Journal of Physical & Theoretical Chemistry
Islamic Azad University of Iran 2 (1)
Science and Research Campus
ISSN: 1735-2126

Ionic Strength Dependence of Formation Constants, Complexation of Glycine with Dioxouranium (VI) Ion

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ABSTRACT

The dependence on ionic strength of protonation of glycine and its complexation with dioxouranium(VI) is reported in sodium perchlorate and sodium chloride solutions as background salts. 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 ≤ 1.0 mol dm^{-3} sodium perchlorate or sodium chloride.

Keywords: Ionic strength; complexation; Formation constant

INTRODUCTION

Uranium is a naturally occurring metal, which is wide speared in nature. It is present in ocean and certain types of soils and rocks. This metal is a trace constituent in rock phosphate, which is extensively used as a source of phosphorous for fertilizers and livestock feed supplements. Calcium phosphate, for example, a source of calcium used as an animal feeding supplement, can present concentrations of uranium as high as 200 ppm.[1] Thus, the investigation of the pathway, uranium (from feeding) → animal → human, is particularly important, as far as the radiological protection of the general population in concerned.

In previous works we have reported the complex formation for uranium(VI) ion with some α-amino acids and have demonstrated that the ligands bind to metal ion through the carboxylate group only, whereas the amino group, in the experimental conditions used, is protonated.[2-3] We had examined the coordination behavior of some amino acids, which have two carboxylic groups in the chain, in order to evaluate the influence of another group on the capacity of amino acids to form stable bonds to uranium ion. Complexation of the uranyl(VI) ion with aspartic and glutamic acids in aqueous solution was studied using spectrophotometric technique. We reported before, below pH 3.5 this ion was bound to one of the carboxylic groups only and at pH more than 3.5 hydrolysis of metal ion occurs. This result has also been confirmed by NMR studies.[4-5] However, the coordination behavior of uranyl(VI) ion with aspartic acid by solvent extraction technique suggests that, at pH 8, the binding of aspartate involves both carboxylate groups, but there is no uranyl-amino group interaction.[6]

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This work deals with the study of complexation of dioxouranium(VI) ion, UO_2^{+2}, with glycine in aqueous solution at 25 °C and different ionic media, 0.1 to 1.0 mol dm^{-3}, of sodium perchlorate and sodium chloride, using a combination of potentiometric and spectrophotometric techniques. The parameters which define this dependency were analyzed with the aim of obtaining further information with regard to their variation as a function of charges involved in the complex formation reaction. Moreover, a general equation was established for the dependence of formation constant on ionic strength. This equation gives the possibility of estimating a formation constant at a fixed ionic strength when its value is known at another ionic strength in the range 0.1 < ionic strength < 1.0 mol dm^{-3}, and therefore may make a significant contribution to solving many analytical and speciation problem.

EXPERIMENTAL SECTION

Chemicals. Glycine, (Merck, 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 (Merck) and its concentration was checked by several titrations with standard HCl. Perchloric acid, sodium perchlorate, sodium chloride, hydrochloric acid, and uranium(VI) acetate were supplied from Merck as analytical reagent grade materials and were used without further purification. Dilute perchloric and hydrochloric acid solutions were 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.[7]

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 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 GDU-20 computer and using thermostated matched 10 mm quartz cells. The measurement cell was of 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 or sodium chloride. The pH-meter was calibrated for the relevant H^+ concentration with a solution of 0.01 mol dm^{-3} perchloric or hydrochloric acid solution containing 0.09 mol dm^{-3} sodium perchlorate or sodium chloride (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 $-\log[H^+] = 2.00$.[8] 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 of hydrogen ion concentration of two different solutions of $HClO_4$ or HCl with sufficient $NaClO_4$ or NaCl solutions to adjust the ionic media.

Procedure. 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 glycine (containing a large excess of the ligand, 0.01 mol dm^{-3}), both in the same ionic strength. The $-\log[H^+]$ and absorbance were measured after addition of a few drops of titrant, and this procedure 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 ion all the measurements were performed at $-\log[H^+] < 3.5$. The complex $M_xH_yL_z^{(nx+y-z)+}$ 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 β_{xyz},[8-9]

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

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

The protonation constant of glycine 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 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 nonlinear least-squares method.[10] These values are listed in Table 1 together with the values reported in the literature, which are in good agreement with those reported before.[11-13]

Table 1. Protonation constants of the carboxylic, β_{011}, and the amino, β_{021}, groups of glycine at 25 °C and different ionic strengths, I, of $NaClO_4$ and NaCl together with the values reported in literature

ionic strength mol dm^{-3}	logβ_{011} ($NaClO_4$)	logβ_{011} (NaCl)	logβ_{021} ($NaClO_4$)	logβ_{021} (NaCl)	experimental conditions	ref.
0.1	2.43±0.04	2.41±0.03	9.80±0.06	9.77±0.08		this work
0.3	2.33±0.05	2.29±0.02	9.71±0.07	9.67±0.05		″
0.5	2.25±0.03	2.20±0.05	9.64±0.05	9.59±0.04		″
0.7	2.22±0.04	2.17±0.06	9.58±0.08	9.52±0.06		″
1.0	2.29±0.06	2.22±0.02	9.62±0.04	9.57±0.07		″
	2.44		9.68		0.1 M $NaNO_3$, 25 °C	11
	2.45		9.69		0.1 M $NaClO_4$, 30 °C	12
	2.45		9.75		1.0 M $NaClO_4$, 25 °C	13

The method of determination of the stability constant 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. Treatments of the spectrophotometric data (each 5 nm) obtained during the titrations as a function of the H^+ concentration was conducted to the computer program.[10] 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, glycine exists in its anionic forms (L^-), zwitterionic species (HL), and cationic form (H_2L^+). Considering the protonation constant of the amino acid, in acidic pH the predominant species for complexation is HL. In the computer program the following complexes were considered: MH_2L, MHL, ML, $M(H_2L)_2$, $M(HL)_2$, ML_2 (the charges are omitted for simplicity). Using the computer program [10] 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

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

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 MH_2L 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 UO_2HL^{+2} and $UO_2(HL)_2^{+2}$, resulted in a satisfactory numerical and graphical fitting. The average values of β_{111} and β_{122} for various wavelengths are listed in Table 2.

In Figure 1 the equilibrium distribution of various species for UO_2^{+2}+ glycine 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 1.4 and 3.5 the mole fractions of the proposed complexes have the maximum values.

Table 2. Average values of logβ_{111} and logβ_{122} of the system UO_2^{+2} + glycine for various wavelengths at 25 °C and different ionic strengths of $NaClO_4$ and NaCl together with the values reported in literature

ionic strength mol dm^{-3}	logβ_{111} ($NaClO_4$)	logβ_{111} (NaCl)	logβ_{122} ($NaClO_4$)	logβ_{122} (NaCl)	experimental conditions	ref.
0.1	7.89±0.09	7.81±0.11	9.62±0.10	9.55±0.11		this work
0.3	7.58±0.08	7.42±0.10	9.26±0.09	9.12±0.12		″
0.5	7.41±0.09	7.18±0.11	9.12±0.08	8.99±0.13		″
0.7	7.39±0.5	7.14±0.12	9.21±0.07	9.05±0.10		″
1.0	7.52±0.08	7.19±0.09	9.35±0.10	9.12±0.11		″
	-		2.14		0.1 M $NaClO_4$, 30 °C	12
	9.43		17.55		1.0 M $NaClO_4$, 25 °C	13

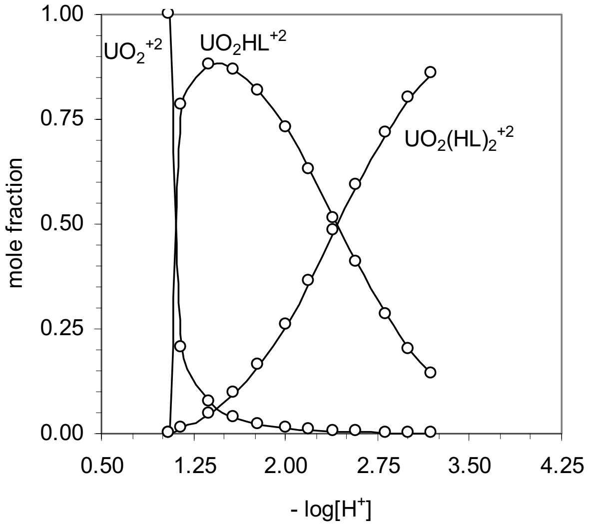

Fig. 1. The equilibrium distribution of the species in UO_2^{+2} + glycine system as a function of –log[H^+] at 25 °C and ionic strength 0.3 mol dm^{-3} sodium chloride.

Ionic strength and ionic medium dependence The dependence of the stability constants on ionic strength for the complex species can be described by a semi-empirical equation [2-3,14-15]

$$\log K(I) = \log K(I^*) - f(I) + CI \qquad (5)$$

where $f(I) = Z^*AI^{1/2}/(1 + BI^{1/2})$, K(I) and K(I*) are the stability constants of the actual and the reference ionic media, respectively. A is the parameter of Debye-Hückel equation, (A = 0.5115 at 25 °C), $Z^* = \sum(\text{charges})^2_{\text{reactants}} - \sum(\text{charges})^2_{\text{products}}$, C is an empirical parameter that its value is considered, and B is set equal to1.5 [16] (a small error in fixing B is absorbed in the linear term C [16]). Results of a series of investigations done by Daniele et al /17-18/, De Stefano et al /19-20/, and Gharib et al [2-3, 5, 14] showed that, when all the interactions occurring in the solution are considered, in the range 0 ≤ ionic strength ≤ 1, the empirical parameters are dependent on the stoichiometry of the formation reaction. If an approximate value of C is known, the stability constant can be determined for the variation of ionic strength from I* to I by the equation

$$\log K(I) = \log K(I^*) - f(I,I^*) + C(I - I^*) \qquad (6)$$

where

$$f(I,I^*) = Z^*A[I^{1/2}/(1+1.5I^{1/2}) - I^{*\,1/2}/(1+1.5I^{*1/2})] \qquad (7)$$

I and I* are the ionic strength of the solution by appropriate electrolyte. A preliminary analysis of the data showed that if a fixed value is assigned to C, the fit with eq 6 is not always good over the whole range of ionic strength from 0.1 to 1.0 mol dm^{-3}. This equation may be useful for small changes of ionic strength, but a better fit is obtained by adding a further term of the from $DI^{3/2}$ and EI^2 (D and E are another adjustable parameters). Therefore the data were fitted to the eq 8.

$$\log K(I) = \log K(I^*) - F(I,I^*) + C(I - I^*) + D(I^{3/2} - I^{*\,3/2}) + E(I^2 - I^{*2}) \qquad (8)$$

It is noticeable that the introduction of the term $D(I^{3/2} - I^{*\,3/2})$ or $E(I^2 - I^{*\,2})$ very often improves the goodness of the fit. For example, for the β_{111} in sodium perchlorate media, from eq 8 we obtained three sets of values depending on whether or not we take into account the term in D and E:

$C = -0.85$, $S = 2.33 \times 10^{-1}$

$C = -3.12$, $D = 2.54$, $S = 1.50 \times 10^{-3}$

$C = -2.50$, $D = 0.94$, $E = 0.99$, $S = 4.10 \times 10^{-4}$

The squares sum, S, shows that there is a significant improvement in the fit when D and E terms are introduced.

The parameters for the dependence on ionic strength (C, D, and E) were calculated by the fitting method and reported in Table 3. The empirical parameters obtained for NaCl media, Table 3, are different with respect to those in $NaClO_4$, and the stability constants in NaCl media are lower from those determined in $NaClO_4$, Tables 1 and 2. This suggesting the complexes of glycine+UO_2^{+2} is less stable in chloride than in perchlorate media.

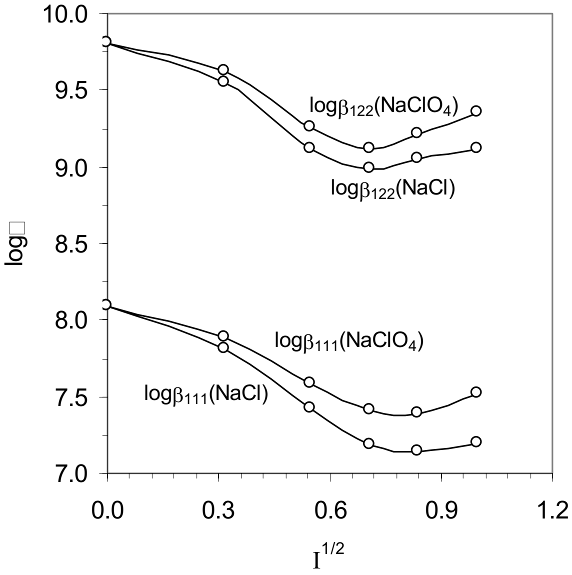

Fig. 2. Plots of logβ versus the square root of ionic strength of glycine + UO_2^{+2} at 25 °C

Table 3. The parameters for dependence on ionic strength for the studied systems in different background electrolytes, $NaClO_4$ and NaCl

species	C	D	E
β_{111} ($NaClO_4$)	- 2.50	0.94	0.99
β_{111} (NaCl)	- 3.78	2.74	0.15
β_{122} ($NaClO_4$)	- 3.20	2.51	0.24
β_{122} (NaCl)	- 4.75	5.46	-1.38

Figure 2 shows a good convergence of logβ to a single value at zero ionic strength in both media, i.e. the thermodynamic constant, which were calculated by the fitting method. The thermodynamic stability constants for $\log\beta_{111}$ and $\log\beta_{122}$ are 8.09 ± 0.09 and 9.81 ± 0.11, respectively.

The different electrolytes used to keep constant the ionic strength may influence the stability constant values in different ways. Indeed, the variation of the nature and the concentration of such electrolytes change the activity coefficient values and hence the formation constants. The effects of the ionic strength and the ionic medium on the values of the formation constants can be classified into two types: (a) the effects of changes in the activity coefficients, and (b) specific interactions. The nature of an ionic strength dependence that can be interpreted in terms of changes in the activity coefficients is related to the charges on the ionic species participating in the equilibrium. The stability constant values obtained in this work both in $NaClO_4$ and NaCl have adjusted to the same ionic strength, so the specific interactions, such as ion-pair formation /21/, should apparently be responsible for the observed differences in the formation constants.

The dependence of logβ on ionic strength determined in $NaClO_4$ and NaCl as background electrolytes, Fig. 2, show a regular trend and are in a good agreement with other complex species.[2-3, 5, 14, 17-20] Our previous results on ionic strength dependence of complex formation constants [2-3, 5, 14] and this work reveal the logβ values are nearly always at their minimum at an ionic strength range 0.3-0.7 mol dm^{-3}, that is a characteristic of the curve logβ = f(I), Figure 2. According to the theory of electrolytic solutions the $AI^{1/2}$ term in equation 8 accounts for ion-ion interaction, while the BI term accounts for disturbances in ion-solvent interaction. Consideration of A and B should therefore yield information about these interactions in the system studied. At low ionic strength, as the ions become separated, the solvent shell of each ion is freed of disturbances and the term BI becomes negligible, making logβ a linear function of $AI^{1/2}$. At higher ionic strength, on the other hand, the term due to the solvent interaction dominates the $AI^{1/2}$ term and logβ is a linear function of ionic strength.

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