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Short communication

Ionophoretic technique for the determination of stability constants of metal–nitrilotriacetate–methionine mixed complexes

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Abstract

A method, involving the use of paper electrophoresis is described for the study of the equilibria in mixed ligand complex systems in solution. Plots of −log [methionine] against mobility were used to obtain information on the formation of mixed complexes and to calculate the stability constants. Metal (M)–methionine and M–nitrilotriacetate (NTA) binary equilibria were also studied since this is a prerequisite for the investigation of mixed complexes. The stability constants (log K) of the M–NTA–methionine complexes were found to be 6.02 ± 0.03 and 4.92 ± 0.01 for M = Al(III) and Th(IV), respectively, at μ = 0.1 mol/l and 35°C.

1. Introduction

Paper electrophoresis has been applied to the study of metal complexes in solution and attempts have been made to determine the stability constants of the complex species [1–3]. The use of paper electrophoresis for the study of metal complex systems with a single ligand seems to be well established [4,5], but there has been no systematic study of mixed complexes. Czakis-Sulikowska [6] made some observations on the formation of mixed halide complexes of Hg^{2+}, but the work was only qualitative and did not throw light either on the nature of the species or on their stabilities. The electrophoretic technique usually suffers from number of defects, e.g., temperature rise during electrophoresis, adsorption and molecular sizing effects and the mobility of the charge moieties [7,8]. The technique described here is almost free from these vitiating factors. Not much work, however, is on record on the application of paper electrophoresis for examining complexation reactions. We previously described [9,10] a method for the study of mixed complexes. The present work is an extension of this technique and reports observations on mixed systems, viz. Al^{3+}/Th^{4+}–nitrilotriacetate–methionine.

2. Experimental

The apparatus, procedure and method of preparation of aluminium(III) and thorium(IV) metal perchlorate solutions were as described previously [9,10].

Metal spots were detected on the paper using aluminon solution (BDH, Poole, UK) for Al(III) and 1-(2-pyridylazo)-2-naphthol (PAN) (Merck, Darmstadt, Germany) for Th(IV). A

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saturated aqueous solution (0.9 ml) of silver nitrate was diluted to 20 ml with acetone. Glucose, as a black spot, was detected by spraying with this solution and then with 2% ethanolic sodium hydroxide.

The background electrolytes used in the study of binary complexes were 0.1 *M* perchloric acid and 0.01 *M* methionine. For the study of ternary system the background electrolytes used were 0.1 *M* perchloric acid, 0.01 *M* NTA and various amounts of 0.01 *M* methionine. The ternary system was maintained at pH 8.5 by the addition of sodium hydroxide.

Stock solutions of 9.0 *M* perchloric acid, 2.0 *M* sodium hydroxide and 0.5 *M* methionine were prepared from AnalaR-grade chemicals (BDH). A 0.01 *M* NTA solution was prepared from the compound obtained from Merck.

3. Results and discussion

3.1. Metal (M)-methionine binary system

The overall ionophoretic mobility of metal ions as a function of pH is given in Fig. 1. There are three and two plateaux on the curves for Al^{3+} and Th^{4+} metal ions, respectively. The first

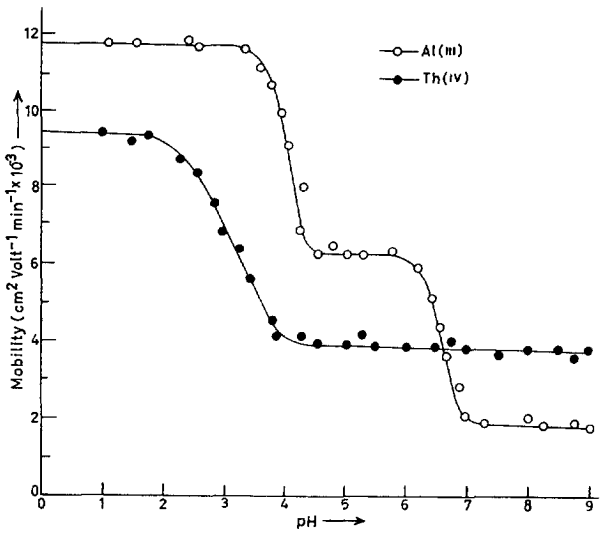

Fig. 1. Mobility curves for the M–methionine systems. ○ = Al(III)–methionine; ● = Th(IV)–methionine.

plateau of positive mobility at lower pH is due to non-complexed cations. In this pH range methionine is present as a non-complexing species. The second plateau in each case, still of positive mobility, indicates a 1:1 complex of cationic nature. The ligand here is the anionic species of methionine. With a further increase in pH, the mobility in the case of Al^{3+} metal ion decreases, giving rise to a third plateau in the positive region, indicating a 1:2 metal complex of positive nature, whereas for Th^{4+} ion, the mobility remains constant with increase in pH, which indicates that only a 1:1 complex is formed in the case of the Th(IV)–methionine system. ML_2 and ML are the highest complexes in the experimental region of pH values for Al^{3+} and Th^{4+}, respectively. Prominent chelating properties have also been assigned to unprotonated anionic species of methionine, ruling out any such property to the zwitterion [11–13]. In general, complexation of metal ions with methionine anion can be represented as

$$M^{3+} + L^- \overset{K_1}{\rightleftharpoons} ML^{2+} \quad (1)$$

$$ML^{2+} + L^- \overset{K_2}{\rightleftharpoons} ML_2^+ \quad (2)$$

$$M^{4+} + L^- \overset{K_1}{\rightleftharpoons} ML^{3+} \quad (3)$$

where M^{3+} and $M^{4+} = Al^{3+}$ and Th^{4+} metal ions, L^- = methionine anion and K_1 and K_2 are first and second stability constants, respectively.

Using the protonation constants of methionine ($pK_1 = 2.25$, $pK_2 = 9.00$) [14,15], the concentration of the complex species, $[L^-]$, was calculated at a particular pH. K_1 and K_2 for the complexes were calculated as described previously [9,10]. The results are given in Table 1.

3.2. Metal–nitrilotriacetate system

The overall mobility of metal spots in the presence of NTA at different pH values is shown in Fig. 2. Two plateaux are obtained; the mobilities of the last plateau in the case of Al(III) and Th(IV) ions are in the zero and positive regions, respectively, showing the neutral and cationic nature of the Al(III)–NTA and Th(IV)–

Table 1
Stability constants of binary and ternary complexes of Al(III) and Th(IV) at ionic strength 0.1 M) and 35°C

Values	Metal	Stability constant[a]			
		Log $K^{M}_{1_{ML}}$	Log $K^{M}_{2_{ML2}}$	Log $K^{M}_{3_{M-NTA}}$	Log $K^{M-NTA}_{4_{M-NTA-L}}$
Calculated (this work)	Al(III)	7.01 ± 0.04	11.50 ± 0.08	10.83 ± 0.01	6.02 ± 0.03
	Th(IV)	8.08 ± 0.07	–	8.17 ± 0.05	4.92 ± 0.01
Literature	Al(III)	–	–	11.40[15]	–
				5.09[15]	–
				5.55[15]	–
				5.28[15]	
				8.81[15]	
				9.50[19]	
				11.37[19]	
	Th(IV)	–	–	8.60[14]	
				13.30[15]	
				8.60[15]	
				16.90[19]	
				13.30[19]	

NTA anion = $N(CH_2COO)_3^{3-}$; methionine anion = $(CH_3)_2C(SCH_3)CH(NH_2)COO^-$.
[a] $K^{M}_{1_{ML}} = [ML]/[M][L]$; $K^{M}_{2_{ML2}} = [ML_2]/[ML][L]$; $K^{M}_{3_{M-NTA}} = [M-NTA]/[M][NTA]$; $K^{M-NTA}_{4_{M-NTA-L}} = [M-NTA-L]/[M-NTA][L]$; M = metal cation; L = ligand (methionine) NTA = nitrilotriacetate.

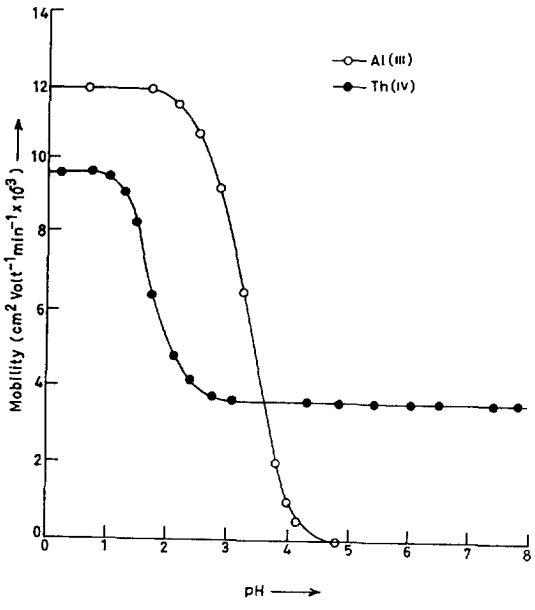

Fig. 2. Mobility curves for the M–NTA systems. ○ = Al(III)–NTA; ● = Th(IV)–NTA.

NTA complexes. Hence only one NTA anion is assumed to combine with one metal ion to give a 1:1 M–NTA complex, which is in conformity with the findings of others [16–18]. The stability constants (K_3) of the complexes with NTA were calculated as described in the preceding paragraph. The calculated values are given in Table 1.

3.3. Metal–nitrilotriacetate–methionine ternary system

This system was studied at pH 8.5 for the same reason as given previously [9,10].

The plot of mobility against log(concentration of added methionine) gives a curve (Fig. 3) containing two plateaux, one at beginning and other at the end. The mobility of the range of the first plateau corresponds to the mobilities of 1:1 M–NTA complexes. The mobility in this range is also in agreement with the mobility of

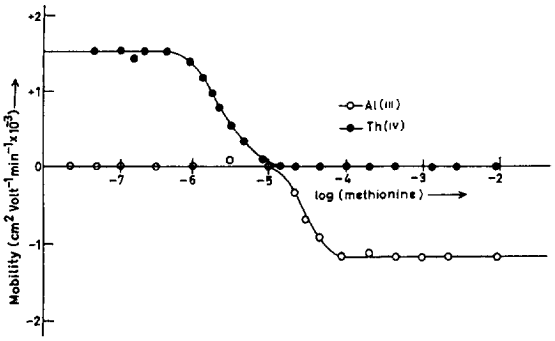

Fig. 3. Mobility curves for the M–NTA–methionine systems. ○ = Al(III)–NTA–methionine; ● = Th(IV)–NTA–methionine.

the 1:1 M–NTA complex evidenced in the study of the binary M–NTA system. The mobility of the last plateau is more negative than that of the first plateau, indicating the formation of a more negatively charged complex. Further, since the mobility in the last plateau does not agree with those of 1:1 and 1:2 metal methionine complexes (observed in our study of binary M–methionine system), it is inferred that the species in the last plateau is formed by coordination of methionine anion to a 1:1 M–NTA complex, resulting in the formation of 1:1:1 M–NTA–methionine mixed complex:

$$\text{M–NTA} + \text{L} \overset{K_4}{\rightleftharpoons} \text{M–NTA–L} \tag{4}$$

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

$$U = \frac{u_0 + u_1 K_4[(CH_3)_2C(SCH_3)CH(NH_2)COO^-]}{1 + K_4[(CH_3)_2C(SCH_3)CH(NH_2)COO^-]} \tag{5}$$

where u_0 and u_1 are the mobilities in the region of the two plateaux of the curve. From Fig. 3, the concentration of methionine anion at pH 8.5 for this methionine concentration was calculated; the stability constant of the mixed complex, K_4, is equal to $1/[(CH_3)_2C(SCH_3)CH(NH_2)COO^-]$. All these values of K_4 are given in Table 1.

The precision of the method is limited to that of paper electrophoresis. However, the uncertainty in the results is ±5%. Although this method clearly cannot replace the most reliable methods, it is a new approach worth developing. This simple electrophoretic technique has been helpful in deciding as whether a mixed complex system is formed or not and, if it is formed, its stability constant can also be determined.

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