Paper Electrophoretic Technique in the Study of Mixed Complexes (M-Nitrilotriacetate - Tryptophan System)

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Paper electrophoresis was applied to the study of metal complexes in solution and attempts were made to determine the stability constants of the complex species [1,2]. A method has been reported for the study of the step-wise complex formation [3,4] from these laboratories. Csakis-sulikowska [5] 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. Publications from our laboratories [6,7] described a new method for study of mixed complexes. The present work is an extension of the work and reports our observation on the mixed system, namely Cu(II) / Co(II) / Zn(II)-nitrilotriacetate - tryptophan.

EXPERIMENTAL

Perchlorates of Cu(II), Co(II) & Zn(II) were prepared starting from corresponding nitrates via carbonates. The precipitates were washed thoroughly with boiling water before treating with a calculated amount of 1% perchloric acid. The resulting mixtures were heated to boiling on a water bath and then filtered. The metal contents in the filtrates were determined and the final cocentration adjusted to 5.0×10^{-3} M.

A 0.1 % w/v solution of 1-(2-pyridylazo)-2-naphtol (PAN), in ethanol was used for detecting the metal ions. A saturated solution of silver nitrate (0.9 ml) was diluted with acetone to 20 ml. Glucose was detected by spraying this solution followed by a spray of 2% ethanolic sodium hydroxide.

Stock solutions of 9.0 M perchloric acid, 2.0 M sodium hydroxide and 0.5 M tryptophane were prepared from AnalaR samples (BDH Poole, Great Britain). 0.01 M nitrilotriacetic acid (NTA) was prepared from E. Merck sample. Each solution was standardised as usual.

The background electrolyte for binary complex study consisted of 0.1 M perchloric acid, 0.01 M tryptophane (or 0.001 M NTA as the case may be) and the pH adjusted to a specific value by the addition of sodium hydroxide solution.

The back ground electrolyte for the study of ternary complexes consisted of 0.1 M sodium perchlorate, 0.001 M NTA, varying amounts of tryptophane and the

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pH adjusted to 8.5. The procedure of measurement remains the same as discussed in detail earlier [7].

RESULT AND DISCUSSION

Metal - Tryptophane Binary System

The plot of overall electrophoretic mobility of metal spot against pH gives a curve with three plateaus shown in Fig.1. The pH range showing a horizontal plateau possibly contains one particular complex species overwhelmingly. Uncomplexed metal ion exists predominantly in the plateau at low pH values. In this pH range, tryptophane exists in protonated form which has low liganding ability. Beyond this range, mobility of metal ion decreases progressively. In this pH range of decreasing mobility, first complex (metal - tryptophane) is being formed. Because of the increase in bulk, the mobility of this species is lower. The second plateau in case of each metal represents the complex of cationic nature (1:1 metal-tryptophane). Further increase in pH results in a plateau of zero mobility and represents neutral complex formed from two anionic tryptophane species with one bivalent metal ion. Literature also assigns prominent liganding property to unprotonated anionic species of tryptophane and poor liganding ability to zwitterion [8,9]. Further increase in pH has no effect on the mobility of metal ion.

The method of calculation of K^{M}_{ML} and K^{ML}_{ML2} is described earlier [7a]. Tryptophane anion concentration is calculated using the acid dissociation constant value of Tryptophane (log K_1 = 9.49, log K_2 = 2.32). The calculated values are presented in Table 1.

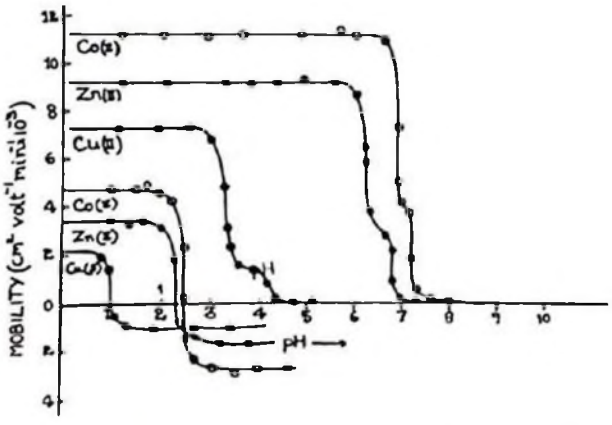


Fig 1 Mobility curves of binary systems
Temperature 25°C;
Ionic Strength 0.1 M
A) Metal-tryptophan System;
B) Metal-NTA System

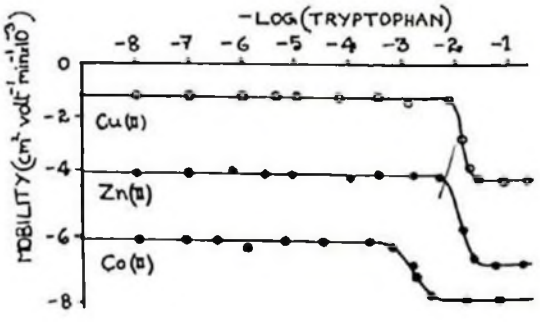


Fig 2 Mobility curves of ternary system
Temperature 25°C;
Ionic Strength 0.1 M; pH = 8.5;
[NTA] = 0.001 M

Table 1

Stability Constants of some Binary and Ternary Complexes of Cu(II), Co(II) and Zn(II)

Ionic Strength 0.1 M; Temp 25° C;
A = NTA; L = Tryptophane

Metal ion	Stability Constant $\log K^{M}_{ML}$	$\log K^{M}_{ML2}$	$\log K^{M}_{MA}$	$\log K^{MA}_{MAL}$
Cu(II)				
This work	8.23	7.29	12.99	5.08
lit.	8.29[8]	7.19[8]	12.94[11]	5.06 [12]
Co(II)				
This work	4.59	4.29	10.37	3.06
lit.	4.58[8]	4.32[8]	10.38[11]	3.08 [12]
Zn(II)				
This work	5.24	4.69	10.66	3.05
lit.	5.18[8]	4.69[8]	10.66[11]	3.02 [12]

$$\log K^{M}_{ML} = \frac{[ML]}{[M]\,[L]} \qquad \log K^{M}_{ML2} = \frac{[ML_2]}{[ML]\,[L]}$$

$$\log K^{M}_{MA} = \frac{[M\text{-}NTA]}{[M]\,[NTA]} \qquad \log K^{MA}_{MAL} = \frac{[M\text{-}NTA\text{-}L]}{[M\text{-}NTA]\,[L]}$$

Metal-Nitrilotriacetate Systems

The observations on the overall mobility of metal spots in presence of NTA at different pH values are also represented in Fig.1. It is evident from the figure that two plateaus are obtained with all the three metal ions. The mobility of the last plateau in the negative region, shows the negatively charged nature of the complexes. Only one NTA anion is assumed to combine with one bivalent metal ion to give a 1:1 M-NTA complex, which is in conformity with the findings of others [10,11]. The stability constants of complexes with NTA are calculated in the manner described earlier [7a]. The calculated values are given in Table 1.

Metal-Nitrilotriacetate - Tryptophan Ternary Systems

It is observed from the mobility curves of M-tryptophan and M- NTA binary systems that M-tryptophan and M-nitrilotriacetate are formed at a pH much lower than 8.5. Thus at this pH, the transformation of the M-NTA complex into M-NTA-tryptophan complex can be studied without any ambiguity.

The plot of mobility against logarithm of concentration of added tryptophan gives a curve (Fig.2) containing two plateaus- one in the begining and the other in the end. The mobility in the range of first plateau corresponds to the mobilities of 1:1 M-NTA complexes as seen in the study of binary M-NTA system. The mobility of the last plateau is more negative than that of first plateau, so it indicates the formation of a more negatively charged complex. Further, since the mobility in the last plateau does not tally with the mobility of the 1:1 and 1:2 metal tryptophan complex (observed in our study of binary M-tryptophan system), it is inferred that the last plateau is due to the co-ordination of the tryptophanate anion to a 1:1 M-NTA moiety, resulting in the

formation of 1:1:1 mixed complex (M-NTA-Tryptophan) as

$$M\text{-}NTA^{-} + L^{-} \underset{}{\overset{k'}{\rightleftharpoons}} M\ NTA\text{-}L^{2-}$$

In the present electrophoretic study, the transformation of a simple complex into a mixed complex takes place. The complexity constants are calculated as described earlier [7b] and presented in Table 1.

The present values determined electrophoretically are compared with the available literature values (Table 1). The slight difference observed may be due to change in temperature, ionic strength and experimental conditions.

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