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A New Ionophoretic Technique for the Study of Metal Complexes

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A new ionophoretic technique has been evolved for the study of thiourea complexes of Cu(II), Ni(II), Co(II) and Zn(II). Two complexes are formed with each metal ion. The stability constants (K_1, K_2) 2.80, 1.70; 2.00, 1.16; 1.80, 1.70; and 1.80, 1.70 respectively have been found out at 35°C and $\mu = 0.1$.

INTRODUCTION

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

EXPERIMENTAL

Procedure

One set of 50 ml solutions each containing 1×10^{-3} M Cu(II)/Ni(II)/Co(II) and Zn(II), 0.1 M $HClO_4$ and 1×10^{-2} M thiourea was prepared at different pH's (by adding NaOH solution). 10 Ml of this aliquot was taken in an electrophoretic tube and then thermostated at 35°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 volume of the solution on both sides of the middle stopper. Two 0.5 × 0.5 cm platinum electrodes were dipped in each arm cup and a 50 volt potential difference 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 thiocyanate complex[1]. The volume was raised to the mark in the flask and then absorbance at $\lambda = 408$ nm was measured with Spekol spectro-colorimeter.

The nickel content of the solution was converted in Ni(II)-dimethyl glyoxime complex[2]. The volume was raised to the mark in the flask and then absorbance at $\lambda = 445$ nm was measured.

In the same manner the cobalt content of the solution was converted into Co(II)-thiocyanate complex[3]. The volume was raised to the mark in the flask and then absorbance at $\lambda = 625$ nm was measured. Finally zinc content of the solution was converted into Zn(II)-zincon complex. In the solution withdrawn from the anodic compartment, 10 ml of a pH 9.0 buffer were added. The solution was diluted to 250 ml and absorbance was taken at 620 nm wavelength.

It was found that absorbance by the Cu(II), Ni(II), Co(II) and Zn(II) ions with different complexing agents obeys Beer's law in the relevant concentration ranges of the metal ion used in the ionophoretic studies and the presence of the thiourea does not interfere in the absorbance measurement.

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:

$$M + L \overset{K_1}{\rightleftarrows} ML$$

$$ML + L \overset{K_2}{\rightleftarrows} ML_2$$

It is obvious that free metal ions and ML and ML_2 complexes constitute $\frac{1}{1 + K_1[L] + K_1K_2[L]^2}$ and $\frac{K_1[L]^2}{1 + K_1[L] + K_1K_2[L]^2}$ 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 a swarm in one direction or the other direction. Hence the environment of the entity remains unchanged in the 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 times during the migration rules out separation of the species in the bulk. Overall effect of this overriding condition is that metal ion will move with a speed which is composite of weighted speeds of free and complexed 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 used by different workers[4, 5]:

$$U = f_1u_1 + f_2u_2 + f_3u_3 + \dots$$

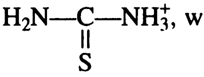
where u_1, u_2, u_3 and f_1, f_2, f_3 are mobility and mole fraction of M, ML^+ and ML_2^+ respectively.

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 a potential gradient in the narrower zone will be more than that in the broader zone. 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 and temperature obviously vitiates the electrophoretic 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 of ion are *ca.* 10^{-5} cm^2 sec^6, which is negligible in comparision to the ionic mobilities which are *ca.* 10^{-3} cm. Thus diffusion cannot affect the electrophoretic mobilities.

Thus ionophoretic measurements obtained with electrophoretic tube are reliable with about ± 1% error.

RESULTS AND DISCUSSION

Figure 1 illustrates the relation between absorbance difference and 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 systems containing metal ions and thiourea. In each figure three plateaus are discernible. The first plateau corresponds to a region of uncomplexed metal ion while the remaining plateaus indicate the formation of different complexes. It is obvious that the protonated ionic species of the ligand  $H_2N-\underset{\underset{S}{\|}}{C}-NH_3^+$, which abound in low pH ranges are non-complexing. Beyond the first plateau metal ion have progressively decreasing velocities and hence complexation of metal ions should be taking place with non-protonated species of this ligand, whose concentration increases with increase in pH of the electrolyte. The decrease in mobility continues till a second plateau in the positive range of mobility is evinced. The second plateau corresponds to overwhelming formation of a complex very likely of the 1:1 complex. The region between first and second plateau corresponds to progressive conversion of uncomplexed metal ion into binary complex with ligands. The overall mobility of the metal ion in this region is due to the individual contribution of the uncomplexed and the complexed metal ions.

On further increase of pH beyond the second plateau, the concentration of unprotonated species of ligands increases further and adduction of another molecule to 1:1 binary complex takes place. The mobility registers a downward trend, ultimately resulting in a third plateau which has positive mobility again tending to zero mobility. The third plateau obviously corresponds to overwhelming formation of 1:2 complex and, with further increase in pH, does not show any change in mobility ruling out formation of any other higher mononuclear complex.

Stability Constant

The equation for overall mobility is a general one. In view of the conclusion

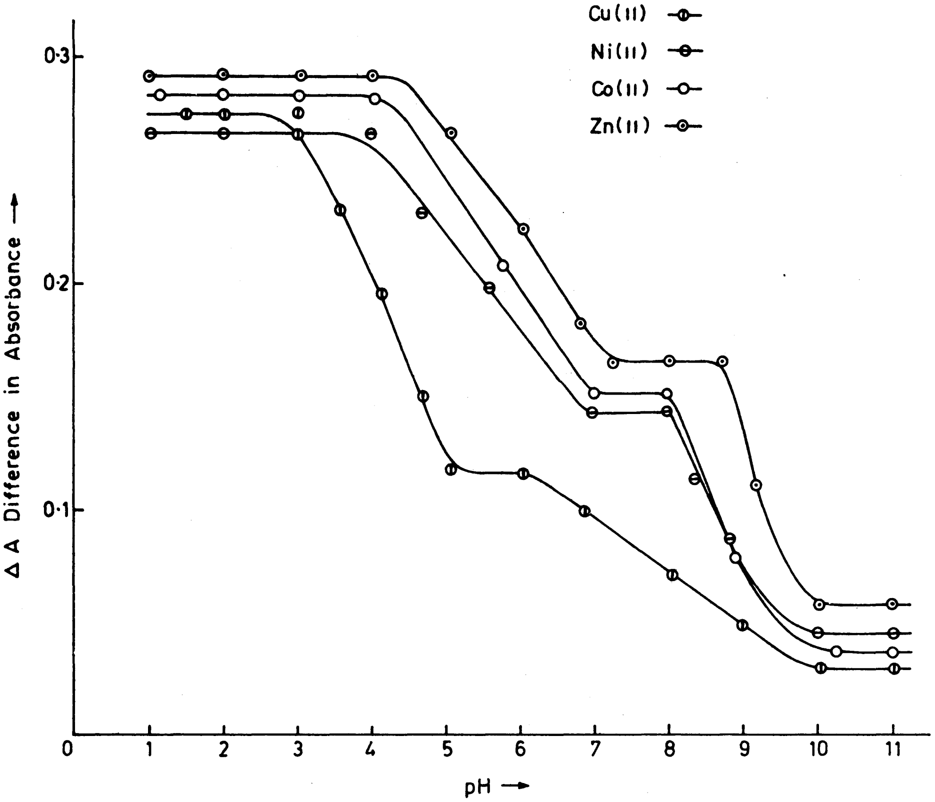


Fig. 1 Mobility curve M(II)-thiourea system (Temp.= 35°C, ionic strength = 0.1)

that unprotonated species of the ligands are the only ligating species and further number of complexes formed being two of 1:1, 1:2 composition. The general equation can be particularized for the systems under investigation as follows:

$$U = \frac{u_0 + u_1K_1[L] + U_2K_1K_2[L]^2}{1 + K_1[L] + K_1K_2[L]^2}$$

Here u_0, u_1, u_2 are mobilities of uncomplexed metal ion 1:1 and 1:2 cationic complexes. L is unprotonated ligand, K_1 and K_2 are stability constants of 1:1 and 1:2 complexes expressed as:

$$K_1 = \frac{ML}{[M][L]}$$

$$K_2 = \frac{[ML_2]}{[ML][L]}$$

Using the principle of average mobility, K_1 can be calculated with the help of mobilities of first plateau and second plateau. Similarly K_2 can be calculated with the help of mobilities of second plateau and third plateau. The concentration of unprotonated ligands at different pH's for calculation of stability constants can be calculated taking help of the equilibria of protonated and deprotonated species of the ligands. Protonation constants help in assessment of the unprotonated species at any pH with the relevant equation:

$$L = \frac{Lt}{1 + K[H]^+}$$

Here L is unprotonated species, Lt is total ligand and K is protonation constant (thiourea = 5.5).

The calculated values of stability constants of 1 : 1 and 1 : 2 complexes are given in Table 1. It is to be noted that the stability constants of the metal ions obtained follow the Erving Williams order of stability constant

$$Zn < Cu > Ni > Co.$$

TABLE 1
STABILITY CONSTANTS

$\mu = 0.1$ Temperature 35°C

Metal ion	Calculated K_1	Value K_2
Cu(II)	2.8	1.7
Ni(II)	2.0	1.6
Co(II)	1.8	1.7
Zn(II)	1.8	1.7

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