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Electrophoretic Elucidation and Determination of Stability Constants of Some Binary Metal Complexes [M-Penicillamine-System]

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A new method involving the use of paper electrophoresis is described for the study of equilibria in metal-ligand complex system in solution. The technique is based on the movement of metal ion under an electric field with the complexants added to the background electrolyte the stability constants of the complex were found to be log k_1 = 14.53 (for Th(IV)); log k_1 = 13.38, log k_2 = 5.42 (for Fe(III)) ; log k_1 = 12.80, log k_2 = 4.04 (for Cr(III)); log k_1 = 12.10, log k_2 = 3.21 (For Al(III)); complexes at 35º and ionic strength 0.1 M.

Key Words: Solution electrophoresis, Stability constant, Th(IV), Fe(III), Cr(III), Al(III), Penicillamine.

INTRODUCTION

The properties and chemical reactions of naturally occurring D-penicillamine have already been subjected to wide investigation. The most important reactions are processes involving participation of the mercapto group and the main biochemical aspects have been reviewed by Jocelyn[1]. The chemical significance of amino acid penecillamine is determined by the mercapto sulphur donor atom, which is soft in character. More biological importance is attached to the study of metal sulphur bonds formed in such processes, primarily in the non-haeme iron proteins[2] and the blue copper proteins[3]. The significance of penicillamine is enhanced by the fact that it display's independent the therapeutic activity. Its most valuable use is for the treatment of wilsons disease, caused by accumulation of copper. As a consequence of its property of forming stable complexes, it can also be employed to advantage for the elimination of other heavy metals (Pb, Hg) from the organism. It has been utilized in connection with rheumatoid arthritis and neonatal Jaundice. Sorensen[4] has demonstrated the antiinflammatory activity of copper-D-penicillamine.

Sulikowska[5] studied the formation of mixed halide complexes of Hg(II). We previously described[6,7] a method for the study of binary complexes. This work is an extension of the previous technique and reports our observations on binary systems.

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:

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

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

$$H_L \xrightleftharpoons{K_1} H_1 L + H$$

(charges have been ignored)

The concentration of protonated species H_PL can be expressed as:

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

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

Total polybasic 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, eqn. 1 becomes,

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

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:

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

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

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

The speed of complex, under the unit potential gradient can be given by the well known equation of Jokl[8].

$U = U_{x.p.} f_{x.p.}$ (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 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:

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

Yadav *et al.*[9] 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 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 penicillamine 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 Th(IV), Fe(III), Cr(III) and Al(III): 1-(O-arsonophenyl 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 reagents[10].

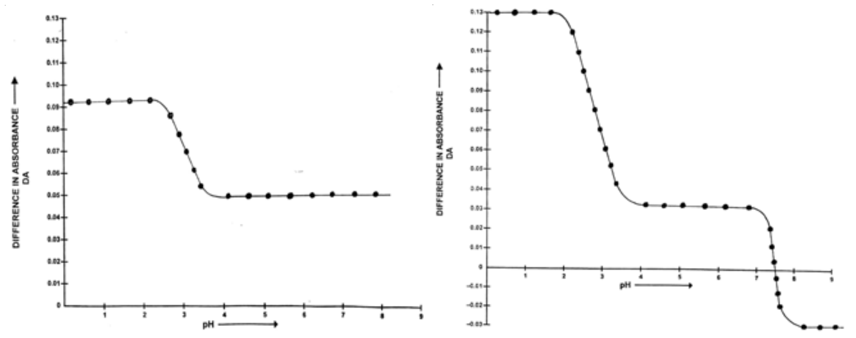
Procedure: At the outset a solution containing 1.0×10^{-2} M and penicillamine, 0.1 M perchloric acid solution and respective amount of metal ion solution [2.0×10^{-3} Th(IV), 2.0×10^{-3} Fe(III) or 1×10^{-4} Cr(III) and Al(III) were prepared, respectively. The pH of the solution was adjusted by adding sodium hydroxide solution. An aliquot of 10 mL ion taken in the electrophoretic tube and then thermostated at 30 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.

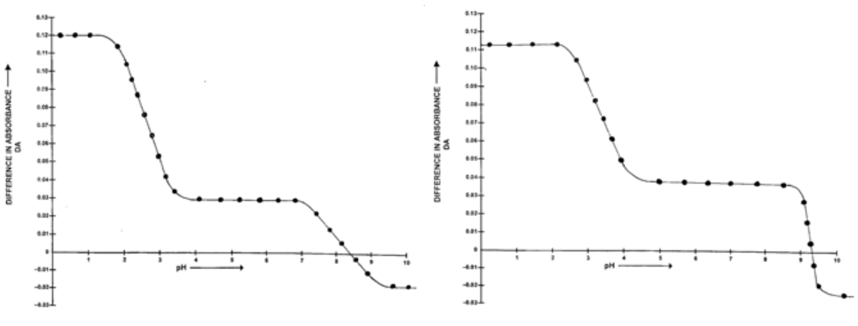
Firstly the absorbance taken before electrolysis (A_0) and the after passing electricity for 0.5 h at potential diff 50 V, the middle stopper was closed. This was A_t. The difference between these two give the mobility of respective ion. Under a potential gradient, a metal ion will move in the field, the speed and its direction depending upon the charges and size of the ion.

RESULTS AND DISCUSSION

Observation on absorbance difference are represented graphically in Fig. 1. The figure show two plateaue with Th(IV), three plateaus for the trivalent metal ion Fe(III), Cr(III) and Al(III). The first plateau represent the region of uncomplexed metal ion while the remaining plateaus indicate the formation of different complexes. Hence Fe(III), Cr(III) and Al(III) form two complexes while only one complex is formed by Th(IV). A strong co-ordaining ability is attributed to the anionic species of penicillamine in literature[11-14]. It is apparent from the present studies that only one coordinating species is assumed to have complex with Th(IV) to give a 1:1 cationic complex. While second plateau in the case of penicillamine lie in positive and its third plateau lie in the negative region of the curve, indication cationic nature of its 1:1 complex and anionic nature of its 1:2 complex. 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. It is significant that anionic species of penicillamine coordinate with metal ion forming variety of binary complexes of 1:1 and 1:2 composition.



Th(IV)-Penicillamine Fe(III)-Penicillamine



Cr(III)-Penicillamine Al(III)-Penicillamine

Fig. 1. Absorbance curve [M-penicillamine system] [temp. 35 ºC; ionic strength 01]

For calculating stability constants of different complexes obtained with penicillamine, the equation mention earlier has been utilized. From the above discussion it is clear that complexes formed with Th(IV) is 1:1 in composition while in trivalent metal ions 1:1 and 1:2. The deprotonated species L *i.e.* anion of penicillamine has been assumed to be ligand species with metal ions. Complexes of amino acids with metal ions are thus formed as a result of coordination of anion of penicillamine in stages. The mathematical equation is simplified as:

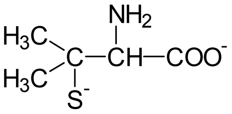
$$U = \frac{u_0 + u_1 k_1 [L] + u_2 k_1 k_2 [L]^2}{1 + k_1 [L] + [L]^2}$$

where u_0 u_1 and u_2 are mobilities of uncomplexed metal ions, 1 : 1 metal complex and 1:2 metal complex, respectively for calculating its stability constant K_1 the region between first and second plateau is pertinent. The overall mobility "U" will be equal to the arithmetic mean of mobility of uncomplexed metal ion (u_0) and that of the first complex u_1 at a pH when $k_1 = 1/[L]$.

With the help of dissociation constant log $k_1 = 10^{2.00}$, log $k_2 = 10^{8.25}$, by $k_3 = 10^{10.35}$, the concentration of anion is determined for that particular pH, from which K_1 can be calculated. Similar procedure is adopted for calculation of K_2, where second and third plateau are considered. The calculated values are given in Table-1.

TABLE-1
STABILITY CONSTANTS OF SOME BINARY COMPLEXES
Th(IV), Fe(III), Cr(III), Al(III) WITH PENICILLAMINE
(TEMP. 35ºC, IONIC STRENGTH = 0.1)

Pencillamine Anion - L =



Metal ion	Calculated value			Literature value		
	$\log K^{M}_{ML}$	$\log K^{ML}_{ML_2}$	$\log \beta\ ML_2$	$\log K^{M}_{ML}$	$\log K^{ML}_{ML_2}$	$\log \beta\ ML_2$
Th(IV)	14.53	–	–	–	–	–
Fe(III)	13.38	5.48	18.86	–	–	–
Cr(III)	12.80	4.04	16.84	–	–	–
Al(III)	12.10	3.21	15.31	–	–	–

The precision of the method is still limited *i.e.* the order of uncertainty is 5 %. It is to be mentioned here that these complexes are studied for the first time. So no comparison is possible.

REFERENCES

1. C.P. Jocelyn, Biochemistry of the SH group, Academic press, London and New York (1972).
2. R.G. Moone and P.J.R. William's, *Coord. Chem. Rev.*, **18**, 125 (1976).
3. A.J. Fee, *Struct. Bonding*, **23**, 1 (1975).
4. R.J. Sorensen, *J. Med. Chem.*, **19**, 135 (1976).
5. M.C. Sulikowska, *Zesz. Nauk, Politech Lodz Chemia*, **6**, 2036 (1967).
6. S. Singh and K.L. Yadav, *Polish J. Chem.*, **59**, 1021 (1985).
7. S. Singh and S.R. Tripathi, *Proc. Nat. Aca. Sci. (India)*, **62A**, 111, 373 (1992).
8. V. Jokl, *J. Chromatogr.*, **14**, 71 (1964).
9. R.K.P. Singh and K.L. Yadav, *J. Electrochem. Soc. (India)*, **35**, 77 (1986).
10. W. Wagner, C.J. Hull and G.E. Markle, Advanced Analytical Chemistry Reinhold Publishing Corporation, New York (1956).
11. H. Shindo and L.T. Brown, *J. Am. Chem. Soc.*, **87**, 1904 (1965).
12. S.F.D. Natusch and J.L. Porter, *J. Chem. Soc. A*, 2527 (1971).
13. B.B. Tewari and K.L. Yadav, *Biomed. Chromatogr.*, **10**, 221 (1996).
14. B.B. Tewari, *J. Chromatogr.*, **310**, 181 (2005).

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