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DETERMINATION OF THE STABILITY CONSTANTS OF ZINC(II) AND CADMIUM (II) MIXED COMPLEXES BY AN ELECTROPHORETIC METHOD

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Abstract : Stability constants of different complex species of Zn^{2+} Cd^{2+} with methionine were determined electrophoretically at an ionic strength of 0.1 perchloric acid at 35°C. The stability constant of complexes metal - nitrilotriacetate - methionine were 3.84 and 3.66 (log K values) for Zn^{2+} and Cd^{2+} complexes respectively.

Key words - Electrophoresis, mobility, mixed complexes, stability constants

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 complex species.[1] A new method has been recently developed for the study of stepwise complex formation.[2,3] Earlier work[4,5] carried out in our laboratory described a new method for the study of mixed complexes. The present work is an extension of this technique and reports our observations on the mixed system Zn(II) and Cd(II) - nitrilotriacetate - methionine.

METHODS AND MATERIALS

The apparatus and procedure were described previously.[2] Triplicate strips were used for the same experiment and value found for the movement was taken as the mean of all the three strips. Variation in mobility was about ± 5%. Zn^{2+} and Cd^{2+} perchlorate solutions were prepared in the laboratory from the nitrates via the carbonates. The solution was standardized and diluted to 5.0×10^{-3} M. Metal spots were detected on the paper using dithizone in carbon tetra chloride (BDH, England) [for Zn(II)] and (PAN) 1-(2-Pyridilazo)-2-naphthol (E. Merck, Germany) [for Cd(II)]. A saturated aqueous solution (0.9 ml) of silver nitrate was diluted with acetone to 20 ml. Glucose was detected by spraying with this solution followed by 2% ethanolic sodium hydroxide. Stock solutions of 9.0 M perchloric acid, 2.0 M sodium

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hydroxide and 0.5 M methionine were prepared from Analar samples (BDH, UK). 0.01 M nitrilotriacetate (NTA) was prepared from a sample obtained from E. Merck.

RESULTS AND DISCUSSION

(I) M (II) - Methionine System: The ionophoretic mobility of metal spots against pH gives a curve with several plateaus as shown in Figure 1. The plateau at the beginning corresponds to a region in which metal ions are uncomplexed. Figure 1 reveals that the second plateau in each case has a positive mobility indicating the formation of 1:1 complex of cationic nature. The third plateau lies in the zero region indicating the neutral nature of the metal complex. Chemical literature also assigns prominent ligating properties to unprotonated anionic species of methionine ruling out any such property to the zwitterion.[6] In view of above observations the complexing of metal ions with methionine anion $[L^-]$ may be represented as,

$$M^{2+} + L^- \overset{K_1}{\rightleftharpoons} ML^+ \qquad \text{...........1}$$

$$ML^+ + L^- \overset{K_2}{\rightleftharpoons} ML_2 \qquad \text{..........2}$$

The metal spot on the paper is thus a conglomeration of uncomplexed metal ion, 1:1 complex and 1:2 complex. The overall mobility is given by equation.

$$U = \frac{u_o + u_1K_1[L^-] + u_2K_1K_2[L^-]^2}{1 + K_1[L^-] + K_1K_2[L^-]^2} \qquad \text{...........3}$$

where,

u_o, u_1 and u_2 are mobility of uncomplexed, 1:1 and 1:2 metal complex respectively.

For calculating the first stability constant K_1, the region between first and second plateau is pertinent. The overall mobility 'U' will be equal to the arithmetic mean of mobility of uncomplexed metal ion, u_o and that of the first complex u_1 at a pH from which $K'_1 = 1/[L^-]$. With the help of dissociation constants of methionine ($K'_1 = 10^{2.25}$, $K'_2 = 10^{9.00}$), the concentration of methione anion $[L^-]$ is determined for the pH from which K_1 can be calculated.

The concentration of ligating amino acid species $[L^-]$ is calculated using the equation.

$$[L^-] = \frac{[L_T]}{1 + \frac{[H]}{K'_2} + \frac{[H]^2}{K'_1K'_2}} \qquad \text{.........4}$$

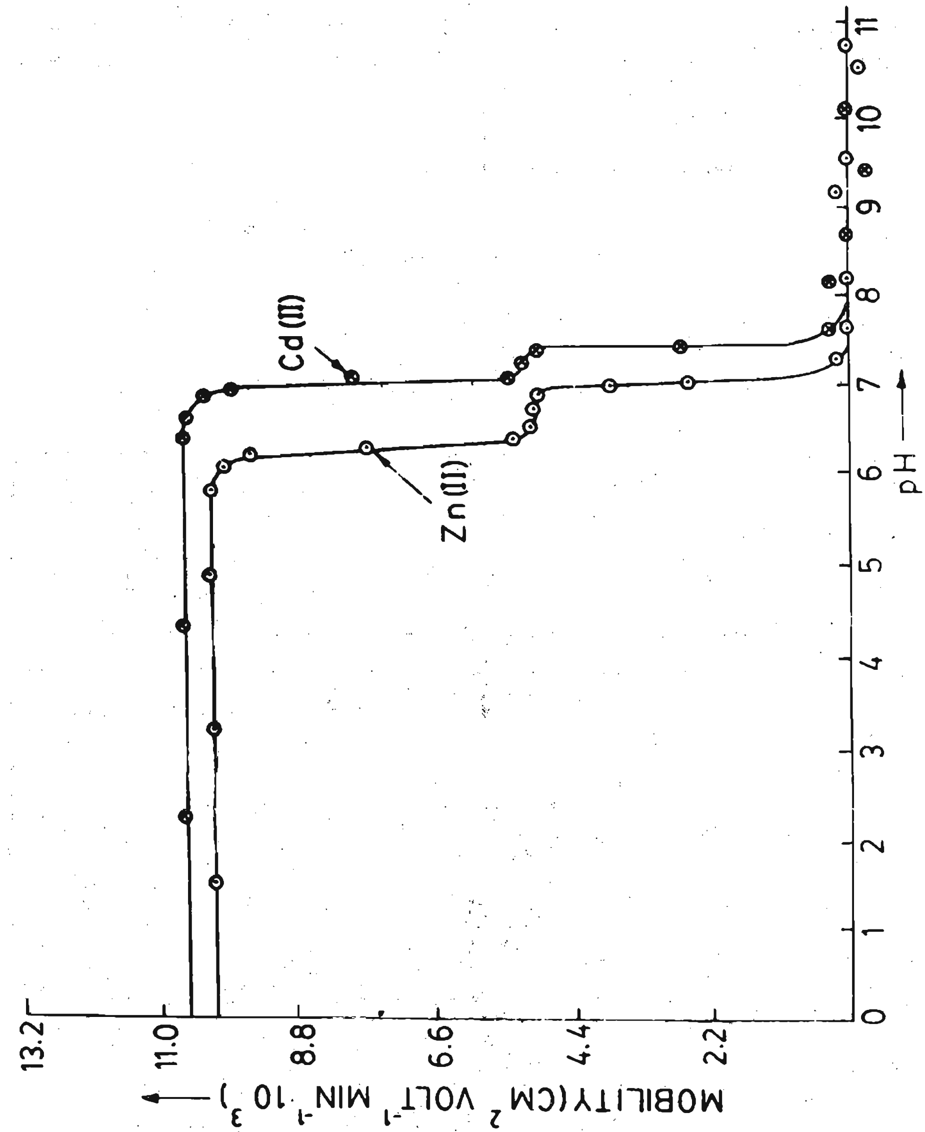

Figure 1: Mobility curve [Zn(II) and Cd(II) - Methionine system]

where,

$[L_T]$ = total concentration.

The stability constant K_2 of the second complex can be calculated by taking into consideration the region between the second and third plateaus of the mobility curve. Their calculated values are given in Table 1.

Table 1: Stability constants of binary and mixed complexes of Zn(II) and Cd (II)

(Ionic strength = 0,1 μ) (Temperature = 35°C)

NTA anion = $N(CH_3COO)_3^{3-}$

Methionine anion = $CH_3 - S - CH_2 - CH_2 - CH(NH_2) - COO^-$

Metal Ions	Calculated value of stability constants			
	$\log K^M_{1_{ML}}$	$\log K^M_{2_{ML}}$	$\log K^M_{M-NTA}$	$\log^{M-NTA}_{M-NTA-L}$
Zn(II)	4.80	8.80	10.66	3.84
Cd(II)	4.00	7.60	9.78	3.66

Metal Ions	Literature value of stability constants			
	$\log K^M_{1_{Ml}}$	$\log K^M_{2_{ML_2}}$	$\log K^M_{M-NTA}$	$\log^{M-NTA}_{M-NTA-L}$
Zn(II)	4.37 + 0.01[7]	8.33 + 0.1[7]	10.66[7]	-
	4.37[8]	8.33[8]	-	-
	4.90[8]	8.50[8]	10.00[9]	-
Cd(II)	3.67 + 0.2[7]	7.03-0.04[7]	9.78[7]	-
	5.40[8]	8.70[8]	-	-
	3.67[8]	7.03[8]	9.40[9]	-

Where, $K^M_{1_{ML}} = \frac{[ML]}{[M][L]}$; $K_{2_{ML_2}} = \frac{[ML_2]}{[ML][L]}$;

$K^M_{M-NTA} = \frac{[M-NTA]}{[M][NTA]}$; $K^{M-NTA}_{M-NTA-L} = \frac{[M-NTA-L]}{[M-NTA][L]}$

M = metal cations.
L = ligand (methionine).
NTA = nitrilotriacetate.

(II) M (II) - (NTA) - Binary System: Figure 2 shows the mobility curve of metal spot with NTA. The mobility of last plateau in each case is negative showing anionic nature of M - NTA complexes. The stability constants of complexes with NTA are calculated in the same manner as for amino acids, with a minor change in equation.[4]

From a knowledge of dissociation contents of NTA,

($K''_1 = 10^{1.68}$, $K''_2 = 10^{2.67}$, $K''_3 = 10^{9.49}$)[9], the concentraion of NTA anion $[L^{3-}]$ is determined for the pH where, $K = 1/[L^{3-}]$, using following equation.

$$[L^{3-}] = \frac{[L_T]}{1 + \frac{[H]}{K''_3} + \frac{[H]}{K''_2 K''_3} + \frac{[H]^3}{K''_1 K''_2 K''_3}} \qquad (4A)$$

The calculated values of $[L^{3-}]$ are used for calculating log K values of M-NTA, complexes. The calculated values are given in Table 1.

(III) M (II) - NITRILOACETATE (NTA) - Methionine System: - The study of this system has been done at pH 8.5 with a purpose. It is observed from mobility curve of M-Methionine and M-NTA binary systems that binary complexes are formed at pH values lower than 8.5. Thus it would be proper to study the transformation of M-NTA-Methionine complex at pH 8.5 in order to avoid any secondary interactions.

The plot of mobility against log of concentration of added methionine gives a curve (Figure 3). The mobility in last plateau does not tally with the mobility of 1:1 and 1:2 M-methionine complex. It is inferred that the moiety in the last plateau is formed by the coordination of the methionine anion 1:1 to the M-nitrilotriacetate moiety resulting in the formation of 1:1:1 mixed complexes as follows:

$$M\text{-}NTA^- + L^- \overset{K'}{\rightleftharpoons} M\text{-}NTA\text{-}L^{2-} \qquad ....5$$

In the present electrophoretic study the transformation of a simple complex to a mixed complex takes place, hence the overall mobility is given by

$$U = u_0 f_{M\text{-}NTA\text{-}L} + u_1 f_{M\text{-}NTA\text{-}L} \qquad ....6$$

where,

u_o, u_1, and $f_{M\text{-}NTA}$ $f_{M\text{-}NTA\text{-}L}$ are mobilities and the mole fractions of $M\text{-}NTA^-$ and $M\text{-}NTA\text{-}L^{2-}$ complexes respectively. The above equation can be transformed to another form by incorporating the values of more fractions.

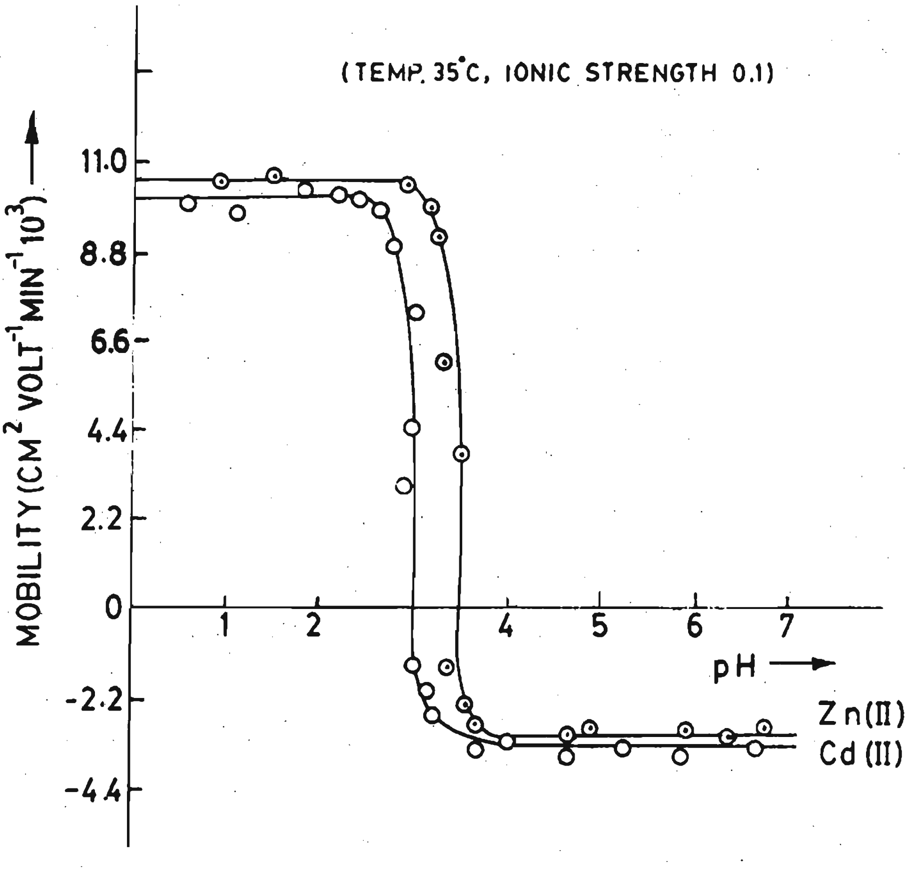

Figure 2: Mobility Curve [M(II) - NTA] system

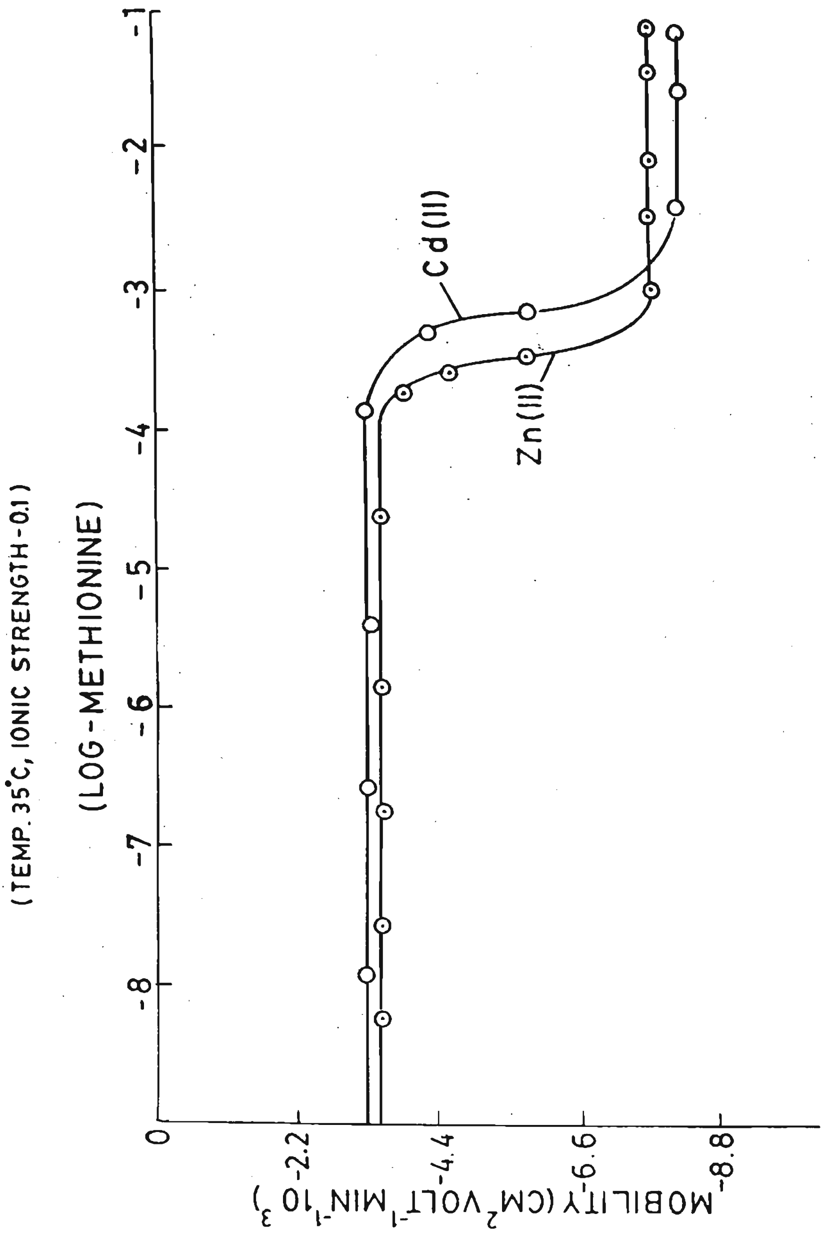

Figure 3: Mobility Curve [Zn(II) and Cd(II)-NTA-Methionine] system

$$U = \frac{u_o + u_1 K'[L]}{1 + K'[L]} \qquad \text{.............7}$$

u_o and u_1 are the mobilities in the regions of the two plateaus of the curve. The concentration of methionine anion at pH 8.5 for this methionine concentration is calculated. K' is equal to $1/[L^-]$ and the values of K' obtained are given in Table 1.

The complexes of Zn (II) and Cd(II) with methionine and other sulphur containing amino acids are of great importance because of the interesting biological role of Zn (II), and the toxic nature of Cd (II). Zinc is an important constituent of many enzymes. It is generally accepted that toxicity of zinc is very low, and a wide range of zinc compounds are permitted for use in food. Very high concentrations of zinc, may cause diarrhoea and vomiting. Cadmium shows no certain indication of being an essential trace element in biological processes. On the contrary, it is highly toxic to a wide variety of living organisms, including man. Inhalation of cadmium rapidly affects the respiratory tract and later the kidneys. Ingestion leads to almost immediate gastro-intestinal poisoning, similar in its symptoms to food poisoning. Kidney and liver damage may result. It may be concluded from these studies that compounds similar to methionine and nitrilotriacetate (NTA) may reduce the level of free Zn (II) and Cd (II) in biological systems.

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