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Determination of formation constants of some mixed complexes of glycocymin and Nitrilotriacetic acid by paper electrophoresis (Cu(II), UO_2(II), Co(II), Zn(II), Cd(II)-Nitrilotriacetic acid-Glycocymin System)

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ABSTRACT

Formation constant of mixed complexes of Cu(II), UO_2(II), Co(II), Zn(II), Cd(II) NTA and Glycocymin was determined by paper electrophoresis. The value of stability constant of studied complexes were found to be 5.35, 5.15, 4.23, 3.67, 3.45, 3.41 for Cu(II), UO_2(II), Co(II), Zn(II), Cd(II) respectively at Ionic strength 0.1M perchloric acid at 35°C.

Key words: Paper electrophoresis stability constant, mobility, mixed complex.

INTRODUCTION

Not much work is on record on the application of this technique to the study of metal complexes. In 1964, Jokl[1] gave a comprehensive account of the use of paper electrophoresis in of determination of stability, of metal ligand system in solutions. He employed electromigration studies of amino acid complexes of several bipositive metal ions. Biernat[2] gave a theoretical treatment similar to that of Jokl[1] for the study of stepwise complexation reactions in solution. Hurnick[3] followed the same technique for study of tartarate complexes of Fe (II), Co (II), Ni (II) in aqueous media and determined stability constants with those obtained from spectrophotometric measurements. Kozak[4] investigated Cu (II), Co (II), Ni (II), Cd (II), Zn (II) and Mg (II) complexes of malonic acid and alkyl derivatives while oxalate and succinate complexes were studied by Koch[5]. In majority of the investigations reported, it is noted that the studies are not extensive and in many cases they are largely qualitative.

In recent years, Singh *et. al.,* have published number of papers in which a new approach have been made for study of complexation reactions in solution with help of paper electrophoresis. Formation of various mixed complexes have also been studied by Singh *et. al.*[6-17].

EXPERIMENTAL

Instruments

Paper electrophoresis equipment used is the same as described earlier (4). Measurements of pH are made with an Elico pH meter model L. 1 - 10 using a glass electrode.

Cu (II), UO_2 (II), Co (II), Zn (II), Cd (II) perchlorates were prepared by prepared by precipitating the corresponding carbonates from solution of nitrates, washing the precipitates thoroughly with boiling water and treating with calculated amount of perchloric acid. Resulting mixture was heated to boiling on a water bath and filtered. The metal content in the filtrate as determined and concentration was adjusted finally to 5M in each case.

A solution (0.1%) of 1-(2-pyrdylazo)-3-naphthol (PAN) was prepared in ethanol and used to detect Cu (II), UO_2 (II), Co (II), Zn (II) ions. Cadmion 2B was used for detecting Cd (II). Glucose spot was detected as usual with silver nitrate and 2% ethanolic sodium hydroxide. Stock solution of 3.0 M perchloric acid, 2.0 M sodium hydroxide and 0.5 M Glycocymin were prepared from AnalaR samples. 0.01 M NTA was prepared from E.Merck sample. Each solution was standardised as usual. The background electrolytes were prepared from these stock solutions.

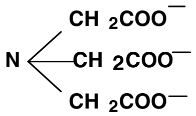
Background electrolyte for binary complex study was 0.1 M perchloric acid containing 0.01 M Glycocymin and adjusted to different pH values. Ionic mobility of the different metal ions was determined. At different pH ; Mobility vs pH plots were prepared. Background electrolyte for ternary complexes was 0.1 M perchloric acid containing 0.01 M Glycocymin and varying amounts of NTA; The pH of this solution was adjusted to pH 8.5 by the addition of sodium hydroxide. The mobility of metal spots was determined in each of the solutions. Plots of mobility vs NTA concentration were prepared.

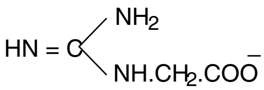
RESULTS AND DISCUSSION

The plot of overall mobility of metal ion spot

Table 1: Stability constant of metal - nitrilotriacetic acid-glycocymin complexes

Temperature 35°C Ionic Strength = 0.1

NTA anion = 

Glycocymin anion ($GC\overline{N}$) = 

Metal ion	Calculated value				
	Log K^{M}_{ML}	Log K^{M}_{ML}	Log K^{M}_{ML}	Log K^{M}_{ML}	Log K^{M}_{ML}
Cu (II)	6.85	5.37	12.65	5.35	18.00
UO_2 (II)	7.12	5.22	9.50	5.15	14.65
Ni (II)	5.12	3.84	10.31	4.23	14.54
Co (II)	4.43	3.91	10.78	3.67	14.45
Zn (II)	4.34	3.83	10.63	3.45	14.08
Cd (II)	4.33	3.88	9.44	3.41	12.85

vs pH gives three plateaus. The plateau of high mobility represents uncomplexed metal ions, the one with near zero mobility represents uncharged metal complex (metal : ligand = 1:2). The middle plateau represents 1:1 complex ML^+. The mid point between the first and second plateau was used to calculate K_1. (The overall mobility, U, at this point is the arithmetic mean of mobility at the first plateau (U_1) and that at second plateau (U_2). The pH of this point was read out from the graph. The ligand concentration, (L), (unprotonated Glycocymin species) at this pH was calculated using the dissociation constant of Glycocymin . $K_1 = 1/[L]$. K_2 was similarly calculated from the mid point between the second and lowest plateau. The values are given in Table-1.

It is observed that the metals form highest complex both with Glycocymin (1:2) and NTA (1:1) at a pH lower than 8.5. So conversion of 1:2 Glycocymin to ternary complex with NTA was studied at a pH of 8.5. The plot of mobility vs log [NTA] at this pH gives a curve with two plateaus. The mobility at low NTA concentration corresponds to mobility of 1:2 metal - Glycocymin binary complex. Negative mobility observed at highest NTA concentration corresponds to ternary complex. The interaction may be represented as :

$$ML' + L \overset{K'}{\rightleftharpoons} ML'L$$

Where
L' = NTA anion
and L = amino acid anion

Under these conditions overall mobility can be given by the expression :

$$U = \frac{u_0 + u_1 k'[L]}{1 + k'[L]}$$

where u_0 and u_1 are mobilities of M-NTA complex and mixed complex (ML'L) respectively. These mobilities pertain to the two plateaus region of the curve. Using again the principle of average mobility k can be determined to be equal to . Now for the formation of ML i.e. M-NTA complex the equilibrium holds good where K is stability constant of M-NTA complex and is determinable as described earlier.

From these two chemical equilibria

$$[ML'\ L] = K'[ML]'[L] = kK'[M][L'][L]$$

$$ML' + L \overset{K}{\rightleftharpoons} ML$$

obviously KK' is overall stability constant of mixed ligand and this can be assessed with the knowledge of K and K'. Calculated value of different mixed complexes are given in table 1.

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