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Electrophoretic Studies on Determination of Stability Constants of Zn(II) and Cd(II) Mixed Complexes (M-Methionine-Cysteine System)

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The stability constant of different complex species of some metal ions viz. Zn^{2+} and Cd^{2+} with methionine were determined electrophoretically at an ionic strength 0.1 perchloric acid and 85°C. The stability constant of complexes M(II)–methionine-cysteine 7.30 and 7.62 (log K values) for Zn(II) and Cd(II) complexes.

INTRODUCTION

The most important reactions are the processes involving participation of the mercapto group; main biochemical aspect of these have been reviewed by Jocelyn[1]. Extremely greater biological importance is attached to the study of metal-sulphur bonds formed in such processes, primarily in the nonheme iron proteins[2] and in the blue copper proteins[3]. Sorensen[4] has demonstrated the antiinflammatory activity of the copper D-Penicillamine. Publications[5,6] from our laboratories described a new method for study of mixed complexes. The present work reports our observation on the inter-ligand mixed complex system *viz* Zn^{2+} and Cd^{2+}-methionine-cysteine.

EXPERIMENTAL

The apparatus and procedure are reported as earlier[5,6], with a minor difference from the precision point of view. Here triplicate strips were used for the same experiment and the find value of the movement was taken as a mean of all the three strips. It was found that the variation in the movement was about $\pm 5\%$.

Zn(II) and Cd(II) perchlorate solutions were prepared in the laboratory from the nitrates viz. carbonate. The solution was standardized and diluted to 5.0×10^{-3}M.

Metal spots were detected on the paper using dithiozone in carbon tetrachloride (for Zn^{2+}) Pan (for Cd^{2+}). Silver nitrate in acetone made alkaline is used for glucose.

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Background Electrolyte

Stock solution of 9.0M perchloric acid, 2.0M sodium hydroxide, 0.5M methionine and 0.5M cysteine were prepared from analaR samples (B. D. H. Poole, Great Britain). It was maintained at pH 8.5 by addition of sodium hydroxide for mixed system.

RESULTS AND DISCUSSION

(I) M(II)–Methionine Binary System

The ionophoretic mobility of metal spot against pH gives a curve with a number of plateaus. The first one in beginning corresponds to a region in which metal ions are uncomplexed. The second plateau in each case with positive mobility indicating the formation of 1 : 1 complex of cationic nature. Further increase of pH mobility decreases giving rise to third plateau lie in zero region, neutral nature of metal complexes indicated. Chemical literature also assigns prominent liganding properties to unprotonated anionic species of methionine, ruling out any such property to *Z*witter ion[7]. In view of above observation the complexation of metal ion with methionine anion $[L^-]$ may be represented as

$$M^{2+} + L^- \overset{K_1}{\rightleftharpoons} ML^+$$

$$ML^+ + L^- \overset{K_2}{\rightleftharpoons} ML_2$$

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

$$U = \frac{u_0 + u_1K_1[L^-] + u_2K_1K_2[L^-]^2}{1 + K_1[L^-] + K_1K_2[L^-]^2}$$

where,

u_0, u_1 and u_2 are mobilities of uncomplexed, 1 : 1 and 1 : 2 metal complex respectively.

For calculating 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_0 and that of the first complex u_1 at a pH where $K_1 = 1/[L^-]$ with the help of dissociation constants of methionine ($k_1 = 10^{2.25}$, $k_2 = 10^{8.55}$).

The concentration of methionine anion $[L^-]$ is determined from which K_1 can be calculated. The concentration of liganding amino acid species $[L^-]$ is calculated with the help of equation,

$$[L^-] = \frac{[L_T]}{1 + \frac{[H]}{k_2} \; \frac{[H^2]}{k_1 k_2}}$$

where,

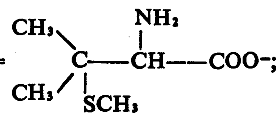
$[L_T]$ = total concentration.

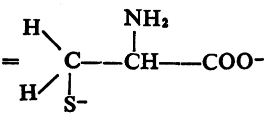
The stability constant K_2 of second complex can be calculated by taking into consideration the region between second and third plateau of mobility curve. These calculated values are given in Table 1.

TABLE 1

STABILITY CONSTANTS OF BINARY AND MIXED COMPLEXES OF Zn(II) AND Cd(II)

(Ionic Strength=0.1; (Temperature=35°C)

Methionine anion = 

Cysteine anion = 

Metal ions	Values of Stability Constant		
	$\log K_1{}^{M}_{ML}$	$\log K_2{}^{M}_{ML_2}$	$\log K'^{M-L}_{M-L-L'}$
Zn(II)			
Calculated value	4.80	8.80	7.30
Literature value	4.37+0.01(8)*	8.33+0.1(8)*	—
	4.37(9)*	8.33(9)*	—
	4.90(9)*	8.50(9)*	—
Cd(II) :			
Calculated value	4.0	7.60	7.62
Literature value	3.67+0.2(8)*	7.03—0.04(8)*	—
	5.40(9)*	8.70(9)*	—
	3.67(9)*	9.03(9)*	—

where, $K_1{}^{M}_{ML} = \frac{[ML]}{[M][L]}$; $K_2{}^{M}_{ML_2} = \frac{[ML_2]}{[ML][L]}$: $K'^{ME}_{MLL'} = \frac{[M-L-L']}{[M-L][L']}$

*References.

On comparing these values with the literature values, it was found that both are not in quite agreement. This difference in the result can be attributed to the different experimental conditions *i.e.* ionic strength and temperature. Though with certain modification in experimental conditions we have tried to remove the error, even then the precision of the method is limited to that of paper electrophoresis and the range of uncertainity in the results is $\pm 5\%$.

(III) M(II)-Methionine-Cysteine Mixed Ligand System

The plot of mobility against log of concentration of added cysteine gives a curve. The mobility of last plateau is more negative than mobility of pure M-methionine complex. It is inferred that the moiety in last plateau is due to coordination of cysteine anion to 1 : 1 M-methionine moiety resulting in the formation of 1 : 1 : 1 mixed complexes (M-methionine-cysteine) as—

$$ML^1 + L \overset{K'}{=} ML'L$$

The overall mobility given by

$$U = u_0 \, f_{m-methionine} + u_1 f_{m-methionine-cysteine}$$

where,

u_0, u_1 and $f_{m-methionine}$, $u_1 f_{m-methionine-cysteine}$ are the mobilities and mole fractions of M-methionine and M-methionine-cysteine complexes respectively. Above equation changes into another form by adding the value of mole fraction

$$U = \frac{{}_0 + u_1 K'[L]}{1 + K'[L]}$$

where,

u_0 and u_1 are mobilities of M-methionine and M-methionine-cysteine complexes respectively.

The concentration of cysteine anion at pH 8.5 for the cysteine concentration is calculated. K′ is obviously equal to $1/[L^-]$. All these values of K′ are given in Table 1.

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