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Short communication

Ionophoretic studies on mixed metal–nitrilotriacetate–penicillamine complexes

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Abstract

Paper ionophoresis is described for the study of equilibria in a mixed ligand complex system in solution. This method is based on the movement of a spot of metal ion in an electric field with the complexants added in the background electrolyte at pH 8.5. The concentration of the primary ligand (nitrilotriacetate) was kept constant, while that of the secondary ligand (penicillamine) was varied. The stability constants of the metal–nitrilotriacetate–penicillamine complexes have been found to be 6.26 ± 0.09 and 6.68 ± 0.13 (log K values) for Al^{3+} and Th^{4+} complexes, respectively, at 35°C and ionic strength 0.1 M. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Paper ionophoresis; Stability constants; Metal complexes; Metal cations; Aluminium; Thorium; Nitrilotriacetic acid; Penicillamine

1. Introduction

Mixed metal complexes play an important role in various biological system [1] and in different fields of chemistry [2,3]. Hence, the formation stability and reactivity of these complexes have been an active field of research [4]. The complexes of Al(III) and Th(IV) with penicillamine are of great importance because of their interesting biochemical role and toxic nature. Aluminium-containing drugs, are routinely given orally to patients with renal failure to control serum phosphate concentrations [5]. An increased Al(III) concentration may cause bone disorders in human [6]. Thorium(IV) was widely

prescribed as tonic in the 1920s and 1930s [7]. The chemical toxicity of thorium is low radiation, toxicity is the controlling hazard [8].

Communications [9–12] from our laboratory described a new method for the study of mixed complexes. The present work is an extension of the technique and reports my observation on the mixed systems viz. Al (III)/Th(IV)–nitrilotriacetate–penicillamine.

2. Experimental

2.1. Instruments

Electrophoresis equipment from Systronic (Naroda, India) model 604 was used. The apparatus

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consists of a Poly(vinyl chloride) PVC moulded double tank vessel. In order to avoid errors due to the heat generated during electrophoresis, two hollow rectangular plates each weighing 1 kg, and covered with thin plastic paper were used through which thermostated water circulated. The tanks were closed with a transparent PVC moulded lid to prevent moisture changes that might upset the equilibrium in the paper strip. Each electrolyte tank contained a separate Pt-wire electrode. Applied voltage was from a stabilized source.

pH measurements were made with an Elico model L₁₋₁₀ pH meter using a glass electrode.

2.2. Chemicals

Solutions of aluminium(III) and thorium(IV) metal perchlorate were prepared by preliminary precipitation of metal carbonate from 0.1 M solution of sodium carbonate (AnalaR grade; BDH, Poole, UK). The precipitate was thoroughly washed with boiling water and treated with a suitable amount of 1% perchloric acid. The resulting mixture was heated to boiling on a water-bath and then filtered. The solutions were standardized and diluted to $5.0 \cdot 10^{-3}$ M.

Metal spots were detected on paper; 0.1%(w/v) 1-(2-pyridylazo)-2-naphthol (PAN) in ethanol was used for Th(IV) and aluminon ammonium acetate mixture in water was used for detecting the Al(III). Glucose was detected by spraying with silver nitrate in acetone then with 2% ethanolic sodium hydroxide.

2.3. Background electrolyte

The background electrolyte used in the study of binary complexes was 0.1 M perchloric acid with 0.01 M penicillamine. For the study of ternary systems the background electrolytes used consisted of 0.1 M perchloric acid, 0.01 M nitrilotriacetic acid (NTA) and various amounts of 0.01 M penicillamine. The ternary system was maintained at pH 8.5 by addition of sodium hydroxide.

Stock solutions of 5.0 M perchloric acid (SDS AnalaR), 2.0 M sodium hydroxide (AnalaR grade),

0.5 M penicillamine (BDH) were prepared. A 0.01 M nitrilotriacetate (E. Merck, Darmstadt, Germany) solution was prepared from the compound. Each solution was standardized using appropriate method.

2.4. Procedure

The hollow base plate in the instrument was verified to be horizontal with spirit level. 150-ml volume of background electrolyte was placed in each tank of the electrophoretic apparatus. The levels of the two tank solutions were equalized by a siphon. These precautions were taken to stop any gravitational and hydrodynamic flow. Paper strips (Whatman No. 1) of 30×1 cm² size were soaked in background electrolyte and then an excess of electrolyte solution was blotted by pressing them gently within the folds of dry filter paper sheets. Paper strips in duplicate were spotted with metal ions and glucose in the centre with a micropipette and were subsequently placed on the base plate and sandwiched under the upper hollow metallic plate with the ends of the strips immersed in the tank solutions on both sides. Then a potential difference of 200 V was applied between the tank solutions and electrophoresis was carried out for 60 min. Afterward the strips were taken out with the help of a glass rod and dried. The spots were developed. The distances recorded in the duplicate strips differed $\pm 5\%$ and the average distance was calculated. The distances travelled towards the anode were given a negative sign and those towards the cathode a positive one. The actual distance of the sample spot moved was corrected for the distance travelled by the reference glucose spot. The mobilities were calculated by dividing the movement by the potential gradient and expressed in $\text{cm}^2 \text{V}^{-1} \text{min}^{-1}$.

3. Results and discussion

3.1. Metal–penicillamine binary complexes

The overall electrophoretic mobility of metal ions as a function of pH is given in Fig. 1. There are three and two plateaus in the curves of Al³⁺ and Th⁴⁺,

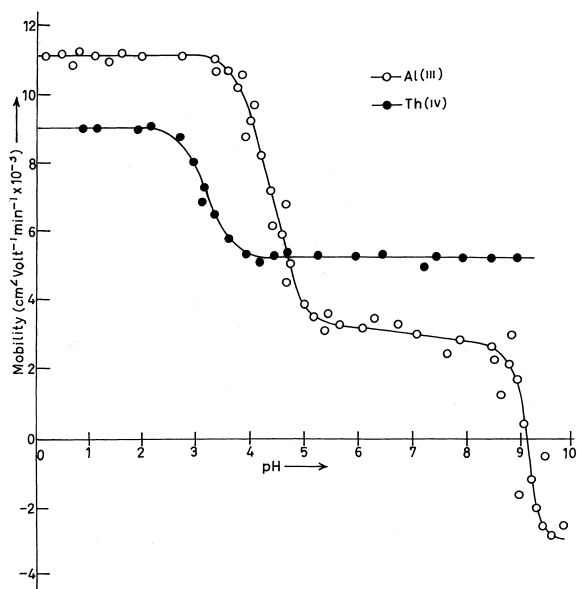


Fig. 1. Mobility curves for the M-penicillamine systems ○ = Al(III)–penicillamine; ● = Th(IV)–penicillamine. Concentration of Al(III) and Th(IV) = $5.0 \cdot 10^{-3}$ M.

cations respectively. The first plateau in each case with positive mobility in the lower pH range is due to non-complexed cations, in this pH range penicillamine is present as a non-complexing species $[(\text{CH}_3)_2\text{C}(\text{SH})\text{CH}(\text{NH}_2)\text{COOH}]$. The second plateau in each case with positive mobility indicates a 1:1 complex of a cationic nature. The ligand here

is the anionic species of penicillamine $[(\text{CH}_3)_2\text{C}(\text{S}^-)\text{CH}(\text{NH}_2)\text{COO}^-]$. At higher pH ranges formation of a third plateau with negative mobility was observed only in case of Al^{3+} metal ion which indicates formation of a 1:2 $(\text{ML}_2)^-$ complex. Further increase of the pH has no effect on the mobility of metal ions. $(\text{ML}_2)^-$ and $(\text{ML})^{2+}$ are the highest complexes in the experimental region of pH values of Al(III) and Th(IV) ions, respectively.

Using the protonation constants of penicillamine (electrophoretically obtained value, $\text{pK}_1=1.90$; $\text{pK}_2=7.85$; $\text{pK}_3=10.55$) the concentration of the complex species $[\text{L}^{2-}]$ was calculated at particular pH. The first stability constant K_1 and second stability constant K_2 for the two complexes were calculated as described earlier [9–12]. The results are given in Table 1.

3.2. Metal–nitrilotriacetate binary complexes

The overall mobility of the metal spots in the presence of NTA at different pH values is presented in Fig. 2. It is evident from Fig. 2 that in both metal ions two plateaus are obtained, the zero and positive mobility of the last plateau in Al(III) and Th(IV) metal ions, respectively showing a neutral and cationic charged nature of complex. Hence, only one NTA anion is assumed to combine with one metal to give a 1:1 metal–NTA complex.

Table 1
Stability constants of binary and mixed complexes of Al(III) and Th(IV)

Ionic strength 0.1 M; temperature 35°C.

NTA anion = $\text{N}(\text{CH}_2\text{COO})_3^{3-}$; Penicillamine anion = $[(\text{CH}_3)_2\text{C}(\text{S}^-)\text{CH}(\text{NH}_2)\text{COO}^-]$

Values	Metal ions	Stability constants ^a		
		M log K_1 ML	M log K_2 ML_2	M-NTA Log K_3 M-NTA-L
Calculated (this work)	Al(III)	11.50 ± 0.07	15.06 ± 0.11	6.26 ± 0.09
	Th(IV)	13.51 ± 0.04	–	6.68 ± 0.13

^a $K_1 \frac{M}{\text{ML}} = \frac{[\text{ML}]/[\text{M}][\text{L}]}{[\text{L}]}$; $K_2 \frac{M}{\text{ML}_2} = \frac{[\text{ML}_2]/[\text{ML}][\text{L}]}{[\text{L}]}$; $K_3 \frac{\text{M-NTA}}{\text{M-NTA-L}} = \frac{[\text{M-NTA-L}]/[\text{M-NTA}][\text{L}]}{[\text{L}]}$; M = metal cation; L = ligand (penicillamine); NTA = nitrilotriacetate.

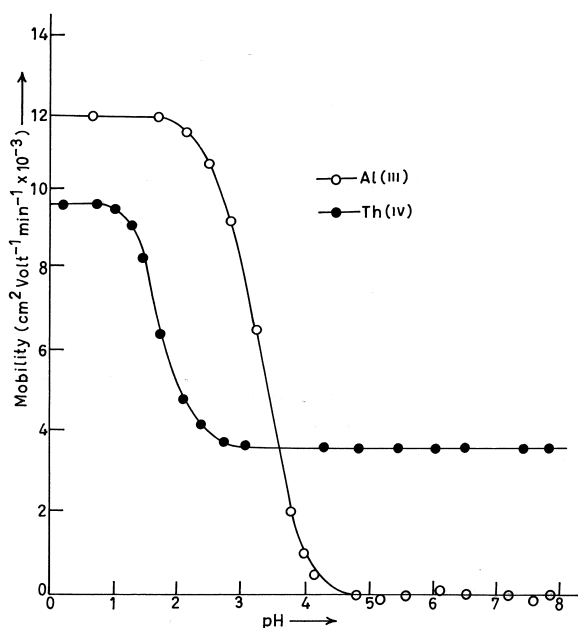


Fig. 2. Mobility curves for the metal-NATA systems. \circ = Al(III)-NTA; \bullet = Th(IV)-NTA. Concentration of Al(III) and Th(IV) = $5.0 \cdot 10^{-3}$ M; Concentration of NTA = $1.0 \cdot 10^{-2}$ M.

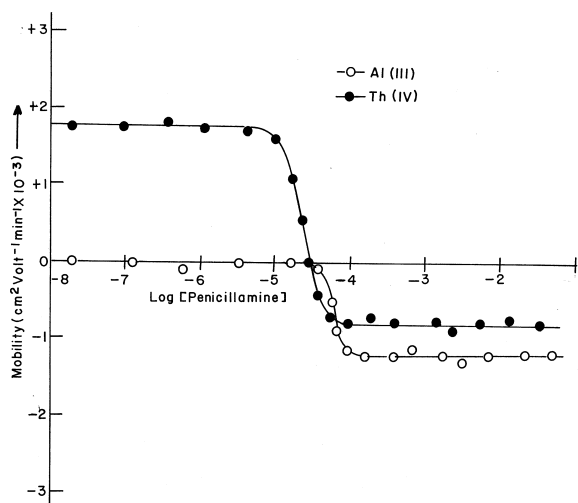


Fig. 3. Mobility curves for the metal-penicillamine systems \circ = Al(III)-NTA-penicillamine; \bullet = Th(IV)-NTA-penicillamine. Concentration of Al(III) and Th(IV) = $5.0 \cdot 10^{-3}$ M; Concentration of NTA = $1.0 \cdot 10^{-2}$ M.

3.3. Metal-nitrilotriacetate-penicillamine mixed complexes

It is observed from the mobility curves of the metal-penicillamine and metal-nitrilotriacetate systems that binary complexes are formed at $\text{pH} < 8.5$. It was therefore considered necessary to study the transformation of binary complexes into metal-nitrilotriacetate-penicillamine mixed complexes at $\text{pH} 8.5$ to avoid any side interaction. The plot of mobility against logarithm of concentration of added penicillamine gives a curve (Fig. 3) containing two plateaus. The mobility in the range of the first plateau corresponds to mobilities of 1:1 metal-NTA complexes as also observed in the study of Metal-NTA complexes. It is inferred that the complex formed in the region of the last plateau is due to co-ordination of penicillamine anion to 1:1 metal-NTA moiety resulting in the formation of 1:1:1 mixed complex (metal-NTA-penicillamine). The stability constants K_3 of mixed complexes are calculated as described earlier [9–12]. All these calculated values of K_3 are given in Table 1.

Table 1 shows that stability constants of binary complexes are higher than those of mixed complexes. It is therefore inferred that the co-ordination tendency of a ligand decreases with a higher state of aggregation. In other words, the metal progressively lessens its tendency of linkage with a ligand on progressive filling of vacant orbitals. This conclusion is of universal validity as evident in the chemical literature [13–15].

The precision of the method is limited to that of paper electrophoresis i.e. the order of uncertainty is $\pm 1\%$. Obviously this method cannot be intended to replace more reliable methods. As far as of uncertainty is concerned the results reported here are fairly reliable.

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