Ternary Complexes of Dioxouranium(VI) with Amino acids and Adenine - A Paper Electrophoretic Study

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The relative mobilities of ternary complexes of dioxouranium (VI) with DL-glycine, DL-α-alanine, DL-valine, L-serine and L-isoleucine as primary ligands and adenine as secondary ligand in 0.1M solution of KNO_3 indicate formation of cationic complexes at 303°K and 3.5 pH. This suggests coordination through carboxylate group of amino acidate zwitter ion. Stabilities of the complexes are reported. The results are supplemented with potentiometric studies.

Paper electrophoretic technique [1,2] has been employed for the determination of dissociation constants of the amino acids [3,4] and formation constants of their complexes [5,6]. The complexation of dioxouranium(VI) ion with amino acids has been investigated electrophoretically to examine the nature of complexation of amino acidate zwitter ion [7].

The present communication reports the values of stability constants of 1:1:1 ternary complexes of dioxouranium (VI) ion with amino acids (aa) [where aa = glycine (gly); DL-α-alanine (ala); DL-valine (val); L-serine (ser) and L-isoleucine (ile)] and adenine (adn). The results of these studies are supplemented with potentiometric investigations.

EXPERIMENTAL

The chemicals and appratus are the same as described earlier [8].

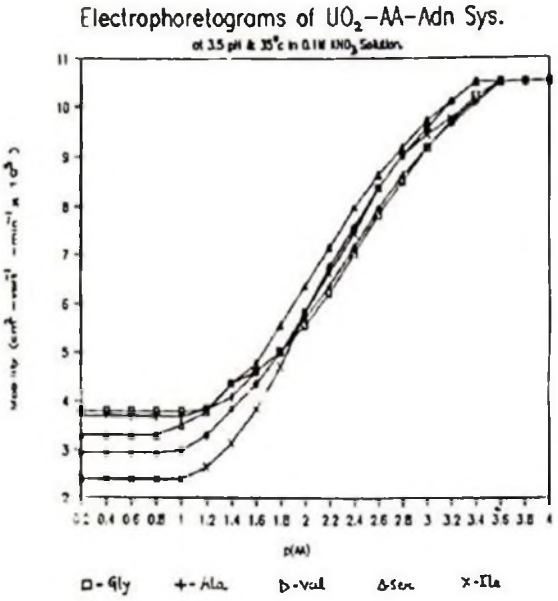
The background electrolyte for this study consists of ternary mixture of 0.1 M solution of KNO_3 with 0.01 M solution of adenine in presence of varying amounts of amino acid and adjusted to pH = 3.5 units by adding dilute nitric acid. The paper strips (40x1 cm^2) were spotted with 0.05 M uranyl nitrate solution using micropipette. The electrophoresis was carried out for 90 minutes at 250 V. The migration of metal ion spot was recorded by spraying the ethanolic solution of PAN on the paper strips. The electrophoretograms were obtained in a usual manner.

The pH titrations of 1:1:1 ternary solution of uranyl nitrate with amino acids and adenine were carried out under nitrogen atmosphere at 303°K in 0.1M KNO_3 solution and formation constants of the complex were calculated [9].

RESULTS AND DISCUSSION

The electrophoretograms (Fig.1) for the ternary system comprises of two plateaus. The upper plateau (at low concentration of amino acid) is due to the mobility of simple complex $[UO_2 (AdnH)]^{+2}$. It has been noticed during the electrophoretic investigation of binary systems that the mobility of free uranyl ion is higher and that of binary complexes of amino acids is much less than the observed value of $[UO_2 (AdnH)]^{+2}$ complex. The second plateau corresponds

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to the migration of the mixed ligand complex; mobility of the uranyl ion spot in this region was towards the cathodic compartment, confirming the formation of a cationic species - $[UO_2 (AdnH) (AA^{\cdot}H)]^{+}$; between the two plateaus, the binary and ternary complexes are in equilibrium with each other.

At low concentration of amino acids, the concentration of adenine in the background electrolyte is about hundred times higher than that of amino acids; only a binary complex $[UO_2 (AdnH)]^{+2}$ is expected in the solution according to the following reaction.

$$UO^{+2}_2 + AdnH \rightleftharpoons [UO_2 (AdnH)]^{+2}$$

With addition of amino acid, amino acidate zwitter ion gradually adds on to the binary complex according to reaction

$$[UO_2 (Adn\ H)]^{+2} + AAH^{\cdot} \rightleftharpoons [UO_2 (Adn\ H) (AAH)]^{+}$$

This leads to the decrease in the mobility. The mobility of ternary complexes with respect to amino acids follow the order: gly > ala > ser > val > ile. It shows that increase in the mass and size of the amino acid molecule results in a decrease in the ionic mobility of the complexes.

The overall mobility for the above system can be given as:

$$U = U_B f_B + U_T f_T$$

where U_B and U_T are the mobilities and f_B and f_T are the mole fractions of the binary and ternary complexes. Substituting the values of mole fractions, the overall mobility is obtained. The values of ternary formation constants (Table 1) have been calculated. These are also determined graphically using the principle of average mobility [4] evaluating stability constant of adenine binary complex potentiometrically. The value of overall stability constants (ß) can be estimated as the product of the step constants.

Table 1

Stability Constants of Ternary Complexes - Paper Electrophoretic Method

pH = 3.5; Temp = 30°; μ = 0.1 M KNO_3

Amino acid	log K_2		log ß		Δlog K	
	Graph	Calc.	Graph	Calc.	Graph	Calc.
DL-gly	2.39	2.42	6.00	6.03	0.30	0.35
DL-α-ala	2.35	2.38	5.96	5.99	0.30	0.34
DL-val	2.22	2.19	5.83	5.80	0.20	0.22
L-ser	2.13	2.14	5.74	5.75	0.23	0.27
L-ile	2.17	2.14	5.81	5.78	0.17	0.13

$$K_2 = \frac{[UO_2 (AdnH) (AAH)]}{[UO_2(AdnH)]\ [AAH]}$$

$$Log K^{UO2}_{UO2IADNH} = 3.61$$

$$ß = \frac{[UO_2 (AdnH) (AAH)]}{[UO_2]\ [(AdnH)]\ [AAH]}$$

Table 2

Stability Constants of Ternary Complexes - Potentiometric Method

Temp = 30°; μ = 0.1 M KNO_3

Amino acid	$logK_1$	$logK_2$	log ß	Δlog K
DL-gly	3.99	2.46	6.07	0.38
DL-α-ala	3.93	2.41	6.02	0.32
DL-val	3.80	2.23	5.84	0.19
L-ser	3.70	2.04	5.65	0.17
L-ile	3.76	2.19	5.80	0.15

$$K_1 = \frac{[UO_2(AAH)(AdnH)]}{[UO_2(AAH)][AdnH]}$$

$$K_2 = \frac{[UO_2(AdnH)(AAH)]}{[UO_2(AdnH)][AAH]}$$

$$ß = \frac{[UO_2(AdnH)(AAH)]}{[UO_2][(AdnH)][AAH]}$$

$$LogK^{UO2}{}_{UO2(ADNH)} = 3.61$$

These values agree well with those obtained from the potentiometric studies (Table 2). This provides a proof for the relaibility of the electrophoretic data and the correctness of approach following the complex equilibria in the ternary systems.

The stability of ternary complexes decreases in the series gly > ala > val > ile > ser. This is in accordance with decreasing order of ligand basicity and is almost similar to the trend exhibited by binary complexes of amino acids.

The relative stability of the ternary complexes over the binary one [8] is quantified in terms of ΔlogK, defined as:

$$\Delta\log K = \log ß - [LogK^{UO2}{}_{UO2(AAH)} + LogK^{UO2}{}_{UO2(ADNH)}]$$

The positive Δlog K, values (Table 1,2) confirm the greater stability of the ternary complexes.

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