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# Interaction of the Dioxouranium(VI) Ion with Aspartate and Glutamate in NaCl(aq) at Different Ionic Strengths

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The formation of complexes species of the dioxouranium(VI) ion with aspartic and glutamic acids was studied in the pH range of 3 to 6 at 25 °C by potentiometric measurements ($H^+$−glass electrode). Results gave evidence for the formation of the following species: $(UO_2)A^0$, $(UO_2)AH^+$, and $(UO_2)_2A(OH)_2{}^0$ ($A^{2-}$ = a glutamic or aspartic ligand). Investigations were carried out in a NaCl ionic medium at $I$ (0.1, 0.25, 0.5, and 1.0) mol $L^{-1}$. The dependence on ionic strength of the formation constants was analyzed by the specific ion interaction theory (SIT) model. The formation constants at infinite dilution, obtained using this model, are $\log \beta_{110} = 8.53 \pm 0.03$, $8.37 \pm 0.05$; $\log \beta_{111} = 13.60 \pm 0.05$, $13.42 \pm 0.02$; and $\log \beta_{21-2} = 3.31 \pm 0.05$, $2.98 \pm 0.03$ for glutamate and aspartate, respectively, where indexes for the overall formation constant $\beta_{pqr}$ refer to the equilibrium $p\,UO_2{}^{2+} + qA^{2-} + rH^+ = (UO_2)_p(A)_qH_r{}^{(2p\,-\,2q\,+\,r)}$. The specific interaction coefficients are also reported. A mononuclear hydroxo species $(UO_2)A(OH)^-$, of great interest for very low naturally occurring concentrations of uranium(VI), was hypothesized, with equilibrium constant log $K$ [$(UO_2)A^0 + H_2O = (UO_2)A(OH)^-$] = −5.4 at $t$ = 25 °C and $I$ = 0 mol $L^{-1}$. Speciation profiles for different concentrations of $UO_2{}^{2+}$ in the presence of both amino acids are discussed.

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## Introduction

Studies on the environmental impact and radiological effects of uranium(VI) compounds have been much improved during the last 50 years, and many articles and compilations have been published on the solution chemistry of the dioxouranium(VI) ion[1−5] to define its chemical behavior in terrestrial and aquatic ecosystems. In previous papers, we reported results on the dependence on the ionic strength of hydrolysis constants of $UO_2{}^{2+}$ in different ionic media[6] and on the speciation of this ion in media simulating the composition of natural waters.[7] Quantitative studies on the interaction of the dioxouranium ion with different carboxylic ligands were also carried out by our research group.[8,9] Despite a very large amount of literature data on the solution chemistry of the uranyl ion, interactions of this ion in aqueous media with molecules of biological interest, such as amino acids, have been little investigated. Most of the results, reported many years ago, are concerned with structural investigations on the complex species formed and were carried out mainly to establish whether the interaction between uranyl and an amino acid occurs via carboxylic or amino groups or both.[10−14] Quantitative studies on the stability of $UO_2{}^{2+}$ amino acid complex species by different authors by means of various techniques[15−23] were performed in fairly concentrated aqueous solutions of the uranyl ion ($10 \times 10^{-3}$ to $30 \times 10^{-3}$ mol $L^{-1}$) and ligand (up to $C_A/C_M$ = 10:1). Under these experimental conditions, measurements were performed generally in a very narrow pH range (2 to 4) to avoid precipitation of uranium(VI) oxide species of low solubility. Most authors report the formation of only the $(UO_2)A^0$ ($A^{2-}$ = aspartic or glutamic ligand) species, often without considering the uranyl hydrolysis occurring in the pH range of 3 to 4.[6,7]

Here we report results of a study on the interactions of $UO_2{}^{2+}$ with aspartic and glutamic acids in the pH range of 2 to 6 in NaCl aqueous solution. Measurements were carried out by a potentiometric technique ($H^+$−glass electrode) at 25 °C at fairly low concentrations of the $UO_2{}^{2+}$ ion (0.5 or 1.0 mmol $L^{-1}$) and with a $C_A/C_M$ ratio ($A^{2-}$ = aspartic or glutamic ligand; M = $UO_2{}^{2+}$) not higher than 5:1. A complex formation model was used where both the hydrolysis of the dioxouranium(VI) ion[1,6,7] and the protonation of amino acids[2−5,24,25] were taken into account. In addition to the simple species $(UO_2)A^0$, ($A^{2-}$ = aspartic or glutamic ligand), protonated $(UO_2)AH^+$ and hydroxo $(UO_2)_2A(OH)_2{}^\circ$ mixed species were also found. Another mononuclear hydroxo species $(UO_2)A(OH)^-$, of great interest for very low naturally occurring concentrations of uranium(VI), was hypothesized. Among the few literature data, formation constants are reported at only one ionic strength value in each work dealing with these systems, mainly 0.1 mol $L^{-1}$ ($NaClO_4$). In this work, data at different ionic strengths (0.1, 0.25, 0.5, and 1.0 mol $L^{-1}$) are reported, and the specific ion interaction theory (SIT) model was used to extrapolate formation constants of all species found at infinite dilution and to calculate specific interaction parameters.

## Experimental Section

***Materials.*** The dioxouranium(VI) cation ($UO_2{}^{2+}$) was used as the nitrate salt (Fluka), and its purity, checked gravimetrically after precipitation as $U_3O_8$ by gaseous ammonia, was >99.5 %. L(+)-aspartic and L(+)-glutamic acids (Carlo Erba, purity >99.5 %) were used without further purification. Sodium chloride was used as the anhydrous salt (Merck) after drying at 140 °C. Hydrochloric acid and sodium hydroxide solutions were prepared by diluting concentrated solutions (Aldrich and Merck, respectively) and were standardized against sodium carbon-

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**Table 1. Experimental Conditions for $UO_2$ Glutamate and Aspartate Systems at $t$ = 25 °C**

| $I$/mol $L^{-1a}$ | $C_{UO_2}$/mol $L^{-1}$ | $C_A$/mol $L^{-1}$ | $C_H$/mol $L^{-1}$ | pH range | $n^b$ | $I$/mol $L^{-1a}$ | $C_{UO_2}$/mol $L^{-1}$ | $C_A$/mol $L^{-1}$ | $C_H$/mol $L^{-1}$ | pH range | $n^b$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $UO_2$ Glutamate | | | | | | | | | | | |
| 0.0920 | 0.00054 | 0.00100 | 0.00237 | 3.36−6.15 | 76 | 0.4660 | 0.00054 | 0.00150 | 0.00341 | 3.33−6.18 | 92 |
| 0.0900 | 0.00054 | 0.00200 | 0.00475 | 3.15−6.07 | 120 | 0.4610 | 0.00054 | 0.00200 | 0.00460 | 3.31−6.10 | 109 |
| 0.0890 | 0.00100 | 0.00200 | 0.00475 | 3.13−6.07 | 150 | 0.4550 | 0.00054 | 0.00260 | 0.00552 | 3.30−5.73 | 126 |
| 0.0910 | 0.00054 | 0.00150 | 0.00336 | 3.35−6.09 | 91 | 0.4520 | 0.00100 | 0.00200 | 0.00446 | 3.27−5.97 | 139 |
| 0.0900 | 0.00054 | 0.00250 | 0.00532 | 3.32−6.23 | 121 | 0.9270 | 0.00054 | 0.00100 | 0.00275 | 3.15−6.06 | 89 |
| 0.2360 | 0.00052 | 0.00103 | 0.00287 | 3.13−6.54 | 86 | 0.9250 | 0.00054 | 0.00150 | 0.00341 | 3.36−6.04 | 92 |
| 0.2310 | 0.00052 | 0.00207 | 0.00493 | 3.13−6.53 | 80 | 0.9140 | 0.00054 | 0.00200 | 0.00446 | 3.33−6.05 | 109 |
| 0.2310 | 0.00051 | 0.00152 | 0.00423 | 2.99−6.48 | 78 | 0.9030 | 0.00054 | 0.00260 | 0.00552 | 3.32−5.95 | 126 |
| 0.2290 | 0.00052 | 0.00255 | 0.00590 | 3.13−6.5 | 89 | 0.8970 | 0.00100 | 0.00200 | 0.00446 | 3.31−6.04 | 137 |
| 0.4760 | 0.00054 | 0.00100 | 0.00235 | 3.36−6.17 | 76 | | | | | | |
| $UO_2$ Aspartate | | | | | | | | | | | |
| 0.0880 | 0.00057 | 0.00198 | 0.00600 | 2.74−6.25 | 128 | 0.4710 | 0.00054 | 0.00101 | 0.00243 | 3.23−6.09 | 79 |
| 0.0930 | 0.00105 | 0.00099 | 0.00279 | 3.05−5.86 | 121 | 0.4660 | 0.00054 | 0.00152 | 0.00345 | 3.18−6.16 | 95 |
| 0.0900 | 0.00105 | 0.00198 | 0.00477 | 2.90−6.06 | 153 | 0.4520 | 0.00109 | 0.00203 | 0.00446 | 3.11−5.99 | 142 |
| 0.0940 | 0.00057 | 0.00158 | 0.00357 | 3.18−6.00 | 100 | 0.4610 | 0.00109 | 0.00101 | 0.00243 | 3.21−5.91 | 110 |
| 0.0950 | 0.00057 | 0.00099 | 0.00239 | 3.24−6.19 | 79 | 0.4600 | 0.00054 | 0.00203 | 0.00446 | 3.14−6.04 | 112 |
| 0.0880 | 0.00057 | 0.00396 | 0.00955 | 2.83−5.79 | 152 | 0.9190 | 0.00054 | 0.00203 | 0.00447 | 3.16−6.07 | 112 |
| 0.2340 | 0.00052 | 0.00108 | 0.00295 | 3.04−6.44 | 74 | 0.9400 | 0.00054 | 0.00101 | 0.00243 | 3.25−5.88 | 79 |
| 0.2280 | 0.00052 | 0.00149 | 0.00418 | 2.90−6.24 | 105 | 0.8920 | 0.00109 | 0.00203 | 0.00487 | 3.02−6.01 | 154 |
| 0.2220 | 0.00091 | 0.00199 | 0.00518 | 2.89−6.30 | 95 | 0.9110 | 0.00054 | 0.00250 | 0.00540 | 3.15−6.02 | 124 |
| 0.2250 | 0.00052 | 0.00202 | 0.00523 | 2.91−6.47 | 81 | 0.9200 | 0.00054 | 0.00152 | 0.00386 | 3.05−6.02 | 109 |
| 0.2270 | 0.00052 | 0.00250 | 0.00580 | 3.00−6.41 | 88 | | | | | | |

[a] Mean values of ionic strength. [b] Number of experimental points (two or three independent titrations).

ate and potassium hydrogen biphthalate, respectively. All of the solutions were prepared by using $CO_2$-free freshly prepared distilled water ($R$ = 18 MΩ) and grade-A glassware.

***Experimental Equipment and Procedure.*** The measurements were carried out using two different potentiometric instruments consisting of a Metrohm model 665 automatic titrant dispenser coupled with a Metrohm model 654 potentiometer and combination Orion-Ross 8102 and 8172 glass electrodes, respectively. The estimated accuracy of this system was ±0.15 mV and ± 0.003 mL for emf and the titrant volume reading, respectively. In titration cells, pure nitrogen was bubbled through the solutions to avoid $O_2$ and $CO_2$ inside, and the solutions were magnetically stirred. A volume of (20 to 25) mL of solution, containing the amino acid under investigation (glutamic or aspartic acid) and $UO_2(NO_3)_2$ in different concentration ratios, in the presence of an appropriate amount of NaCl to adjust the ionic strength to different values (0.1, 0.25, 0.5, and 1.0 mol $L^{-1}$) was titrated with sodium hydroxide standard solutions at (25.0 ± 0.1) °C. For each experiment, independent titrations of hydrochloric acid solutions with NaOH standard solutions were performed under the same experimental conditions of ionic strength and temperature as for the systems under study to determine the formal electrode potential; therefore, potentiometric readings were in terms of pH = $-\log [H^+]$. All titrations were carried out up to pH ~6 before the precipitation of uranium(VI) oxide species of low solubility. Table 1 shows the experimental conditions used for each titration carried out on the $UO_2$ glutamate and $UO_2$ aspartate systems. In this Table, $C_H$ refers to the total $[H^+]$ concentration derived from both the amino acids under study and a slight excess of standard HCl added to check the internal formal electrode potential and to compare it with the external one.

***Calculations.*** The nonlinear least-squares computer program ESAB2M[26] was used to calculate all of the parameters of an acid−base titration (analytical concentration of the reagents, electrode potential, junction potential coefficient, and ionic product of water). The following additional computer programs[27] were also used: STACO and BSTAC to calculate formation constants, LIANA for fitting linear and nonlinear equations for the calculation of protonation and formation constants, and ES4ECI to draw distribution diagrams of the species in solution and to compute species formation. In all calculations, both the hydrolysis constants of the uranyl ion[1,6,7] and the protonation constants of aspartic and glutamic acids[5,24,25] in NaCl aqueous medium were taken into account. All formation constants ($\beta_{pqr}$) are expressed according to the equilibrium

$$p\mathrm{UO_2}^{2+} + q\mathrm{A}^{2-} + r\mathrm{H}^+ = (\mathrm{UO_2})_p(\mathrm{A})_q\mathrm{H}_r^{(2p-2q+r)} \quad (1)$$

***Ionic Strength Dependence of Formation Constants.*** The dependence on ionic strength was taken into account by using the SIT model,[28] according to which formation constants can be expressed as

$$\log K_m = \log {}^{\mathrm{T}}K_m - z^*\mathrm{DH} + L(\epsilon, I) \quad (2)$$

where $K_m$ is the molal formation constant; ${}^{\mathrm{T}}K_{\mathrm{m}}$ is the relative value at infinite dilution; $z^*$ is the difference of the square of the charges; DH is the Debye−Huckel term $[0.51I^{0.5}/(1+1.5I^{0.5})]$; and $L(\epsilon, I)$ is a linear term dependent on ionic strength and interaction coefficients. In the base theory, for a simple equilibrium

$$\mathrm{M}^{z+} + \mathrm{A}^{z-} = \mathrm{MA}^{y-}$$

(in the supporting electrolyte BX), the linear term assumes the form

$$L(\epsilon, I) = I[(\epsilon(\mathrm{M}^{z+}, \mathrm{X}^-) + \epsilon(\mathrm{A}^{z-}, \mathrm{B}^+) - \epsilon(\mathrm{MA}^{y-}, \mathrm{B}^+)]$$

The interaction coefficients of uncharged species with ions of the supporting electrolyte are equal to zero, but the activity coefficient can be obtained from the well-known relationship[28]

$$\log \gamma = \lambda I$$

and therefore $\epsilon$(uncharged species, supporting electrolyte) $\equiv \lambda$. Often, when some interaction coefficients are not known, eq 2 is written as

$$\log K_m = \log {}^{\mathrm{T}}K_m - z^*\mathrm{DH} + I\Delta\epsilon \qquad (2a)$$

In other words,

$$L(\epsilon, I) = I\Delta\epsilon$$

## Results and Discussion

***Hydrolysis Constants of the Dioxouranium(VI) Ion and Protonation Constants of Aspartic and Glutamic Acids.*** The dioxouranium(VI) ion undergoes strong hydrolysis with the formation of stable soluble hydroxo species (at pH >3) before the precipitation of oxide species of low solubility at pH ~6. Most of the hydrolysis products are polynuclear species even for quite low $UO_2^{2+}$ concentration.[1] Therefore, the hydrolysis of the uranyl ion cannot be neglected when the interactions of $UO_2^{2+}$ with organic and/or inorganic ligands in aqueous solution have to be investigated. In previous papers,[6,7] we reported hydrolysis constants of $UO_2^{2+}$ and parameters for the ionic strength dependence determined in different aqueous media and at different ionic strength values. The hydrolysis constants of the uranyl ion at the ionic strength (NaCl medium) investigated in this work are reported in Table 2. Protonation of aspartic and glutamic acids was also considered in the calculations to determine formation constants of complex species in the $UO_2$ amino acid systems. Protonation constants of aspartic and glutamic acids at different ionic strengths in NaCl were reported in previous papers[24,25] and are shown in Table 3.

***Formation and Stability of $UO_2^{2+}$ Aspartate and Glutamate Complexes.*** Least-squares analysis of potentiometric data was performed by taking into consideration many speciation models. We found that the best set of the species is represented, for both systems, by $(UO_2)A^0$, $(UO_2)AH^+$, and $(UO_2)_2A(OH)_2^\circ$ ($A^{2-}$ = aspartate, glutamate). In Table 4 we report, for some experimental data, the comparison between different speciation models carried out on the basis of the residual variance of models. Formation constants of $UO_2$ glutamate/aspartate complex species were determined at different ionic strengths in NaCl medium, and the experimental values, on the molal and molar concentration scales, are shown in Tables 5 and 6, respectively. Errors in formation constants are given as ≥95 % confidence intervals; these were obtained by performing separate calculations on four sets of experimental data. This procedure also partially accounts for systematic errors.

The dependence of formation constants on ionic strength was taken into account by the SIT model as described in the Experimental Section. To this end, we needed to know several interaction coefficients, $\epsilon$, for the different species. In Table 7, we report the values of $\epsilon(A^{2-}, Na^+)$, $\epsilon(HA^-, Na^+)$, and $\epsilon(H_3A^+, Cl^-)$ calculated from the dependence of protonation constants on ionic strength (assuming $\lambda_{H_2A} = 0.1$, on the basis of several values reported for similar systems[28]) and $\epsilon(H^+, Cl^-)$ and $\epsilon(UO_2^{2+}, Cl^-)$ obtained from the literature.[8,29] Using these coefficients, we calculated $\epsilon$ values for the complex species of aspartate and glutamate by fitting formation constants at different ionic strengths to eq 2. This fitting also allows us to obtain the infinite dilution formation constants. The relative results, together with formation constants at infinite dilution, are reported in Table 8. Values of $\epsilon$ and $\lambda$ are fairly low, indicating small interactions between complexes and the supporting electrolyte.

**Table 2. Hydrolysis Constants[a,b] of the Dioxouranium(VI) Ion at Different Ionic Strengths in NaCl(aq) at $t$ = 25 °C[6]**

| $I$/mol kg$^{-1}$ | $-\log \beta_{11}$ | $-\log \beta_{22}$ | $-\log \beta_{34}$ | $-\log \beta_{35}$ | $-\log \beta_{37}$ |
|---|---|---|---|---|---|
| 0.10 | 5.45 | 5.98 | 12.22 | 16.54 | 29.67 |
| 0.25 | 5.57 | 6.06 | 12.32 | 16.75 | 29.75 |
| 0.50 | 5.71 | 6.13 | 12.37 | 16.91 | 29.76 |
| 1.02 | 5.95 | 6.23 | 12.39 | 17.10 | 29.75 |

[a] Equilibrium constants refer to the reaction $pUO_2^{2+} + qH_2O = (UO_2)_p(OH)_q^{(2p-q)} + qH^+(\beta_{pq})$. [b] Molal concentration scale.

**Table 3. Protonation Constants[a,b] of Aspartate and Glutamate at Different Ionic Strengths in NaCl at $t$ = 25 °C[24,25]**

| $I$/mol kg$^{-1}$ | $\log \beta^{H}_1$ | $\log \beta^{H}_2$ | $\log \beta^{H}_3$ |
|---|---|---|---|
| | Aspartate | | |
| 0.10 | 9.65 | 13.36 | 15.30 |
| 0.25 | 9.58 | 13.24 | 15.21 |
| 0.50 | 9.56 | 13.21 | 15.21 |
| 1.00 | 9.55 | 13.21 | 15.32 |
| | Glutamate | | |
| 0.10 | 9.64 | 13.86 | 16.07 |
| 0.25 | 9.56 | 13.73 | 15.97 |
| 0.50 | 9.55 | 13.72 | 15.99 |
| 1.00 | 9.55 | 13.72 | 16.09 |

[a] Protonation constants refer to the equilibrium $A + nH = AH_n$ (A = aspartate or glutamate; $n$ = 1, 2, 3). [b] Molal concentration scale.

**Table 4. Different Models Tried for the $UO_2$ Aspartate and Glutamate Systems at $I$ = 0.1 mol L$^{-1}$**

| | $UO_2$ aspartate system | | | $UO_2$ glutamate system | | |
|---|---|---|---|---|---|---|
| species | $\log \beta$ | $\sigma_0^2/\sigma^{2a}$ | mean dev. [b] | $\log \beta$ | $\sigma_0^2/\sigma^{2a}$ | mean dev.[b] |
| | | | Model 1 | | | |
| MA | 7.588 | 1.000 | 0.405 | 7.745 | 1.000 | 0.499 |
| MAH | 12.634 | | | 12.740 | | |
| $M_2A(OH)_2$ | 1.984 | | | 2.218 | | |
| | | | Model 2 | | | |
| MA | 7.823 | 1.552 | 0.973 | 7.977 | 1.371 | 0.940 |
| MAH | 12.455 | | | 12.500 | | |
| | | | Model 3 | | | |
| MA | 7.85 | 2.654 | 2.848 | 8.055 | 2.172 | 2.359 |

[a] $\sigma_0^2$ variance of the best model. [b] Mean deviation in emf.

The stability of dioxouranium(VI) complexes with both amino acids is quite high and indicates that in addition to the two carboxylate groups the amino group is also effective in the coordination. In fact, at $I$ = 0.1 mol L$^{-1}$ in NaCl we have $\log \beta_{110}$ = 5.71 and 7.58 for malonate[9] and aspartate $UO_2$ systems, respectively. Moreover, for the analogous complex species of glycine it was found at $I$ = 0.1 mol L$^{-1}$ (P. G. Daniele, personal communication) that $\log \beta_{110}$ = 6.59. This means an increment in stability of 1.9 and 1 log units for the aspartate system in comparison with malonate and glycinate, respectively. Analogous considerations can be made for the protonated species $(UO_2)AH^+$ by writing the partial equilibrium

$$UO_2^{2+} + HA^- = (UO_2)AH^+ \qquad (K_{111})$$

By considering this equilibrium, we have (for the above experimental conditions) $\log K_{111}$ = 3.0, 5.4, and 1.2 for aspartate, malonate, and glycinate,[9] respectively, with the aspartate value being very close to the average value of glycinate and malonate [$(\log K_{111(\mathrm{gly})} + \log K_{111(\mathrm{mal})})/2 = 3.3$]. For the hydroxo species, the following equilibrium can be taken into account:

$$(UO_2)_2(OH)_2^{2+} + A^{2-} = (UO_2)_2A(OH)_2^{0} \qquad (K_{21-2})$$

**Table 5. Formation Constants[a] of $UO_2$ Glutamate Complex Species at Different Ionic Strengths[b] and $t$ = 25 °C**

| $I$/mol kg$^{-1}$ | log $\beta_{110}$[c] | log $\beta_{111}$ | log $\beta_{21-2}$ | $I$/mol L$^{-1}$ | log $\beta_{110}$ | log $\beta_{111}$ | log $\beta_{21-2}$ |
|---|---|---|---|---|---|---|---|
| 0.092 | 7.75 ± 0.03[d] | 12.75 ± 0.03 | 2.24 ± 0.03 | 0.092 | 7.75 | 12.75 | 2.24 |
| 0.232 | 7.44 ± 0.06 | 12.64 ± 0.03 | 2.06 ± 0.03 | 0.230 | 7.44 | 12.65 | 2.06 |
| 0.465 | 7.72 ± 0.04 | 12.65 ± 0.03 | 2.03 ± 0.04 | 0.460 | 7.72 | 12.66 | 2.03 |
| 0.935 | 7.63 ± 0.03 | 12.66 ± 0.03 | 1.95 ± 0.04 | 0.917 | 7.64 | 12.68 | 1.95 |

[a] Molal and molar concentration scales. [b] NaCl ionic medium. [c] log $\beta_{pqr}$ values refer to equilibrium 1. [d] ≥95 % confidence interval.

**Table 6. Formation constants[a] of $UO_2$ aspartate complex species at different ionic strengths[b] and $t$ = 25 °C**

| $I$/mol kg$^{-1}$ | log $\beta_{110}$[c] | log $\beta_{111}$ | log $\beta_{21-2}$ | $I$/mol L$^{-1}$ | log $\beta_{110}$ | log $\beta_{111}$ | log $\beta_{21-2}$ |
|---|---|---|---|---|---|---|---|
| 0.092 | 7.59 ± 0.02[d] | 12.64 ± 0.02 | 1.99 ± 0.02 | 0.092 | 7.59 | 12.64 | 1.99 |
| 0.232 | 7.22 ± 0.05 | 12.44 ± 0.02 | 1.72 ± 0.03 | 0.230 | 7.22 | 12.45 | 1.72 |
| 0.465 | 7.37 ± 0.02 | 12.43 ± 0.02 | 1.72 ± 0.02 | 0.460 | 7.37 | 12.44 | 1.72 |
| 0.935 | 7.30 ± 0.03 | 12.50 ± 0.01 | 1.73 ± 0.03 | 0.917 | 7.31 | 12.52 | 1.73 |

[a] Molal and molar concentration scales. [b] NaCl ionic medium. [c] log $\beta_{pqr}$ values refer to equilibrium 1. [d] ≥95 % confidence interval.

**Table 7. SIT Interaction Coefficients**

| SIT coefficients | glutamic acid | aspartic acid |
|---|---|---|
| $\epsilon(A^{2-}, Na^+)$ | 0.42 | 0.38 |
| $\epsilon(HA^-, Na^+)$ | 0.16 | 0.16 |
| $\lambda_{H_2A}$ | 0.1 | 0.1 |
| $\epsilon(H_3A^+,Cl^-)$ | 0.04 | 0.05 |
| $\epsilon(H^+, Cl^-)$[a] | 0.12 | |
| $\epsilon(UO_2{}^{2+}, Cl^-)$[b] | 0.25 | |

[a] Reference 29. [b] Reference 8.

**Table 8. Formation Constants at Infinite Dilution and Interaction Coefficients of $UO_2$ Glutamate and Aspartate Complex Species in NaCl at $t$ = 25 °C**

| | glutamate | aspartate |
|---|---|---|
| log $\beta_{110}$ | 8.53 ± 0.03 | 8.37 ± 0.05 |
| log $\beta_{111}$ | 13.60 ± 0.05 | 13.42 ± 0.02 |
| log $\beta_{21-2}$ | 3.31 ± 0.05 | 2.98 ± 0.03 |
| $\lambda_{(UO_2)2A(OH)_2}$ | −0.046 | −0.188 |
| $\lambda_{UO_2A}$ | −0.113 | 0.043 |
| $\epsilon(UO_2HA^+, Cl^-)$ | 0.049 | 0.010 |
| $\Delta\epsilon_{110}$ | 0.78 | 0.59 |
| $\Delta\epsilon_{111}$ | 0.74 | 0.74 |
| $\Delta\epsilon_{21-2}$ | 0.73 | 0.83 |

For this equilibrium, we have log $K_{21-2}$ = 8.0 and 7.0 for aspartate and malonate, respectively. These considerations support the involvement of all of the potential ligand groups in the uranyl aspartate system. Complex species in the uranyl glutamate system show a slightly higher stability that is likely due to a better steric arrangement.

It is probable that other species can be formed under other experimental conditions. In particular, it is well known that at very low metal concentrations the formation of mononuclear species prevails, but the possibility of having data at very low reactant concentrations is of fundamental importance in the speciation studies of natural fluids. Therefore, for the systems here studied it should be of great interest to have an estimate of the stability of the mononuclear hydroxo species $(UO_2)A(OH)^-$, and to this end, we may resort to empirical predictive methods. For several uranyl complexes, it was shown that formation constants are a linear combination of the species stoichiometric coefficients,[9] and for the reaction $(UO_2)A^0 + H_2O = (UO_2)A(OH)^-$, a value of formation constant log $K = -5.4$ (at $t$ = 25 °C and $I$ = 0 mol L$^{-1}$) was found. This means that we may predict the formation constant of the species $(UO_2)A(OH)^-$ to be log $\beta_{11-1}$ = 3.1 and 3.0 ($I$ = 0 mol L$^{-1}$) for glutamate and aspartate, respectively (log$\beta_{11-1}$ = 2.2 and 2.1 at $I$ = 0.5 mol L$^{-1}$). The confidence interval for these estimates (95 % confidence interval) was predicted to be ±0.4 log units.

**Table 9. Literature Data of the $UO_2$ Aspartate and $UO_2$ Glutamate Systems**

| ionic medium | $I$/mol L$^{-1}$ | t/°C | log $\beta_{110}$ | log $K_{111}$[a] | log $K_{122}$[b] | ref |
|---|---|---|---|---|---|---|
| | | $UO_2$ Aspartate System | | | | |
| $NaClO_4$ | 1 | 25 | | 2.41 | 4.14 | 17 |
| $NaClO_4$ | 0.1 | 30 | 8.71 | | | 20 |
| | 0.5 | 25 | 8.40 | | | 21 |
| | 0.5 | 25 | 8.62 | | | 21 |
| $NaClO_4$ | 0.1 | 30 | 8.34 | | | 22 |
| $NaClO_4$ | 0.1 | 40 | 8.93 | | | 22 |
| $NaClO_4$ | 0.1 | 50 | 10.40 | | | 22 |
| $KNO_3$ | 0.2 | 25 | | 2.61 | | 13 |
| KCl | 0.1 | 30 | 8.00 | | | 15 |
| | | $UO_2$ Glutamate System | | | | |
| $NaClO_4$ | 0.1 | 30 | 8.43 | | | 20 |
| $KNO_3$ | 0.1 | 25 | 8.25 | | 14.75 | 23 |
| $KNO_3$ | 0.2 | 25 | | 2.66 | | 13 |

[a] The equilibrium constant refers to the reaction $UO_2{}^{2+} + HA^- = (UO_2)AH^+$. [b] The equilibrium constant refers to the reaction $UO_2{}^{2+} + 2HA^- = (UO_2)(AH)_2{}^0$.

Literature data on the formation of $UO_2$ glutamate and aspartate complexes are reported in Table 9, where one can see that only mononuclear species were considered. As concerns the species $(UO_2)A^0$ and $(UO_2)AH^+$, the stability is comparable with that found in this work but with slightly higher formation constants. Literature data are given mostly in perchlorate and nitrate media, and this explains the significantly higher values of stability constants with respect to present data in the chloride medium. (See also, in ref 6, some consideration of the interaction of $Cl^-$ with $UO_2{}^{2+}$). Some authors report, for both amino acids, formation species having stoichiometric coefficients of the ligand of >1; these species can be formed in excess ligand for protonated species such as $(UO_2)(AH)_2{}^\circ$ (acidic range) or at pH values close to neutrality where the formation of hydroxo complexes is highly probable.

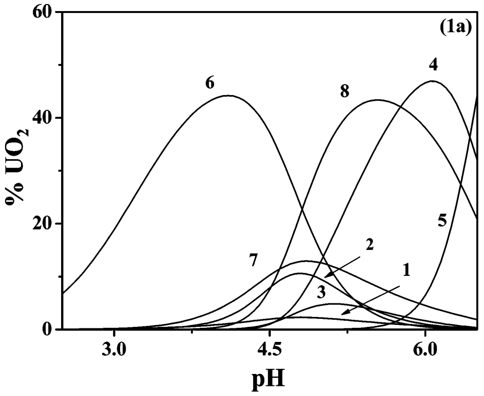
The stability of uranyl glutamate and aspartate complexes can also be compared with that of analogous complexes of other metal ions. Some formation constants for $Cu^{2+}$, $Ni^{2+}$, $Cd^{2+}$, and $Co^{2+}$ glutamate and aspartate complexes are reported in Table 10, where the stability trend $Cu^{2+} > UO_2{}^{2+} > Ni^{2+} > Cd^{2+} < Co^{2+}$, in accordance with the stability of analogous series,[2–5] can be observed.

Because the main purpose of this work is to contribute to the speciation studies of dioxouranium(VI), we must underline that the complexes of amino acids are generally strongly dependent on temperature. In fact, in a study at different temperatures Triverdi et al.[22] found (for the aspartate complex) log $\beta_{110}$ = 8.34, 8.93, and 10.40 at (30,

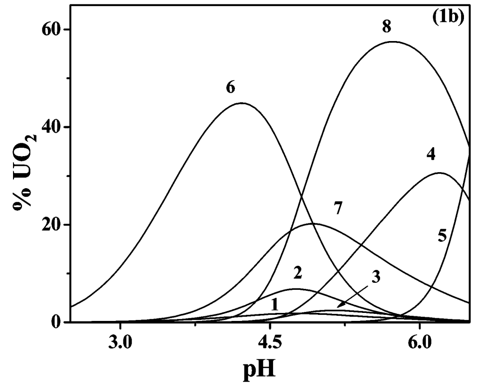
**Table 10. Literature Stability Constants[2–5] of Some Metal Glutamate and Aspartate Systems at $t$ = 25 °C and $I$ = 0.1 mol $L^{-1}$**

| metal ion | $\log \beta_{110}$ | $\log K_{111}$[a] |
|---|---|---|
| | M Glutamate Species | |
| $Cu^{2+}$ | 8.32 | 2.89 |
| $Ni^{2+}$ | 5.61 | |
| $Cd^{2+}$ | 3.8 | |
| $Co^{2+}$ | 4.56 | |
| | M Aspartate Species | |
| $Cu^{2+}$ | 8.89 | 2.92 |
| $Ni^{2+}$ | 7.16 | 1.52 |
| $Cd^{2+}$ | 4.35 | |
| $Co^{2+}$ | 5.95 | |

[a] The equilibrium constant refers to the reaction $M^{2+} + HA^- = MAH^+$.



$C_{NaCl}$ = 0.5 mol $L^{-1}$; $C_{UO_2}$ = 0.5 $10^{-3}$ mol $L^{-1}$
$C_{asp}$ = 2 $10^{-3}$ mol $L^{-1}$ (figure 1a)

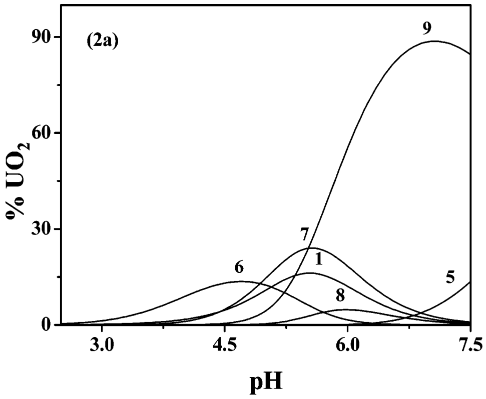


$C_{NaCl}$ = 0.5 mol $L^{-1}$; $C_{UO_2}$ = 0.5 $10^{-3}$ mol $L^{-1}$
$C_{glu}$ = 2 $10^{-3}$ mol $L^{-1}$ (figure 1b)

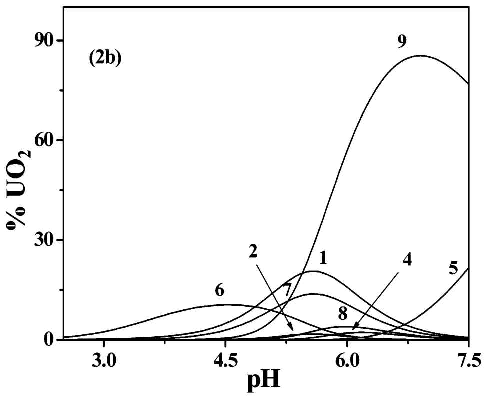
**Figure 1.** Distribution of species vs pH in the systems (a) $H^+–Na^+–UO_2^{2+}–asp^{2-}–Cl^-$ and (b) $H^+–Na^+–UO_2^{2+}–glu^{2-}–Cl^-$ at $t$ = 25 °C. Species: 1, $(UO_2)(OH)^+$; 2, $(UO_2)_2(OH)_2^{2+}$; 3, $(UO_2)_3(OH)_4^{2+}$; 4, $(UO_2)_3(OH)_5^+$; 5, $(UO_2)_3(OH)_7^-$; 6, $(UO_2)AH^+$; 7, $(UO_2)A^0$; 8, $(UO_2)_2A(OH)_2°$.

40, and 50) °C, respectively; if these data are correct (generally $\beta$ values are given with an error of <0.2 log units), then we have a temperature gradient of 0.1 log units/K. Direct calorimetric measurements are in progress in our laboratories to deal with this important problem.

***Speciation Profiles.*** In Figures 1a and b, the speciation diagrams of uranyl glutamate and aspartate species are shown. Under the simulated conditions (similar to the experimental ones), the main species are the monoprotonated $(UO_2)AH^+$ in the acidic pH range (more than 40 % yield for both $UO_2$ asp and $UO_2$ glu systems) and the mixed hydroxo species $(UO_2)_2A(OH)_2°$ at higher pH values (about 42 % and 58 % formation for $UO_2$ asp and $UO_2$ glu systems, respectively). The simple $(UO_2)A^0$ species arises at about 10 % and 20 % formation at pH ~4.8 in the $UO_2$ asp and $UO_2$ glu systems, respectively. Other simple $(UO_2)_p(OH)_q^{(2p-q)}$ hydroxo species are formed in accordance with the hydrolysis speciation model for $UO_2^{2+}$, which was previously reported.[6,7] The species distribution picture changes considerably if we consider a significantly lower concentration of uranyl ($10^{-6}$ mol $L^{-1}$) and a 10 times lower concentration of ligands (0.2 × $10^{-3}$ mol $L^{-1}$). In this case, we must take into account the formation of the predicted mixed hydroxo mononuclear species $(UO_2)A(OH)^-$ (see Formation and Stability of Complex Species) and the fact that the distribution diagrams change thoroughly (Figure 2a and b). Mononuclear species $(UO_2)A(OH)^-$ shows the highest formation percentage (~90 % at pH 7). In these last diagrams, the pH range is larger than that reported in the former ones to underline the importance of the $(UO_2)A(OH)^-$ species at higher pH.



$C_{NaCl}$ = 0.5 mol $L^{-1}$; $C_{UO_2}$ = $10^{-6}$ mol $L^{-1}$
$C_{asp}$ = 0.2 $10^{-3}$ mol $L^{-1}$ (figure 2a)



$C_{NaCl}$ = 0.5 mol $L^{-1}$; $C_{UO_2}$ = $10^{-6}$ mol $L^{-1}$
$C_{glu}$ = 0.2 $10^{-3}$ mol $L^{-1}$ (figure 2b)

**Figure 2.** Simulation of distribution of species vs pH in the systems (a) $H^+–Na^+–UO_2^{2+}–asp^{2-}–Cl^-$ and (b) $H^+–Na^+–UO_2^{2+}–glu^{2-}–Cl^-$ at $t$ = 25 °C. Species: 1, $(UO_2)(OH)^-$; 2, $(UO_2)_2(OH)_2^{2+}$; 3, $(UO_2)_3(OH)_4^{2+}$; 4, $(UO_2)_3(OH)_5^+$; 5, $(UO_2)_3(OH)_7^-$; 6, $(UO_2)AH^+$; 7, $(UO_2)A^0$; 8, $(UO_2)_2A(OH)_2°$; 9, $(UO_2)A(OH)^-$.

## Conclusions

The main final remarks of this work can be summarized as follows:

(i) Interactions of the dioxouranium(VI) ion with dicarboxylate amino acids were defined in the pH range that was investigated before the precipitation of uranium(VI) species of low solubility.

(ii) Owing to the strong hydrolysis of the $UO_2^{2+}$ cation in aqueous solution, mixed hydroxo species are formed in both $UO_2$ asp and $UO_2$ glu systems. The formation of the soluble $(UO_2)_2A(OH)_2^{\circ}$ species in the pH range immediately before the uranium oxides precipitation allowed us to extend the pH range of our investigations slightly.

(iii) For the first time, in this work interactions of $UO_2^{2+}$ with aspartic and glutamic acids were studied at different ionic strengths (NaCl) in order to investigate the dependence of the formation constants on ionic strength. The use of the SIT model allowed us to calculate the formation constant values at infinite dilution and the specific interaction coefficients.

(iv) Speciation profiles of $UO_2^{2+}$ in the presence of the two ligands, also for low cation concentrations, show considerable formation percentages of simple $(UO_2)A^0$, mixed protonated $(UO_2)AH^+$, and hydroxo $(UO_2)_2A(OH)_2^{\circ}$ species in the different pH ranges investigated.

(v) Because of the importance of speciation at low ligand and metal concentrations (natural fluid conditions) in which mononuclear hydroxo species are formed, we used an empirical predictive method to establish the stability of predicted species $(UO_2)A(OH)^-$ in the two systems investigated. We found log $\beta_{11-1}$ values of 2.2 and 2.1 ($I$ = 0.5 mol $L^{-1}$) for glutamate and aspartate ligands, respectively. As can be seen in the simulated distribution diagrams reported in Figure 2a and b, where we also extended the pH range up to 7.5, this species is the mean species at pH >6.

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