A New Method for Study of Mixed Complexes in Solution (M-Nitrilotriacetate-threoninate system)

S.SINGH, R.CHANDER, P. KUMAR, S.R.TRIPATHI AND K.L.YADAVA*

Electrochemical Laboratories, Department of Chemistry, University of Allahabad, Allahabad-211002, India.

(Received 4th August, 1985, Revised 12th October, 1986)

Summary: A new method, involving the use of paper electrophoresis is described for the study of equilibria in mixed ligand complex systems in solution. This method is based on the migration of a spot of a metal ion, with the complexants added in the background electrolyte (0.1M perchloric acid). The concentration of one of the complexants (NTA) is kept constant, while that of second ligand (threonine) is varied. A graph of log threonine against mobility is used to obtain information on the formation of mixed ligand complex and to calculate the stability constants.

Introduction

Paper electrophoresis was applied to the study of metal complexes in solution, attempts were made to determine the stability constant of the complex species [1,2]. In recent work of these laboratories a new method has been developed for the study of the stepwise complex formation [3-6]. Although the use of paper electrophoresis for the study of metal complex systems with single ligand seems to be well established, there is no systematic study for mixed complexes. However, Czakis-Sulikowska [7] made some observations on the formation of mixed halide complexes of Hg(II), but it is only qualitative and does not throw light either on the nature of the species or on their stabilities. Publications [8-11] from our laboratories described a new method for study of mixed complexes. The present work is an extension of the technique and reports our observation on the mixed system viz. Be(II)/Ni(II)/Pb(II)-nitrilotriacetate-threoninate.

Experimental

Horizontal cum vertical type No.604 PE equipment (systronics) was used together with various accessories supplied with instrument. In each case electrophoresis was carried out for 60 min. at 200 volt at 35°C. Whatman No.1 paper strips (30 x 1 cm) was used. PH measurements were made with an Elico Model L_{1-10} pH meter using glass electrode.

Metal perchlorates were prepared by appropriate method and final concentrations were kept at 5.0×10^{-3}M. PAN (0.1% w/v) in ethanol was used for detecting Ni(II) and Pb(II) ions. Aluminon ammonium acetate mixture in water was used for detecting Be(II) ions. A saturated solution of silver nitrate in acetone was sprayed on the paper and subsequently fumed with ammonia to detect glucose spot.

The background electrolyte in the study of binary complexes consists of

* To whom all correspondence should be addressed.

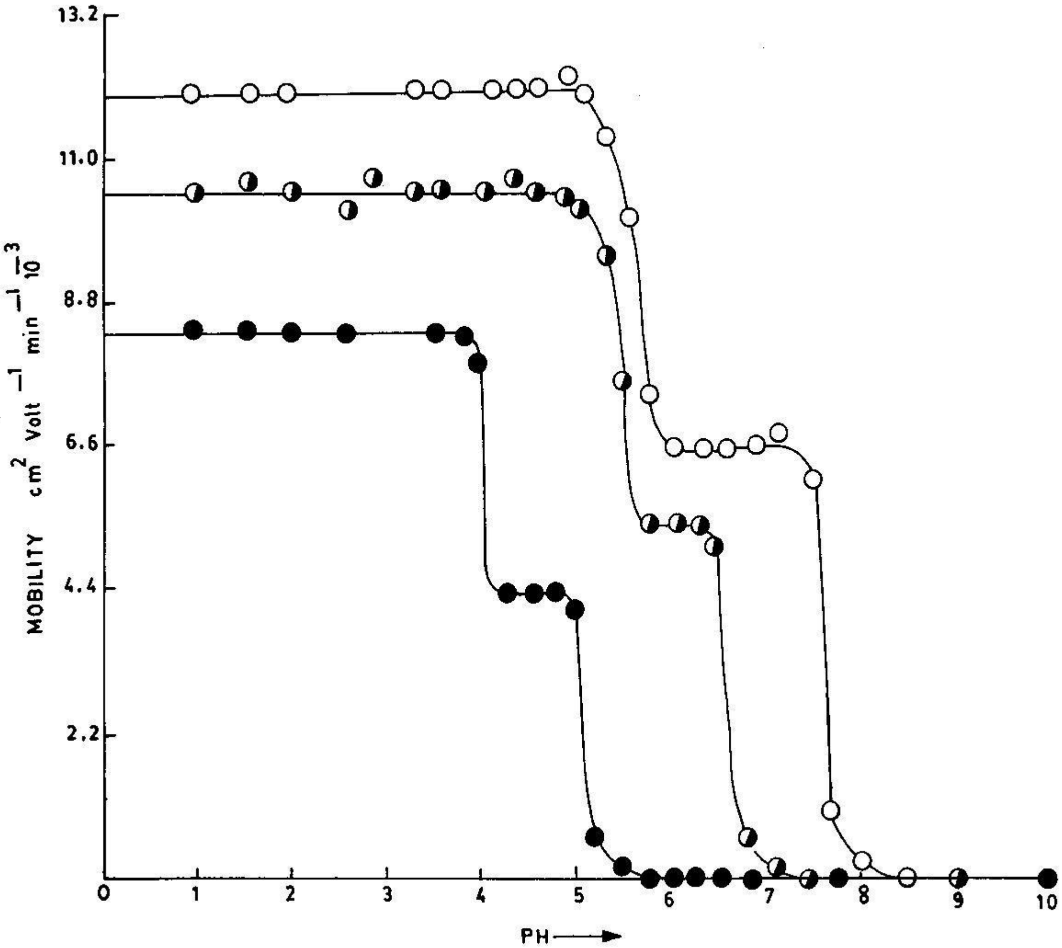

Fig-1: Mobility curves of [M-Threonine] system (Temp. 35°C, Ionic Strength 0.1).

0.1M perchloric acid and 1.0×10^{-2}M threonine/1.0×10^{-3}M NTA. While in study of ternary complexes, it consists of 0.1M sodium perchlorate, 1.0×10^{-3}M NTA and varying amounts of 1.0×10^{-2}M threonine, it was maintained at pH 8.5 by addition of sodium hydroxide solution.

Procedure:

I) For binary complexes:

Paper strips Whatman No.1 (30x1 cm) in duplicate are spotted in middle with metal ions. An extra strip is marked with glucose. The strips are sandwitched between two insulated hollow metal plates. The plates are then mounted on the electrophoresis equipment with end of paper strips dipping in two tanks of the instrument. Electrophoresis is carried out for 60 minutes. The strips are then removed from tank, dried and migrated spots are detected with specific reagents. Duplicate strips always recorded less than 5% variation in travelled distance. Mean of two was taken for calculation of mobility. Movement of glucose is used as correction factor for electrosmosis.

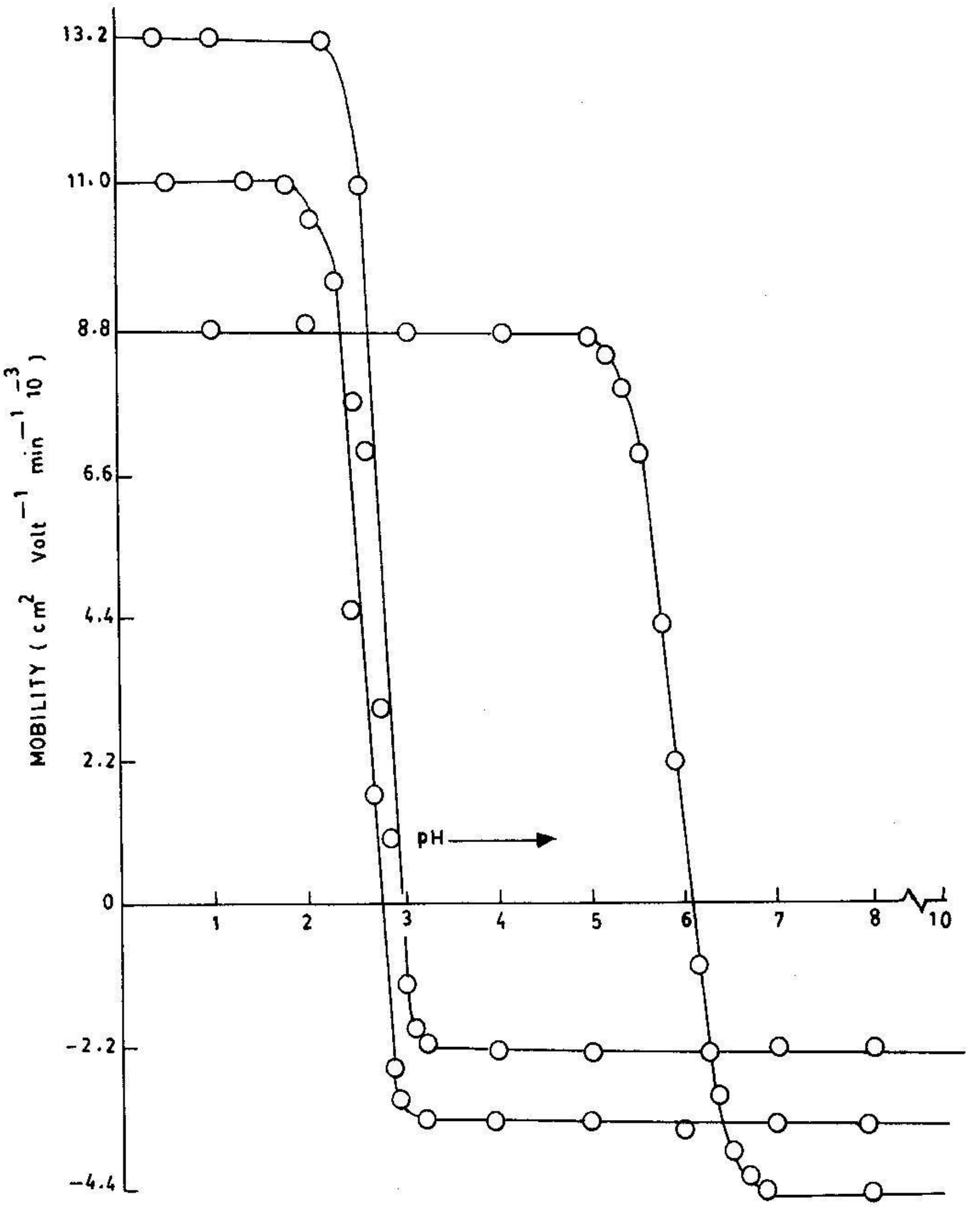

Fig-2: Mobility curve [M-NTA] system [Temp. 35°C Ionic Strength 0.1).

The electrophoretic migration of metal spot on paper was observed at different pH's of the background electrolyte. Dividing movements by potential gradient yields mobility which is plotted in figure 1 and 2.

II) For Ternary Complexes:

Strips are marked with metal ions in duplicate along with additional one marked with glucose. After drenching the strips with the background electrolyte the electrophoresis is carried for one hour at a same potential difference as in case of binary complexes. For subsequent observations, the threonine solution : maintained at pH 8.5 is added progressively and ionophoretic mobility is recorded. A plot of mobility against log threonine is made, which is shown in Figure-3.

Results and Discussion

1. Metal - Threoninate Binary Systems:

The plot of overall electrophoretic mobility of metal spot against pH gives a curve with a number of plateaus shown in Figure (1). A plateau is obviously indication of a pH range where speed is practically constant. This is possible only when a particular complex is overwhelmingly formed. Thus every plateau indicates the formation of a certain complex species. The first one in beginning corresponds to region in which metal ions are uncomplexed. It lies in low pH region where concentration of protonated species of threonine is obviously maximum. Hence it is concluded that this protonated species of threonine is non-complexing. Beyond this metal ion spot has progressively decreasing velocity and hence complexation of metal ion should be taking place with other ionic species of threonine whose concentration increases progressively with increase of pH. The figure reveals that the second plateau in each case with positive mobility indicates formation of 1:1 complex of cationic nature. Further increase in pH gives rise to a third plateau with zero mobility in each case which indicates formation of electrically neutral metal complex. This is possible only when two anionic species of threonine combine with one bivalent metal ion. Chemical literature also assigns prominent liganding property to unprotonated anionic species of threonine ruling out any such property to the Zwitter ion [12-14]. Further increase of pH has no effect on the mobility of metal ions.

The metal spot on the paper is thus a conglomeration of uncomplexed metal ions, 1:1 complex and 1:2 complex. This spot is moving under the influence of electric field, its overall mobility is given by equation [1]:

$$U = \Sigma_n u_n f_n$$

where u_n and f_n are mobility and mole fraction of a particular complex species respectively. This equation is transformed into the following form on taking into consideration different equilibria:

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

where u_o, u_1 and u_2 are mobilities of uncomplexed metal ion; 1:1 metal complex and 1:2 metal complex respectively. This equation has been used for calculating stability constants of the complexes of metal ions with threonine. For calculating first stability constant k_1, the region between first and second plateau is pertinent. The overall mobility 'U' will be equal to the arithmatic mean of mobility of uncomplexed metal ion, u_o and that of the first complex u_1 at a pH where $K_1 = 1/[L^-]$ with the help of dissociation constants of threonine ($k_1=10^{2.21}, k_2=10^{8.97}$) [15]. The

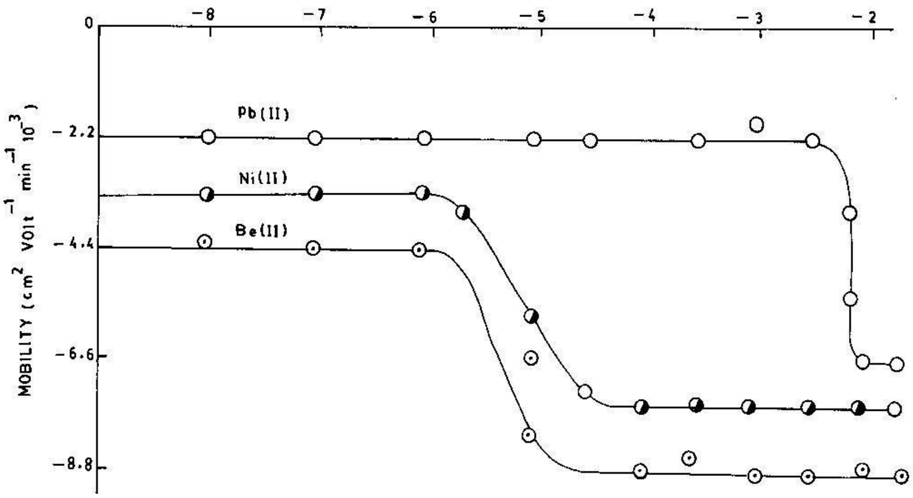

Fig-3: Mobility curve [M-NTA-Threonine] system [Temp. 35°C, Ionic Strength 0.1).

concentration of threoninate anion (L) is determined for the pH, from which K_1 can be calculated. The stability constants K_2 of second complex can be calculated by taking into consideration the region between second and third plateau of the mobility curve. These calculated values are given in Table-1.

2. M-Nitrilotriacetate Systems:

The observations on overall mobility of metal spots in presence of NTA at different pH values are represented in figure (2). As it is evident from figure that with all the three metal ions two plateaus are obtained, the mobility of last plateau lies in the negative region, showing negatively charged nature of the complexes. Hence only one NTA anion is assumed to combine with one bivalent metal ion to give 1:1 $M\text{-}NTA^-$ complex which is in conformity with finding of others [16-18]. The stability constants of complexes with NTA are calculated in a manner described in preceding paragraph. The calculated values are given in Table-1.

3. Metal-Nitrilotriacetate-Threoninate Ternary Systems:

The study of this system has been done at pH 8.5 with purpose. It is observed from the mobility curves M-threonine and M-NTA binary systems that binary complexes, M-threonine and M-nitrilotriacetate 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-threoninate complex at pH 8.5 in order to avoid any side interaction.

The plot of mobility against logarithm of concentration of added threonine gives a curve (fig.3) containing two plateaus- one in beginning and other in the end. The mobility of the range of first plateau corresponds to the mobilities of 1:1 M-NTA complexes. The mobility in this range is also in agreement with mobility of 1:1 M-NTA complex as evinced in the

Table-1: Stability constants of some binary and ternary complexes of Be(II), Ni(II) and Pb(II) (Ionic strength = 0.1); Temperature = 35°C

NTA anion = $N(CH_2COO)_3)^{-3}$; Threoninate anion = $CH_3 - \underset{OH}{CH} - \underset{NH_3}{CH} - COO^-$

Metal ion	Calculated value of stability constants				Literature value			
	$\log K^M_{1ML}$	$\log K^M_{2ML2}$	$\log K^M_{M-NTA}$	$\log K^{M-NTA}_{M-NTA-L}$	$\log K^M_{1ML}$	$\log K^M_{2ML2}$	$\log K^M_{M-NTA-L}$	$\log K^{M-NTA}_{M-NTA-L}$
Be(II)	6.90	5.90	7.22	5.70	-	-	7.11[19]	-
							7.11[15]	
Ni(II)	5.50	4.40	11.42	5.59	5.50[19]	4.44[19]	11.54[19]	-
					5.42[19]	4.34[19]	11.50[15]	
					5.28[19]	4.19[19]	11.53[15]	
							11.26[20]	
Pb(II)	5.30	3.30	11.21	3.59	-	-	11.47[19]	-
							12.40[20]	
							11.83[20]	
							10.64[20]	

where K = $K^M_{1ML} = \frac{[ML]}{[M]\,[L]}$; $K^M_{2ML_2} = \frac{[ML_2]}{[ML\,[L]}$; $K^M_{M-NTA} = \frac{[M-NTA]}{[M]\,[NTA]}$; and $K^{M-NTA}_{M-NTA-L} = \frac{[M-NTA-L]}{[M-NTA]\,\,[L]}$

study of binary M-NTA system. The mobility of the last plateau is more negative than that of first plateau so it indicates, the formation of more negatively charged complex. Further, since the mobility in the last plateau does not tally with the mobility of 1:1 and 1:2 metal threonine complex (observed in our study of binary M-threoninate systems) it is inferred that the moiety in least plateau is due to co-ordination of threoninate anion to 1:1 M-NTA moiety resulting in the formation of 1:1:1 mixed complex (M-nitrilotriacetate-threoninate) as:

$$M\text{-}NTA^- + L^- \xrightarrow{K^1} M\text{-}NTA\text{-}L^{2-}$$

In the present electrophoretic study the transformation of a simple complex into mixed complex takes place, hence the overall mobility is given by:

$$U = u_o f_{M\text{-}NTA} + u_1 f_{M\text{-}NTA\text{-}L}$$

where u_o, u_1 and $f_{M\text{-}NTA}$; $f_{M\text{-}NTA\text{-}L}$ are the mobilities and the mole fractions of $M\text{-}NTA^-$ and $M\text{-}NTA\text{-}L^{2-}$ complexes respectively. Substituting the values of mole fractions the overall mobility is given by:

$$U = \frac{u_c + u_1 K^1 [L]^-}{1 + K^1 [L^-]}$$

From the figure, concentration of threonine at which overall mobility is mean of the mobilities of two plateaus is determined. The concentration of threoninate anion at pH 8.5 for this threonine concentration is calculated. K' is obviously equal to $1/[L^-]$. All these values of K' are given in Table-1.

The precision of the method is limited to that of paper electrophoresis. However, uncertainty in the result is 5%. No doubt it cannot replace the most reliable methods even then it is a new approach worthwhile to develop.

References

1. V. Jokl, *Chromatography*, **14**, 71 (1964).
2. J. Biernat and Roczniki, *Chem.Ann.Soc.Chim.Polonoium*, **38**, 343 (1964).
3. R.K.P. Singh, J.K. Sircar, J.R. Yadava, P.C. Yadava and K.L. Yadava, *Electrochem. Acta*, **26**, 395 (1980).
4. R.K.P. Singh, J.K. Sircar, R. Khelawan and K.L. Yadava, *Chromatographia*, **13**, 709 (1980).
5. R.K.P. Singh, J.R. Yadava, P.C. Yadava and K.L. Yadava, *Z.Phys.Chemie Leipzig*, **3**, 264 (1983).
6. S. Singh, H.L. Yadava and K.L. Yadava, *Rev. Chim. Minerale*, (1984) (In press).
7. M. Czakis-Sulikowska, *Zesz. nauk. Politech. Ledz. Chem.*, **6**, 2038 (1967).
8. P.C. Yadava, J.K. Ghose, K.L. Yadava, and A.K. Dey, *J. Chromatography*, **9**, 416 (1976).
9. J.R. Yadava, J.K. Sircar and K.L. Yadava, *Electrochem. Acta*, **26**(3), 391 (1981).
10. R.K.P. Singh, J.R. Yadava and K.L. Yadava, *J. Electrochem. Soc.*, **30**, 250 (1981).
11. R.K.P. Singh and K.L. Yadava, *Trans. SEAST*, **16**, 3 (1981).
12. A. Gergly, I. Sovago, I. Nagpal and R. Kiraly, *Inorg. Chem. Acta*, **6**, 43 (1972).

13. A. Raghavan and M. Santappa, *J. Inorg. Nucl. Chem.*, **35**, 3363 (1973).
14. O. Farrok and N. Ahmed, *J. Electro. Anal. Chem. Interfacial Electrochem.*, **53**(3), 457 (1974).
15. A.E. Martell and R.M. Smith, "Critical Stability Constants" Vol.1, (Amino Acids) Plenum Press, New York (1977).
16. N.G. Elenkova and R.A. Troneva, *J. Inorg. Nucl. Chem.*, **35**, 841 (1973).
17. D.L. Rabenstein and G. Elakney, *Inorg. Chem.*, **12**, 128 (1973).
18. V.V. Ramanujam, M. Rajlakshmi and M. Shivashankar, *Ind. J. Chem.*, **20A**, 531 (1981).
19. L.G. Sillen and A.E. Martell, Stability constants of metal ion complexes. Special publication No.17. Chemical Society, London, page 465 (1964).
20. D.D. Perrin, Stability constant of metal ion complexes. Part B (organic ligand), Pergamon Press, Oxford, I.U.P.A.C. data series.