

Determination of stability constants of Th (IV), Fe(III), Cr(III), Al(III) binary complexes with methionine by solution electrophoresis

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ABSTRACT

A method involving the use of solution electrophoresis is described for the study of equilibria in metal-ligand binary complex systems in solution. The technique is based on the migration of metal ion in solution under an electric field with the complexants added to the background electrolyte at different pH in an electrophoretic tube.

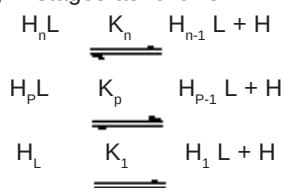
Key words : Solution electrophoresis, stability constant, methionine.

INTRODUCTION

The use of paper electrophoresis for the study of metal complex system seems to be well established¹⁻⁵. The present work is an extension of the technique. It is to be mention here that the solution electrophoresis is used for the first time in which metal ion travels in electrophoretic tube under constant potential gradient. The present paper reports some of our observation on Th (IV), Fe (III) Cr (III) and Al (III) - Methionine system at 35°C and Ionic strength 0.1.

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 :



(charges have been ignored)

the concentration of protonated species H_pL can be expressed as :

$$[\text{H}_p\text{L}] = K_p [\text{H}_{p-1}\text{L}] [\text{H}] = K_p \cdot K_{p-1} \dots \dots K_1 [\text{L}] \cdot [\text{H}]^p = {}_p[\text{H}]^p [\text{L}] \quad \dots(1)$$

Where $\alpha_p = K_1 \cdot K_2 \dots \dots K_p$

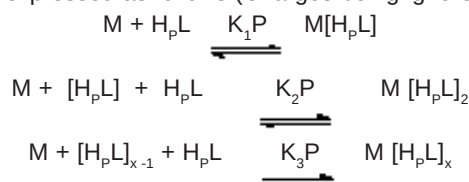
Total poly basic acid thus distributes it self in the form of different anionic species. The following expression holds good for the total concentration :

$$T_A = \sum_{p=0}^P \alpha_p [\text{H}]^p \cdot [\text{L}] \quad \dots(2)$$

In view of this expression, eq. (1) becomes,

$$[\text{H}_p\text{L}] = \frac{T_A \cdot \alpha_p \cdot [\text{H}]^p}{p \sum_{p=0}^P \alpha_p \cdot [\text{H}]^p}$$

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



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

$$[M(H_pL)_x] = K_{xp} [M(H_pL)_{x-1}] [H_pL] = \beta_{x,p} [H_pL]_x [M]$$

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

$$\beta_{xp} = K_{1p} \cdot K_{2p} \dots K_{xp} \quad \dots (4)$$

The speed of complex, under the unit potential gradient can be given by the well known equation of Jokl⁶.

$$U = U_{x,p} \cdot f_{x,p} \quad \dots (5)$$

Where $U_{x,p}$ is the speed and $f_{x,p}$ is the mole fraction of the general complex $M(H_pL)_x$ present in the conglomeration.

$$\text{obviously, } f_{xp} = \frac{[M(H_pL)_x]}{\sum [M(H_pL)_x]}$$

This expression, in view of equation (3) simplifies to :

$$f_{xp} = \frac{\beta_{xp} [H_pL]^x}{\sum \beta_{xp} [H_pL]^x}$$

Now, equation (5) can be expressed as : . . . (6)

$$U = \frac{U_{xp} \beta_{xp} [H_pL]^x}{\sum \beta_{xp} [H_pL]^x}$$

Yadav *et al.*⁷ 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

$$U = \frac{U_0 + U_1 K_1 [L] + U_2 K_2 [L]^2 + \dots}{1 + K_1 [L] + K_1 K_2 [L]^2 + \dots}$$

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

$$\begin{aligned} K_1 &= ML/M.L \\ K_2 &= ML_2 / ML.L \\ K_3 &= ML_3 / ML_2.L \end{aligned}$$

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

$$L = \frac{L_t}{1 + \frac{[H^+]}{K_1} + \frac{[H^+]^2}{K_1 K_2} + \frac{[H^+]^3}{K_1 K_2 K_3} + \dots}$$

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 Methionine 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 standardised 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-arsenophenyl azo)-2- naphthol-3, 6-disulphonic acid, for Th (IV), Ammonium thiocyanate solution for Fe (III), 1, 5-diphenyl carbazide for Cr (III) and Eriochrome Cyanine R solution for Al (III) is being used as developing Regents⁸.

Procedure

At the outset a solution containing 1.0×10^{-2} M and Methionine, 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 $\lambda_{\max}$ 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.

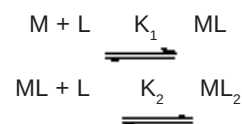
Firstly the absorbance taken before electrolysis (A_0) and the after passing electricity for 30 minutes at potential diff 50V, the middle stopper was closed. This was A_t . The difference between these two give the mobility of respective Ion. Under

a potential gradient, a metal ion will move 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 curve with a number of plateaus (Fig. 1). The figure shows two plateaus with Th (IV) Three plateaus for the trivalent metal ion viz., Fe (III) Cr (III) and Al (III). The first plateau represents the region of uncomplexed metal ion while the remaining plateaus 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 Thorium to give a 1 : 1 cationic complex. Since the absorption difference of the second and third plateaus for Fe (III) Cr (III) and Al (III) in case of Methionine 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 methionine in literature⁹⁻¹⁴.

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



The metal ion is in 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).

$$u = \sum u_n f_n^{(6)}$$

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

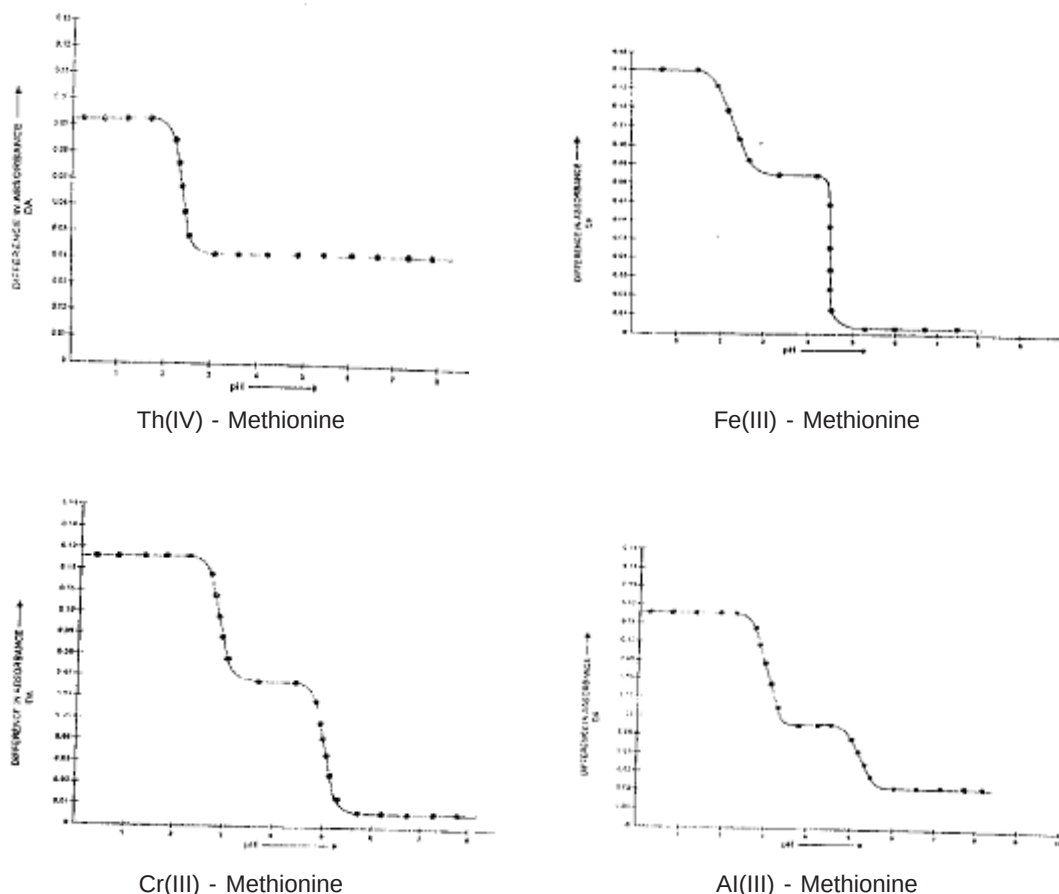


Fig. - 1: Absorbance cuve [M-Methionine system] [Temp-30°C, ; Ionic strength 01]

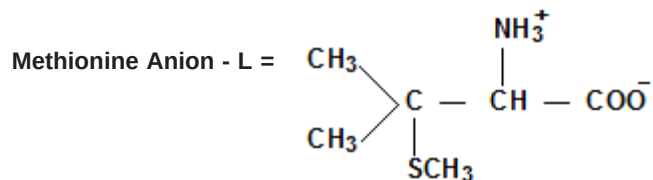
$$u = \frac{u_0 + u_1 K_1 [L] + u_2 K_1 K_2 [L]^2}{1 + K_1 [L] + K_1 K_2 [L]^2}$$

(Charges being ignored)

Whose u_0 , u_1 and u_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 u will be

equal to the arithmetic mean of nobilities of 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 constant of Methionine (electrophoretically obtained values $K_1 = 10^{2.25}$ $K_2 = 10^{9.00}$ ^{8,9}, 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 curves. 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 Methionine (Temp - 35°C, Ionic strength = 0.1)



Metal Ion	Calculated Value			Literature Value			Ref. No.
	$\text{LogK}_{M_1}^M$	$\text{LogK}_{ML_2}^{ML}$	$\text{Log } \beta_{ML_2}$	$\text{LogK}_{M_1}^M$	$\text{LogK}_{ML_2}^{ML}$	$\text{Log } \beta_{ML_2}$	
Th (IV)	8.17	-	-	-	-	-	-
Fe (III)	7.62	5.20	12.82	-	-	-	-
Cr (III)	7.34	4.87	12.21	-	-	-	-
Al (III)	7.12	4.71	11.83	-	-	-	-

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