Ionic Strength Dependence of Formation Constants: Complexation of Glutamic Acid with Uranium(VI) Ion[1]

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Abstract—The dependence on ionic strength of protonation of L-glutamic acid and its complexation with dioxouranium(VI) are reported in sodium perchlorate solution as a background salt. Measurements have been performed at $25 \pm 0.1°C$ 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, and with a good approximation, at another ionic strength, if $0.1 \leq$ ionic strength ≤ 1.0 mol dm^{-3} sodium perchlorate.

INTRODUCTION

A considerable amount of work has been carried out on some aminocarboxylic acid complexes with uranyl ion using different techniques [1–7]. Many researchers have claimed that amino acids are bidentated chelating ligands towards uranyl ion, the chelation being effected through carboxyl oxygen and amino nitrogen [9–11]. These authors have also reported data on uranyl ion complexes on the above basis. However, some others have reported that the amino nitrogen is not involved in coordination [6, 12]. The stability constant values of the chelation that were reported by these authors vary considerably. These values vary within the range of 2.4 to 12.4 in log unit for the uranyl ion(VI)+glutamic acid system. The differences are mostly due to the fact that at pH > 3.5 uranyl ion undergoes hydrolysis and the constants calculated at pH > 3.5 do not represent the true equilibrium of the metal ion with the ligands. Some of the differences are also due to the different ionic strengths and various techniques that were employed. In most cases measurements were performed at a fixed ionic strength, and in some other cases no special attempts were made to control the ionic strength. However, in all cases some uncertainties are still present. This fact is mainly due to the uncertainties in the numerical values of stability constants. For example, when maintaining two different ionic strengths of 0.1 and 1.0 mol dm^{-3} sodium perchlorate, we observed a difference of about 1.1 log unit for the stability constant of uranyl ion with glutamic acid.

The present work describes the complexation of uranium(VI) ion with glutamic acid in an ionic strength range of 0.1 to 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 regards to their variation as a function of the charges involved in the complex reaction. Moreover, a general equation was drawn for the dependence of the formation constants on the ionic strength. This equation allows the possibility of estimating a stability constant at a fixed ionic strength when its value is known in another ionic media, $0.1 \leq I \leq 1.0$ mol dm^{-3} sodium perchlorate and, therefore, may make a significant contribution to solving many analytical and speciation problems.

EXPERIMENTAL

Chemicals. L-glutamic acid, glu, (Fluka, analytical reagent grade) was recrystallized from hot water, washed with ethanol, and dried over P_2O_5, and its 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 ± 0.1 $\mu\Omega^{-1}$ cm^{-1}. The concentration of the uranyl ion, UO_2^{2+}, in aqueous solution was determined by pulse polarography using a standardized solution of $UO_2(NO_3)_2$ (a sample of the stock solution was diluted in aqueous 0.5 mol dm^{-3} hydrochloric acid [13]).

Apparatus. An Eyela pH meter (PHM 2000) was used for $-\log[H^+]$ measurements. A purified nitrogen atmosphere was maintained in the reaction vessel during the titrations. The hydrogen ion concentration was

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Table 1. Protonation constants of the first and second carboxylic, β_{031} and β_{021}, and amino, β_{011}, groups of glutamic acid at 25°C and different ionic strengths, I, of NaClO$_4$

I, mol dm^{-3}	log β_{031}	log β_{021}	log β_{011}	Experimental conditions	Ref.
0.1	2.21 ± 0.03	4.24 ± 0.05	9.64 ± 0.08		This work
0.3	2.15 ± 0.04	4.03 ± 0.04	9.27 ± 0.07		This work
0.5	2.11 ± 0.04	3.76 ± 0.06	9.10 ± 0 10		This work
0.7	2.10 ± 0.02	3.74 ± 0.05	9.04 ± 0.07		This work
1.0	2.10 ± 0 03	3.60 ± 0.04	8.98 ± 0.06		This work
		4.15	9.49	I = 0.15 M NaClO$_4$, T = 25°C	16
		4.21	9.54	I = 0.1 M NaNO$_3$, T = 25°C	17
		4.05	9.46	I = 0.1 M NaClO$_4$, T = 30°C	18
		4.15	9.61	I = 0.1 M KNO$_3$, T = 25°C	19
		3.71	9.63	I = 0.1 M NaClO$_4$, T = 30°C	1

measured with an Ingold UO 3234 glass electrode and an Ingold UO 3236 calomel electrode. Spectrophotometric measurements were performed on a UV-vis Shimadzu 2100 spectrophotometer with a GDU-20 computer using thermostated matched 10 mm quartz cells. The measurement cell was of the flow type. A Masterflex pump allowed circulation of the solution under study from the potentiometer cell to the spectrophotometric cell, so the absorbance and $-\log[H^+]$ of the solution could be measured simultaneously.

Measurements. All measurements were carried out at 25 ± 0.1°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 $-\log[H^+]$ = 2.00 [4]. The junction potential corrections have been calculated from Eq. 1

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

a and b were determined by measuring the hydrogen ion concentration of two different solutions of HClO$_4$ with sufficient NaClO$_4$ to adjust the ionic media.

Procedure. A 25 cm^3 acidic solution of UO$_2^{2+}$ (10^{-3} mol dm^{-3}) was titrated with an alkali solution (0.1 mol dm^{-3} NaOH) of glutamic acid (containing a large excess of the ligand, 10^{-2} mol dm^{-3}), both having the same ionic strength. The $-\log[H^+]$ and absorbance were measured after addition of a few drops of the titrant, and this procedure was extended up to the required $-\log[H^+]$. 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 $-\log[H^+]$ < 3.5. The complex $M_xH_yL_z^{(nx+y-zi)+}$ 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 β_{xyz} [4, 14]

$$xM^{+n} + yH^+ + zL \rightleftharpoons M_xH_yL_z^{(nx+y-zi)+} \quad (2)$$

$$\beta_{xyz} = [M_xH_yL_z^{(nx+y-zi)+}]/([M^{+n}]^x[H^+]^y[L^{-i}]^z). \quad (3)$$

The protonation constant of glutamic acid has been used for computation of the stability constants β_{xyz} of the metal-ligand. The protonation constants of the ligand have been extensively studied in different kinds of background electrolytes, and the results have been reported in the literature. The protonation constants have been determined using potentiometric techniques and calculated using a computer program, which employs a least-squares method [15]. These values are listed in Table 1 together with the values reported in the literature. They are in good agreement with those reported before [1, 16–19].

The method of determination of the stability constant is based on the relation $A = f([H^+])$. Absorbance A and $-\log[H^+]$ 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

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

| $-\log[H^+]$	A				$-\log[H^+]$	A			
	260 nm	265 nm	270 nm	275 nm		260 nm	265 nm	270 nm	275 nm
$I = 0.1$ mol dm^{-3}									
1.18	0.155	0.124	0.100	0.080	1.72	0.108	0.087	0.071	0.057
1.23	0.146	0.117	0.096	0.077	1.82	0.106	0.085	0.070	0.056
1.28	0.138	0.110	0.090	0.072	1.96	0.105	0.085	0.070	0.056
1.33	0.131	0.105	0.085	0.069	2.16	0.105	0.085	0.070	0.057
1.39	0.125	0.101	0.082	0.066	2.34	0.107	0.088	0.072	0.058
1.45	0.120	0.096	0.079	0.063	2.60	0.114	0.093	0.077	0.063
1.52	0.116	0.094	0.077	0.063	3.02	0.136	0.112	0.093	0.077
1.61	0.112	0.090	0.074	0.059	3.37	0.170	0.141	0.119	0.099
$I = 0.3$ mol dm^{-3}									
1.12	0.160	0.129	0.106	0.087	1.83	0.112	0.091	0.075	0.063
1.21	0.145	0.117	0.096	0.079	2.24	0.112	0.092	0.076	0.063
1.32	0.134	0.109	0.090	0.074	2.47	0.117	0.096	0.089	0.067
1.38	0.129	0.104	0.086	0.071	2.62	0.124	0.102	0.086	0.072
1.45	0.124	0.100	0.083	0.068	2.82	0.133	0.110	0.092	0.078
1.54	0.119	0.096	0.080	0.066	3.09	0.148	0.123	0.104	0.088
1.63	0.117	0.095	0.079	0.065	3.24	0.162	0.135	0.114	0.097
1.75	0.114	0.093	0.077	0.064	3.41	0.180	0.151	0.128	0.108
$I = 0.5$ mol dm^{-3}									
1.17	0.158	0.126	0.104	0.085	2.16	0.109	0.088	0.073	0.061
1.21	0.146	0.117	0.096	0.078	2.40	0.114	0.093	0.077	0.065
1.24	0.139	0.111	0.091	0.074	2.57	0.120	0.099	0.082	0.068
1.31	0.126	0.101	0.082	0.068	2.80	0.132	0.109	0.091	0.077
1.36	0.120	0.097	0.079	0.066	2.95	0.143	0.118	0.099	0.083
1.48	0.112	0.090	0.074	0.061	3.11	0.157	0.130	0.109	0.093
1.67	0.108	0.087	0.072	0.059	3.28	0.176	0.147	0.124	0.105
1.80	0.105	0.085	0.070	0.058	3.44	0.199	0.167	0.142	0.120
$I = 0.7$ mol dm^{-3}									
1.06	0.160	0.128	0.104	0.085	1.70	0.112	0.090	0.074	0.062
1.09	0.152	0.122	0.099	0.082	2.19	0.116	0.094	0.078	0.066
1.16	0.138	0.111	0.091	0.075	2.50	0.125	0.102	0.086	0.072
1.20	0.132	0.106	0.086	0.071	2.75	0.140	0.115	0.096	0.082
1.25	0.127	0.102	0.084	0.069	2.89	0.150	0.124	0.104	0.088
1.31	0.123	0.098	0.080	0.067	3.07	0.166	0.138	0.116	0.099
1.40	0.118	0.095	0.077	0.064	3.24	0.183	0.152	0.129	0.109
1.61	0.113	0.091	0.074	0.062	3.41	0.208	0.175	0.148	0.127
$I = 1.0$ mol dm^{-3}									
1.08	0.167	0.136	0.113	0.093	1.97	0.113	0.093	0.078	0.065
1.15	0.149	0.122	0.101	0.084	2.31	0.120	0.099	0.083	0.070
1.21	0.137	0.113	0.094	0.077	2.48	0.126	0.104	0.088	0.074
1.25	0.132	0.109	0.091	0.076	2.71	0.138	0.115	0.097	0.081
1.30	0.128	0.105	0.087	0.073	2.85	0.148	0.123	0.105	0.088
1.37	0.125	0.103	0.086	0.072	3.01	0.162	0.136	0.115	0.097
1.46	0.116	0.096	0.079	0.066	3.18	0.181	0.154	0.130	0.110
1.56	0.114	0.094	0.078	0.065	3.36	0.212	0.180	0.155	0.131
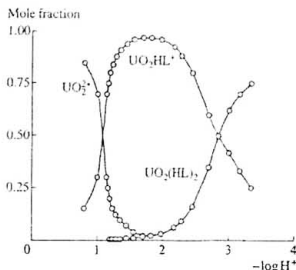
Fig. 1. The equilibrium distribution of the species in the UO$_2^{2+}$ + L-glutamic acid system as a function of $-\log[\,H^+]$ at 25°C, 275 nm. and ionic strength 1.0 mol dm^{-3} sodium perchlorate.

a function of the H$^+$ concentration were conducted using a computer program [15]. The program allows calculation of stability constants for different stoichiometric models. The degree of refinement then guides the choice between models. In aqueous solution, glutamic acid exists in its anionic forms (HL$^-$ and L^{2-}), zwitterionic species (H$_2$L), and cationic form (H$_3$L$^+$). Considering the protonation constant of the amino acid, in acidic pH the predominant species for complexation is H$_2$L. Using the computer program, the following complexes were considered: MH$_2$L, MHL, ML, M(H$_2$L)$_2$, M(HL)$_2$, ML$_2$ (the charges are omitted for simplicity). Also using the computer program [15], the data were fitted to estimate the formation constant of Eq. 2. We used the Gauss–Newton nonlinear least-

squares method in the computer program to refine the absorbance by minimizing the error squares sum from Eq. 4

$$U = \Sigma(a_i - b_i)^2, \qquad (4)$$

where a_i is quasi-experimental and b_i is calculated. As was expected, all the proposed species were systematically rejected by the computer program except for MHL and M(HL)$_2$. A value for the MH$_2$L formation constant was calculated by the program, but the species was not considered further, because the estimated error in its formation constant was unacceptable, and its inclusion does not improve the goodness of the fit. The model finally chosen, formed by UO$_2$HL$^+$ and UO$_2$(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. In Figure 1 the equilibrium distribution of various species for the UO$_2^{2+}$ + glu system is shown as a function of $-\log[\,H^+]$. The calculations are based on the stability constants given before. This figure shows when $-\log[\,H^+]$ approaches 1.82 and 3.36, the mole fractions of the proposed complexes have the maximum values.

Comparison with the literature data. Some of the stability constant values for uranyl ion complexes of glutamic acid or its homologous aspartic acid found in the literature have some differences with those determined in this work. This is certainly due to the different stoichiometry model and the difference in the experimental conditions. For uranyl ion complexes Shelke and Jahagirdar [1] have, respectively, obtained log β_{101} = 8.43 and 8.71 for glutamic and aspartic acids by potentiometric titration method at 30°C. Petit-Ramel and Mosoni [3] have found log β_{111} = 12.4 and log β_{101} = 8.25 for glutamic acid by spectrophotometric technique. They explained that both carboxyl groups, as well as the amino group of glutamic acid, are

Table 3. Average values of logβ_{111} and logβ_{122} of the system UO$_2^{2+}$ + glutamic acid for various wavelengths at 25°C and different ionic strengths of NaClO$_4$

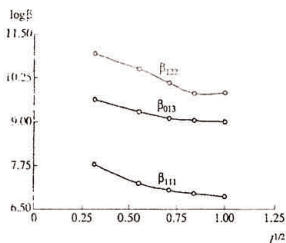| I. mol dm^{-3}	logβ_{111}	logβ_{122}	logβ_{101}	Experimental conditions	Ref.
0.1	7.78 ± 0.10	10.94 ± 0.15			This work
0.3	7.25 ± 0.11	10.51 ± 0.17			This work
0.5	7.05 ± 0.11	10.10 ± 0.15			This work
0.7	6.95 ± 0.10	9.79 ± 0.12			This work
1.0	6.87 ± 0.09	9.82 ± 0.11			This work
			8.43	I = 0.1 M NaClO$_4$, T = 30°C	1
	12.4		8.25	I = 0.1 M NaClO$_4$, T = 25°C	3
	2.72			I = 0.2 M KNO$_3$, T = 25°C	12

Fig. 2. Plots of $\log\beta$ versus the square root of ionic strength for protonation of L-glutamic acid and the stability constants.

probably involved in chelation, but binding by the amino nitrogen is insignificant for a steric reason. By a potentiometric titration method the values of $\log\beta_{111}$ = 2.41 and $\log\beta_{112}$ = 4.14 were obtained by Bismondo and Rizzo [2] for aspartic acid in 1.0 mol dm^{-3} sodium perchlorate as the ionic strength. The authors have described that the ligand binds to the oxometal ion through one carboxylate group only, the one furthest from the positive amino group, whereas the amino group, in the experimental conditions used, is protonated and not involved in coordination.

Ionic strength dependence. The dependence of the stability and protonation constants on ionic strength can be described by a Debye–Hückel type equation [20–27]

$$\log\beta(I) = \log\beta(I^*)^-$$
$$-AZ^*[I^{0.5}/(1 + BI^{0.5}) - I^{*0.5}/(1 + BI^{*0.5})] \quad (5)$$
$$+ C(I - I^*) + D(I^{1.5} - I^{*1.5}),$$

where I and I^* are the actual and reference ionic

Table 4. Parameters for the dependence on ionic strength of the protonation of glutamic acid and the stability constants of UO_2HL^+ and $UO_2(HL)_2$

Species	C	D	Z^*
011	−0.60	0.44	0
022	−1.39	0.83	2
011	−1.81	1.40	4
111	−3.72	2.73	2
122	−4.65	3.13	0

strength, respectively, and according to equation 6,

$$pM^{+m} + qL^{-n} + rH^+(M_pL_qH_r)^{pm + qn + r} \quad (6)$$

$Z^* = pm^2 + qn^2 + r - (pm + qn + r)^2$, where m and n are the charges on the metal ion and the ligand, respectively [21]. Considering

$$A = 0.5115 + 8.885 \times 10^{-4}(T - 25)$$
$$+ 2.953 \times 10^{-6}(T - 25)^2,$$

$$B = 1.489 + 8.772 \times 10^{-4}(T - 25)$$
$$+ 4.693 \times 10^{-6}(T - 25)^2,$$

where T is the temperature in °C, Eq. 5 can be simplified at $T = 25$°C as

$$\log\beta(I) = \log\beta(I^*)$$
$$-Z^*[I^{0.5}/(2 + 3I^{0.5}) - I^{*0.5}/(2 + 3I^{*0.5})] \quad (7)$$
$$+ C(I - I^*) + D(I^{1.5} - I^{*1.5}),$$

where C and D are empirical coefficients whose values were obtained by a regression method with a suitable computer program [15] and are shown in Table 4.

The dependences on ionic strength of the $\log\beta$ values are shown in Tables 1 and 3 and Fig. 2, which are in agreement with the results obtained for other complex species in our previous studies [20–27].

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