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

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According to our knowledge, no work has been reported on the ionic strength dependence of dioxouranium(VI) + aspartic acid. This study deals with the complexation of dioxouranium(VI) ion with L-aspartic acid in an ionic strength range 0.1-1.0 mol dm^{-3} sodium perchlorate using a combination of potentiometric and spectrophotometric techniques. 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 ≤ 1.0 mol dm^{-3} sodium perchlorate.

Introduction

In previous work we reported the complexation of uranyl(VI) ion with glutamic acid at different ionic strengths 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(1). 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.

Experimental Section

Reagents. L-aspartic acid (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. Sodium perchlorate, perchloric acid, sodium hydroxide and uranium(VI)

acetate were obtained from E. Merck as analytical reagent grade materials and were used without further purification. Dilute perchloric acid solution was standardized against $KHCO_3$. In all experiments double-distilled water with specific conductance equal to (1.3 ± 0.1) $\mu S.cm^{-1}$ have been used.

Measurements

All measurements were carried out at (25 ± 0.1) °C. A 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}) was employed as a standard solution of hydrogen ion concentration. The same procedure was performed for the other ionic strengths. The calibration has been done for the whole pH(pH = -log[H$^+$]) range used. Spectrophotometric measurements were performed on a UV-vis Shimadzu 2101 spectrophotometer with an Acer Mate 486 SX/250 computer using thermostated, matched 10-mm quartz cells.

Results and Discussion

(a) Dissociation Constants

The dissociation equilibria of aspartic acid have been studied in different kinds of background electrolytes but there are no reports about the ionic strength dependence of the dissociation constants of aspartic acid. The dissociation constants, β_{031}, β_{021} and β_{011} have been determined using potentiometric techniques and calculated using Microsoft Excel 2000 program(1-3).

(b)Complexation of Dioxouranium(VI) with Aspartic Acid

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 aspartic acid (containing a large excess of the ligand, 0.01 mol dm^{-3}), both in the same ionic strength. The pH and absorbance were measured after addition of a few drops of titrant, and this procedure extended up to the required pH. In all cases the procedure was repeated at least three times. All measurements were performed at pH < 3.5. Spectrophotometric data obtained as a function of the concentration were conducted to the computer program. The program allows calculation of stability constants for different stoichiometry models and degree of refinement then guides the choice between models. In the computer program the following complexes considered: MH_2L, MHL, ML, $M(HL)_2$(The charges are omitted for simplicity). We used the Gauss-Newton nonlinear least –squares method in computer program to refine the absorbance by minimizing the error squares sum from eq 1:

$$U = \sum_i (a_i - b_i)^2 \qquad (i = 1,2,3,...) \qquad (1)$$

where a is a quasi-experimental quantity 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$_2$L 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$_2$HL$^+$ and UO$_2$(HL)$_2$, resulted in a satisfactory numerical and graphical fitting.

The dependence of the dissociation and stability constants on the ionic strength can be described according to the previous works (1-3):

$$\log \beta(I) = \log \beta(I_1) - AZ^*\left(\frac{I^{0.5}}{1+BI^{0.5}} - \frac{I_1^{0.5}}{1+BI_1^{0.5}}\right) + C(I - I_1) + D(I^{1.5} - I_1^{1.5})$$

$$(2)$$

where I and I_1 are the actual and reference ionic strengths, respectively and according to eq 3 :

$$M^{m+} + qL^{n-} + rH^+ \rightleftharpoons (M_pL_qH_r)^{pm-qn+r} \qquad (3)$$

$Z^* = pm^2 + qn^2 + r - (pm + qn + r)^2$ where m and n are the charges on the metal ion and the ligand respectively. Considering, A = 0.5115 and B = 1.489 eq 2 can be simplified :

$$\log \beta(I) = \log \beta(I_1) - Z^*\left(\frac{I^{0.5}}{2+3I^{0.5}} - \frac{I_1^{0.5}}{2+3I_1^{0.5}}\right) + C(I - I_1) + D(I^{1.5} - I_1^{1.5})$$

$$(4)$$

where C and D are empirical coefficients and their values were obtained by minimizing the error squares sum,(U), and the Gauss-Newton nonlinear least squares method in eq 1. The values of C and D are shown in Table 1. By using eq 4 and the values of C and D it is very easy to calculate the values of stability constants for this complex in the desired range of the ionic strength without any further experimental work. We have used $I_1 = 0.1$ as the reference ionic strength in order to obtain better consistency between experimental and calculated stability constants.

Table 1. Parameters for the Dependence on Ionic Strength of Dissociation
and Stability Constants of UO_2HL^+ and $UO_2(HL)_2$

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

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