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Determination of Stability Constants of Some Metal Mixed Complexes in Solution by Solution Electophoresis [Be(II), Mn(II), Pb(II), Cd(II)-Methyl Cysteine-NTA System]

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An innovative solution electrophoresis technique has been used for the study of mixed ligand complexes of some divalent metals ions *viz.*, Be(II), Mn(II), Pb(II) and Cd(II) with methyl cysteine as primary ligand and NTA as secondary ligand. The stability constants of the mixed complexes formed were found to be: 4.81, 4.67, 3.54, 3.65 (log k values) for Be(II), Mn(II), Pb(II) and Cd(II), respectively at 30 ± 0.5 ºC an ionic strength 0.1 M.

Key Words: Stability constants, Mixed complexes, Electophoresis, Metal(II)-Methyl Cysteine-NTA system.

INTRODUCTION

For the study of metal-ligand equilibria partition technique, solvent extraction, ion exchange method and paper electropheresis have been mainly employed by a number of workers. Jokl [1] has done a significant work for the determination of stability constants of metal complexes adopting the electro migration studies. From the migration mobility curve, Jokl[1] 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 stepwise complex formation. The technique subsequently attracted the attention of few workers[3-5] who applied it to examine various complexing system in an aqueous medium.

In recent years, Singh *et al.*[6-8] and Tiwari *et al.*[9-12] 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 electrohoresis.

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 speices moves, depends on the mode of manufacturer of the 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 little work has been done on the transference number of ions in mixtures, although, both Hittorf and moving

boundary methods have been employed. It is possible, to derive the required transference numbers by the analysis of the anodic and cathodic compartments before and after electrophoresis.

In the present work, methyl cysteine as primary ligand and NTA as secondary ligand has been studied from the point of the view of the complexation with Be(II), Mn(II), Pb(II), Cd(II).

THEORETICAL

Electrophoretic technique used in these studies consists in examining the speed of metal ions in a mixture containing ligand solution under a definite potential gradient in a tube. The absorbance are recorded at different pH's of the mixture solution.

A ligand may be assumed to be polybasic acid dissociating in stages as follows:

$$H_nL \underset{}{\overset{K_n}{\rightleftharpoons}} H_{n-1}\,L + H$$

$$H_PL \underset{}{\overset{K_P}{\rightleftharpoons}} H_{P-1}\,L + H$$

$$H_L \underset{}{\overset{K_1}{\rightleftharpoons}} H_{L-1} + H$$

(charges have been ignored)

the concentration of protonated species H_PL can be expressed as:

$$[H_PL] = K_P\,[H_{P-1}L]\,[H] = K_P \cdot K_{P-1} \ldots\ldots K_1[L]\cdot[H]\,P = {}_P[H]\,P\,[L] \qquad (1)$$

where $\alpha p = K_1 . K_2 . \ldots\ldots . K_P$

Total polybasic acid thus distributes itself in the form of different anionic species. The following expression holds good for the total concentration:

$$T_A = \sum_{p=0} \alpha_P\,[H]^P . [L]$$

In view of this expression, eqn. 1 becomes,

$$[H_PL] = \frac{T_A . \alpha_P . [H]^P}{p\sum_{p=0} \alpha_P . [H]^P} \qquad (2)$$

A metal ion M may complex with any deprotonated species of acid and the reaction can be expressed as follows (charges being ignored):

$$M + H_PL \underset{}{\overset{K_1P}{\rightleftharpoons}} M\,[H_PL]$$

$$M + [H_PL] + HPL \underset{}{\overset{K_2P}{\rightleftharpoons}} M\,[H_PL]_2$$

$$M + [H_PL]_{x-1} + HPL \underset{}{\overset{K_3P}{\rightleftharpoons}} M\,[H_PL]_x$$

The concentration of a general complex species can be expressed as:

$$[M(H_PL)_x] = K_{XP}\,[M(H_PL)_{X-1}]\,[H_PL] = \beta_{X.P}[H_PL]_{X.}\,[M] \quad (3)$$

where as β_x, p is the overall stability constant of the complex acid is given by the expression:

$$\beta_{xp} = K_1p.\ K_2p..... K_{xp} \quad (4)$$

The speed of complex, under the unit potential gradient can be given by the well known equation of Jokl[1].

$$U = U_{x.p.}\ f_{x.p.} \quad (5)$$

where $U_{X.P.}$ is the speed and f_{xp} is the mole fraction of the general complex $M[H_PL]_X$ present in the conglomeration. obviously,

$$f_{XP} = \frac{[M(H_PL)_X}{\sum[M(H_PL)_X]}$$

This expression, in view of eqn. 3 simplifies to:

$$f_{xp} = \frac{\beta_{XP}\,[H_PL]^X}{\sum\beta_{X.P}[H_PL]^X}$$

Now, eqn. 5 can be expressed as:

$$U = \frac{U_{X.P}\,\beta_{X.P.}\,[H_PL]^X}{\sum\beta_{X.P.}\,[H_PL]^X} \quad (6)$$

Yadav *et al.*[14] have pioneered the relation between the mobility of metal ion and its concentration in the cathodic compartment, with the help of spectrometer, measuring the absorbance of the solution, before and after electrolysis. This was found experimentally that mobility of ion were reciprocally related to the difference of absorbance.

For the calculation of stability constants eqn. 6 can be simplified as:

$$U = \frac{U_0 + U_1K_1[L] + U_2K_2[L]_2 + ...}{1+K_1\,[L]+ K_1K_2\,[L]^2 + ...}$$

where K_1, K_2, K_3 are stability constants of complexes, expressed as:

$$K_1 = ML/M.L$$
$$K_2 = ML_2/ML.L$$
$$K_3 = ML_3/ML_2.L$$

The concentration of liganding species L or HL at different pH's during process of neurtralization of background electrolyte with sodium hydroxide have been calculated with well known mathematical calculation:

$$L = \frac{L_T}{1 + \frac{[H^+]}{K_1} + \frac{[H^+]^2}{K_1K_2} + \frac{[H+]^3}{K_1K_2K_3} + ...}$$

where as L_T is the total concentration of amino acid existing in different stages of protonation. K_1, K_2 and K_3 are dissociation constants of amino acids. The technique of mean mobility has been used to find out the stability constants.

EXPERIMENTAL

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: CP901 Century digital pH-meter having glass electrode assembly and working on 220 volts/50 cycles stabilized AC main was used.

Colorimeter: A colorimeter of visible range 400-750 nm of Carlzeiss (Jena Specol) was employed.

Be(II), Mn(II), Pb(II), Cd(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 methyl cysteine were prepared by dissolving accurately weighed amounts in water. Solutions of required strengths were then prepared by suitable dilutions.

Perchloric acid as background electrolyte: A stock solution (1.0 M) was prepared by suitable dilution of 70 % perchloric acid. The solution was standarized by titrating a suitable volume of its dilute solution against a standard NaOH solution.

Detecting reagent for Be(II), Mn(II), Pb(II) and Cd(II): 4-Nitro benzenazoresorcinol for Be(II), dithizone for Pb(II), cadmion-2B/2-2' dipyridyl for Cd(II). Manganese is determined calorimetrically by oxidation to per managonic acid with the use of potassium per iodate (0.5 g) by boiling[15].

Procedure: At the outset a solution containing 1.0×10^{-2} M and methyl cysteine, 0.1 M perchloric acid solution and respective amount of metal ion solution [2.0×10^{-3} Be(II), 2.0×10^{-3} Mn(II) or 1×10^{-4} Pb(II) and Cd(II) were prepared, respectively. The pH of the solution was adjusted by adding sodium hydroxide solution. An aliquot of 10 mL ion taken in the electrophoretic tube and then thermostated at 30 ºC. After allowing electrolysis 0.5 h, the middle stopper was closed and developing the solution

of anodic compartment by adding developers. The absorbance of the solution was taken at λ_{max} 625 nm, respectively.

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

First the absorbance taken before electrolysis (A_0) and the after passing electricity for 0.5 h at potential difference of 50 V, the middle stopper was closed. This was A_t. The difference 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.

RESULTS AND DISCUSSION

M(II)-methycysteine binary system: The plot of the overall mobility of a metal spot against pH gives a curve with a number of plateaus, as shown in Fig. 1. The first, at the beginning, corresponds to a region in which metal ions are uncomplexed. A second plateau in each instance with positive mobility indicates the formation of 1:1 complex of a cationic nature. A further increase of pH results in third plateau with zero mobility, which indicates the formation of an electrically neutral metal complex. The literature also assigns prominent ligational properties to unprotonated anionic species of methylcysteine, ruling out any such property due to the zwitter ion[6]. In view of the above observation, the complexation of a metal ion with the methycystine anion L-may be represented by

$$M^{2+} + L^- \underset{}{\overset{K_1}{\rightleftharpoons}} ML^+$$

$$ML^+ + L^- \underset{}{\overset{K_2}{\rightleftharpoons}} ML_2$$

when M represents Zn or Cd and ML^+ and ML_2 are their complexes with methylcysteine.

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

$$U = \frac{u_0 + u_1K_1[L^-] + u_2\ K_1K_2\ [L^-]^2}{1+K_1[L^-]+ K_1\,K_2[L^-]^2}$$

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 plateau 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 methylcysteine ($k_1 = 10^{2.55}$, $k_1 = 10^{8.55}$)[16,17].

The concentration of methylcysteine, L^-, is calculated with the equation

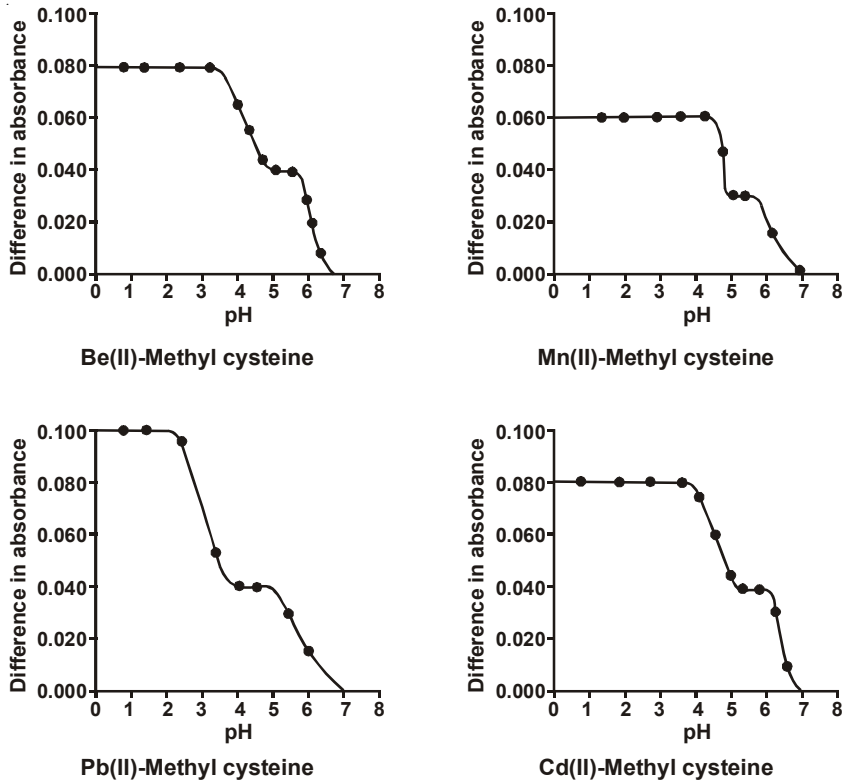

Fig. 1. Absorbance curve [M-methyl cysteine system] [Temp. 35 ºC; Ionic strength 01]

$$[L^{-}] = \frac{[L_T]}{1 + \frac{[H]}{K_2} + \frac{[H]^2}{k_1 k_2}}$$

where $[L_T]$ = total concentration.

The stability constant K_2 of the second complex can be calculated by taking into consideration the region between the second and third plateaus of the mobility curve. The 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 graphically shown in Fig. 2. The absorbance difference of last plateau in case of Be(II), Mn(II), Pb(II) and Cd(II) is negative. Hence this indicate anionic nature of metal NTA complex. Hence only one NTA in anioned to combine with metal ion to give 1:1 complexes, which is in conformity with the finding of previous workers[18]. The stability constant of complexes with NTA were calculated as described in metal methylcysteine complexes and is given in Table-1.

TABLE-1
STABILITY CONSTANTS OF SOME BINARY AND TERNARY COMPLEXES OF Be(II), Mn(II), Pb(II) AND Cd(II)
Ionic strength (μ) = 0.1; Temperature = 35 ºC. NTA anion = $N(CH_2COO)_3^{3-}$, Methylcysteine anion = $CH_3SCH_2CH(NH_2)COO^-$

Metal ion	Calculated value of stability constants*			
	$\log K^{M}_{1ML}$	$\log K^{M}_{2ML_2}$	$\log K^{M}_{M-NTA}$	$\log K^{M-TNA}_{M-NTA-L}$
Be(II)	5.26	9.32	7.89	4.81
Mn(II)	4.33	8.73	7.55	4.67
Pb(II)	3.53	6.51	7.21	3.57
Cd(II)	3.91	7.10	7.41	3.65
	Literature values of stability constants*			
	$\log K^{M}_{1ML}$	$\log K^{M}_{2ML_2}$	$\log K^{M}_{M-NTA}$	$\log K^{M-TNA}_{M-NTA-L}$
Be(II)	5.55[19]	10.50[19]	7.11[19]	–
			7.35[19]	
			7.44[19]	
			7.89[19]	
			7.76[19]	
Mn(II)	–	–	7.11[19]	–
Pb(II)	–	–	7.15[19]	–
Cd(II)	–	–	7.78[19]	3.54[9]

$$* K^{M}_{1ML} = \frac{[ML]}{[M][L]}; K^{M}_{2ML_2} = \frac{[ML_2]}{[ML][L]}; K^{M}_{M-NTA} = \frac{[M-NTA]}{[M][NTA]}; K^{M-NTA}_{M-NTA-L} = \frac{[M-NTA-L]}{[M-NTA][L]}$$

M-Methyl cysteine-NTA-mixed complexes: The study of this system was made at pH 8.5. From the absorbance difference *vs.* pH curves for metal-methylcysteine and Metal-NTA binary complex system that binary complexes are form at pH 8.5. Hence it was considered appropriate to study the transformation of ML_2 to ML-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 methylcysteine with progressive addition of secondary ligand NTA from 1×10^{-7} to 5×10^{-3} M at a fixed pH 8.5. The observations are recorded graphically (Fig. 3). These figures elucidate the transformation, of ML_2 in to M-L-NTA complexes on progressive addition of NTA. The figure shows two plateaus. The first plateau corresponds to M-(methyl cysteine)$_2$ whereas the second plateau corresponds 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 new complex may also be a mixed complex of M-L-NTA as $M\text{-}L_2^+ + NTA \rightarrow M\text{-}L\text{-}NTA + L$ in which the NTA adds on to ML giving an anionic species.

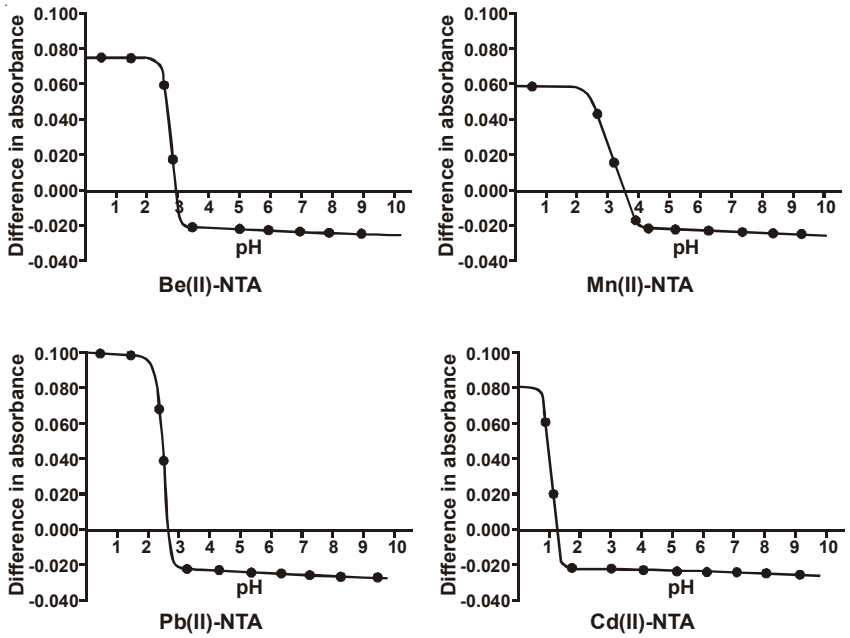

Fig. 2. Absorbance curve [M-NTA system] [Temp. 35 ºC; Ionic strength 01]

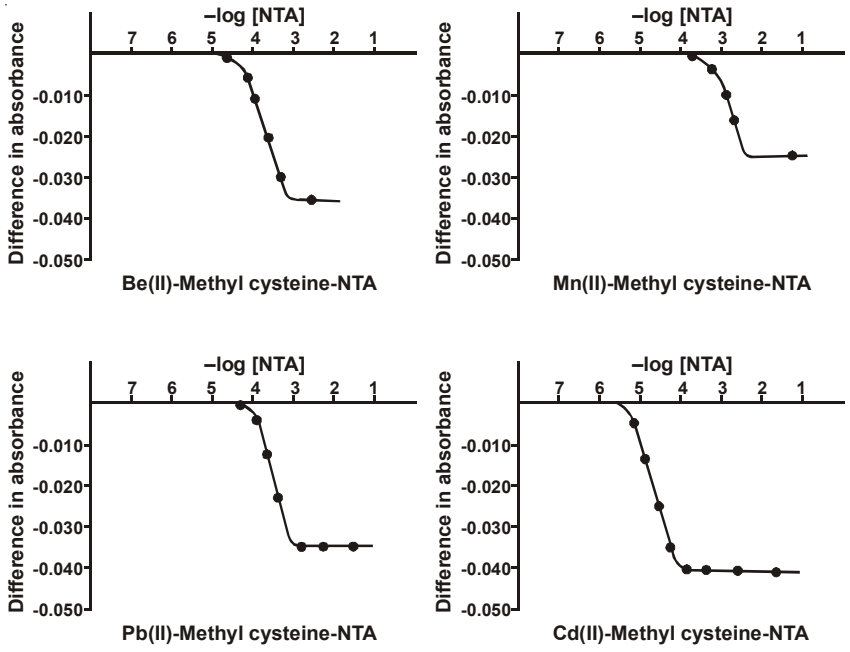

Fig. 3. Absorbance curve [M-methyl cysteine-NTA system] [Temp. 35 ºC; Ionic strength 01]

Obviously the final plateau corresponds to the absorbance difference of M-NTA or M-L-NTA, whichever is formed, in interaction. It was found that the absorbance difference of the new species 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 between the two plateaus represent the progressive transformation of binary complex ML_2 into ML-NTA mixed complex as:

$$ML_2 + NTA \overset{K_1}{\rightleftharpoons} M\text{-}L\text{-}NTA + L$$

The K' can be calculated with the help of the method of mean mobility obviously K' will be given by reciprocal of the trinegative anion concentration of NTA at the mid point of two plateaus. The calculated value of stability constant are given in Table-1.

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