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Ionophoretic Study of Mixed Ligand Complexes of Mn(II), Pb(II) and Th(IV)-Adenosine Triphosphate Nitrilotriacetate System

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Use of paper electrophoresis has been described for the study of metal-ligand equilibria in solution. This technique is based on the movement of a spot of metal ion under an electric field with the complexant added in the background electrolyte at a fixed pH 8.5. The concentration of primary ligand adenosine triphoshate (ATP) was kept constant while that of secondary ligand nitrilotriacetate (NTA) was varied. Valuable information is obtained from the plots of –log [NTA] against mobility regarding the mixed complexes. The overall stability constants of the M-ATP-NTA have been found to be $10^{10.09}$, $10^{10.39}$ and $10^{11.64}$ for mixed ligand complexes of Mn(II), Pb(II) and Th(IV) respectively at $u = 0.1$ and temperature 30 ± 0.1°C.

INTRODUCTION

Disposal of certain metal ions like Mn(II), Pb(II) and Th(IV) on land affects soil, vegetation and environment around disposal ponds[1]. Mn(II) ion has various roles in catalytic cycle in biological redox systems[2] and lead poisoning has been long known[3] whereas thorium belongs to the family of radioactive elements. Thus, the Mn(II), Pb(II) and Th(IV) ions with regards to their bioavailability, mobility and complex formation has become a matter of concern in recent years[4, 5]. The studies on their complex formation with biologically relevent systems appears to be interesting. There are limited reports on the systematic study of the mixed ligand complexes of metal ions using paper electrophoresis[6, 7]. In the present communication, we report our studies on the mixed ligand complexes of Mn(II), Pb(II) and Th(IV) with adenosine triphosphate (ATP)-nitrilotriacetate (NTA) using paper electrophoresis.

EXPERIMENTAL

Electrophoresis equipment (Systronics Model-604, India) with built in power AC-DC, which is directly fed to a paper electrophoresis tank, was used. To control

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the temperature, two hollow metallic plates coated outwardly with thin paper plastic were used for sandwiching paper strips and thermostated water (30 ± 0.1°C) was circulated through them. Whatman No. 1 paper strips (25 × 1 cm) were used for electrophoresis. Elico Model L_{1-10} pH-meter with glass electrode was used for pH measurements.

Mn(II), Pb(II) and Th(IV) perchlorate were prepared by precipitating the corresponding carbonates treating with a suitable amount of 1% perchloric acid. The final concentration was kept at 5.0×10^{-3} M.

1-(2-Pyridylazo)-2-naphthol (PAN), 0.1% (w/v) in ethanol was used for detecting Mn(II), Pb(II) and Th(IV) ions. Glucose spot, electro-osmotic indicator, was detected by spraying aqueous silver nitrate in acetone and 2% ethanolic caustic soda.

The background electrolyte for the study of binary complexes was 0.1 M perchloric acid, 2.0×10^{-3} M ATP and 3.3×10^{-3} M-NTA with varying amounts of sodium hydroxide solution to obtain desired pH values. For the study of ternary complexes, the background electrolyte consisted of 0.1 M perchloric acid, 2.0×10^{-3} M ATP and varying amounts of NTA maintained at pH 8.5 by addition of sodium hydroxide.

Procedure

Whatman No. 1 paper strips (25 × 1 cm) in duplicate were spotted at the centre with metal ion solution. One strip was marked with glucose solution. The strips were sandwiched between two insulated metal hollow plates. The plates were then mounted in electrophoresis equipment with ends of the paper strips dipping in the two tanks of the instrument. Each tank was filled with 150 mL of the background electrolyte. Half an hour was allowed for the strips to get wet by diffusion with the background electrolyte solution. Then electrophoresis was carried out for 1 h under the influence of 200 volts of potential difference between the two tank solutions. The electrophoresis was repeated at different pH values of the background electrolyte. Then strips were removed, dried and the migrated spots were detected with specific reagents. The distances travelled by the spots were measured from the initial marks. Duplicate strips always recorded less than ± 3% variation. Mean of the two was taken for the calculation of mobility. Glucose movement was used as a correction factor for electro-osmosis. The distance travelled towards anode were assumed to be negative and those towards cathode to be positive. The length of unimmersed strips above the tank containing the background electrolyte is 20 cm, hence the potential gradient applied in each set of experiments is 10 V/cm. Dividing movement by potential gradient yields mobilities, which are plotted against pH in Figs. 1 and 2.

For ternary complexes, similar procedure was followed as described above in case of binary complexes except for the background electrolyte. For the subsequent observations, the NTA solution was added progressively maintaining the pH 8.5 of the background electrolyte solution by adding NaOH solution. The ionophoretic mobilities were recorded and plotted against –log [NTA] as shown in Fig. 3.

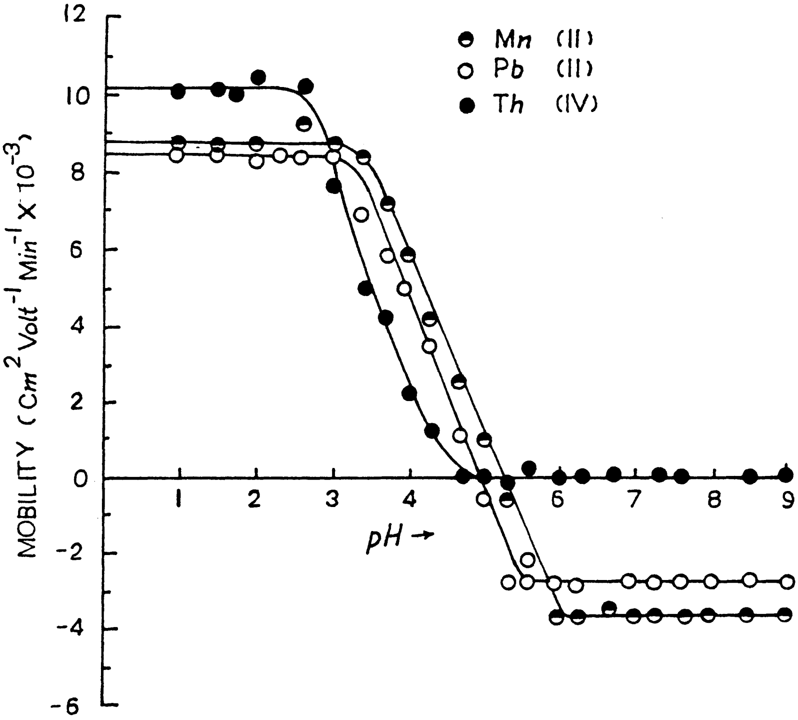

Fig. 1. Mobility curves for metal-ATP systems

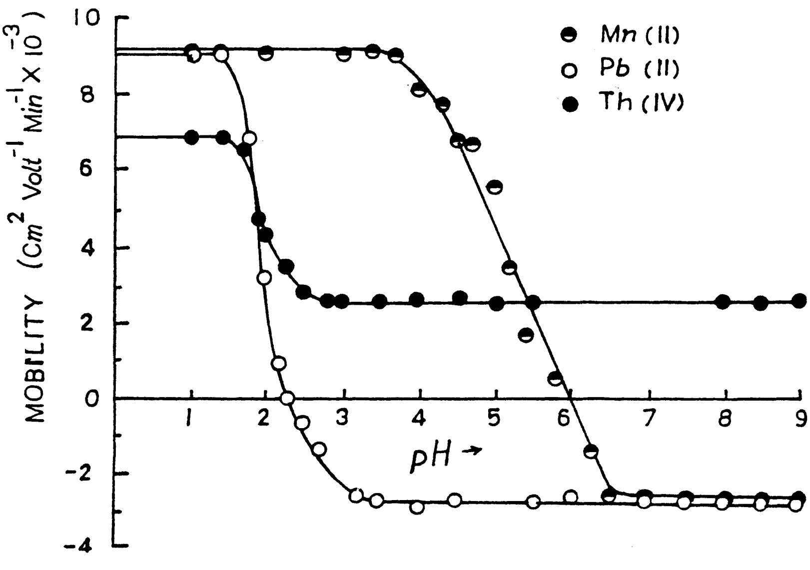

Fig. 2. Mobility curves for metal-NTA systems

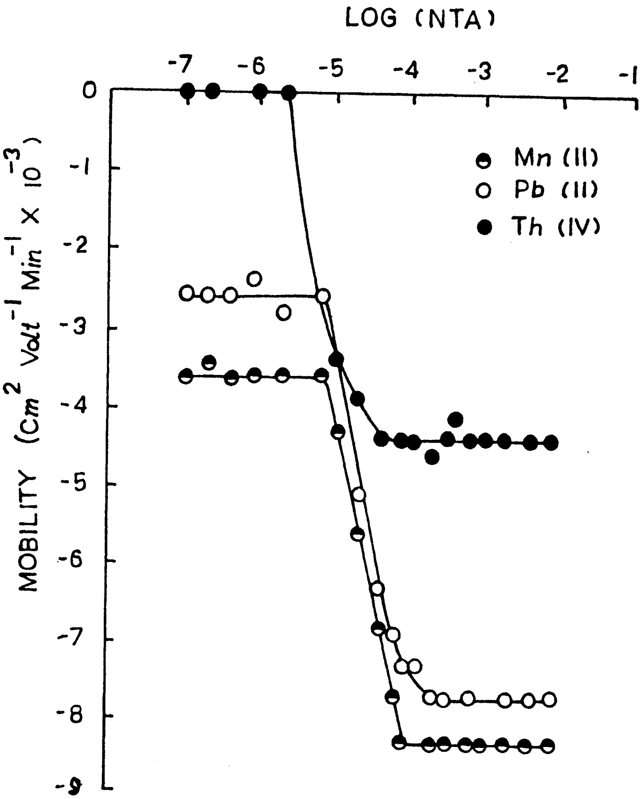

Fig. 3. Mobility curves for metal-NTA-ATP systems

RESULTS AND DISCUSSIONS

Mn(II), Pb(II) and Th(IV) with Adenosine Triphosphate System

It is evident in Fig. 1, which is the plot of overall ionic mobility of the metal ion spot against the pH of the background electrolyte containing the ligand, that a curve with two plateaus is obtained. A plateau is indication of the pH range over which mobility is practically constant. The first plateau corresponds to a region in which metal ions are uncomplexed. It lies in the low pH region. Beyond this region, metal ions spots have shown progressive decrease in mobility. The complexation of the metal ions should be taking place in this region with other ionic species of ATP whose concentration gradually increases with the increase of the pH of the background electrolyte. The second plateau in each case corresponds to the formation of a metal-ligand complex, which is very likely 1 : 1 complex. The region between the first and second plateau is an indication of the progressive conversion of uncomplexed metal ion into binary complex with ATP. Further increase in the pH of the background electrolyte has no effect on the mobility of the metal ion spots. This leads to the conclusion that the ligating ionic species is ATP^{4-}.

The overall mobility of the metal ion spot is given by the equation

$$U = \sum_{n} U_n f_n \tag{1}$$

where U_n and f_n are the mobility and mole fraction of a particular complex species. As it has been already concluded that the ultimate anionic species of the ligand (ATP^{4-}) is the only ligating species in 1 : 1 complex, the above general equation can be modified for the system under consideration as follows:

$$U = \frac{U_0 + U_1 K_1[L]}{1 + K_1[L]} \tag{2}$$

where U_0 and U_1 are the mobilities of the uncomplexed metal ions and 1 : 1 metal ion-ATP complex respectively, L is the ligating species (neglecting the charge for simplicity) and K_1 is the stability constant for 1 : 1 complex.

Using the principle of average mobility, K_1 can be calculated with the help of mobilities of both the plateaus. The average mobility will be equal to the arithmetic mean of the mobility of uncomplexed metal ion U_0 and that of 1 : 1 metal complex U_1 at a pH where $K_1 = 1/L$. With the help of dissociation constants of ATP ($K^{ATP^{2-}}_{ATP^{3-}} = 4.2$ and $K^{ATP^{3-}}_{ATP^{4-}} = 6.5$) the value of ATP anion [L^{4-}] is determined at this pH and then $K^{M}_{M\text{-}ATP}$ can also be calculated which is given in Table-1.

Mn(II), Pb(II) and Th(IV) with Nitrilotriacetate System

Dissociation constant of NTA has been determined electrophoretically in our laboratories and the values $K_1 = 1.78$, $K_2 = 2.40$ and $K_3 = 9.56$ at 30°C have been found, which were used for calculation of stability constants. Observations on overall mobility of metal ion spots in the presence of NTA at different pH values are presented in Fig. 2. Each metal ion gives two plateaus. The mobility of first plateau is positive for all the three metal ions while the mobility of the second plateau is positive for Th(IV) and negative for Mn(II) and Pb(II). It is inferred that metal ion forms 1 : 1 M-NTA complex in agreement with the findings of others[8–11]. The stability constants of complexes with NTA are calculated in the same manner as described for M-ATP system and are presented in Table-1.

TABLE-1
STABILITY CONSTANTS OF SOME BINARY AND TERNARY COMPLEXES OF Mn(II), Pb(II) AND Th(IV) WITH ATP AND NTA

Stability constants	Mn(II)		Pb(II)		Th(IV)	
	Calc. value	Lit. value	Calc. value	Lit. value	Calc. value	Lit. value
log $K^{M}_{M\text{-}ATP}$	4.70	4.76	4.90	—	5.50	—
log $K^{M}_{M\text{-}NTA}$	7.08	7.46	11.90	11.34	11.33	13.30
log $K^{M\text{-}ATP}_{M\text{-}ATP\text{-}NTA}$	5.39	—	5.49	—	6.14	—
log $K^{M}_{M\text{-}ATP\text{-}NTA}$	10.09	—	10.39	—	11.64	—

Mn(II), Pb(II) and Th(IV) with ATP-NTA System

The study of these mixed ligand complexes has been carried out in the presence of primary ligand ATP with progressive addition of the secondary ligand NTA to the background electrolyte at a fixed pH 8.5. The pH for the background electrolyte has been purposely chosen as it is evident from the mobility curves of M-ATP (Fig. 1) and M-NTA (Fig. 2) that binary complexes in both the cases are formed up to this pH. Observations on overall mobility have been presented in Fig. 3. These figures elucidate the transformation of M-ATP complexes into M-ATP-NTA complexes on progressive addition of NTA. The figures show two plateaus. The negative mobility of Mn(II) and Pb(II) and zero mobility of Th(IV) in the region of the first plateau is due to M-ATP complex (Fig. 1 at pH 8.5). The mobility in the second plateau corresponds to the mobility of the new mixed complex M-ATP-NTA, since it does not agree with the mobility of a 1 : 1 M-NTA complex (Fig. 2).

In this electrophoretic study, the transformation of a binary complex into ternary complex takes place; the overall mobility is given by

$$U = U_0 f_{\text{M-ATP}} + U_1 f_{\text{M-ATP-NTA}} \qquad (3)$$

where U_0 and U_1 are the mobilities and $f_{\text{M-ATP}}$ and $f_{\text{M-ATP-NTA}}$ are the mole fractions of M-ATP and M-ATP-NTA complexes respectively. The overall stability constants $K^{\text{M}}_{\text{M-ATP-NTA}}$ are calculated by multiplying the stability constants of the M-ATP complex with the stability constants of the M-ATP-NTA complex (Table-1). The calculated values of the stability constants based on our paper on electrophoresis experiments are in good agreement with literature values[12, 13].

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