Study of Mn(II) Complexes with Sulphur containing Ligands by Paper Electrophoretic Technique

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The complexation data involving body toxic or essential metal ion and bioactive sulphur containing ligands give insight into many physico-chemical processes. Manganese is an essential metal [1] and known to participate in photosynthetic mechanism [2]. The use of paper electrophoresis for the study of metal complex is well established [3]. This method has been used to study the binary complexes of Mn(II) with methyl cysteine, methionine, cysteine and penicillamine.

EXPERIMENTAL

The apparatus, procedure of paper electrophoresis and method of preparation of manganese(II) perchlorate solution are as described earlier [3]. The background electrolytes used are 0.1 M perchloric acid containing 0.01 M solution of the studied ligand. Metal spot is detected on the paper using indicator solution of 1-(2-pyridylazo)-2-naphthol (PAN of Merck Darmstadt, Germany). Glucose spot is detected as a black spot by spraying silver nitrate solution in aqueous acetone followed by alcoholic sodium hydroxide.

RESULTS AND DISCUSSION

The plot of overall ionophoretic mobility of metal spot against pH gives curves with two plateaus in every case (Fig 1 & 2). The plateau at low pH value is due to uncomplexed metal. The second plateau in the case of methyl cysteine and methionine (Fig 1) have positive mobility indicating the complex to be cationic in nature (ML^+), the ligand being monodentate anionic species [L^-]. In the case of cysteine and penicillamine (Fig

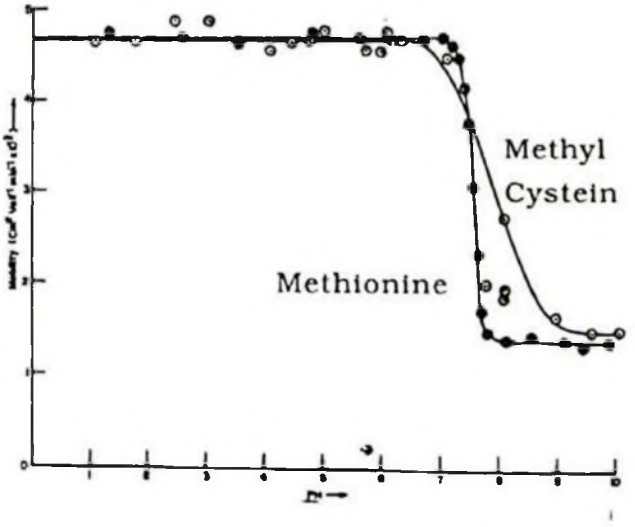


Fig.1 Mobility curves for M-amino acid systems. Temperature = 35° C Ionic strength = 0.1M

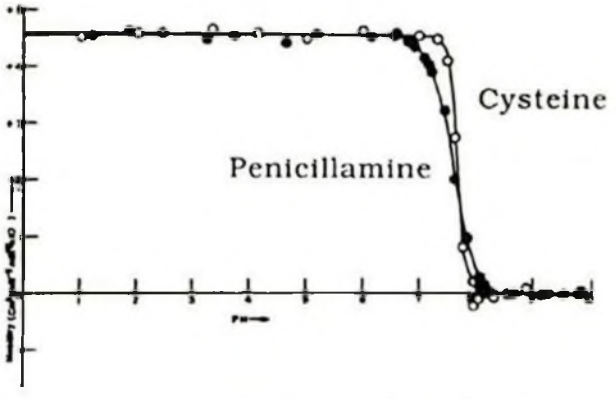


Fig.1 Mobility curves for M-amino acid systems. Temperature = 35° C Ionic strength = 0.1M

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2), the second plateau has zero mobility indicating a neutral complex species, the ligand being bidentate anionic species (L^{2-}). Further increase of pH in each case has no effect on the mobility of metal ion.

The concentration of the mononegative anionic ligands of methyl cysteine and methionine and dinegative anionic ligands of cysteine and penicillamine at the pH corresponding to the mid point of the ionophoretic mobility plot are calculated from the concentration and protonation constants of the ligands. The values of protonation constants used in the calculations for the four ligands [4,5] are given in the Table.

The value of the complexity constant K_1 of different complexes are calculated by the relation

K_1 = 1 / [Ligand species]

Ligand species being $[L^{-1}]$ and $[L^{2-}]$ and included in the Table.

The complexing tendency with manganese (II) is highest for penicillamine anion and lowest for methyl cystein. The order of the complexation tendency is found to be in the order:Methyl cysteine < Methionine < Cysteine < Penicillamine.

The divergence in the values obtained from different sources as seen in the Table is mainly due to the difference in temperature and ionic strength used by different workers. Further, the uncertainity attending on the mobility measurements is known to be slightly on the higher side (±5%). In view of these,

Table 1

Protonation Constants of Ligands and Stability Constants of Manganese Complexes

Ionic Strength = 0.1 M Temperature 35°C

Const.	Methyl cysteine	Methionine	Cysteine	Penicillamine
Protonation Constants of the Ligands [Ref 4, 5]				
pK_1	2.55	2.55	2.00	1.90
pK_2	9.00	8.55	8.25	7.85
pK_3			10.35	10.55
Stability Constants - Present Work				
log K_1	2.80±0.07	3.40±0.09	5.40±0.05	5.72±0.10
Stability Constants - Literature Values [Ref 4,5 and 6]				
log K_1	2.52 [5,6]	2.85[4]	4.70[5]	-
		2.77[5]	4.56[6]	-
		3.20 [6]		
log K_2	1.75 [5,6]	1.80[5]	-	-
		1.50 [6]		

the agreement with the literature values is considered as satisfactory.

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