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Mixed Ligand Complexes of Mn(II), Pb(II) and Th(IV) with Adenosine Diphosphate and Nitrilotriacetate

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A new method, paper electrophoresis, involving the use of ionophoretic technique, is described for the study of equilibria in mixed ligand system in solution. Migration of a metal ion spot (M), under an electric field, with complexant added in the background electrolyte at fixed pH 8.5, is studied. For the study of ternary complexes, the concentration of the primary ligand adenosine diphosphate (ADP) is kept constant while that of the secondary ligand nitrilotriacetate (NTA) is varied. Plot of -log [NTA] against mobility provided information about the mixed ligand complex to calculate the stability constants. As a prerequisite, binary equilibrium M-ADP and M-NTA have also been studied. The overall stability constants of M-ADP-NTA complexes have been found to be $10^{9.04}$, $10^{9.72}$ and $10^{10.49}$ for Mn(II), Pb(II) and Th(IV) complexes respectively at ionic strength $\mu = 0.1$ and temp. $30° \pm 0.1°C$.

INTRODUCTION

In these laboratories, a new method has been developed for the study of stepwise complex formations.[1–3] Although the use of paper electrophoresis for the study of metal complexes with a single ligand seems to be well established but there is no systematic study of the mixed ligand complexes. Publications[4–8] from our laboratories described a new method for the study of mixed ligand complexes. The present work is an extension of the technique and this paper reports our observations on the mixed ligand systems Mn(II)-ADP-NTA, Pb(II)-ADP-NTA and Th(IV)-ADP-NTA.

EXPERIMENTAL

Electrophoresis equipment was used together with various accessories which include power supply, paper electrophoresis tank and two insulated hollow metal plates circulating thermostated water ($30° \pm 0.1°C$) to control the temperature. Electrophoresis was carried out for 1 h at 200 volts. Whatmann no. 1 paper strips (25×1 cm) were used. pH measurements were done with Elico Model L_{1-10} pH meter using glass electrodes.

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Mn(II), Pb(II) and Th(IV) 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 Mn(II), Pb(II) and Th(IV) ions. Glucose spot, the electro-osmotic indicator was detected by spraying aqueous silver nitrate in acetone and 2% ethanolic NaOH.

Background electrolyte for the study of binary complexes was 0.1 M perchloric acid 2.0×10^{-3} M ADP and 3.3×10^{-3} M NTA. For the study of ternary complexes, background electrolyte consisted of 0.1 M perchloric acid and 2.0×10^{-3} M ADP with varying amounts of NTA, maintained at pH 8.5 by adding NaOH solution.

RESULTS AND DISCUSSION

(i) M-ADP systems

The plot of the overall electrophoretic mobility of the metal spot against pH gives a curve with two plateaus shown in Fig. 1. A plateau is obviously an indication of the pH range over which mobility is practically constant. This could be possible only when a particular complex is formed in abundance. Thus, every plateau indicates the formation of a certain complex species. The first plateau corresponds to a region in which metal ions are uncomplexed. It lies in low pH region where the concentration of protonated species of ADP is maximum; hence it is concluded that this protonated species is non-complexing. Beyond this region, metal ion spots have progressively decreasing mobility. The complexation of the metal ion should be taking place in this region with other ionic species of ADP whose concentration gradually increases as the pH of the background electrolyte increases. The second plateau corresponding to zero mobility in each case indicates the formation of 1 : 1 electrically neutral complex. Further increase in the pH of the background electrolyte has no effect on the mobility of the metal ion. This leads to the conclusion that liganding ionic species of ADP is the ultimate ionic species ADP^{3-}. There are allusions in literature[9, 10] regarding the formation of complexes with ultimate ionic species of the ligand.

The metal spot on the paper is thus a combination of uncomplexed metal ions and 1 : 1 complex. For the spot moving under the influence of electric field, overall mobility U is given by the equation:

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

where U_n and f_n are mobility and mole fraction of particular complex species. This equation can be modified for the system under consideration as follows:

$$U = \frac{U_0 + U_1 K[ADP^{3-}]}{1 + K[ADP^{3-}]} \quad (2)$$

U_0 and U_1 are the mobilities of uncomplexed metal ion and 1 : 1 metal ligand complex respectively. For calculating stability constant $K^{M}_{M\text{-}ADP}$ the region between the first and second plateau is pertinent. The overall mobility U will be equal to the arithmatic mean of mobilities of uncomplexed metal ion U_0 and that of the 1 : 1 metal ligand complex U_1 at the pH where $K^{M}_{M\text{-}ADP} = 1/[ADP^{3-}]$. The dissociation constants of ADP are $K^{ADP^{-}_{2}}_{ADP^{2-}} = 10^{4.0}$ and $K^{ADP^{2-}_{3}}_{ADP^{3-}} = 10^{6.4}$. The concentration of ADP^{3-} is determined at a particular pH from which $K^{M}_{M\text{-}ADP}$ can be calculated. These values are given in Table-1.

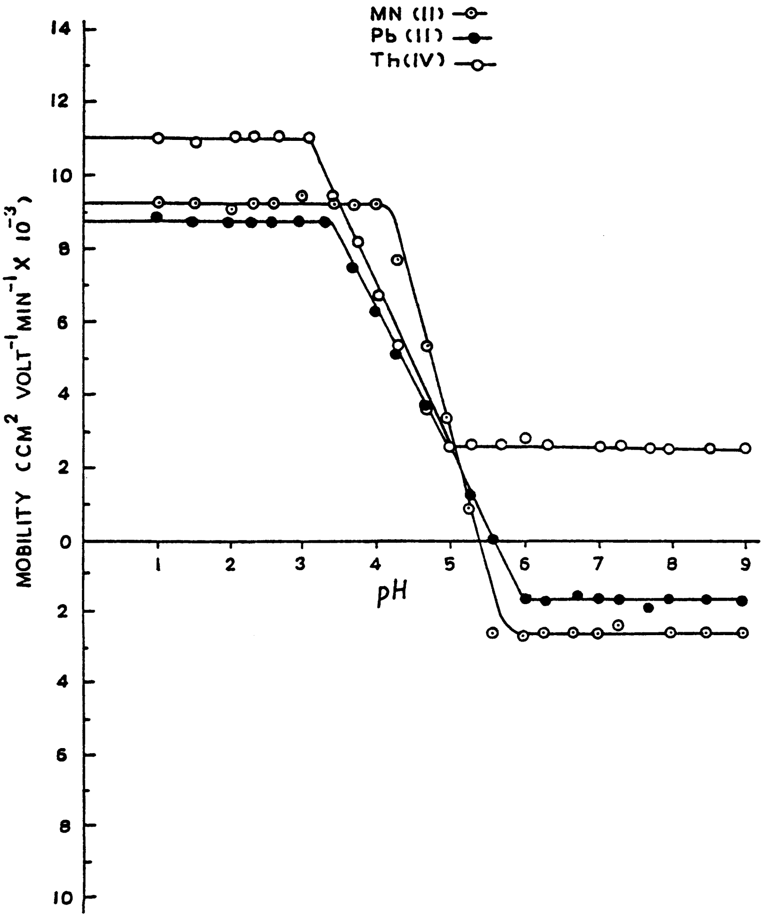

Fig. 1. Mobility curve M-ADP system

(ii) M-NTA system

Observations on overall mobility of metal spots in the presence of NTA at different pH values are represented in Fig. 2. It is evident from the figure that, in all the metal ions, two plateaus are obtained; the mobility of the last plateau lies in the negative region for Mn(II) and Pb(II) and in the positive region for Th(IV). Hence only one NTA^{3-} is assumed to combine with one metal ion to give a 1 : 1 M-NTA complex which is in agreement with the findings of others[11–14]. The stability constants of the metal complexes with NTA ($K^{M}_{M\text{-}NTA}$) were obtained in the similar manner as described for M-ADP system and are given in Table-1.

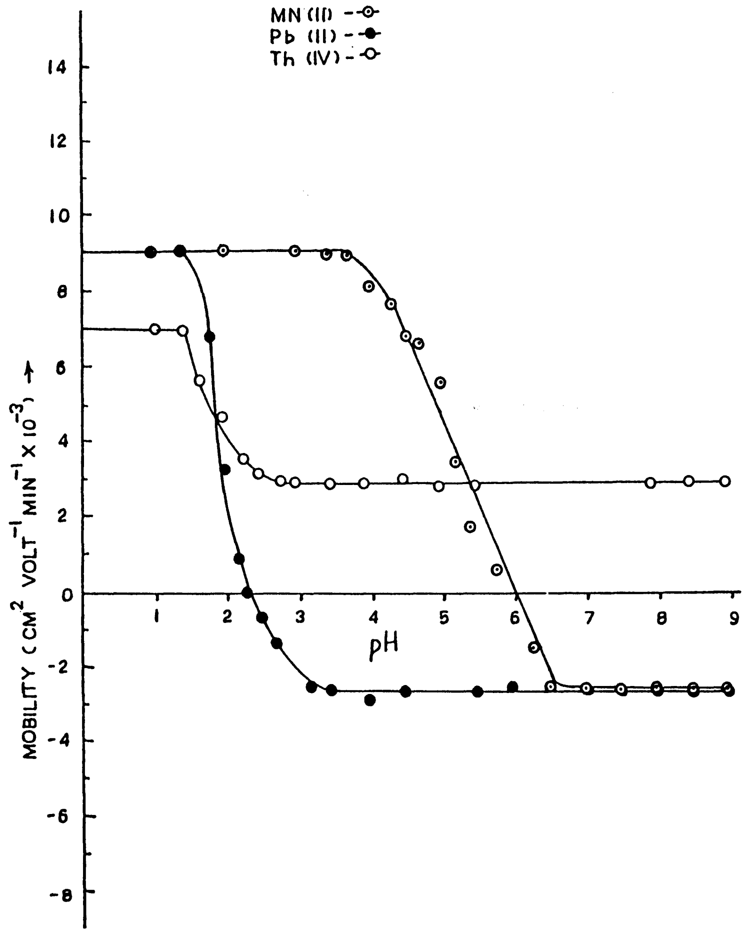

Fig.2. Molbility curve M-NTA system

(iii) M-ADP-NTA system

Study of this system has been done at pH 8.5 due to specific reason. It was observed from mobility curves for M-ADP nd M-NTA binary systems that binary complexes M-ADP and M-NTA are formed at pH lower than 8.5. Thus it could be proper to study the transformation of M-ADP complexes into M-ADP-NTA complexes at pH 8.5 in order to avoid any side interaction.

Plots of mobility against –log [NTA] are shown in Fig. 3 which exihibits two plateaus. Negative mobility in the region of the first plateau for Mn(II) and Pb(II) while positive mobility for Th(IV) corresponds to the mobilities of 1 : 1 M-ADP complexes (Fig. 1 at pH 8.5). The mobility corresponding to the second plateau is more negative for Mn(II) and Pb(II) and negative for Th(IV), indicating the formation of a more negatively charged complex. Since the mobility in the second plateau does not tally with the mobility of 1 : 1 M-NTA complex (Fig. 2), it is inferred that the species corresponding to the second plateau is due to the combination of NTA^{3-} anion to a 1 : 1 M-ADP moiety resulting in the formation of a 1 : 1 : 1 (M-ADP-NTA^{3-}) mixed complex according to

$$\text{M-ADP} + NTA^{3-} \rightleftharpoons (\text{M-ADP-}NTA^{3-}) \quad (3)$$

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

$$U = U_0 f_{\text{M-ADP}} + U_1 f_{\text{M-ADP-NTA}} \quad (4)$$

where U_0 and U_1 are the mobilities and $f_{\text{M-ADP}}$ and $f_{\text{M-ADP-NTA}}$ are the mole fractions of M-ADP and M-ADP-NTA complexes respectively.

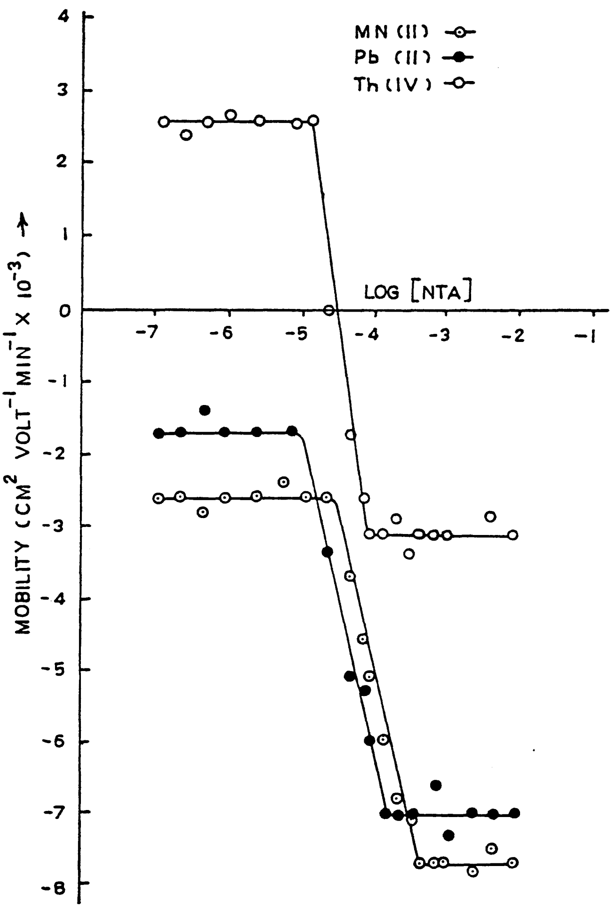

Fig. 3. Mobility curve M-ADP-NTA system

From Fig. 3 the total concentration of NTA at which the overall mobility is the mean of the mobilities of the two plateaus was determined. From this the concentration of NTA^{3-} at pH 8.5 is obtained, $K^{\text{M-ADP}}_{\text{M-ADP-NTA}}$ is equal to

$1/[NTA^{3-}]$. The overall stability constant is obtained by multiplying $K^{M}_{M\text{-}ADP}$ and $K^{M}_{M\text{-}ADP\text{-}NTA}$. All these values are given in Table-1.

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

Stability constants	Mn(II)		Pb(II)		Th(IV)		Ref.
	Calculated value	Literature value	Calculated value	Literature value	Calculated value	Literature Value	
$\log K^{M}_{M\text{-}ADP}$	4.12	4.05	4.41	–	5.10	–	15
$\log K^{M}_{M\text{-}NTA}$	7.08	7.46	11.09	11.34	11.33	13.30 18.60	16
$\log K^{M}_{M\text{-}ADP\text{-}NTA}$	4.92	–	5.31	–	5.39	–	–
$\log B^{M}_{M\text{-}ADP\text{-}NTA}$	9.04	–	9.72	–	10.49	–	–

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