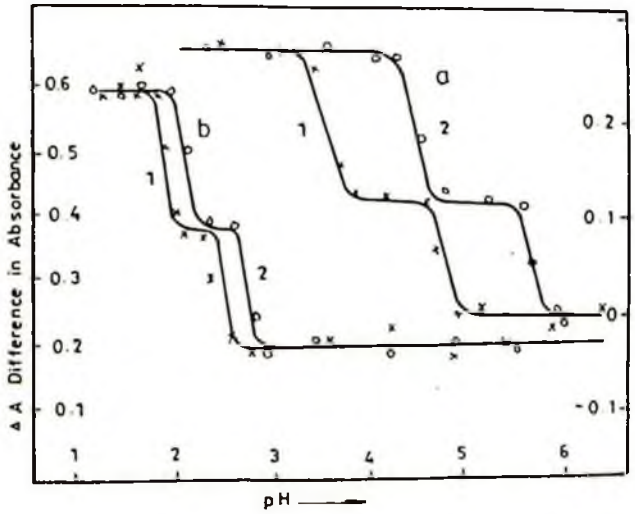


Fig. 1a Cu(II) - Glycenate System
1) 10^{-2} M Glycine; 2) 10^{-3} M Glycine

Fig. 1b Fe(III) - Glycinate System
1) 5×10^{-2} M Glycine; 2) 2.5×10^{-2} M Glycine

of pH where metal ion is uncomplexed. Further increase in ligating glycinate anion concentrations, 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 in the figure is reached beyond which mobility of the metal ion species remains constant regardless of increase of pH of reaction mixture. This is second plateau which corresponds to a pH region in which 1:1 metal: ligand complex is overwhelmingly formed. Beyond this plateau, increase of pH further decreases the mobility till a third plateau is obtained. This plateau corresponds to overwhhelming formation of 1:2 metal ligand complex. The second plateau in case of Cu(II) -glycinate system and second and third plateaus in case of Fe(III) -glycinate system indicates the movement of the complex metal ion species towards cathode and hence positive charges on 1:1 Cu(II) -glycinate and 1:1 and 1:2 Fe(III) -glycinate complexes are confirmed. The movement in the region of third plateau of the Cu(III) -glycinate system is zero which substantiates electroneutrality of the 1:2 Cu(II) -glycinate complex. It is apparent from the figures that the curves remain unaffected upto 10 pH and hence no other complexes are formed upto this pH.

Stability Constant

The overall mobility U as mentioned earlier is a composite parameter contributed by different ionic species of the metal ions. It would be given by the following equation:

$$U = \frac{u_o + u_1 K_1 [L] + u_2 K_1 K_2 [L]^2 + \cdots\cdots}{1 + K_1 [L] + K_1 K_2 [L]^2 + \cdots\cdots}$$

Where K's are stability constants of complexes and [L] is the concentration of glycinate anion. U's are the ionic mobilities of the different species of the metal ions which can be assessed from the plateaus of the figures. In the region between first and second plateau, the system contains overwhelmingly a mixture of free metal and 1:1 complex. The existence of 1:2 complex can be excluded and hence the third term in the numerator and denominator of the above equation can be justifiably neglected. U would be equal to ($u_o + u_1$) /2 provided $K_1 [L] = 1$. Accordingly the pH corresponding to the average value of u_o and u_1 is found from figures. From the dissociation constants of glycine cited in literature $pK_1 = 2.40$ $pK_2 = 9.60$) [6]. The concentration of glycinate ion at this pH is calculated. Its reciprocal gives the stability constant K_1 of the 1:1 complex. Considering the region between the second and third plateau, the stability constant K_2 of the 1:2 complex is calculated likewise. The values along with literature values are given in Table 2. It is to be noted that our values are in fair agreement with the literature values in case of Cu complexes

TABLE 2

STABILITY CONSTANTS
μ = 0.1 Temperature = 25° C

Metal ion	Glycine Conc.(M)	Stability constants pK_1	pK_2	Literature value [6]
Fe(III)	5.0×10^{-2}	9.71	8.40	
		9.72	8.45	10.0
Fe(III)	2.5×10^{-2}	9.74	8.50	
Cu(II)	10^{-2}	8.10	6.90	
		8.15	6.95	8.25
Cu(II)	10^{-3}	8.19	7.00	6.85

whereas there is some variation in case of Fe(III) complex. The cause of variation in latter case is probably the fact that hitherto no other worker has been able to pinpoint the formation of 1:2 complex of this metal ion and naturally their evaluation of stability constant of 1:1 complex must have been vitiated.

The transition from first to second plateau and second to third plateau may be conjectured to be due to formation of pure or mixed hydroxy complexes. If it is possible, then the stability constants of these hydroxy complexes would be given by an equation $K_1 \times [OH] = 1$ and $K_2 \times [OH]^2 = 1$ in the region between first and second plateau and between second and third plateau respectively. As such the average of the plateau mobilities would correspond to fixed pH value irrespective of glycine concentration. With each metal ion two separate curves are obtained for the two different glycinate concentrations. The average value of mobility in the two curves in each case lies at different pH's which clearly indicates that hydroxy complexes are not formed in this system. Moreover of the stability constants calculated from the two curves for a given metal are quite consistent which each other.

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