Asian Journal of Chemistry Vol. 15, No. 1 (2003), 353–358

Ionophoretic Technique in the Study of Mixed Complexes [M(II)-Nitrilotriacetate-Valine System]

SATYENDRA SINGH* and KANCHAN GAUR†
Department of Chemistry, Faculty of Science, Kashi Naresh Government Postgraduate College, Gyanpur, Sant Ravidas Nagar-221 304 Bhadohi, India

Binary equilibria of M(II)-valine and also mixed complexes formation have been studied using paper electrophoresis. The log k values for mixed complexes have been found to be 5.24, 3.21 and 3.13 for Hg(II), Cd(II) and Mn(II) complexes respectively at $\mu = 0.1$ and 35°C.

Key Words: Ionophoretic, Mixed Complexes, Mn(II), Cd(II), Hg(II), Nitrilotriacetate, Valine.

INTRODUCTION

Publications from our laboratories described a method for study of mixed complexes[1–4]. The present work is an extension of the technique and reports our observation on the mixed system, *viz.*, Mn(II)/Hg(II)/Cd(II)-nitrilotriacetate-valine.

EXPERIMENTAL

Systronics model no. 604, India horizontal-cum-vertical type paper electrophoresis equipment has been used. It has a built-in power supply (AC–DC) which is directly fed to a paper electrophoretic tank.

The electric current running through paper strips generates heat which causes evaporation of background electrolyte leading to serious error. In order to eliminate it, two hollow metallic plates coated outwardly with thin plastics have been used for sandwiching paper strips and thermostated water (35°C) is circulated through them. pH measurements were made with Elico model L_{1-10} pH meter using glass electrode.

Hg(II), Cd(II) and Mn(II) perchlorates were prepared by precipitating the corresponding carbonates from solutions of nitrates, washing the precipitate thoroughly with boiling water and treating with a suitable amount of 1% perchloric acid. The resulting mixture was heated to boiling on a water-bath and then filtered. The metal contents of the filtrates were determined as usual and final concentration was kept at 5.0 mmol L^{-1}.

1-(2-Pyridylazo)-2-naphthol (PAN), 0.1% w/v in ethanol was used for detecting the metal ions. A saturated solution of silver nitrate in acetone was sprayed on the paper and subsequently fumed with ammonia to detect glucose in the spot.

---

†Department of Physics, Faculty of Science, Kashi Naresh Govt. P.G. College,

Background Electrolyte

Stock solution of 5.0 mol L^{-1} perchloric acid, 2.0 mol L^{-1} sodium hydroxide and 0.5 mol L^{-1} complexant valine were prepared from analaR samples (BDH, Poole, Great Britain); 0.01 mol L^{-1} nitrilotriacetic acid (NTA) was prepared from a sample obtained from E. Merck (Dermstadt, G.F.R.). Each solution was standardized as usual. The background electrolyte in studies of binary complexes consists of 0.1 mol L^{-1} perchloric acid and 1.0×10^{-1} mol L^{-1} valine/1.0×10^{-3} mol L^{-1} NTA, while in studies of ternary complexes, it consists of 0.1 mol L^{-1} sodium perchlorate, 1.0×10^{-3} mol L^{-1} NTA and varying amounts of 1.0×10^{-2} mol L^{-1} valine. It was maintained at pH 8.5 by addition of sodium hydroxide.

Procedure

(i) For Binary Complexes

150 mL of background electrolyte is filled in the two electrode vessel. Paper strips, Whatman no. 1 (30 × 1 cm), in duplicate are spotted in the middle with different metal ions. An extra strip is marked with glucose. These strips are mounted on the insulated hollow plates lengthwise of the electrophoresis equipment with the end of the paper strips dipping into the two tanks. An hour is allowed for the strips to get wet by diffusion with background electrolyte solution. The second insulated hollow plates are placed on these paper strips to press them. The whole instrument is made air-tight to prevent the moisture change which may upset the equilibria on the paper strips. Subsequently electrophoresis is carried out for 1 h under the influence of 200 V potential difference between the two tank-solutions. The strips are then removed from the tanks, dried and migrated spots detected with specific reagents. The electrophoretic migration of metal spot on paper is observed at different pH of background electrolyte. Dividing movement by potential gradient yields mobility. These are plotted as a function of pH as shown in Fig. 1.

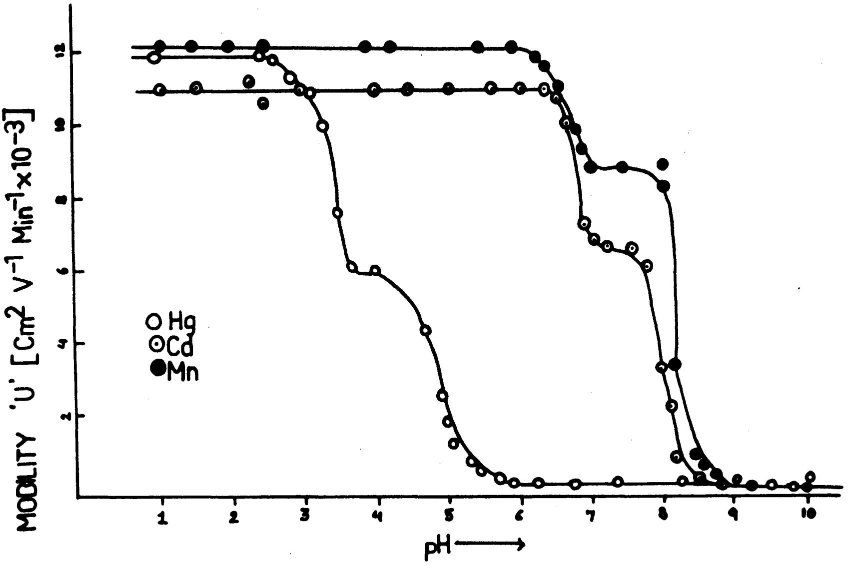

Fig. 1. Mobility Curve of [M(II)–Valine] System.

(ii) For Ternary Complexes

Same procedure is adopted as described in case of binary complexes. But in ternary complexes the background electrolyte is fixed at 8.5 pH by addition of NaOH. The secondary ligand valine is added progressively into the background electrolyte containing the primary ligand. Mobility is recorded at every addition of secondary ligand. A plot of mobility against log [valine] is made as shown in Fig. 2.

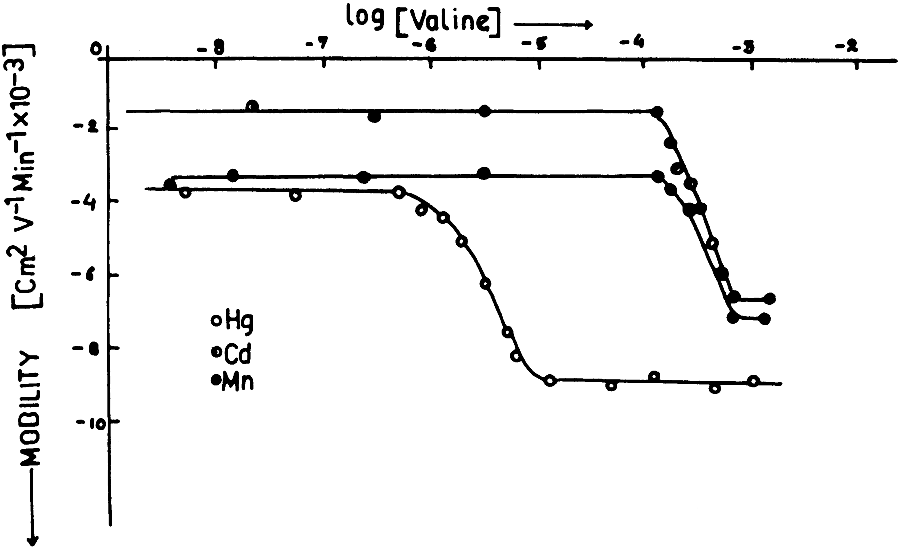

Fig. 2. Mobility Curve [M(II)–NTA–Valine] System

RESULTS AND DISCUSSION

Metal-Valine Binary System

The plot of overall mobility of a metal spot against pH gives a curve with a number of plateaus (Fig. 1). A graphic plateau indicates a pH range with practically constant velocity, where a particular complex is formed. Thus every plateau corresponds to the formation of certain complex species. The first plateau, at low pH, with a maximum of highly protonated, non-complexing species of valine corresponds to uncomplexed metal ions. Beyond this range, the metal ions exhibit decreasing mobility, indicating complexion with other ionic species of valine whose concentration increases with increasing pH. The second plateaus in each case, with positive mobility, indicate the formation of 1 : 1 complexes of cationic nature. Further increase in pH gives rise to the third plateau with positive mobility coresponding to 1 : 2 metal complexes of cationic nature, formed by two anionic species of valine with one bivalent metal ion. Literature also assigns prominent ligational property unprotonated anionic species of valine, however ruling out any such property for zwitter ions[5–7]. Further increase of pH has no effect on mobility of metal ions. The complexation of metal (M) ion with valine anion (L^-) may be represented as

$$M^{2+} + L^- \overset{K_1}{\rightleftharpoons} ML^+$$

$$ML^+ + L^- \overset{K_2}{\rightleftharpoons} ML_2$$

The overall mobility is given by Eq. (1):

$$U = \sum_n u_n f_n \tag{1}$$

where u_n and f_n are the mobility and mole fraction of a particular complex species. Eq. (1) is transformed into the following form on taking into consideration different equilibria:

$$U = \frac{U_0 + U_1k_1[L^-] + U_2k_1k_2[L^-]^2}{1 + k_1[L^-] + k_1k_2[L^-]^2} \tag{2}$$

where U_0, U_1 and U_2 are mobilities of uncomplexed metal ions, 1 : 1 metal complex and 1 : 2 metal complex, respectively.

Eq. (2) has been used for calculating stability constants of the complex of metal ions with the valine anion. For calculating the first stability constant, k_1, the region between the first and second plateau is pertinent. The ovrall mobility, U, will be equal to the arithmetic mean of the mobility of the uncomplexed metal ion, U_0, and that of the first complex U_1 at a pH where $k_1 = 1/[L^-]$. With the help of the dissociation constants of valine [$k_1 = 2.2$ and $k_2 = 9.4$][8, 9] the concentration of the valine anion (L^-) can be determined for the pH from which k_1 can then be calculated. The stability constant k_2 of the second complex can be calculated by taking into consideration the region between the second and third plateaus of the mobility (Table-1).

TABLE-1
STABILITY CONSTANTS OF BINARY AND TERNARY COMPLEXES OF Hg(II), Cd(II) and Mn(II)

Metal ion	$\log K^{M}_{ML}$	$\log \beta_{ML_2}$	$\log K_{M\text{-}NTA\text{-}L}$	$\log \beta_{M\text{-}NTA\text{-}L}$
Hg(II)	8.12	14.52	5.24	18.54
Cd(II)	4.31	8.01	3.21	13.74
Mn(II)	4.20	7.81	3.13	13.53

where $\log K^{M}_{ML} = \frac{[ML]}{[M][L]}$; $\log \beta_{ML_2} = \frac{[ML_2]}{[M][L]^2}$, $\log K^{M\text{-}NTA}_{M\text{-}NTA\text{-}L} = \frac{[M\text{-}NTA\text{-}L]}{[M\text{-}NTA][L]}$

Metal-Nitrilotriacetate Valine Ternary System

It is observed from the mobility curve of M(II)-valine and M(II)-NTA system[10–12] that binary complexes M(II)-valine and M(II)-NTA are formed at a pH lower than 8.5. Thus it would be proper to study the transformation of M-NTA complex into M-NTA-valine at pH 8.5 in order to avoid any side interaction.

The plot of mobility against logarithm of concentration of added valine gives a curve with two plateaus at both ends (Fig. 2). The mobility in the range of the first plateau corresponds to mobilities of 1 : 1 M-NTA complexes, in agreement with results in binary M-NTA system.

The mobility of the second plateau indicates the formation of a more negatively charged complex. The formation of the mixed complex can be represented as:

$$\text{M-NTA}^- + \text{L}^- \overset{K'}{\rightleftharpoons} \text{M-NTA-L}^{2-}$$

The overall mobility is given by

$$U = U_0 f_{M-NTA} + U_1 f_{M-NTA-L} \quad (3)$$

where U_0, U_1 and $f_{M\text{-}NTA}$ and $f_{M\text{-}NTA\text{-}L}$ are the mobilities and the mole fractions of M-NTA$^-$ and M-NTA-L$^-$ complexes respectively. Substituting the values of ion fractions the overall mobility is given in Eq. (4).

$$U = \frac{U_0 + U_1 K'[L^-]}{1 + K'[L^-]} \quad (4)$$

where U_0 and U_1 are the mobilities in the regions of the two plateaus of the curve. From the figure, the concentration of valine, for which the overall mobility is the mean of the mobilities of both the plateaus, can be determined. The concentration of anionic species of valine at pH 8.5, for this valine concentration of K′ is calculated and is obviously equal to 1/[L$^-$] (Table-1). The stability constant of the mixed complex is determined for the first time; so no comparison can be made from the literature.

Precision

The precision of the method, roughly ±5%, is limited to that of paper electrophoresis. Obviously this method cannot replace more reliable methods but it provides a new technique which is developing and, with further refinements, may prove valuable.

Conclusion

The ionophoretic technique, as modified in our laboratory, is simple as compared to other techniques. It helps determine the composition of mixed complexes and its stability constants with a fair degree of accuracy. It has its limitations in not being applicable in the cases of unchanged complex species.

REFERENCES

1. S. Singh, A.K. Bajpai and K.L. Yadav, *Electrophoresis*, **7**, 187 (1986).
2. S. Singh, B. Radha Rani, M. Vyas and K.L. Yadav, *Chemica Scripta*, **26**, 363 (1986).
3. M. Vyas, S. Singh, S.R. Tripathi and K.L. Yadav, *Croat. Chim. Acta*, **56**, 907 (1986).
4. S. Singh, S.R. Tripathi and K.L. Yadav, *Pak. J. Chem. Soc.*, **59**, 515 (1987).
5. A.A. Khan and W.U. Malik, *J. Indian Chem. Soc.*, **40**, 564 (1963); *Biochemistry*, **3**, 1169 (1964).
6. Jejowska, B. Triebiatowska and A. Antonow, *Bul. Acad. Pol. Ser. Chem.*, 226 (1974).
7. S.R. Saxena and G.L. Sharma, *J. Indian Chem. Soc.*, **59**, 635 (1982).
8. Y. Gergely, E. Parkas, I. Nagpal and E. Kas, *J. Inorg. Nucl. Chem.*, **50**, 1709 (1978).
9. B.A. Goodman, B. Donald, H. Kipton and J. Powell, *J. Chem. Soc.*, 822 (1981).
10. S. Singh, D. Gupta and K.L. Yadav, *J. Electrochem. Soc.*, **1**, 35 (1986).
11. S. Singh, M. Vyas and K.L. Yadav, *Anali Di Chimica*, **75**, 377 (1985).
12. S. Singh, D. Gupta and K.L. Yadav, *Himalayan Chem. Pharm. Bull.*, **2**, 34 (1985).

(*Received:* 15 July 2002; *Accepted:* 9 September 2002) AJC-2844
