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Ionic Strength Dependence of Formation Constants, Complexation of Molybdenum(VI) with Glutamic Acid

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The complexation of molybdenum(VI) with glutamic acid was investigated in aqueous solution ranging in pH from 4 to 9, using polarimetric and spectrophotometric techniques. The composition of the complex was determined by the continuous variations method. It was shown that molybdenum(VI) forms a mononuclear 1:1 complex with glutamic acid of the type MoO_3L^{-2} at pH 5.8. The protonation constants of glutamic acid (using the potentiometric technique) and the stability constant of the complex (using the spectrophotometric technique) were determined at 25 °C and at ionic strengths ranging from (0.1 to 1.0) mol dm^{-3} sodium perchlorate. The dependence of the protonation of glutamic acid and the stability constants of the complex on ionic strength is described by a Debye−Huckel-type equation.

Introduction

The stability constant of Mo(VI) complexes with some amino acids in aqueous solution has been determined by various authors using different techniques, but according to literature, no work has been reported on ionic strength dependence of these complexes. However, in a potentiometric study of molybdenum(VI) chelates with glutamic acid, Rabestein et al.[1] reported the stability constant at 25 °C and at ionic strength of 0.2 mol dm^{-3} KNO_3; Raymond et al.[2] have synthesized and proved the composition of the complex using the spectroscopic technique; and Gharib et al.[3] have proved the composition of glutamic acid complex and reported its stability constant, using the polarimetric and spectrophotometric techniques. In mentioned cases measurements were carried out at a fixed ionic strength, but in some other cases no special attempts were made to control the ionic strength. However, in all cases of constant ionic strength, some uncertainties are still present. This fact is due mainly to the uncertainties in numerical values of stability constants. For example, when maintaining two different ionic strengths, 0.1 and 1 mol dm^{-3} sodium perchlorate, we observed a difference of about 0.8 log unit in the stability constant of molybdenum chelate by glutamic acid.

The present paper describes the complexation of Mo(VI) with L-glutamic acid in an ionic strength range of (0.1 to 1.0) mol dm^{-3} sodium perchlorate. The parameters that define the dependence on ionic strength were analyzed with the aim of obtaining further information regarding to their variation as a function of the charges involved in the complex reaction. Moreover, a Debye−Huckel-type equation was established for the dependence of formation constants on ionic strength. This equation makes it possible to estimate a stability constant at a fixed ionic strength when its value is known at another ionic media in the range ($0.1 \leq I \leq 1.0$) mol dm^{-3}; therefore, the eauation may make a significant contribution solving many analytical and speciation problems.

Experimental Section

Reagents. Sodium perchlorate, perchloric acid, sodium hydroxide, sodium molybdate, and L-glutamic acid were obtained from E Merck as analytical reagent grade materials and were used without further purification. Dilute perchloric acid solution was standardized against $KHCO_3$. Dilute solutions were prepared from double-distilled water, with specific conductance equal to (1.3 ± 0.1) $\mu\Omega^{-1}cm^{-1}$.

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. A Horiba pH-meter, D-14, was used for pH measurements. The pH-meter had a sensitivity of 0.01 units. The hydrogen ion concentration was measured with a Horiba combination electrode, model S8720. A 1.00×10^{-2} 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.

Spectrophotometric measurements were performed on a UV−vis Shimadzu 2101 spectrophotometer with an Acermate 486 SX/250 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 potentiometric cell to the spectrophotometric cell so the absorbance and pH of the solution could be measured simultaneously. Polarimetric measurements were performed with an Atago model Polax-D polarimeter equipped with a sodium lamp. A water-jacketed cell of 200 mm length and 20 cm^3 total volume was used.

For each experiment (for both the spectrophotometric and the polarimetric methods), two solutions of Mo(VI) + L-glutamic acid were prepared with the same concentration,

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Table 1. Protonation Constants of the Amino, K_1, and the Second Carboxylic Acid Groups, K_2, of L-Glutamic Acid at Different Ionic Strengths, I, of $NaClO_4$

I/mol dm^{-3}	log K_2	log K_1	experimental condition	ref
0.1	4.24 ± 0.05	9.64 ± 0.05		this work
0.3	4.03 ± 0.05	9.27 ± 0.05		this work
0.5	3.76 ± 0.05	9.19 ± 0.05		this work
0.7	3.74 ± 0.05	9.04 ± 0.05		this work
1.0	3.60 ± 0.05	8.98 ± 0.05		this work
	4.15	9.49	I = 0.15 M, $NaClO_4$, t = 25 °C	3
	4.21	9.54	I = 0.1 M, $NaNO_3$, t = 25 °C	11
	4.05	9.46	I = 0.1 M, $NaClO_4$, t = 30 °C	12
	4.15	9.61	I = 0.1 M, KNO_3, t = 25 °C	13
	3.71	9.63	I = 0.1 M, $NaClO_4$, t = 30 °C	14

but the ionic strength of the first was maintained with sodium perchlorate, and that of the second, with sodium hydroxide or perchloric acid. The first solution was then titrated with the second. The pH and absorbance or optical activity 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, and the resulting average values and corresponding standard deviations are shown in the text and tables.

Results and Discussion

The protonation equilibria of glutamic acid have been extensively studied in different kinds of background electrolytes, and the results are reported in the literature. However, no studies have been performed on the ionic strength dependence of protonation constants of glutamic acid. The following equilibria were studied:

$$H^+ + L^{-2} \rightleftharpoons HL^- \quad K_1 = [HL^-]/[H^+][L^{-2}] \qquad (1)$$

$$H^+ + HL^- \rightleftharpoons H_2L \quad K_2 = [H_2L]/[H^+][HL^-] \qquad (2)$$

where L^{-2} represents the fully dissociated amino acid anion. The protonation constants of the amino, K_1, and the second carboxylic acid groups, K_2, of the side chain of the amino acid have been determined using potentiometric techniques and calculated using a computer program that employs a least-squares method.[4] These values are listed in Table 1 together with the values reported in the literature, which are in good agreement with those reported before.

Complexation of Molybdenum with Glutamic Acid. (1) Polarimetric Studies. Assuming that the optical activity of L-glutamic acid would change upon complexation, we performed polarimetric measurements to determine whether Mo(VI) is complexed by the ligand. Thus, we determined the optical rotations of various solutions of Mo(VI) + L-glutamic acid, as well as those of and L-glutamic acid alone with the same concentration but at different pH. The effect of pH on the optical rotation of such solutions is shown in Figure 1. As Figure 1 shows, when the pH is less than 7, the optical rotation of the Mo + glutamic acid solution becomes increasingly different from that of glutamic acid alone, indicating complexation by Mo. The difference reaches a maximum between pH 5 and pH 6 and decreases as the pH is decreased below 5, indicating that the largest amount of complex is formed in the pH range 5−6. At higher pH, the complex dissociates[5] as a result of the competitive formation of MoO_4^{-2},while at low pH values, isopolymolybdates are formed.[6]

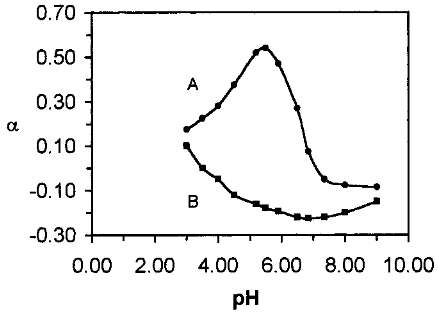

Figure 1. Effect of pH on optical rotation, α, of (A) [Mo(VI)] (0.03 mol dm^{-3}) + [L-glutamic acid] (0.03 mol dm^{-3}) and (B) [L-glutamic acid] (0.03 mol dm^{-3}).

Table 2. Continuous Variations Data for the Mo(VI) + L-Glutamic Acid System at pH 5.8, Wavelength 265 nm, and Ionic Strength 0.1 M $NaClO_4$

mole fraction of Mo(VI)	A[a]	mole fraction of Mo(VI)	A[a]
0.00	0.000	0.60	0.284
0.05	0.099	0.80	0.213
0.10	0.121	0.90	0.111
0.20	0.169	0.95	0.054
0.40	0.245	1.0	0.000
0.50	0.291		

[a] The corrected absorbance of [Mo(VI)] + [glutamic acid] = 0.02 mol dm^{-3}.

(2) Spectrophotometric Studies. Using the continuous variations method, we determined the absorbances of solutions of Mo(VI) and glutamic acid of total concentration 0.02 mol dm^{-3} in the UV range (260 to 265 nm) at a constant pH of 5.8. The observed absorbances were corrected for unreacted Mo, from eq 3, and are summarized in Table 2 and plotted in Figure 2.

$$A_c = A_{obs} - \epsilon_0[Mo] \qquad (3)$$

where A_c, A_{obs}, and ϵ_0 are the absorbance of the complex, the observed absorbance, and the molar absorp tivity of Mo, respectively. Values of ϵ_0 were calculated at the mole fraction of Mo equal to 1, and are shown in Table 3. In Figure 2 a rather sharp maximum at a mole fraction of Mo equal to 0.5 was obtained, indicating a 1:1 complex. The molar absorptivity of the complex, ϵ_1, was calculated from the linear part of the curve at a low mole fraction of Mo, where essentially all the metal ions were in the form of a complex. The molar absorptivities are listed in Table 3. At the maximum point of the plot, the concentration of the complex is

$$[C] = A_c/\epsilon_1 \qquad (4)$$

Raymond et al.[2] synthesized $Na[MoO_3(Glu)]H_2O$, among other molybdenum chelate complexes. The IR spectrum of this compound that was crystallized at pH = 6 shows the glutamate ion as a tridentate ligand coordinated to a *cis*-trioxo molybdenum core. A *cis*-dioxo molybdenum core was

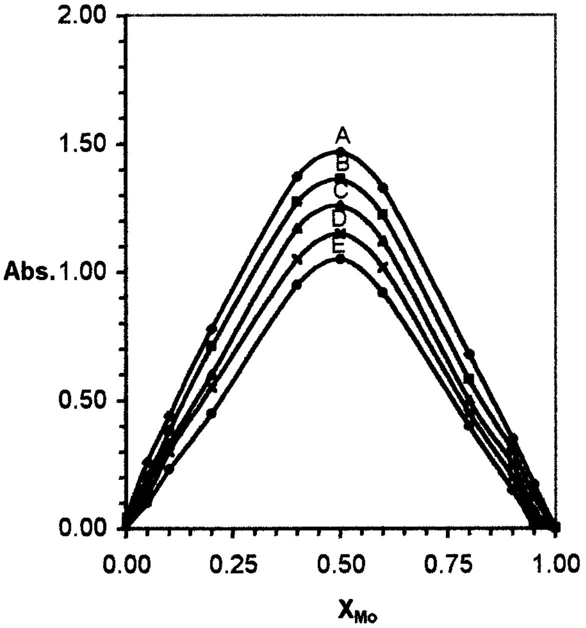

Figure 2. Continuous-variations plots of absorbances of MoO_3L^{-2}, abs, versus mole fraction of Mo(VI), x, at 260 nm, [Mo] + [glutamic acid] = 0.02 mol dm^{-3}, pH = 5.8, and different ionic strengths $NaClO_4$ of (A) 0.1, (B) 0.3, (C) 0.5, (D) 0.7, and (E) 1.0 mol dm^{-3}.

Table 3. Molar Absorptivities of Mo(VI), ϵ_0, and MoO_3L^{-2}, ϵ_1, at pH 5.8, Different Wavelengths, and Various Ionic Strengths, *I*, $NaClO_4$

	ϵ_0		ϵ_1	
I/mol dm^{-3}	260 nm	265 nm	260 nm	265 nm
0.1	183.5	163.5	273.5	98.8
0.3	176.9	158.5	285.1	109.5
0.5	175.9	156.6	268.1	94.4
0.7	180.1	160.6	269.9	97.4
1.0	186.9	160.2	265.1	98.8

formed with tetradentate ligands, and, in the case of glycine, with two bidentate ligands. The formation of a *cis*-trioxo Mo(VI) core requires two hydrogen ions:

$$MoO_4^{-2} + 2H^+ \rightleftharpoons MoO_3 + H_2O \tag{5}$$

whereas a *cis*-dioxo molybdenum(VI) species requires four:

$$MoO_4^{-2} + 4H^+ \rightleftharpoons MoO_2^{+2} + 2H_2O \tag{6}$$

If glutamic acid at a lower pH value has one of its ligating sites occupied by a hydrogen ion, it might be expected that a complex with two glutamic acid molecules per molybdate could be formed. However, Johansen and Jons[6] (1981) concluded that at pH 5.8, the composition of the complex indicated by the optical rotation and spectrophotometric measurements is MoO_3L^{-2}. The formation of a 1:1 complex with tridentate glutamic acid thus has Mo ligand proton equal to 1:1:2 stoichiometry as

$$MoO_4^{-2} + L^{-2} + 2H^+ \rightleftharpoons MoO_3L^{-2} + H_2O \tag{7}$$

with the stability constant, K_S, as:

$$K_S = \frac{[MoO_3L^{-2}]}{[MoO_4^{-2}][L^{-2}][H^+]^2} \tag{8}$$

Equations can be written for the total concentration of Mo, C_M, and the total concentration of the ligand, C_L, at the maximum point on the plot of Figure 2:

Table 4. Average Values of logK_S at pH 5.8, and Different Ionic Strengths, I, $NaClO_4$

I/mol dm^{-3}	log K_S	experimental condition	ref
0.1	17.54 ± 0.30		this work
0.3	16.94 ± 0.40		this work
0.5	16.93 ± 0.50		this work
0.7	16.84 ± 0.35		this work
1.0	16.76 ± 0.40		this work
	16.78	$I = 0.2$ M KNO_3, $t = 25$ °C	1
	16.73	$I = 0.15$ M $NaClO_4$, $t = 25$ °C	3

$$C_M = [Mo] + [C] \tag{9}$$

$$C_L = [L] + [C] \tag{10}$$

Combining eqs 4 and 9−10 in eq 8 and solving for K_S gives the stability constant of eq 7, and its values at different ionic strengths are shown in Table 4 together with the values reported in the literature.

The structure of sodium molybdate is tetrahedral in solid state and is believed to be octahedral in solution,[5] with three positions to form its complexes. On the other hand, glutamic acid is potentially a tridentate ligand toward metal ions, with three donor sites, on the terminal amino and carboxyl groups as well as on the second carboxyl group on the side chain of the molecule. Thus, Mo(VI) will bond with this tridentate ligand, and it seems unlikely that the complexes of 1:2 and 1:3 stoichiometry exist in the pH range 5 to 6.

The dependence of the stability constants on ionic strength can be described by a Debye−Huckel-type equation[7,8]

$$\log K_S(I) = \log K_S(I_1) - AZ^*\left(\frac{I^{0.5}}{1 + BI^{0.5}} - \frac{I_1^{\,0.5}}{1 + BI_1^{\,0.5}}\right) + C(I - I_1) + D(I^{1.5} - I_1^{\,1.5}) \tag{11}$$

where I and I_1 are the actual and reference ionic strengths, respectively, and according to eq 12

$$pM^{+m} + qL^{-n} + rH^+ \rightleftharpoons (M_pL_qH_r)^{pm+qn+r} \tag{12}$$

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

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

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

where t is the temperature in degrees Celsius,[9] eq 11 can be simplified at $t = 25$ °C as

$$\log K_S(I) = \log K_S(I_1) - Z^*\left(\frac{I^{0.5}}{2 + 3I^{0.5}} - \frac{I^{0.5}{}_1}{2 + 3I^{0.5}}\right) + C(I - I_1) + D(I^{\,1.5} - I_1^{\,1.5}) \tag{13}$$

where C and D are empirical coefficients, and their values were obtained by a regression method in a suitable computer program. These values shown in Table 5. We used the Gauss−Newton nonlinear least-squares method

Table 5. Parameters for the Dependence on Ionic Strength of Protonations and MoO_3L^{-2}

species	C	D	Z^*
K_1	−2.087	1.457	4
K_2	−0.706	0.380	2
MoO_3L^{-2}	−2.188	1.840	6

in a computer program to refine the parameters of eq 13 by minimizing the error squares sum from eq 14:

$$U = \sum_i (a_i - b_i)^2 \quad (i = 1, 2, 3, ...) \tag{14}$$

where a_i is a quasi-experimental quantity and b_i is a calculated one.

The dependences on ionic strength of log K_1, log K_2, and log K_S are shown in Tables 1 and 4, which are in agreement with the results obtained for other species.[10] Using the above values of C and D, from Table 5, one can rewrite eq 13 for K_1, K_2, and K_S as:

$$\log K_2 = 4.727 - \frac{I^{0.5}}{0.5 + 0.75I^{0.5}} - 0.706I + 0.38I^{1.5} \tag{15}$$

Equations 15−17 give the possibility of estimating the

$$\log K_1 = 10.017 - \frac{I^{0.5}}{0.5 + 0.15I^{0.5}} - 2.087I + 1.457I^{1.5} \tag{16}$$

$$\log K_S = 18.344 - \frac{I^{0.5}}{0.333 + 0.5I^{0.5}} - 2.188I + 1.84I^{1.5} \tag{17}$$

protonation and the stability constants of glutamic acid and its complex by molybdenum at each ionic strength in the range of ($0.1 \le I \le 1.0$).

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