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Study of Simple and Mixed Ligand Complexes of Glycyl Glycine with Cu (II), Ni (II), Co (II) and Zn (II)

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Abstract: An innovative solution electrophoresis technique has been used for study of mixed complexes of some divalent metal ions viz, Cu(II), Ni(II), Co(II) and Zn(II) with glycyl glycine as primary ligand and NTa as a secondary ligand. The stability constants of mixed complexes formed were found to be : 5.75, 4.26 ,3.25 ,3.15 (log k values)for Cu(II), Ni(II), Co(II) and Zn(II) respectively at 30^0 C and ionic strength 0.1 M.

Key Words: Solution Electrophoresis, Stability constants, Glycyl glycine, mixed complexes.

1. Introduction

For the study of Metal- Ligand equilibria partition technique, solvent extraction, paper electrophoresis and ion exchange method have been employed by a number of workers. Jok[1] has done a significant work for the determination of stability constants for metal complexes adopting the electro migration studies. From the migration mobility curve, he succeeded in determining the stability constants of amino acid complex of some bivalent metal ions. A theoretical treatment was given by Biernet[2] for the study of step wise complex formation. The technique subsequently attracted the attention of few workers,[3-5] who applied it to examine various complexing system in a aqueous medium . In recent years, Singh et.al.[6-12] have published a number of papers in which a new approach have been made for the study of complexation reaction in solution with the help of paper electrophoresis.

The gel or paper electrophoresis has the striking drawback in the sense that the path of migrating ion is not uniform. The surface of paper of gel medium, on which the charged species moves, depends on the mode of manufacturing of paper of gel. Keeping the discrepancies in mind, a venture to work in pure solution in this paper has been undertaken. According to Glasstone[13] relatively a little work has been done on the transference number of ions in mixtures, although Hittorf and Moving boundary methods have employed. It is possible, to derive the required transference numbers by the analysis of the anodic and catholic compartments before and after electrophoresis.

In the present work glycyl glycine as a primary ligand and NTA as a secondary ligand has been studied from the point of the view of the complexation with four metal ions viz Cu (II), Ni (II), Co (II) and Zn (II).

2. Experimental Instruments

Electrophoretic tube:

A simple electrophoretic tube, 18 cm long and of 5 mm bore with a stopper in middle and is fused perpendicularly at the ends with short wider tubes of 1.2 cm bore, arms have been utilized to insert the platinum electrodes. These electrodes are connected with an electrophoresis voltage supply. The voltage can be varied through three different ranges viz. 0-100, 100-200, and 200-300 volts.

pH-indicator and Accessories:

CP 901 century digital pH- meter having glass electrodes assembly and working on 220 volts/ 50 cycles stabilized A.C. main was used.

Colorimeter:

A colorimeter of visible range 400-750 nm of carlzeiss (jena specol) was employed.

Chemicals:

Cu (II), Ni (II), Co (II), ZN (II) perchlorate solutions were prepared by precipitating the corresponding carbonates from 0.1 M solution of sulphates of metal with solution of sodium carbonate, washing the precipitates with water and treated with AR grade 1% perchloric acid. These were boiled on a water bath and filtered to get stock solution of the metal perchlorate 5.0× 10^{-3}M (approx). Stock solution of the complexing reagents glycyl valines were prepared by dissolving accurately weighted amounts in water. Solutions of required strengths were then prepared by suitable dilutions.

Perchloric acids as background electrolyte:

A stock solution (1.0M) was prepared by suitable dilution of 70% perchloric acid. The solution was standarised by titrating a suitable volume of its dilute solution against a standard NaOH solution.

Detecting reagent for Cu(II), Ni(II), Co(II) and Zn(II):

Ammonium thiocynate solution for Cu(II), dimethyl glyoxime for Ni (II) k ,stannous chloride solution , ammonium thiocynate and acetone for Co(II), Zncon {5-(2-Corboxy-phenyl}-1- (2-Hydroxy5-sulpho phenylformazon}for Zn(II)[14]

3. Procedure

At the outmost a solution containing 1x10^{-2} M and glycyl glycine ,0.1 m perchloric solution and respective amount of metal ion solution, [2x10^{-3} Cu (II), 2x10^{-3} Ni(II) or 1x10-4, Co (II) and Zn(ii) were prepared. respectively. The pH of the solution was adjusted by adding sodium hydroxide solution .An aliquot of 10 ml ion is taken in the electrophoretic tube and then thermo stated at 30^0C. after allowing electrolysis30 minutes , the middle stopper was closed and developing the solution of anodic compartment by adding developer. The absorbance of the solution was taken at ^max625 nm respectively.

The observed mobility of migrating cation was calculated by measuring the change in the absorbance of the solution contained in the anodic compartment.

Firstly the absorbance taken before electrolysis (A_0) and after passing electricity for 30 minutes at potential difference 50 volts, the stopper was closed. This was A_i. The differences between these two give the mobility of respective ion. Under a potential gradient, a metal ion will more in the field, the speed and its direction depending upon the charges and size of the ion.

4. Results and Discussion

M(II)- Glycyl glycine binary system:

The plot of the overall mobility of a metal spot against pH gives a curve with a number of plateus. At the beginning, corresponds to a region in which metal ions are uncomplexed. A second plateu in each instance with positive mobility indicates the formation of 1:1 complex of a cationic nature. A further increase of pH results in a third plateu with zero mobility, which indicates the formation of an electrically neutral metal complex. The literature also assigns prominent liganding properties to unprotonated anionic species of glycyl glycine, ruling out any such property to the Zwitterion6. In view of the above observation, the complexation of metal ion with the glycyl glycine anion L may be represented by

$$M^{2+} + L^{-} \rightarrow ML$$
$$ML^{+} + L^{-} \rightarrow ML_2$$

The metal spot on the paper is thus a conglomeration of uncomplexed metal ion and1:1 and1:2 complexes. The overall mobility,U is given by

$$u = \frac{u_0 + u_1 K_1 [L-] + u_2 K_1 K_2 [L-]2}{1 + K_1 [l-] + k_1 K_2 [L-]2}$$

where u_0, u_1 and u_2 are the mobilities of the uncomplexed metal ion, 1:1 complex and 1:2 complex respectively. For calculating the first stability constant, K_1, the region between the first and second plateu is pertinent. The overall mobility U will be equal to the arithbmetic mean of the mobility of the uncomplexed metal ion, u_0, and that of first complex, u_1, at a pH where K_1=1/{L} with the help of dissociation constants of Glycyl glycine (K_1=10 ^{334}, K_1=10 ^{1036})[16,17].

The concentration of the liganding Glycyl glycine, L-, is calculated with the equation

$$[\ L\ ] \underline{\qquad\qquad} \frac{[LT]}{1+\{H\}/K_2 + \{H\}^2/k_1k_2}$$

where [LT] = total concentration.

The stability constant K2 of the second complex can be calculated by taking into consideration the region between the second and third plateus of the mobility curve. These calculated values are given in table -1.

Metal–Nta System

The absorbance difference of metal ion solution in presence of NTA at different pH are plotted. The absorbance difference of last plateuin case of Cu(II), Ni(II), Co(II) and Zn(II) is negative. Hence this indicates the anionic nature of metal NTA complex. Hence only one NTA anion to combine with metal ion to give 1:1 complexes. The stability constant of complexes with NTA were calculated as mentioned in metal penicillamine complexes and is given in Table -1.

M-Glycyl Glycine–Nta–Mixed Complexes

The study of this system was made at pH 8.5. From the absorbance difference VspH curves for metal-glycyl glycine and metal-NTA binary complex system that binary complexes are formed at pH 8.5. Hence it was considered appropriate to study the transformation of ML_2 to M –NTA at pH 8.5 in order to avoid any side interaction. The study of these mixed complexes have been carried out in presence of Glycyl glycine with progressive addition of secondary ligand NTA from $1x10^{-7}$M to $5x10^{-3}$M at a fixed pH 8.5. The observations are plotted. These figures elucidates the transformation, of ML_2 to M–L-NTA complexes on progressive addition of NTA. The figure shows two plateus. The first plateu correspond to M-(glycyl Glycine)$_2$ whereas the second plateu correspond to a new complex. This new complex may be a binary complex M–NTA produced in accordance with the interaction, where the ligand L is completely replaced by the NTA.

The complex may also be a mixed complex of M–L–NTA as M-L_2 ++NTA M-L-NTA+L in which the NTA adds on to ML giving an anionic species.

Obviously the final plateu corresponds to the absorbance difference of M-NTA or M-L-NTA, whichever is formed is not identical to the absorbance difference of M-NTA (binary complex) as observed in pure metal ion and NTA interaction. The new absorbance is greater in magnitude than that of M-NTA. This confirms the formation of M- L –NTA complex. The area between the two plateus represent the progressive transformation of binary complex ML2 into ML-NTA mixed complex as :

$$ML_2 + L^- \rightarrow\rightarrow ML - NTA + L$$

The K' can be calculated with the help of the method of mean mobility obviously K' will be given by the reciprocal of the tri negative anion

concentration of NTA at the midpoint of two plateus. The calculated value of stability constant are given in table -1.

Table -1

Stability constants of some binary and tertiary complexes of Cu(II), Ni(II), Co(II) and Zn(II):

Metal Ion	Calculated Value of Stability Constants			
	Log K_1 ML	Log log ML2	Log KM-NTA	K-M-NTA-L
Cu (II)	5.75	10.44	12.24	5.75
Ni(II)	4.26	11.55	10.81	4.26
Co(II)	3.25	8.85	10.32	3.25
Zn(II)	3.15	8.65	10.59	3.15

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