

Ionic Strength Dependence of Formation Constants: Complexation of Dioxouranium (VI) with Aspartic Acid

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ABSTRACT

The dependence on ionic strength of protonation of L-aspartic acid and its complexation with dioxouranium(VI) is reported in sodium perchlorate solution as a background salt. The measurements have been performed at 25 ± 0.1 °C and various ionic strengths in the range 0.1 to 1.0 mol dm⁻³, using a combination of potentiometric and spectrophotometric techniques. The overall analysis of the present and the previous data dealing with the determination of stability constants at different ionic strengths allowed us to obtain a general equation, by which a formation constant determined at a fixed ionic strength can be calculated, with a good approximation, at another ionic strength, if $0.1 \leq$ ionic strength \leq 1.0 mol dm⁻³ sodium perchlorate.

Keywords: Ionic strength; Formation constant; Complexation.

INTRODUCTION

In previous work we reported the complexation of uranyl(VI) ion with glutamic acid at different ionic strength [1] and showed that glutamic acid bind to the metal ion through one of the carboxylate group, whereas the amino group, in the experimental conditions used, remained protonated. The same result was reported by Bismondo and Rizzo [2] on chelation of uranyl(VI) ion by some dicarboxylic acids, such as glutamic acid. The authors have examined the coordination behaviour of some amino acids, which have two carboxylic groups in the chain, in order to evaluate the influence of another carboxylic group on the capacity of amino acids to form stable bonds to metal ion and concluded below pH 3.5 uranyl(VI) ion was bound to one of the carboxylic groups only.

Chelation of uranyl(VI) ion by amino acids appears to be uncertain. Many workers have reported that amino acids are bidentate chelating ligands towards uranyl(VI) ion, the chelation being effected through carboxyl oxygen and amino nitrogen [3-7]. The present authors have also reported the data on uranyl complexes on the above basis.

In determining a stability constant at a fixed ionic strength, in all cases, some uncertainties are present. This fact is mainly due to the uncertainties in numerical values of stability constants. For example, when

maintaining two different ionic media, 0.1 and 0.7 mol dm⁻³ sodium perchlorate, we observed a difference of about 1.5 log units in the stability constant of dioxouranium(VI) chelate of aspartic acid.

According to the literature, no work has been reported on the ionic strength dependence of dioxouranium(VI)+aspartic acid. This paper deals with the study of complexes of dioxouranium(VI) ion with L-aspartic acid in an ionic strength range 0.1-1.0 mol dm⁻³ sodium perchlorate. The parameters which define the dependence on ionic strength were analyzed with the aim of obtaining further information with regard to their variation as a function of the charges involved in the complexation reaction. Moreover, a general equation was established for the dependence of formation constants on ionic strength. This equation gives the possibility of estimating a stability constant at a fixed ionic strength when its value is known for another ionic media in the range of $0.1 \leq$ ionic strength \leq 1.0 mol dm⁻³ NaClO₄ and may be a significant contribution to solving many analytical and speciation problems.

EXPERIMENTAL SECTION

Chemicals. L-aspartic acid, asp, (Fluka, analytical reagent grade) was recrystallized from hot water, washed with ethanol, and dried over P₂O₅, and its

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concentration was determined by titration against standard alkali. The NaOH solution was prepared from titrisol solution (E. Merck) and its concentration was checked by several titrations with standard HCl. Perchloric acid, sodium perchlorate and uranium(VI) acetate were supplied from E. Merck as analytical reagent grade materials and were used without further purification. Dilute perchloric acid solution was standardized against standard NaOH solution. All dilute solutions were prepared from double-distilled water with specific conductance equal to $1.3 \pm 0.1 \mu\Omega^{-1} \text{ cm}^{-1}$. The concentration of the uranyl ion, UO_2^{+2} , in aqueous solution was determined by pulse polarography using a standardized solution of $\text{UO}_2(\text{NO}_3)_2$ (a sample of the stock solution was diluted in aqueous 0.5 mol dm^{-3} hydrochloric acid [8]).

MEASUREMENTS

All measurements were carried out at $25 \pm 0.1 \text{ }^\circ\text{C}$. The ionic strength was maintained from 0.1 to 1.0 mol dm^{-3} with sodium perchlorate. The pH-meter was calibrated for the relevant H^+ concentration with a solution of 0.01 mol dm^{-3} perchloric acid solution containing 0.09 mol dm^{-3} sodium perchlorate (for adjusting the ionic strength to 0.1 mol dm^{-3}). The same procedure was performed for the other ionic strengths. For these standard solutions, we set $-\log[\text{H}^+] = 2.00$ [9]. Junction potential corrections have been calculated from eq 1

$$-\log[\text{H}^+]_{\text{real}} = -\log[\text{H}^+]_{\text{measured}} + a + b[\text{H}^+]_{\text{measured}} \quad (1)$$

a and b were determined by measuring of hydrogen ion concentration of two different solutions of HClO_4 with sufficient NaClO_4 to adjust the ionic media.

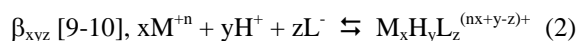
PROCEDURE

25 cm^3 acidic solution of UO_2^{+2} ($10^{-3} \text{ mol dm}^{-3}$) was titrated with an alkali solution (0.1 mol dm^{-3} NaOH) of aspartic acid (containing a large excess of the ligand, 0.01 mol dm^{-3}), both in the same ionic strength. The $-\log[\text{H}^+]$ and absorbance were measured after addition of a few drops of titrant, and this procedure extended up to the required $-\log[\text{H}^+]$. In all cases, the procedure was repeated at least three times and the resulting average values and corresponding standard deviations are shown in the text and Tables.

RESULTS AND DISCUSSION

In order to avoid hydrolysis of oxometal ions all the measurements were performed at $-\log[\text{H}^+] < 3.5$. The complex $\text{M}_x\text{H}_y\text{L}_z^{(nx+y-z)+}$ formed, is characterized by its stoichiometry (x:y:z), where M and L represent the

metal ion and the ligand, respectively. To determine the stability constant of the complexation or the protonation, eq 2 is defined by



$$\beta_{xyz} = [\text{M}_x\text{H}_y\text{L}_z^{(nx+y-z)+}] / ([\text{M}^{+n}]^x [\text{H}^+]^y [\text{L}^-]^z) \quad (3)$$

The protonation constant of aspartic acid has been used for computation of the stability constants, β_{xyz} , of the metal-ligand. The protonation constants of the ligand has been extensively studied in different kind of background electrolytes, and the results were reported in literature. The protonation constants have been determined using potentiometric techniques and calculated using a computer program which employs a least-squares method [11]. These values are listed in Table 1 together with the values reported in the literature, which are in good agreement with those reported before [12-16]. If the values of protonation constants obtained here compare with the data for simple α -amino acids such as glycine or alanine, it can be said that the carboxylic acid groups in aspartic acid lead to a significant increase in protonation constant value for the amino group. The method of determination of the stability constant based on the relation $A=f([\text{H}^+])$. Absorbance, A, and $-\log[\text{H}^+]$ were measured for a solution containing UO_2^{+2} with a large excess of the ligand, and the results are listed in Table 2. Treatments of the spectrophotometric data (each 5 nm) obtained during the titrations as a function of the H^+ concentration were conducted to the computer program [11]. The program allows calculation of stability constants for different stoichiometry models. The degree of refinement then guides the choice between the models. In aqueous solution, aspartic acid exists in its anionic forms (HL^- and L^{2-}), zwitterionic species (H_2L), and cationic form (H_3L^+). Considering the protonation constant of the amino acid, in acidic pH the predominant species for complexation is H_2L . In the computer program the following complexes were considered: MH_2L , MHL , ML , $\text{M}(\text{H}_2\text{L})_2$, $\text{M}(\text{HL})_2$, ML_2 (the charges are omitted for simplicity). Using the computer program [11] the data were fitted to estimate the formation constant of eq 2. We used the Gauss - Newton nonlinear least - squares method in computer program to refine the absorbance by minimizing the error squares sum from eq 4

$$S = \sum(a_i - b_i)^2 \quad (4)$$

Table 1. Protonation constants of the first and second carboxylic, β_{031} and β_{021} , and amino, β_{011} , groups of aspartic acid at 25 °C and different ionic strengths, I, of NaClO₄

I / mol dm ⁻³	log β_{031}	log β_{021}	log β_{011}	experimental conditions	ref.
0.1	2.58 ± 0.03	3.88 ± 0.05	9.93 ± 0.08		this work
0.3	2.38 ± 0.04	3.71 ± 0.04	9.71 ± 0.07		this work
0.5	2.32 ± 0.04	3.58 ± 0.06	9.49 ± 0.10		this work
0.7	2.27 ± 0.02	3.42 ± 0.05	9.42 ± 0.07		this work
1.0	2.24 ± 0.03	3.56 ± 0.04	9.51 ± 0.06		this work
		2.88	9.77	I = 2.25 M NaNO ₃ , t = 25°C	12
		3.75	9.48	I = 0.1 M NaClO ₄ , t = 25°C	13
		3.70	9.62	I = 0.1 M NaNO ₃ , t = 25°C	14
		3.71	9.63	I = 0.1 M NaClO ₄ , t = 30°C	15
		3.79	9.75	I = 0.1 M KNO ₃ , t = 25°C	16

Where a_i is a quasi-experimental and b_i is a calculated one. As expected, all the proposed species were systematically rejected by the computer program except MHL and M(HL)₂. A value for MH₂L formation constant was calculated by the program, but the species was not further considered because the estimated error in its formation constant is unacceptable, and its inclusion does not improve the goodness of the fit. The model finally chosen, formed by UO₂HL⁺ and UO₂(HL)₂, resulted in a satisfactory numerical and graphical fitting. The average values of β_{111} and β_{122} for various wavelengths are listed in Table 3.

It is known that an approximate relationship exists between the protonation constants of a series of amino acids and the stability constants of their 1:1 and 1:2 complexes with a given metal ion. Such a relationship can be used to estimate the stability constants of the metal ion complexes of closely related substances, if their protonation constant values and one β value are known. Figure 1 demonstrate such a relationship for the stability constants of aspartic acid and its homologous glutamic acid complexes with UO₂²⁺, (from our previous work [1]). In Figure 2 the equilibrium distribution of various species for UO₂²⁺+ asp system is shown as a function of $-\log[H^+]$. The calculations are based on the stability constants given before. This Figure shows when the $-\log[H^+]$ approaches to 1.80 and 3.29 the mole fractions of the proposed complexes have the maximum values.

DEPENDENCE ON IONIC STRENGTH

A general equation [17-19], $\log\beta = f(I)$, can be used for all the formation constants if allowance is made for the stoichiometry and for the charges involved in the reaction. The semi-empirical Debye-Huckel type equation, eq [5], can be used for taking into account the

dependence of $\log\beta_{xyz}$ on ionic strength, I, for each complex species [20].

$$\log\beta(I) = \log\beta(I^*) - AZ^*[I^{0.5}/(1+BI^{0.5}) - I^{*0.5}/(1+BI^{*0.5}) + C(I - I^*) + D(I^{1/2} - I^{*1/2})] \quad (5)$$

where I and I* are the actual and reference ionic strength, respectively. According to eq 5, $Z^* = 1 + Z_L^2 - Z_j$ (where Z_L and Z_j are the charges on the anion and the species H_jL, respectively) for β_{031} , β_{021} , β_{011} , and $Z^* = Z_L^2 + Z_M^2 - jZ_C - 1$ (where Z_M and Z_C are the charges on the metal ion and the formed complexes, respectively) for β_{111} and β_{122} . Considering $A = 0.5115 + 8.885 \times 10^{-4}(t - 25) + 2.953 \times 10^{-6}(t - 25)^2$ and $B = 1.489 + 8.772 \times 10^{-4}(t - 25) + 4.693 \times 10^{-6}(t - 25)^2$, where t is the temperature in degrees Celsius, equation 5 can simplified at t = 25 °C as

$$\log\beta(I) = \log\beta(I^*) - Z^*[I^{0.5}/(2+3I^{0.5}) - I^{*0.5}/(2+3I^{*0.5}) + C(I - I^*) + D(I^{3/2} - I^{*3/2})] \quad (6)$$

where C and D are empirical coefficients whose values are considered. The validity of eq 6 has been discussed in previous papers mainly with speciation problems [21-25] where the possibility of calculating $\log\beta$ values, at the desired ionic strength using literature values, is of great importance. The parameters C and D were determined by a regression method with a suitable computer program [11] and reported in Table 4 for each species.

Table 2. Absorbance, A, of the system UO_2^{+2} + aspartic acid at 25 °C and different $-\log[\text{H}^+]$, wavelengths, and ionic strengths, I, of NaClO_4

$-\log[\text{H}^+]$	A				$-\log[\text{H}^+]$	A			
	260nm	265nm	270nm	275nm		260nm	265nm	270nm	275nm
$I = 0.1 \text{ mol dm}^{-3}$									
1.12	0.161	0.129	0.106	0.086	2.16	0.137	0.113	0.094	0.079
1.18	0.142	0.114	0.094	0.076	2.31	0.150	0.124	0.104	0.086
1.25	0.129	0.104	0.086	0.070	2.49	0.169	0.141	0.118	0.099
1.34	0.121	0.097	0.080	0.065	2.72	0.199	0.166	0.141	0.119
1.40	0.118	0.095	0.078	0.064	2.98	0.235	0.198	0.168	0.143
1.57	0.114	0.093	0.077	0.063	3.13	0.255	0.215	0.184	0.156
1.69	0.115	0.094	0.078	0.064	3.27	0.274	0.232	0.198	0.169
1.95	0.124	0.101	0.085	0.070	3.42	0.289	0.246	0.210	0.178
$I = 0.3 \text{ mol dm}^{-3}$									
1.12	0.158	0.126	0.102	0.083	2.30	0.133	0.109	0.090	0.075
1.19	0.139	0.111	0.090	0.074	2.45	0.145	0.119	0.099	0.083
1.27	0.126	0.102	0.082	0.068	2.65	0.165	0.137	0.114	0.096
1.38	0.118	0.095	0.077	0.063	2.89	0.194	0.162	0.136	0.115
1.53	0.112	0.090	0.073	0.061	3.03	0.212	0.178	0.149	0.128
1.78	0.111	0.090	0.073	0.061	3.16	0.230	0.194	0.163	0.139
1.91	0.114	0.092	0.075	0.063	3.30	0.246	0.208	0.175	0.150
2.07	0.120	0.091	0.080	0.066	3.44	0.263	0.222	0.188	0.161
$I = 0.5 \text{ mol dm}^{-3}$									
1.06	0.159	0.127	0.104	0.084	2.27	0.132	0.109	0.091	0.075
1.14	0.141	0.113	0.092	0.075	2.43	0.145	0.119	0.100	0.083
1.22	0.129	0.104	0.085	0.069	2.62	0.163	0.136	0.114	0.095
1.34	0.120	0.096	0.079	0.064	2.85	0.190	0.159	0.134	0.113
1.50	0.113	0.091	0.076	0.061	2.98	0.207	0.173	0.147	0.124
1.75	0.113	0.091	0.075	0.062	3.12	0.225	0.189	0.160	0.136
1.88	0.115	0.094	0.078	0.063	3.26	0.242	0.204	0.174	0.147
2.04	0.120	0.098	0.082	0.067	3.40	0.259	0.219	0.186	0.158
$I = 0.7 \text{ mol dm}^{-3}$									
1.03	0.161	0.130	0.106	0.087	2.25	0.134	0.111	0.093	0.078
1.11	0.142	0.115	0.094	0.078	2.40	0.144	0.120	0.100	0.085
1.20	0.131	0.106	0.087	0.072	2.59	0.161	0.134	0.113	0.096
1.31	0.122	0.099	0.081	0.067	2.82	0.186	0.156	0.132	0.113
1.48	0.116	0.095	0.078	0.065	2.95	0.203	0.172	0.144	0.124
1.74	0.115	0.095	0.078	0.065	3.08	0.221	0.167	0.158	0.136
1.87	0.117	0.096	0.080	0.067	3.22	0.238	0.202	0.171	0.147
2.03	0.122	0.101	0.084	0.070	3.35	0.255	0.216	0.184	0.157
$I = 1.0 \text{ mol dm}^{-3}$									
0.96	0.159	0.128	0.104	0.086	2.21	0.134	0.110	0.091	0.077
1.04	0.141	0.114	0.092	0.077	2.37	0.146	0.121	0.099	0.085
1.13	0.130	0.105	0.085	0.071	2.56	0.163	0.136	0.113	0.097
1.25	0.121	0.098	0.079	0.067	2.79	0.191	0.160	0.133	0.115
1.33	0.118	0.095	0.077	0.065	2.92	0.208	0.175	0.146	0.126
1.54	0.113	0.092	0.074	0.063	3.06	0.225	0.191	0.160	0.138
1.81	0.117	0.095	0.077	0.066	3.20	0.244	0.207	0.174	0.151
1.98	0.122	0.100	0.082	0.070	3.33	0.261	0.221	0.187	0.1612

Table 3. Average values of $\log\beta_{111}$ and $\log\beta_{122}$ of the system UO_2^{+2} + aspartic acid for various wavelengths at 25 °C and different ionic strengths of NaClO_4

$I / \text{mol dm}^{-3}$	$\log \beta_{111}$	$\log \beta_{122}$	$\log\beta_{101}$	experimental conditions	ref.
0.1	8.81 ± 0.12	11.52 ± 0.14			this work
0.3	8.03 ± 0.11	10.85 ± 0.16			this work
0.5	7.56 ± 0.13	10.44 ± 0.13			this work
0.7	7.23 ± 0.10	10.22 ± 0.14			this work
1.0	7.50 ± 0.09	10.66 ± 0.12			this work
	2.41	4.14		$I = 1.0 \text{ M NaClO}_4, t = 25 \text{ }^\circ\text{C}$	2
			8.71	$I = 0.1 \text{ M NaClO}_4, t = 30 \text{ }^\circ\text{C}$	15

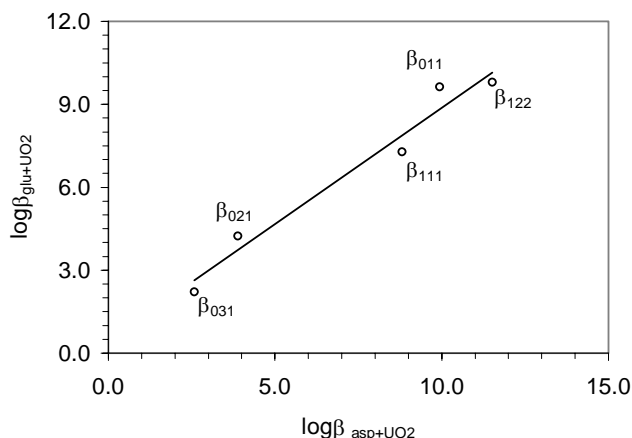


Fig. 1. Linear plot of the protonation and the stability constants of aspartic acid versus the homologous values of glutamic acid at 0.1 mol dm⁻³ NaClO₄ and 25 °C.

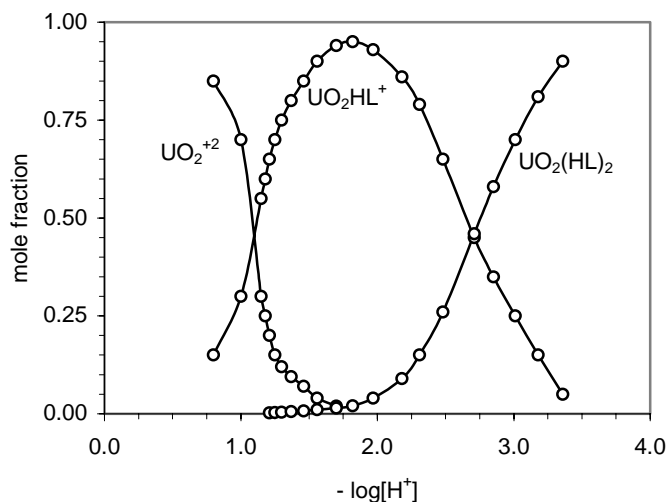


Fig. 2. The equilibrium distribution of the species in UO₂⁺² + L-aspartic acid system as a function of $-\log[\text{H}^+]$ at 25 °C and ionic strength 0.1 mol dm⁻³ sodium perchlorate.

The dependence of $\log\beta$ on ionic strength determined in NaClO₄ as background electrolyte is shown in Figure 3 and listed in Tables 1 and 3. The dependencies show a regular trend and is in a good agreement with other complex species [21-25]. Using the values of C and D from Table 4, one can rewrite eq 6 as:

$$\log\beta_{031} = -1.59I + 1.14I^{3/2} + 2.70 \quad (7)$$

$$\log\beta_{021} = -I^{0.5}/(1 + 1.5I^{0.5}) - 1.47I + 1.19I^{3/2} + 4.20 \quad (8)$$

$$\log\beta_{011} = -I^{0.5}/(0.5 + 0.75I^{0.5}) - 1.39I + 1.23I^{3/2} \quad (9)$$

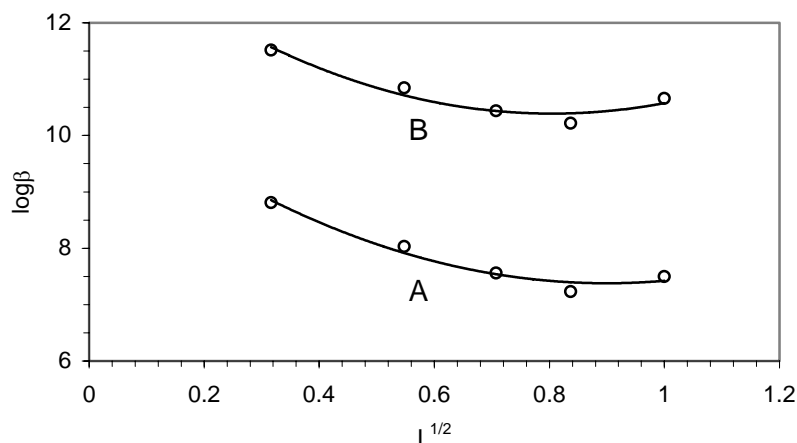
$$\log\beta_{111} = -I^{0.5}/(1 + 1.5I^{0.5}) - 0.77I + 5.98I^{3/2} + 9.61 \quad (10)$$

$$\log\beta_{122} = -8.06I + 6.56I^{3/2} + 12.12 \quad (11)$$

The equations, 7-11, give the possibility of estimating the protonation and the stability constants of aspartic acid and its complexes by dioxouranium(VI) at each ionic strength in the range of $0.1 \leq I \leq 1.0$ mol dm⁻³ NaClO₄.

Table 4. Parameters for the dependence on ionic strength of the protonation of aspartic acid and the stability constants of UO_2HL^+ and $\text{UO}_2(\text{HL})_2$

species	C	D	Z*
β_{031}	- 1.59	1.14	0
β_{021}	- 1.47	1.19	2
β_{011}	- 1.39	1.23	4
β_{111}	- 7.72	5.98	2
β_{122}	- 8.06	6.56	0

**Fig. 3.** Plots of $\log\beta$ versus the square root of ionic strength of L-aspartic acid + UO_2^{+2} at 25 °C, (A) for β_{111} , and (B) for β_{122} .

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