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Study of mixed ligand complexes of leucine and nitrilotriacetic acid (NTA) by paper electrophoresis

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ABSTRACT

Paper electrophoresis has been used to determine the stability constants of mixed complexes. The present work is an extension of the method and reports results on a mixed system. Th(IV), Cr(III) and Al(III) - NTA - Leucine.

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

INTRODUCTION

The importance of mixed ligand complex in various fields of chemical and biological sciences are manifold. The stabilities of mixed complex are important in biological systems as many metabolic and toxicological functions are to a large extent dependent upon them. Also, mixed ligand complex formation is of fundamental importance in many enzyme-catalysed reactions. Most enzymes contain coordinatively bound metal ions and during the enzymatic process coordination of the substrate also takes place and thus a mixed ligand complex is formed. Mildvan and Cohn[1] discussed the mechanism of Conversion of the substrate complex into the product complex in the pyruvate kinase reaction. Similarly, inhibitors preferentially coordinate to the metal ion of the enzyme and thereby the coordination of the substrate is hindered. Williams et al[2] illustrated the formation of an ion mixed ligand complex in enzyme-inhibitor metal systems. Also, in the action of enzyme model mixed ligand complex formation plays an analogous role.

The different types of mixed ligand complex play a significant role in various other reactions as well. They are formed as intermediates in ligand-catalysad complex formation reactions. Mixed ligand complex formation is also responsible for some catalytic effects in several redox reactions. Present paper report our observations on mixed system viz. Th(IV), Cr(III) and Al(III) - nitrilotriacetate-Leucine by paper electrophoresis[3-12].

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.

Th(IV), Cr(III) and Al(III) 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 Th(IV), Cr(III) and Al(III) ions. 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 Leucine 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 Leucine 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 Leucine 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

M-Leucine system

The plot of overall electrophoretic mobility of metal ion spot against pH gives number of plateaus. A plateau is obviously show pH range where mobility is practically constant. This is possible only when a particular complex is overwhelmingly formed. Thus every plateau indicates formation of certain complex species. The first one in beginning corresponds to pH range in which metal ions are uncomplexed. It lies in low pH region where concerned of a highly protonated species of amino acid is obviously maximum, hence it is concluded that this protonated species of amino acid is non-complexing. Beyond this pH range metal ion spot has progressively decreasing mobility. Complexation of metal ion should be taking place with other ionic species of amino acids, whose concentration increases with increase in pH. The reveals that second plateau in each case with positive mobility indicate the formation of 1:1 complex of cations nature. Further increase of pH, the mobility in case of Th(IV) remained unchanged while mobility decreases giving rise to third and fourth plateau in case of Cr(III) and Al(III). Since the mobility of third and fourth plateau lie in positive region, cationic nature of metal complex is indicated. In view of zero mobility of subsequent complex formed in the region of the fourth plateau, the complexes should be electro neutral in nature and so composition of this complexes should be 1:3. The earlier complex should consequently be 1:2 with respect to metal ion and ligand ion. The metal spot on t he paper is thus a conglomeration of uncomplexed metal ions and 1:1, 1:2 and 1:3 complexes. The overall mobility, U is given by

$$U = \frac{u_0 + u_1 K_1 [L] + u_2 K_1 K_2 [L]^2 + u_3 K_1 K_2 K_3 [L]^3}{1 + K_1 [L] + K_1 K_2 [L]^2 + K_1 K_2 K_3 [L]^3}$$

where u_0, u_1, u_2 and u_3 are the mobilities of the uncomplexed metal ion, 1:1 complex and 1:2 and 1:3 complex, respectively.

For calculating the first stability constant, K_1, the region between the first and second plateaus is pertinent. The overall mobility U will be equal to the arithmetic mean of the mobility of the 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 Leucine ($k_1 = 10^{2.2}$, $k_2 = 10^{8.9}$).

The concentration of liganding Leucine, L, is calculated with the 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 and K_3 of the second and third complex can be calculated by taking into consideration the region between the second, third and fourth plateaus of the mobility curve. These calculated values are given in Table-1.

M (II) - NTA binary system

The overall mobilities of the metal ion spots were plotted against the pH of the background electrolyte containing NTA. As the mobility of the second plateau being positive in case of Th(IV) and zero in case of Cr(III) and Al(III). It is inferred that

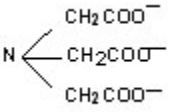
metal ion should from 1:1, M-NTA complexes. The stability constants of these complexes were calculated in the same manner as for complexes with value. These values are recorded in Table 1.

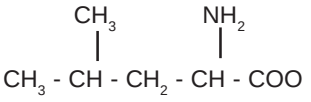
Metal-NTA-Leucine system

The study of this system was done at pH 8.5 for a purpose. It is observed from the mobility curves for Leucine and M-NTA binary systems that

Table 1: Stability Constant of Metal - NTA - Leucine complexes

Temperature 35°C Ionic Strength = 0.1

NTA anion = 

Valine anion = L = 

Metal ion	Calculated value					
	$Log\ K^{M}_{ML}$	$Log\ K^{M}_{ML_2}$	$Log\ K^{M}_{ML_3}$	$Log\ K^{M}_{M-NTA}$	$Log\ K^{M}_{M-NTA-L}$	$Log\ \beta_{M-NTA-L}$
Th(IV)	8.81	—	—	11.64	6.74	18.38
Cr(III)	8.50	15.20	20.70	11.58	5.56	17.14
Al(III)	7.92	14.01	18.90	9.13	5.43	14.56

binary complexes are formed at pH < 8.5. Therefore, it would be preferable to study the transformation of the M-NTA complex into the M-NTA-Leucine complexes at pH 8.5 in order to avoid any side interactions. On the plot of mobility versus log (concentration of added amino acid) a curve is obtained. The first plateau of constant value of mobility obviously corresponds to the mobility of M_NTA complex whereas mobility in second plateau would correspond to the mobility of second complex. This new complex cannot be metal- Leucine complex for which mobilities of later complex species are different from mobility of new complex. Since the mobility of new complex in case of Th(IV) is zero and more negative in case of Cr(III) and Al(III), it is inferred that anionic species of Leucine and have added to M-NTA complex to from N-(NTA.L) mixed complex. The interaction may be represented by

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

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 $\frac{1}{[L]}$. Now for the formation of ML i.e. M-NTA complex the equilibrium M + L' ML holds good where K is stability constant of M-NTA complex and is determinable as described earlier.

From these two chemical equilibria

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

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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