

## Study of Mixed Complexes of Sulphur Containing Amino Acids by Ionophoretic Method (M(II)-Methionine-Penicillamine System)

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The formation constants of different complex species of some metal ions viz., Hg(II), Be(II) and Ni(II) with methionine were determined electrophoretically at an ionic strength of 0.1 M perchloric acid and 35°C. The investigations have also been extended to mixed ligand systems using methionine and penicillamine as primary and secondary ligand respectively. This technique is based on the movement of a spot of metal ion under an electric field with the complexants added in background electrolyte at pH 8.5. The stability constants of complexes, M(II)-methionine-penicillamine have been found to be 10.23, 11.20 and 9.03 (log K values) for Hg(II), Be(II) and Ni(II) complexes respectively.

### INTRODUCTION

Paper electrophoresis was applied to the study of metal complexes in solution; attempts were made to determine the stability constant of the complex species<sup>1</sup>. In recent years a new method has been developed for the study of stepwise complex formation<sup>2</sup>. Although the use of paper electrophoresis for the study of metal complex systems with single ligand seems to be well established, there is no systematic study for mixed complexes. However, Czakis-Sulikowska<sup>3</sup> made some observations on the formation of mixed halide complexes of Hg(II), but it is only qualitative and does not throw light either on the nature of the species or on their stabilities. Tiwari *et al.*<sup>4,5</sup> have described a new method for study of inter-ligand mixed complexes. The present work is an extension of the technique and reports on our observations on the inter ligand mixed complex system viz. Hg(II), Be(II) and Ni(II)-methionine-penicillamine.

### EXPERIMENTAL

The apparatus and procedure were same as reported earlier<sup>2</sup>. Hg(II) Be(II) and Ni(II) perchlorates were prepared by precipitating the corresponding carbonates with sodium carbonate from solutions of nitrates. The metal contents of the filtrates were determined as usual and final concentration was kept at  $5.0 \times 10^{-3}$  M.

Hydrogen sulphide water was used for detecting of Hg<sup>2+</sup>. Aluminon ammonium acetate 0.1 (w/v) solution in water was used for detecting Be<sup>2+</sup>. DMG solution

in  $\text{NH}_4\text{OH}$  was used for detecting  $\text{Ni}^{2+}$ . Silver nitrate in acetone made alkaline is used for glucose.

Stock solutions of 9.0 M perchloric acid, 2.0 M sodium hydroxide, 0.5 M methionine and 0.5 M penicillamine were prepared from AnalaR samples (B.D.H., Poole, Great Britain).

The background electrolyte in the study of binary complexes consists of 0.1 M perchloric acid and  $1.0 \times 10^{-2}$  M methionine. While in study of ternary complexes, it consists of 0.1 M sodium perchlorate,  $1.0 \times 10^{-2}$  M methionine and varying amount of  $1.0 \times 10^{-2}$  M penicillamine. It was maintained at pH 8.5 by addition of sodium hydroxide.

## RESULTS AND DISCUSSION

(i) *M-Methionine-Binary System*: The ionophoretic mobility of metal spot against pH gives a curve with a number of plateaus shown in Fig. 1. Every plateau indicates the formation of a certain complex species. The first one in beginning corresponds to a region in which metal ions are uncomplexed. Fig. 1 reveals that

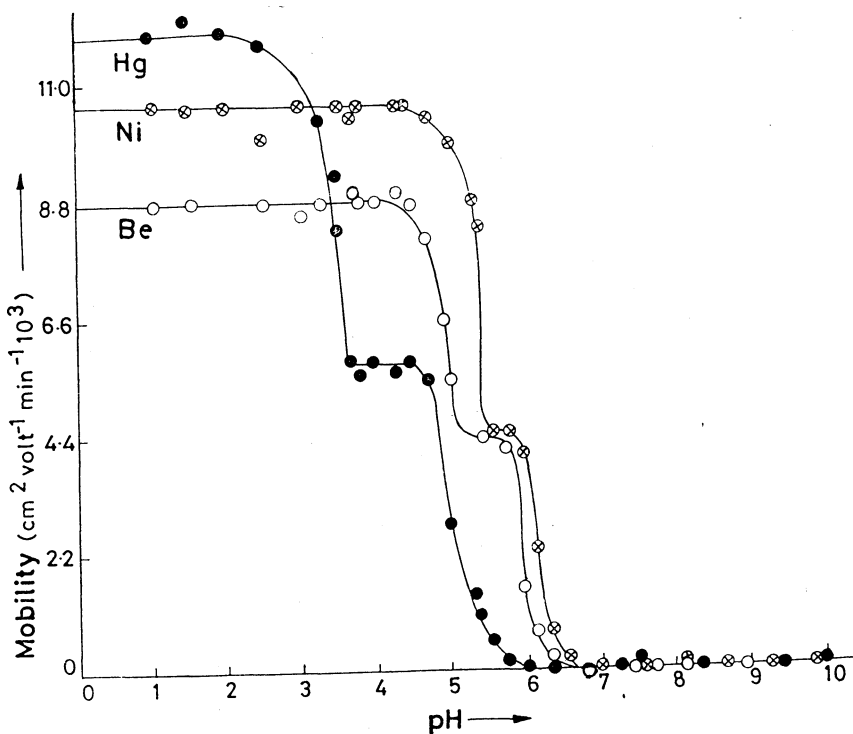


Fig. 1 Mobility curves of [Hg(II), Be(II) and Ni(II). Methionine] system (Temp. 35°C, Ionic strength 0.1 M)

second plateau in each case with positive mobility indicates the formation of 1:1 complexes of cationic nature. On further increase of pH, mobility decreases giving rise to third plateau lying in zero region; neutral nature of metal complexes is indicated. Chemical literature also assigns prominent liganding properties to

unprotonated anionic species of methionine ruling out any such property to zwitter ion<sup>6</sup>.

In view of the above observation, the complexation of metal ion with methionine anion  $[L^-]$  may be represented as



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

$$U = \sum_n u_n f_n \quad (3)$$

where  $u_n$  and  $f_n$  are mobility and mole fraction of particular complex species respectively.

This equation is transformed into the following form on taking into consideration different equilibria:

$$U = \frac{u_0 + u_1 K_1 [L^-] + u_2 K_1 K_2 [L^-]^2}{1 + K_1 [L^-] + K_1 K_2 [L^-]^2} \quad (4)$$

where,  $u_0$ ,  $u_1$  and  $u_2$  are mobility of uncomplexed, 1 : 1 and 1 : 2 metal complexes respectively.

This equation has been used for calculating stability constants of the complex of metal ions with methionine. 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 the first complex  $u_1$  at a pH where  $K_1 = 1/[L^-]$  with the help of dissociation constants of methionine ( $K_1 = 10^{2.55}$ ,  $K_2 = 10^{8.55}$ ). The concentration of methionine anion  $[L^-]$  is determined for the pH, from which  $K_1$  can be calculated. The mobility curve of pure methionine is shown in Fig. 2.

The concentration of liganding amino acid species  $[L^-]$  is calculated with the help of equation

$$[L^-] = \frac{[L_T]}{1 + \frac{[H]}{K_2} + \frac{[H]^2}{K_1 K_2}} \quad (5)$$

where  $[L_T]$  = total concentration

$K_1$ ,  $K_2$  = dissociation constants of methionine.

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.

(ii) *M-Methionine-Penicillamine Mixed Ligand System*: The plot of mobility against log of concentration of added penicillamine gives a curve (Fig. 3) containing two plateaus, one in the beginning and other in the end. The mobility of the range of first plateau corresponds to mobilities 1 : 1 M-methionine complexes. The mobility of last plateau is more negative than mobility of pure M-methionine

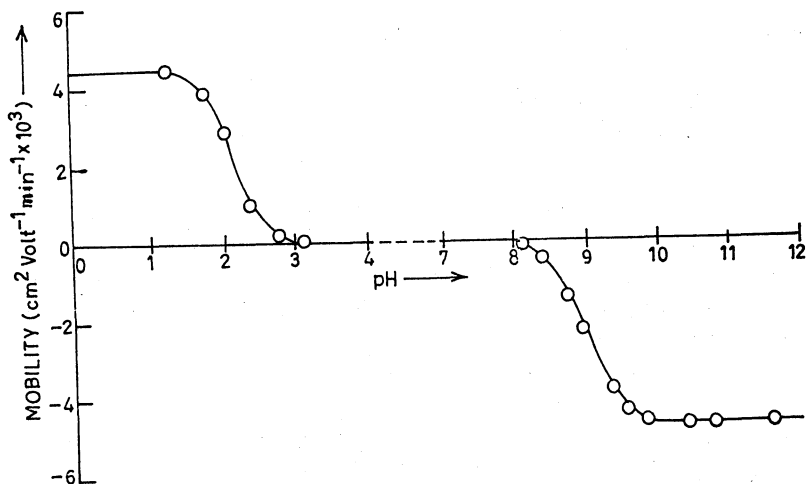
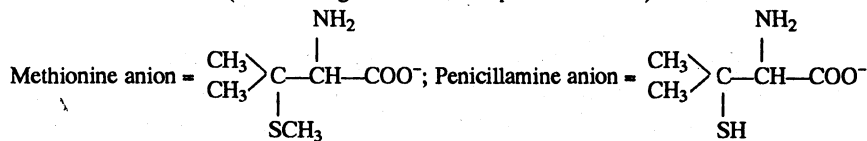


Fig. 2 Mobility curve of H<sup>+</sup> methionine (Temp. 35°C, Ionic strength 0.1 M)

TABLE 1  
STABILITY CONSTANTS OF BINARY AND MIXED COMPLEXES  
OF Hg(II), Be(II) AND Ni(II)

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

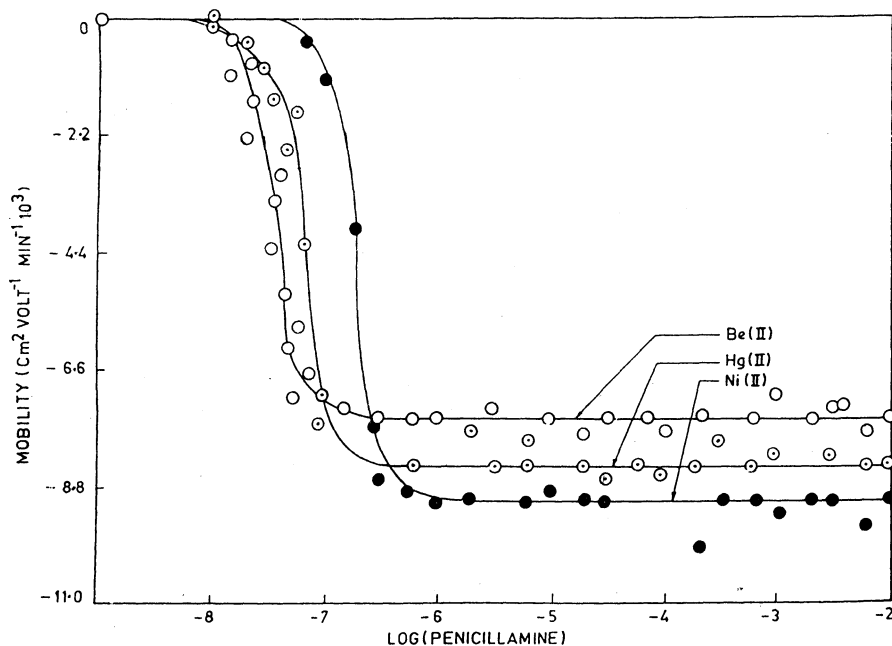


Metal ions	Calculated values of stability constants			Literature values of stability constants		
	$\log K_{1ML}^M$	$\log K_{2ML_2}^M$	$\log K_{M-L-L'}^{M-L}$	$\log K_{1ML}^M$	$\log K_{2ML_2}^M$	$\log K_{M-L-L'}^{M-L}$
Hg(II)	7.62	13.62	10.23	6.52(09) 6.52(07)	11.45(09) 11.45(07)	—
Be(II)	6.00	11.00	11.20	—	12.00(09)	—
Ni(II)	5.60	10.40	9.03	5.70(09) 5.19(09) 5.41(08) 5.19(07)	9.40(09) 9.84(09) 10.81(08) 9.84(07)	12.43(08) <sup>3</sup>

$$\text{where } K_{1ML}^M = \frac{[M]}{[M][L]}, K_{2ML_2}^M = \frac{ML_2}{[ML][L]}, K_{M-L-L'}^{M-L} = \frac{[ML-L']}{[ML][L']}$$

complex. Further since 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 last plateau is due to coordination of penicillamine anion to 1 : 1 M-methionine moiety resulting in the formation of 1 : 1 : 1 intermixed ligand complex (M-methionine-penicillamine) as—





**Fig. 3** Mobility curves of [M(II) Methionine-penicillamine] system (Temp. 35°C, Ionic strength 0.1 M)

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

$$U = u_0 f_{M\text{-methionine}} + u_1 f_{M\text{-methionine-penicillamine}} \quad (7)$$

where,  $u_0$ ,  $u_1$  and  $f_{M\text{-methionine}}$ ;  $f_{M\text{-methionine-penicillamine}}$  are mobilities and the mole fractions of M-methionine and M-methionine-penicillamine complexes respectively. The above equation changes into another form by adding the values of mole fractions:

$$U = \frac{u_0 + u_1 K' [L]}{1 + K' [L]} \quad (8)$$

where,  $u_0$  and  $u_1$  are the mobilities in the regions of the two plateaus of the curve.

The concentration of penicillamine is determined from Fig. 3. The concentration of penicillamine anion at pH 8.5 for this concentration is calculated.  $K'$  is obviously equal to  $1/[L]$ . All these values of  $K'$  are given in Table 1.

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