



ELSEVIER

Journal of Chromatography A, 667 (1994) 371–376

JOURNAL OF
CHROMATOGRAPHY A

Short Communication

Ionophoretic technique in the study of Cu(II), Ni(II), Co(II) and Mn(II)–hydrazine–nitrilotriacetate mixed-ligand complexes

Urmila Mishra*, R.K.P. Singh

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

(First received October 18th, 1993; revised manuscript received January 17th, 1994)

Abstract

A method involving the use of paper electrophoresis is described for the study of equilibria in mixed-ligand complex systems in solution. The method is based on the migration of a spot of a metal ion (M) with the complexants added to the background electrolyte (0.1 M sodium perchlorate). For the study of ternary complexes, the concentration of one of the complexants, hydrazine, is kept constant, while that of the second ligand, nitrilotriacetate (NTA), is varied. A graph of mobility against $-\log [\text{NTA}]$ is used to obtain information on the formation of the mixed-ligand complex and to calculate the stability constants. The overall stability constants of M–hydrazine and M–hydrazine–NTA complexes were found to be $10^{5.6}$, $10^{2.7}$ and $10^{4.7}$ for Cu(II), $10^{2.7}$, $10^{1.8}$ and $10^{5.5}$ for Ni(II), $10^{2.0}$, $10^{1.7}$ and $10^{4.7}$ for Co(II) and $10^{4.9}$, $10^{1.7}$ and $10^{6.1}$ for Mn(II) complexes at $\mu = 0.1$ and 35°C.

1. Introduction

Paper electrophoresis has previously been applied to the study of metal complexes in solution and attempts have been made to determine the stability constants of the complex species [1,2]. In previous work a method was developed for the study of stepwise complex formation [3–5]. Although the use of paper electrophoresis for the study of metal complex systems with a single ligand seems to be well established, there has been no systematic study of mixed-ligand complexes. However, Czakis Sulikowska [6] made some observations on the formation of mixed halide complexes of Hg(II), but the studies were only qualitative and did not throw light either on the nature of the species or on their stabilities.

In previous papers [7,8] a method was described for the study of mixed-ligand complexes. This work represents an extension of that technique and this paper reports our observations on the Cu(II), Ni(II), Co(II) and Mn(II)–hydrazine–nitrilotriacetate (NTA) mixed-ligand-system.

2. Experimental

Horizontal–vertical-type electrophoresis equipment (Systronics Model 604) was used together with various accessories. In each instance electrophoresis was carried out for 60 min at 200 V at 35°C. Whatman No. 1 paper strips (25 × 1 cm) were used. pH measurements were made with an Elico Model L₁₋₁₀ pH meter using a glass electrode.

* Corresponding author.

Metal perchlorates were prepared by an appropriate method and the final concentrations were kept at 5.0×10^{-3} M. 1-(2-Pyridylazo)-2-naphthol (PAN) [0.1% (w/v) in ethanol] was used for detecting Cu(II) Mn(II) and Co(II) ions and dimethylglyoxime for detecting Ni(II) ions. A saturated solution of silver nitrate in acetone was sprayed on the paper, which was subsequently fumed with ammonia to detect glucose spots.

The background electrolyte for the study of binary complexes was 0.1 M perchloric acid, 0.02 M hydrazine or $3.3 \cdot 10^{-3}$ M NTA with sodium hydroxide added to produce the desired pH and for the study of ternary complexes it was 0.1 M perchloric acid–0.02 M hydrazine with various amounts of NTA, maintained at pH 9.0 by addition of sodium hydroxide solution.

2.1. Procedure for binary complexes

Whatman No. 1 paper strips (25 × 1 cm) in duplicate are spotted in the middle with metal ion solutions. An extra strip is marked with glucose. The strips are sandwiched between two insulated hollow metal plates and the temperature of the system is maintained by water supplied within the plates at a fixed temperature. The plates are then mounted on the electrophoresis equipment with the end of the paper strips dipping in the tank solutions on both sides of the instrument. Electrophoresis is carried out for 60 min. The strips are then removed from the tank and dried and the migrated spots are detected with specific reagents. The movement of a metal spot towards the negative electrode is taken as positive mobility and in the reverse direction as negative mobility. Duplicate strips always recorded less than a 5% variation in the distance travelled and the mean of the two was taken for calculation of mobility. The movement of glucose is used as a correction factor for electroosmosis. The electrophoretic migration of metal spots on the paper was observed at different pH values of the background electrolyte. Division of movements by the potential gradient yields mobilities, which are plotted in Figs. 1 and 2.

2.2. Procedure for ternary complexes

Strips are marked with metal ion solutions in duplicate along with an additional strip marked with glucose. After drenching the strips with the background electrolyte, electrophoresis is carried out for 60 min at the same potential difference as for binary complexes. For subsequent observations, the NTA solution (pH 9.0) is added progressively and the ionophoretic mobility is recorded. Mobility is plotted against $-\log[\text{NTA}]$ (Fig. 3).

3. Results and discussion

3.1. M–hydrazine system

The plot of the overall electrophoretic mobility of a metal spot against pH gives a curve with three plateaux, as shown in Fig. 1. A plateau is an indication of the pH range where the speed is virtually 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 plateau corresponds to the region in which metal ions are non-complexed. Beyond the first plateau the metal ion spots have progressively decreasing velocities and hence complexation of metal ions should be taking place with non-protonated species of the hydrazine ligand, whose concentration increases with increasing pH of the background electrolyte. The decrease in mobility continues until a second plateau in the positive range of mobility is reached. The second plateau corresponds to the overwhelming formation of a 1:1 complex. The region between first and second plateaux corresponds to the progressive conversion of non-complexed metal ion into a binary complex with the ligand (hydrazine). On further increasing the pH beyond the second plateau, the concentration of unprotonated species of the ligand 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 tends to have zero mobility. The third

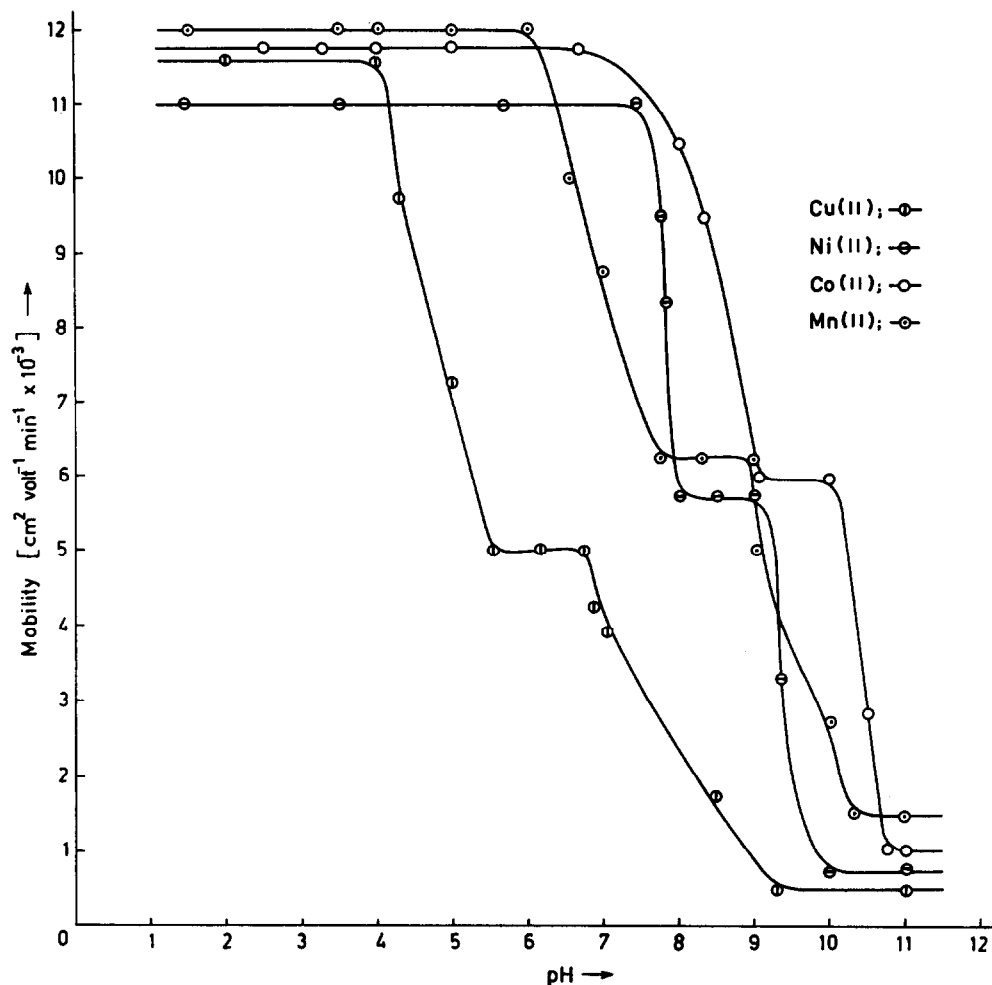


Fig. 1. Plots of mobility versus pH for the metal-hydrazine system.

plateau corresponds to the overwhelming formation of a 1:2 complex of the metal ion with the unprotonated species. Further increase in pH does not lead to any change in mobility, ruling out the formation of any other higher mononuclear complex.

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

$$U = \sum U_n f_n \quad (1)$$

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

$$U = \frac{U_0 + U_1 K_1 [L] + U_2 K_1 K_2 [L]^2}{1 + K_1 [L] + K_1 K_2 [L]^2} \quad (2)$$

where U_0 , U_1 and U_2 are the mobilities of the uncomplexed metal ion and 1:1 and 1:2 complexes, respectively, $[L]$ is the concentration of the unprotonated ligand, which takes part in com-

plex formation, and K_1 and K_2 are stability constants of the 1:1 and 1:2 complexes, respectively, which are expressed as

$$K_1 = \frac{[ML]}{[M][L]} \quad (3)$$

$$K_2 = \frac{[ML_2]}{[ML][L]} \quad (4)$$

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

$$[L] = \frac{[L_t]}{1 + k/[H^+]}$$

where $[L]$ is the concentration of the unprotonated species, $[L_t]$ is the total ligand concentration and k is the protonation constants for (hydrazine $k = 10^{8.3}$) [9,10]. The calculated values of the stability constants of 1:1 and 1:2 complexes are given in Table 1.

3.2. M-NTA system

The overall mobilities of the metal spots in the presence of NTA at different pH values are

Table 1
Stability constants of M-hydrazine complexes at 35°C and ionic strength = 0.1

Metal ion	Calculated values		Literature values		Ref.
	Log K_1	Log K_2	Log K_1	Log K_2	
Cu(II)	5.6	2.7	—	—	—
Ni(II)	2.7	1.8	2.8	2.4	11
Co(II)	2.0	1.7	1.6	0.6	12
Mn(II)	4.9	1.7	—	—	—

presented in Fig. 2. It is evident that with all the metal ions two plateaux are obtained, the mobility of the second plateau lying in the negative region, showing the negatively charged nature of the complex. Hence only one NTA anion is assumed to combine with one bivalent metal ion to give a 1:1 M-NTA complex, which is in conformity with the findings of other workers [13,14]. The stability constants of complexes with NTA were calculated as described for the M-hydrazine system and are given in Table 2.

3.3. M-hydrazine-NTA system

This system was studied at pH 9.0 with a specific purpose. It was observed from the mobility curves for M-hydrazine and M-NTA binary systems that binary complexes are formed

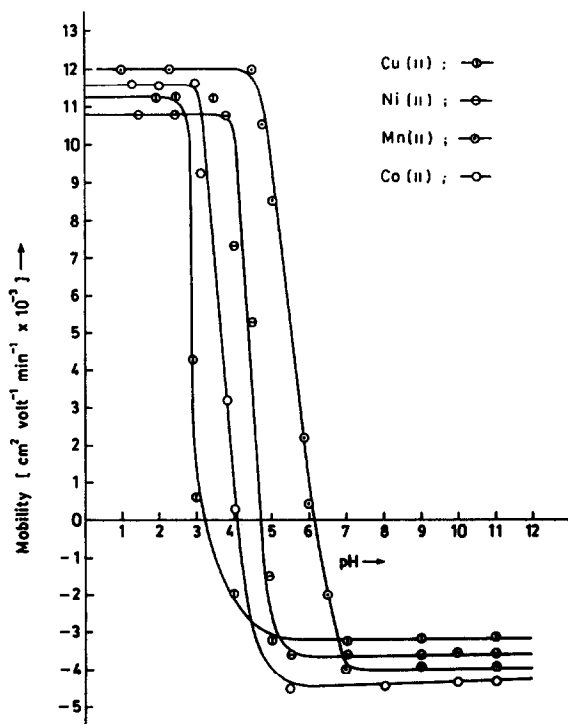


Fig. 2. Plots of mobility versus pH for the metal-NTA system.

Table 2
Stability constants of M–NTA complexes at 35°C and ionic strength = 0.1

Metal ion	Log K_{M-NTA}	
	Calculated values	Literature values [15]
Cu(II)	11.5	13.0
Ni(II)	11.4	11.5
Co(II)	10.5	10.4
Mn(II)	8.9	7.5

up to 9.0 pH. Fig. 3 illustrates the transformation of ML_2 into the M–L–NTA complex on progressive addition of NTA. There are two plateaux. At the first plateau the constant value of the mobility obviously corresponds to the mobility of M–hydrazine complexes, whereas the mobility of second complex corresponds to the mobility of a new complex.

This new complex may be a binary complex of M–NTA, as $ML_2 + NTA \rightleftharpoons M-NTA + 2L$, where the two ligand units of the complex have been completely replaced with one NTA. The new complex may also be a mixed complex in accordance with the reaction $M-L_2 + NTA \rightleftharpoons ML-NTA + L$.

Obviously the final plateau will correspond to the mobility of M–NTA or M–L–NTA, whichever is formed in the interaction. Both the complexes will carry one negative charge, but as the mixed complex is bulkier than the pure M–NTA complex the latter will have greater mobility in the negative direction than the former. The higher mobility for the binary M–NTA complex confirms the formation of mixed complexes in the interaction. From Fig. 3, the total concentration of NTA at which the overall mobility is the mean of the mobilities of the two plateaux was determined. For this the concentration of $[NTA^{3-}]$ anion at pH 9.0 was calculated and log K is obviously $= 1/[L]$. These values of the

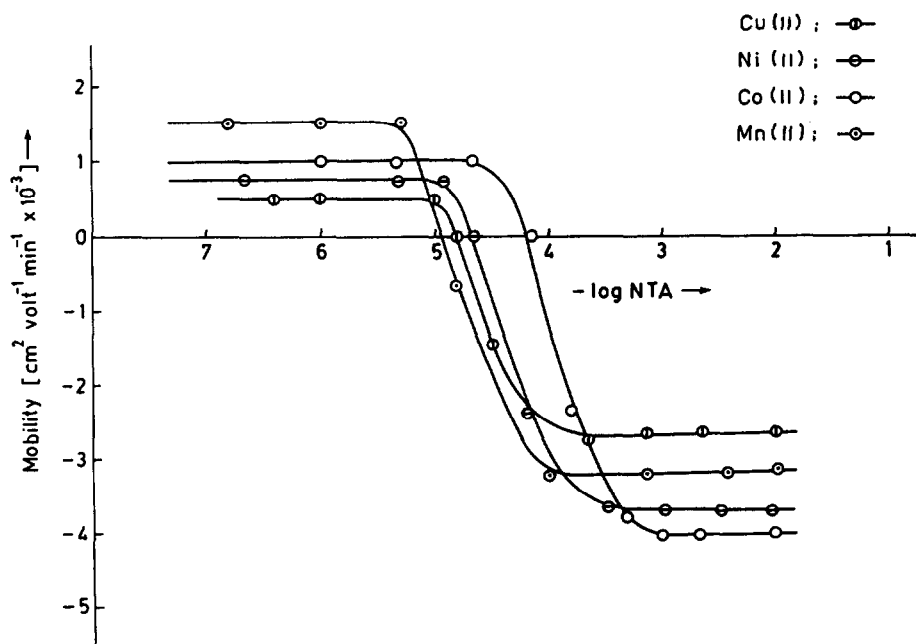


Fig. 3. Plots of mobility versus $-\log [NTA]$ for the metal–hydrazine system.

Table 3
Stability constants of M–NTA–hydrazine complexes at 35°C
and ionic strength = 0.1

Metal ion	Calculated Log K
Cu(II)	4.7
Ni(II)	5.5
Co(II)	4.7
Mn(II)	6.1

stability constants of the mixed-ligand complexes are reported in Table 3.

4. References

- [1] V. Jokl, *J. Chromatogr.*, 14 (1964) 71.
- [2] J. Biernat, *Rocz. Chem.*, 38 (1964) 343; *C.A.*, 61 (1964) 6456b.
- [3] R.K.P. Singh, J.K. Sircar, J.R. Yadav, P.C. Yadav and K.L. Yadava, *Electrochim. Acta*, 26 (1980) 305.
- [4] R.K.P. Singh, J.K. Sircar, R. Khelawan and K.L. Yadava, *Chromatographia*, 13 (1980) 709.
- [5] R.K.P. Singh, J.R. Yadava, P.C. Yadava and K.L. Yadava, *Z. Phys. Chem. (Leipzig)*, 264 (1983) 464.
- [6] M. Czakis Sulikowska, *Zesz. Nauk. Politech. Lodz., Chem.*, 6 (1967) 2038; *C.A.*, 65 (1966) 1746e.
- [7] P.C. Yadava, A.K. Ghosh, K.L. Yadava and A.K. Dey, *Chromatographia*, 9 (1976) 410.
- [8] J.R. Yadava, J.K. Sircar and K.L. Yadava, *Electrochim. Acta*, 26 (1981) 391.
- [9] G.W. Ware, J.B. Sulnik and E.C. Gilbert, *J. Am. Chem. Soc.*, 58 (1936) 1605.
- [10] G. Schwarzenbach, *Helv. Chim. Acta*, 19 (1936) 178.
- [11] G. Schwarzenbach and A. Zobrist, *Helv. Chim. Acta*, 35 (1952), 1291.
- [12] M. Sieprawski, J. Said and R. Cohen-Adad, *J. Chim. Phys.*, 70 (1973) 1417.
- [13] M.M. Taquikhan and A.E. Martell, *J. Am. Chem. Soc.*, 89 (1967) 5585.
- [14] C.M. Fray and J.E. Stuehr, *J. Am. Chem. Soc.*, 94 (1972) 8898.
- [15] A.E. Martell and R.M. Smith, *Critical Stability Constants. Amino Acids*, Vol. 1, Plenum Press, New York, 1974, p. 141.