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Study of chelating tendency of sulphur-containing amino acids by solution electrophoresis

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ABSTRACT

An innovative solution electrophoresis technique has been used for this study of methyl cysteine complexes of some metals ions viz. Th (IV), Fe (III), Cr (III) and Al (III). 1 : 1 complex is formed by Th (IV) while 1:1 and 1:2 complex is form by Fe (III), Cr (III) and Al (III). The stability constant of the complexes formed were found to be : log k_1 = 8.25 (for Th (IV)), log k_1 = 7.84, log k_2 = 6.83 (for Fe (III)), log k_1 = 7.64, log k_2 = 4.72 (for Cr (III)), log k_1 = 7.33, log k_2 = 5.15 (for Al (III)) at 35°C and ionic strength 0.1 M.

(Key words : Solution Electrophoresis, Stability constant, Methyl Cysteine**)**

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, 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 stepwise complex formation. The technique subsequently attracted the attention of a few workers[3-5] who applied it to examine various complexing system in a aqueous medium.

In recent years, Singh et. al. have published a number of paper in which a new approach have been made for the study of complexation reaction in salvtion with the help of paper electrohoresis[6-12].

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, deponds 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 under taken. 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 sulphur containing amino acid methyl cysteine has been studied from the point of the view of the complexation with four metal ions viz., Th (IV), Fe (III), Cr (III), Al ((III).

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 poly basic acid dissociating in stages as follows :

$H_nL \xrightleftharpoons{K_n} H_{n-1}L + H$

$H_PL \xrightleftharpoons{K_P} H_{P-1}L + H$

$H_L \xrightleftharpoons{K_1} H_1L + H$

(charges have been ignored)

the concentration of protonated species H_PL can be expressed as :

$[H_PL] = K_P [H_{P-1}L] [H] = K_P . K_{P-1} ..... K_1 [L]. [H] P = {}_P[H] P [L] ....$ (1)

Where $\alpha p = K_1 . K_2 ..... K_P$ ...(1)

Total poly basic acid thus distributes it self 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, eq. (1) becomes,

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

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

$M + H_PL \xrightleftharpoons{K_1P} M[H_PL]$

$M + [H_PL] + H_PL \xrightleftharpoons{K_2P} M[H_PL]_2$

$M + [H_PL]_{x-1} + H_PL \xrightleftharpoons{K_3P} M[H_PL]_x$

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

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

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

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

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

$U = U_{x.p.} f_{x.p.}$ ...(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 equation (3) simplifies to :

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

Now, equation (5) can be expressed as :

$$U = \frac{U_{X.P} \beta_{X.P.} [H_PL]^X}{\sum \beta_{X.P.} [H_PL]^X}$$

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 equation (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

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

CP901 Century digital pH - meter having glass electrode 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

Th (IV), Fe (III), Cr (III), Al (III) 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 weighted 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 standarised by titrating a suitable volume of its dilute solution against a standard NaOH solution.

Detecting Reagent for Th (IV), Fe (III), Cr (III) and Al (III) :

1-(O-arsonophenyl azo)-2- naphthol-3, 6-disulphonic acid, for Th (IV), Ammonium thio cyanate solution for Fe (III), 1, 5-diphenyl carbazide for Cr (III) and Eriochrome Cyanine R solution for Al (III) is being used as developing Regents[15].

Procedure

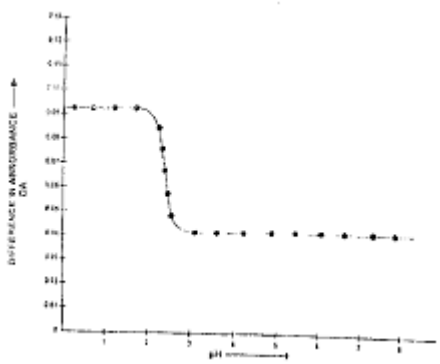
At the outset a solution containing 1.0×10^{-2} M and Methyl Cysteine, 0.1 M Perchloric Acid solution and respective amount of metal ion solution [2.0×10^{-3} Th (IV), 2.0×10^{-3} Fe (III) or 1×10^{-4} Cr (III), and Al (III) were prepared Respectively. The pH of the solution was adjusted by adding sodium hydroxide solution. An Aliquot of 10 ml ion taken in the electrophoretic tube and then thermostated at 30°C. After allowing electrolysis 30 minutes, 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.

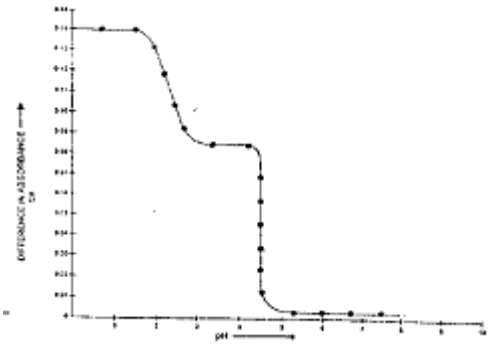
Firstly the absorbance taken before electrolysis (A_0) and the after passing electricity for 30 minutes at potential diff 50V, the middle stopper was closed. This was A_t. The difference between these two give the mobility of respective Ion. Under a potential gradient, a metal ion will more in the field,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

RESULTS AND DISCUSSION

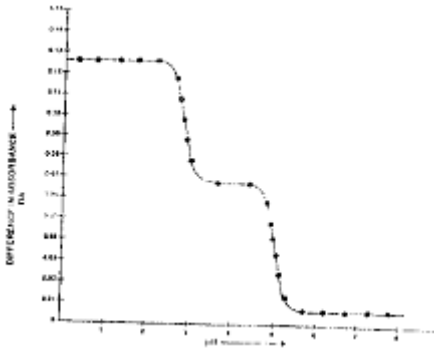
A plot of Absorption difference against pH gives a conve with a number of plateaus (Fig. 1). The figure shows two plateau with Th (IV) Three plateau for the trivalent metal ion viz., Fe (III) Cr (III) and Al (III). The first plateau represent the region of uncomplexed metal ion while the remaining plateau indicate the formation of different complexes hence Fe (III) Cr (III) Al (III) from two complexes while one complex is formed by Th (IV). It is apparent from the present studies that only one coordinating species is assumed to have complex with tetravalent,



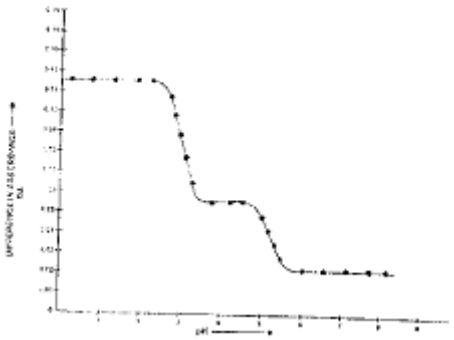
Th(IV) - Methyl cysteine



Fe(III) - Methyl cysteine



Cr(III) - Methyl cysteine



Al(III) - Methyl cysteine

Fig. - 1 Absorbance curve [M-Methyl cystenine system]
[Tem. 30°, : Ionic strength01]

Thorium to give a 1 : 1 cationic complex. Since the absorption difference of the second and third plateau for Fe (III) Cr (III) and Al (III) in case of Methyl Cysteine lie in a positive region, a cationic nature of both 1 : 1 and 1 : 2 complexes is indicated. No change in the absorbance beyond the third plateau is evinced even at higher pH values. Thus 1:2 binary complex of Fe (III) Cr (III) and Al (III) with anionic species of the Ligand is the ultimate complex. A strong coordinating ability is attributed to anionic species of methyl cysteinein literature also[16-19].

In view of the above observations the complexation of metal ions with these ligands may be represented as -

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

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

The metal ion is conglomeration of uncomplexed metal ions, 1 : 1 & 1 : 2 complexes. The metal ion moving under the influence of electrical field, the overall mobility is given by the equation (1).

$$u = \sum u_n f_n \quad (1)$$

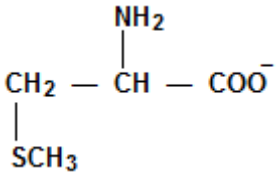
Where u_n and f_n are mobility of mole fraction of a particular complex species. This equation is transformed in to the following form on taking in to consideration different equilibria -

$$u = \frac{u_0 + u_1 k_1 [L] + u_2 k_2 k_1 [L]^2}{1 + k_1 [L] + k_1 k_2 [L]^2}$$

(Charges being ignored)

Whose μ_0 μ_1 and μ_2 are motilities of uncomplexed metal ion, 1 : 1 metal complex and 1:2 metal complex respectively. The equation has been used for the calculation of stability constants of the complexes of metal ion with anionic species of Ligands the region between the First and Second plateau is pertinent for the calculation of First stability constant K_1. The overall mobility μ will be equal to the arithmetic mean of nobilities of uncomplexed metal ion μ_0 and that of first complex μ_1 at a pH, where K_1 = 1/[L] . With the help of dissociation constant of Methyl Cysteine (electrophoretically obtained values $K_1 = 10^{2.55}$ $K_2 = 10^{8.55}$ [18, 19], the concentration of complexing species [L] was determined at particular pH, from which K_1 can be calculated. The stability constant K_2 of second complex can be calculated by taking in to consideration the region between second and third plateau of the mobility carves. The calculated values are given in table 1.

Table - 1: Stability constants of binary complexes Th (IV), Fe (III), Cr (III) and Al (III) with Methyl Cysteine (Temp - 35°C, Ionic strength = 0.1)

Methyl Cysteine Anion - L = 

Metal Ion	Calculated Value			Literature Value			Ref.
	$LogK^{ML}_{ML}$	$LogK^{ML}_{ML2}$	$Log\beta ML_2$	$LogK^{ML}_{ML}$	$LogK^{ML}_{ML2}$	$Log\ \beta ML_2$	No.
Th (IV)	8.25	-	-	-	-	-	-
Fe (III)	7.84	6.83	14.67	-	-	-	-
Cr (III)	7.64	4.72	12.36	-	-	-	-
Al (III)	7.33	5.15	12.48	-	-	-	-

REFERENCES

1. Jokl, V. : *J. Chromatography* **14**, 71, 1964.
2. Biernet, J. : *Rocz. Chem.* **38**, 343, 1964.
3. Hurnick, B. : *Rocz, Chem.* **39**, 137 (1965).
4. Koch, H. & Lovchev, M. : *Isotopanpraxis*, **7**, 401 (9171).
5. Kozak, J. : *Acta fae. Perum Nature Univ. Comenianeae, Chem.* 23 (1971).
6. Singh, S., Yadav, K.L. : *Annli Di Chimica*, **75**, 377 (1985).
7. Tiwari B.B. and Yadav, K.L. ; *Trans. Saest.* **25** (4), 124 (1990).
8. Tewari B.B. and Yadav, K.L. : *J. Chromatogr.* 542-537 (1991).
9. Tewari B.B. and Yadav, K.L. : *Biomed. Chromatogr.* **10** (5), 221 (1996).
10. Tewari B.B. : *J. Chromatogr.* **910**(1), 181 (2001).
11. Singh, S., Bajpai, A.K. and Yadav, K.L. : *Electrophoresis*, **7**, 187 (1986).

12. Singh, S., Gupta, D. and Yadav, K.L. : *J. Electrochem. Soc*. **35**, 1 (1986).
13. Glasstone, S. *Electrochemistry* (2001).
14. Tewari B.B. and Pandey A.K. and Singh R.K.P. : *Proc. Nat. Acad. Sci.* **65** (A), 35, (1995).
15. Wagner, W., Hull, C.J., and Markle, G.E. : Advanced Analytical Chemistry Reinhold Publishing Corporation, New York (1956).
16. Walker, D.M. and Williams, R.D. : *J. Chem. Soc. Dalton,* 1186 (1974).
17. Hojo, Y., Sugivra, Y. and Tankaka, H. : *J. Inorg. Nucl. Chem.,* **38**, 641 (1976).
18. Change, W.J. and Martin : *J. Phys. Chem.,* **73**, 4277 (1969).
19. Muskar, K.W. and Neagley, H.C. : *Inorg. Chem.*, **14**, 1728 (1975).