Ionophoretic Study of Phenyl Thiourea Complexs of Bivalent Metals

Urmila Mishra, R.K.P. Singh & K.L. Yadava

Chemistry Department, University of Allahabad, ALLAHABAD-211 002

Migration of ions of pure electrolyte solutions has been widely studied. This paper deals with migration of mixed electrolyte solution to assess the stability constants of mono-nuclear complexes formed in a system containing various electrolyte ingradients. A simple electrophoretic tube has been designed for this purpose.

PROCEDURE

Details of electrophoretic tube and procedure are described earlier [1]. Solutions containing 1 x 10^{-3} M Cu(II) / Ni(II) / Co(II) / Zn(II) in 0.1 M $HClO_4$ and 1 x 10^{-2} M phenyl thiourea were prepared and adjusted to different pH values by adding NaOH solution. An aliquot of 10 ml of this solution was taken in the electrophoretic tube and thermostated at 35°C. The position of the tube was adjusted in such a way that the level of the solution in wide arm (at one end) reaches the circular mark on it. This adjustment fixes the volume of the solution on either side of the middle stopper. Two platinum electrodes, 0.5 cm x 0.5 cm, were dipped in the cup on each arm. Using 50 volt potential difference, electrolysis of the solution was carried out for 30 minutes. After this, the middle stopper was closed. The solution of the anodic compartment was taken out in a 10 ml volumetric flask.

It was found that absorbance by the Cu(II) thiocyanate complex, Ni(II) - dimethyl glyoxime complex, Co(II) - thiocyanate complex and Zn(II) - zincon complex obey Beer's law in the relevant concentration ranges of the metal ion used in the ionophoretic studies; the presence of thiourea does not interfere in the absorbance measurements. So metal content in the solution was determined colorimetrically as follows:

The copper content of the solution was converted into copper thiocyanate complex [2]. The solution was made upto the mark in the flask and then absorbance was measured at λ = 408 nm with spekol spectro colorimeter.

The nickel content of the solution was converted to Ni(II)-dimethyl glyoxime complex [3]. The solution was made upto the mark in the flask and then absorbance was measured at λ = 445 nm.

In the same manner the cobalt content of the solution was converted in Co(II) - thiocyanate complex [2b]. The solution

© ECSI, Bangalore

was made upto the mark in the flask and then absorbance was measured at λ = 625 nm.

Zinc in solution was converted to Zn - zincon complex in the following manner: 10 ml of a pH 9.0 buffer was added to the solution withdrawn from the anodic compartment and 3 ml of prepared zincon solution was added. The solution was diluted to 50 ml and absorbance was taken at λ = 620 nm.

It is obvious that a potential gradient in the electrophoretic tube is 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 necessary conclusion that the number of ions passing out through any cross-sectional area per unit time would be the same regardless of non-uniformity of the tube.

A number of factors - e.g. diffusion, ionic strength, temperature - vitiate the electrophoretic mobility of a particular ion. Diffusion should be significant in the vicinity of electrodes. A perusal of the literature reveals that the diffusion coefficients of ions are 10^{-5} cm^2 sec^{-1} which is very small in comparison to the ionic mobilities which are of the order of 10^{-3} cm[6]. Thus diffusion cannot affect the electrophoretic mobilities. It is found that the ionophoretic measurements obtained with electrophoretic tube is reliable with about ± 1% error.

RESULTS AND DISCUSSION

Figure 1 illustrates relation between absorbance difference and pH's and thus give an idea of the change in overall mobility of the metal ion species with change in hydrogen ion status of the

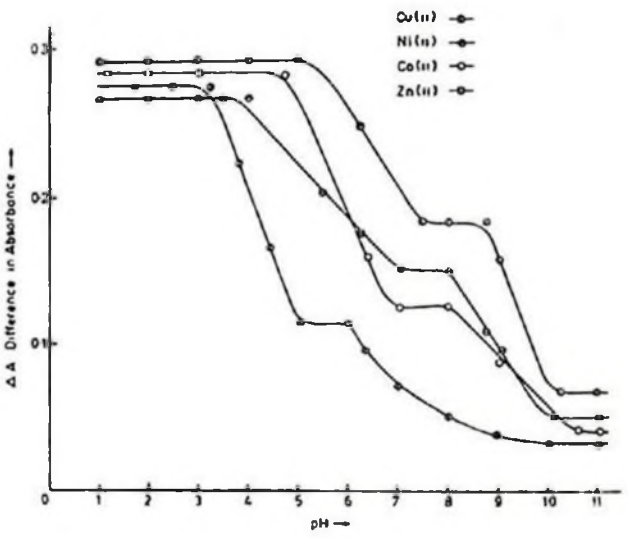


Fig 1 Mobility Curve of MetalPhenyl Thiourea System.
Temp. 35°C; Ionic Strength = 0.1M

systems containing metal ions and phenyl thiourea. In each curve, three plateaus are discernible. The first plateau represent the region of uncomplexed metal ion. The protonated ionic species of the ligand C_6H_5-NH-C(S)-NH_3^+ is in large excess in low pH ranges and this is non complexing. Beyond the first plateau, the absorbance difference decreases. Complexation of metal ions should be taking place with non protonated species of this ligand and complex metal ion have progressively decreasing velocities. Concentration of

non protonated species increases with increase in pH of the electrolyte. So more complexation should be occuring. The mobility continues to decrease till a second plateau in the positive range of mobility is reached. The second plateau corresponds to overwhelming formation of 1:1 complex. The region between first and second plateau corresponds to progressive conversion of uncomplexed metal ion into binary complex with uncharged phenyl thiourea.

On further increase of pH beyond the second plateau, one more uncharged phenyl thiourea molecule adds on to 1:1 binary complex. The mobility registers a downward trend. Ultimately a third plateu is noticed. The third plateau represents a region where 1:2 complex of metal ion predominates in the solution. Further increase of pH does not show any change in mobility ruling out formation of any other higher mono nuclear complex.

Stability Constant

The overall mobility as mentioned earlier [1] is a composite parameter contributed by different ionic species of the metal ions - free metal ion, 1:1 complex and 1:2 complex. In any given solution, the concentration of the three species is given as

$$\text{free metal ion} = \frac{1}{1 + K_1[L] + K_1K_2[L]^2}$$

$$\text{1:1 complex} = \frac{K_1[L]}{1 + K_1[L] + K_1K_2[L]^2}$$

$$\text{1:2 complex} = \frac{K_1K_2[L]^2}{1 + K_1[L] + K_1K_2[L]^2}$$

and overall mobility is given by

$$U = \frac{u_0 + u_1 K_1[L] + u_2 K_1K_2[L]^2}{1 + K_1[L] + K_1K_2[L]^2}$$

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 neglected in this region and hence the third term in the numerator and denominator of the above equation can justifiably be neglected. U would be equal to $(u_0 + u_1)/2$ provided $K_1[L] = 1$. The pH corresponding to average value of u_0 and u_1 is found from the figure. Using the dissociation constants of phenyl thiourea ($K_1 = 6.7$), the concentration of unprotonated phenyl thiourea at this pH is calculated. The reciprocal of this 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 are depicted in Table.

Table 1

Stability Constants

$\mu = 0.1$; Temperature = 35° C

Metal ion	Log K_1	Log K_2
Cu(II)	4.2	1.5
Ni(II)	2.7	1.7
Co(II)	1.8	1.7
Zn(II)	2.2	1.7

It is to be noted that the stability constants of the metal ions obtained, follow the Irving Williams order of stability constant Zn < Cu > Ni > Co.

REFERENCES

1. Snehalatha Tripathi, S. R. Tripathi and K. L. Yadava, *J.ElectroChem. Soc. India*, **41-4** (1992) 231-4.
2. *Colorimetric Methods or Analysis*, Snell & Snell, Volume II (a) page 67 (b) page 203.
3. A.I. Vogel, *Textbook of Quantitative Inorganic Analysis*, (IV Ed), **ELBS** (1978) p. 794.
4. J. Biernat, *Rocz. Chem.*, **38** (1964) 343: *C.A.* **61** (1964) 6456b.
5. V. Jokl. *J. Chromatogr.*, **14** (1964) 71.
6. *Hand book of Electrochemical Constants* Ed. Roger Parsons, **Butterworths Scientific Publication, London,** (1959) page 79.

FORM IV
(SEE RULE VII)

1.	Place of Publication	:	BANGALORE
2.	Periodicity of Publication	:	QUARTERLY
3.	Printer's Name Whether Citizen of India Address	: : :	Sri G.V. MAHESH, SECRETARY YES THE ELECTROCHEMICAL SOCIETY OF INDIA, INDIAN INSTITUTE OF SCIENCE CAMPUS, BANGALORE-560012.
4.	Publisher's Name Whether Citizen of India Address	: : :	Sri G.V. MAHESH, SECRETARY YES THE ELECTROCHEMICAL SOCIETY OF INDIA, INDIAN INSTITUTE OF SCIENCE CAMPUS, BANGALORE-560012.
5.	Editor's Name Whether Citizen of India Address	: : :	Dr. S.K. VIJAYALAKSHAMMA, YES THE ELECTROCHEMICAL SOCIETY OF INDIA, INDIAN INSTITUTE OF SCIENCE CAMPUS, BANGALORE-560012.
6.	Name and Address of Individuals who own the Periodical	: :	THE ELECTROCHEMICAL SOCIETY OF INDIA INDIAN INSTITUTE OF SCIENCE CAMPUS, BANGALORE-560012.

I, Sri G.V. Mahesh, hereby declare that the particulars given above are true to the best of my knowledge and belief.

Sd./-
(Sri G.V. MAHESH)