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Solution Complexation of Amino Acidate Zwitter Ion with Uranyl(VI): Electrophoresis and pH-metric Studies

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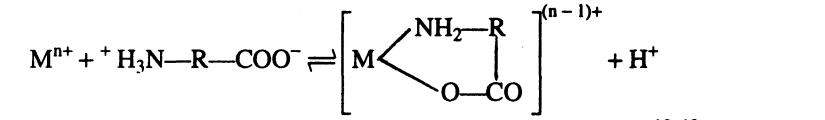
Paper electrophoretic investigation of uranyl complexes with amino acids (L-threonine, L-leucine, L-asparagine, DL-β-phenyl alanine) have been carried out in 0.1 M KNO_3 solution at 35°C and 3.5 pH, to elucidate the nature of coordination in these complexes. Electrophoretograms are supportive of coordination through carboxylate group of the amino acidate zwitter ion. The relative mobilities and stabilities of the complexes are reported. The results are supplemented with pH-metric studies.

INTRODUCTION

Paper electrophoretic technique[1, 2] has been employed for the determination of dissociation constants[3, 4] of amino acids and stability constants of their complexes[5, 6] with metal ions. It is generally believed that transition metal ions coordinate with amino acids[7–9] according the equation:



(1)

Contrary to this reaction scheme (Eq. (1)), some authors[10–13] have reported that uranyl(VI) ions coordinate through carboxylate group of amino acidate zwitter ion without deprotonation of NH_3^+ group in the acidic region of pH. As the ionic mobilities are sensitive to charge, mass, size and shape of moving particles, the paper electrophoretic studies were undertaken to investigate the nature of complexation of amino acidate zwitter ion with uranyl(VI) ion. This paper is an extension of a paper already published.[14] Electrophoretic technique is applied for the determination of the formation constants of 1 : 1 uranyl(VI) amino acid (AA) [where AA = L-threonine (L-thr), L-leucine (L-leu), L-asparagine (L-asp), DL-β-phenyl alanine (DL-β-pheala)] binary complexes, prior to hydrolysis. The results of these studies are supplemented with pH-metric investigation under similar conditions.

EXPERIMENTAL

Reagents: Uranyl nitrate (BDH) and amino acids (ROMALI) were recrystallised and their standard solutions were used. Spots of uranyl(VI) ions were developed using 0.1% ethanolic solution of 1-(2-pyridylazo)-2-naphthol (PAN). The spots due to glucose were detected by spraying $AgNO_3$ solution in acetone and subsequently fuming with ammonia. A 0.1 M KNO_3 solurion was used as background electrolyte.

Apparatus: Horizontal type paper electrophoresis (PE) equipment (Toshniwal, India) along with the accessories and Whatman No.1 paper strips (40×1 cm^2) were used for measuring ionic mobilities of the free and complexed uranyl(VI) ion. The pH measurements were carried out employing pH-meter (Systronics, India) along with glass and calomel electrodes after necessary calibrations.

Procedure: The compartments of the paper electrophoresis (PE) equipment were filled with 1000 mL of background electrolyte containing varying amounts of amino acid. The paper strips in triplicate were spotted uniformly with uranyl(VI) ion and glucose solution and were placed horizontally in PE equipment. Electrophoresis was carried out for 60 min at 3.5 pH and 35°C. The strips were taken out, dried and developed with the help of spraying reagents. The ionic mobilities were calculated by taking the ratio of the distance moved to the potential gradient and time. Each set of experiments was repeated for the various concentrations of amino acid in the background electrolyte.

pH-titrations were carried out under nitrogen atmosphere at 35°C in 0.1 M KNO_3 solution. The acid dissociation constants of the amino acids and 1 : 1 formation constants with metal ion were calculated according to the method proposed by Martell.[15]

RESULTS AND DISCUSSION

The distribution of various species of amino acid existing in different regions of pH and their dissociation constants can be determined from the electrophoreto-

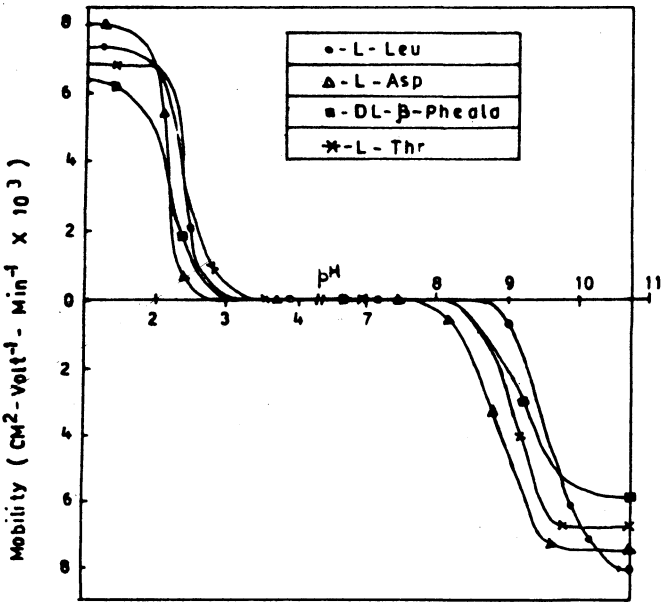


Fig. 1. Mobility curves of amino acids at 35°C in 0.1 M KNO_3 solution.

grams (*i.e.* the plot of overall mobility against pH) according to the procedure described by Yadav *et al.*[3] These electrophoretograms (Fig. 1) consist of three plateaus, each one indicating a definite pH range in which a particular ionic species of amino acid exists.

The values of dissociation constants derived from the electrophoretogram using the principle of average mobility[3] (pK graph) and those calculated using overall mobility (pK calc) along with the results obtaining from the pH-metric data are reported in Table-1.

TABLE-1
ACID DISSOCIATION CONSTANTS OF AMINO ACIDS
AT $\mu = 0.1$ M KNO_3 AND t = 35°C

AA	Electrophoretic values				Potentiometric values	
	pK_a		pK_{2a}		pK_a	pK_{2a}
	Calc.	Graph	Calc.	Graph		
L-thr	2.25	2.28	9.15	9.10	2.34	9.12
L-leu	2.38	2.40	9.60	9.60	2.38	9.59
L-asp	2.12	2.10	8.85	8.80	8.80	8.82
DL-β-pheala	2.20	2.18	9.20	9.25	2.25	9.20

It is of interest to note that the values determined from electrophoretic method are in fairly good agreement with those obtained from pH-metric method.

The electrophoretograms of the metal ligand systems (Fig. 2) show two plateaus. The first plateau at higher mobility values (*i.e.* 11.72 cm^2 $volt^{-1}$ $min^{-1} \times 10^3$) corresponds to the free uranyl(VI) ion whereas the second at lower pertains to the 1 : 1 uranyl(VI)-AA complexes.

The mobilities of free metal and its complex with various amino acids have positive values. The variation in ionic mobilities of the uranyl(VI) -AA complexes follow an order L-thr > L-asp > L-leu > DL-β-pheala, which can be correlated with the increasing trend in the molecular masses. Representing the solution equilibria as

$$UO_2 + AAH \underset{}{\overset{K^{UO_2}_{UO_2(AAH)}}{\rightleftharpoons}} UO_2(AAH) \qquad (2)$$

The equilibrium constant for the above reaction can be expressed as

$$K^{UO_2}_{UO_2(AAH)} = \frac{[UO_2(AAH)]}{[UO_2][AAH)]} \qquad (3)$$

At the equilibrium the total concentration of metal (T_m) can be given as

$$T_m = [1 + K^{UO_2}_{UO_2(AAH)}[AAH]][UO_2] \qquad (4)$$

The mole fractions of free f_m and complex metal f_c can be expressed by the following equations:

$$f_m = \frac{[UO_2]}{[1 + K^{UO_2}_{UO_2(AAH)}[AAH]][UO_2]} \quad (5)$$

$$f_c = \frac{[UO_2(AAH)]}{[1 + U^{UO_2}_{UO_2(AAH)}[AAH]][UO_2]} \quad (6)$$

The overall mobility in each electrophoretic run is given by the expression:

$$U = u_m f_m + u_c f_c \quad (7)$$

where u_m and u_c are the mobilities of free and complex metal ion respectively.

Substituting the values of f_m and f_c in equation (7),

$$U = \frac{u_m + u_c K^{UO_2}_{UO_2(AAH)}[AAH]}{1 + K^{UO_2}_{UO_2(AAH)}[AAH]} \quad (8)$$

According to the principle of average mobility the stability constant $K^{UO_2}_{UO_2(AAH)}$ can be determined and is equal to $1/[AAH^+]$. The values of $\log K^{UO_2}_{UO_2(AAH)}$ for 1 : 1 binary complexes of uranyl(VI) ion with different amino acids determined in the above manner and calculated by using equation (8) are reported in Table-2. The data obtained by pH-metric studies are also included in the table for the sake of comparison. It is evident that electrophoretic technique although being simple and handy offers the determination of these data with a good measure of comparable accuracy.

TABLE-2
STABILITY CONSTANTS OF BINARY UO_2(VI)-AA COMPLEXES
AT μ = 0.1 M KNO_3, t = 35°C AND $\mu = 11.72\ cm^2\ volt^{-1}\ min^{-1} \times 10^3$

AA	μ	$\log K^{UO_2}_{UO_2(AAH)}$				
		Electrophoretic values		Potentiometric values		
		Calc.	Graph	This study	Liter.	Ref
L-thr	3.40	1.96 ± (0.03)	1.99	2.01 ± (0.14)	—	—
L-leu	2.62	2.03 ± (0.06)	2.04	2.05 ± (0.12)	7.13	9
L-asp	2.92	1.83 ± (0.03)	1.88	1.78 ± (0.06)	6.85	8
DL-β-pheala	2.16	1.74 ± (0.04)	1.88	1.76 ± (0.11)	6.77	9

*Standard deviations are given in parentheses.

It may be pointed out that the higher values of stability constants of binary complexes as reported by some authors[8, 9] are probably due to different conjectures about the nature of ligating species and the use of different pH regions of the potentiometric titration curves for calculation of stability constants. These regions actually correspond to neutralization of the protons dissociated from coordinated water molecules rather than the displacement of protons bound to the amino nitrogen atoms of the ligands which usually occur at high pH. It can be inferred from the electrophoretograms for amino acids (Fig. 1) that at pH 3.5 the

concentration of zwitter ion is very large. It has been shown[18] that at this pH, hydrolysis of uranyl(VI) ion is minimum and the most predominant species is $[UO_2(H_2O)_6]^{2+}$. Therefore, complexation of uranyl(VI) ion must involve its aquo ion and zwitter ionic form of the ligand as given below:

$$[UO_2(H_2O)_6]^{2+} + OOC—R—NH_3^- \overset{K^{UO_2}_{UO_2(AAH)}}{\rightleftharpoons} [(H_2O)_5UO_2(OOC—R—^+NH_3)]^+ + H_2O \quad (9)$$

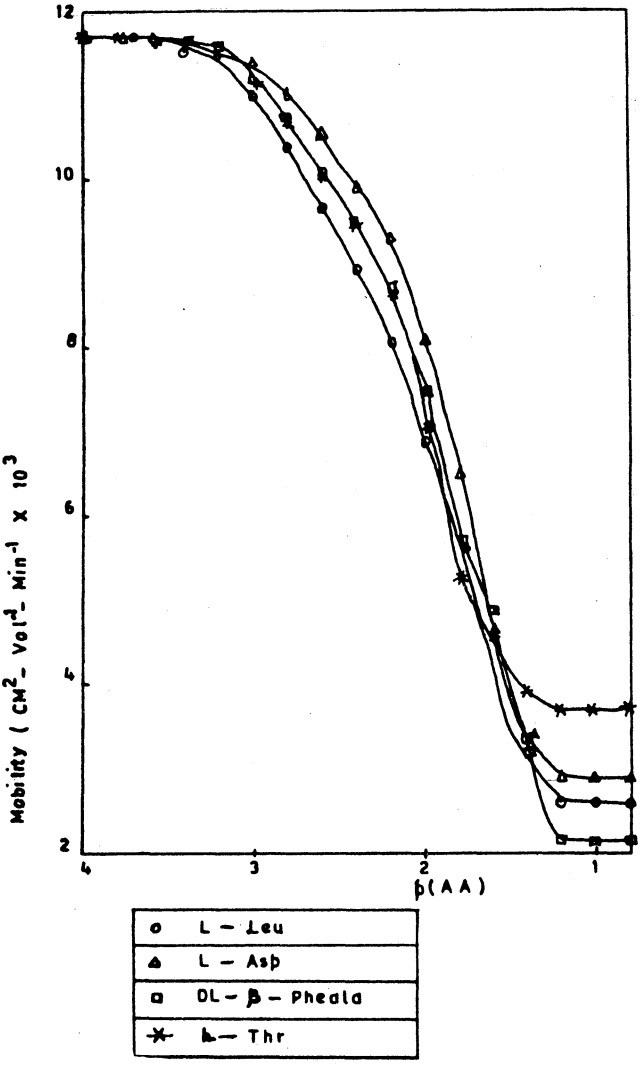


Fig. 2. Mobility curves of UO_2(VI)-AA systems at 3.5 pH and 35°C in 0.1 M-KNO_3 solution.

Thus, paper electrophoretic technique provides an experimental evidence to support the carboxylate complexation of the zwitter ionic amino acidate with uranyl(VI) ion particularly at low pH (pH < 4). (Fig. 2).

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