Ionic Strength Dependence of Formation Constants: Complexation of Mo(VI) with Aspartic Acid

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The formation constants of species formed in the systems H^+ + Mo(VI) + aspartic acid and H^+ + aspartic acid have been determined in aqueous solution for $4 \leq pH \leq 9$ at 25 °C and different ionic strengths ranging from (0.1 to 0.8) mol dm^{-3} ($NaClO_4$), using polarimetric, spectrophotometric, and potentiometric 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 aspartic acid of the type MoO_3L^{-2} at pH = 5.8. The dependence of the protonation of aspartic acid and the stability constant of the complex on ionic strength is described by a Debye−Huckel-type equation, and finally the results have been compared with data previously reported.

Introduction

Aspartic acid is a compound that forms complexes with almost all metal ions. Recently, we published a paper on complexation of aspartic acid with molybdenum(VI) at a constant ionic strength.[1] By pursuing our systematic study on complexation of transition metal ions by natural and biological ligands, we thought it interesting to investigate the protonation and complexation of aspartic acid with Mo(VI) at different ionic strengths of sodium perchlorate.

In recent years considerable studies have been performed on the ionic strength dependence of the formation constants of some weak complexes of alkali and alkaline earth metals with some organic and inorganic ligands,[2−7] but little work has been reported for more stable complexes of α-amino acids with transition metal ions.[8−10]

On determining the stability constants of weak or strong complexes, there are always some uncertainties present. This fact is mainly due to the uncertainties in the numerical values of the stability constants. For example, when maintaining two different ionic strength of 0.1 and 0.4 mol dm^{-3} of sodium perchlorate, we observed a difference of about 0.9 log units in the stability constants of aspartic acid and Mo(VI).

The present paper describes the complexation of Mo(VI) with L-aspartic acid in the ionic strength range (0.1 to 0.8) mol dm^{-3} of sodium perchlorate. The parameters that define the dependence on ionic strength were analyzed with the aim of obtaining further information regarding 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 in another ionic medium in the range ($0.1 \leq I \leq 0.8$) mol dm^{-3} and therefore may give a significant contribution to solving many analytical and speciation problems.

Experimental Section

Reagents. Sodium perchlorate, perchloric acid, sodium hydroxide, sodium molybdate, and L-aspartic acid were obtained from E. Merck as analytical reagent grade materials and were used without further purification. The NaOH solution was prepared from titrisol solution, from Merck, and its concentration was determined by several titrations with standard $HClO_4$ solution. All 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 with sodium perchlorate. An Eyela pH-meter, PHM 2000, was used for pH measurements. The hydrogen concentration was measured with an Ingold UO 3234 glass electrode and an Ingold UO 3236 calomel electrode. The electrode and pH-meter were standardized before each use with Fisher pH 4.0 and 7.0 or 10.0 buffers, leading to estimated errors in the pH reading of ±0.01 pH units. Spectrophotometric measurements were performed on a UV−vis Shimadzu 2100 spectrophotometer with a GDU computer and using thermostated matched 10 mm quartz cells. The measurement cell was a 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 solutions could be measured simultaneously.

Polarimetric measurements were performed at (25 ± 0.1) °C 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-aspartic acid were prepared with the same concentration, but the ionic strength of the first was maintained with

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

I/mol dm^{-3}	log K_2	log K_1	experimental conditions	ref
0.1	3.88 ± 0.02	9.93 ± 0.05		this work
0.2	3.71 ± 0.02	9.71 ± 0.05		this work
0.4	3.58 ± 0.03	9.49 ± 0.05		this work
0.6	3.42 ± 0.03	9.42 ± 0.05		this work
0.8	3.56 ± 0.03	9.51 ± 0.05		this work
	2.881	9.771	$I = 2.25$ M, $NaNO_3$, $t = 25$ °C	12
	3.75	9.48	$I = 0.1$ M, $NaClO_4$, $t = 25$ °C	13
	3.70	9.62	$I = 0.1$ M, $NaNO_3$, $t = 25$ °C	14
	3.71	9.63	$I = 0.1$ M, $NaClO_4$, $t = 30$ °C	15
	3.79	9.75	$I = 0.1$ M, KNO_3, $t = 25$ °C	16

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 and corresponding standard deviations were shown in the text and tables.

Results and Discussion

The protonation constants of aspartic acid have been extensively studied in different kinds of background electrolytes, and the results are reported in the literature. The following equilibria were studied,

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

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

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.[11] The protonation constants, expressed as log K, are collected in Table 1 together with the values reported in the literature, which are in good agreement with those reported before.

If the values of protonation constants obtained here compare with the data for simple α-amino acids such as glycine or alanine, it can be said that the carboxylic acid groups in aspartic acid lead to a significant increase in protonation constant value for the amino group.

Complexation of Molybdenum(VI) with Aspartic Acid. (1) Polarimetric Studies. Assuming that the optical activity of L-aspartic 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-aspartic acid, as well as those of L-aspartic 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(VI) + aspartic acid solution becomes increasingly different from that of aspartic acid alone, indicating complexation by Mo(VI). The difference reaches a maximum between pH 5 and pH 6 and decrease 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[17] as a result of the competitive formation of MoO_4^{2-}, while, at low pH values, isopolymolybdates are formed.[18]

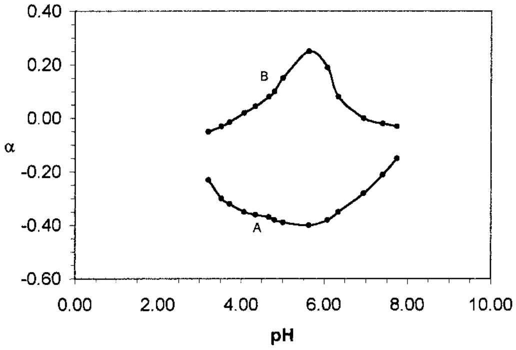


Figure 1. Effect of pH on optical rotation, α, of (A) [L-aspartic acid] (8.0 × 10^{-3} mol dm^{-3}) and (B) [Mo(VI)] (8.0 × 10^{-3} mol dm^{-3}) + [L-aspartic acid] (8.0 × 10^{-3} mol dm^{-3}), at 25 °C and ionic strength 0.1 mol dm^{-3} $NaClO_4$.

Table 2. Continuous Variations Data for the Mo(VI) + L-Aspartic Acid System at pH 5.8, Ionic Strength 0.1 mol dm^{-3} $NaClO_4$, and Different Wavelengths

mole fraction of Mo(VI)	A^a		
	260 nm	270 nm	280 nm
0.00	0.000	0.000	0.000
0.05	0.189	0.071	0.046
0.10	0.352	0.123	0.078
0.15	0.475	0.143	0.094
0.20	0.639	0.198	0.127
0.30	0.900	0.249	0.165
0.40	1.080	0.285	0.176
0.50	1.128	0.305	0.190
0.60	1.030	0.281	0.171
0.70	0.880	0.241	0.164
0.80	0.632	0.199	0.124
0.90	0.315	0.125	0.075
1.00	0.000	0.000	0.000

[a] The corrected absorbance of [Mo(VI)] + [aspartic acid] = 1.502 × 10^{-2} mol dm^{-3}.

Almost similar results were obtained for the system molybdenum(VI) + glutamic acid in our previous studies.[9] The small difference could be due to the formation of a sodium + aspartic acid complex.[19]

(2) Spectrophotometric Studies. Using the continuous variations method, we determined the absorbances of solutions of Mo(VI) and aspartic acid of total concentration 1.502 × 10^{-2} mol dm^{-3} in the UV range (260 to 280 nm) at a constant pH of 5.8. The observed absorbances were corrected for unreacted Mo(VI) from eq 3 and are listed in Table 2 and plotted in Figure 2

$$A_C = A_{obs} - \epsilon_0[Mo] \quad (3)$$

where A_C, A_{obs}, and ϵ_0 are the absorbance of the complex, the observed absorbance, and the molar absorptivity of Mo(VI), respectively. Values of ϵ_0 were calculated at the mole fraction of Mo(VI) equal to 1. In Figure 2 a rather

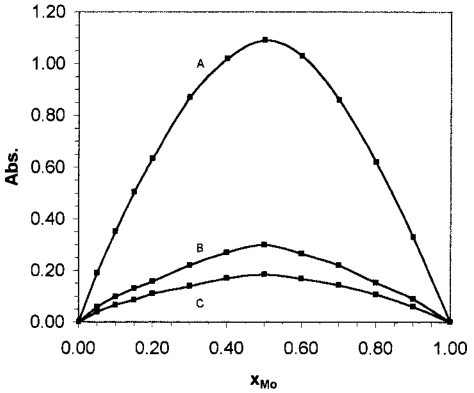


Figure 2. Continuous variations plots of absorbances of MoO_3L^{-2}, Abs, versus mole fraction of Mo(VI), x_{Mo}, at 25 °C, ionic strength 0.2 mol dm^{-3} $NaClO_4$, and different wavelengths: (A) 260, (B) 270, and 280 nm.

sharp maximum at a mole fraction of Mo(VI) 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 the complex. At the maximum point of the plot, the concentration of the complex is

$$[C] = A_C/\epsilon_1 \tag{4}$$

Raymond et al.[20] synthesized $Na[MoO_3(asp)]H_2O$, among other molybdenum chelate complexes. The IR spectrum of this compound that was crystallized at pH = 6 shows that aspartate ion as a tridentate ligand coordinated to a *cis*-trioxo molybdenum core. A *cis*-dioxo molybdenum core was formed with tetradentate ligands. Since Mo(VI) complexes generally contain either a MoO_2 or a MoO_3 core with the coordination sphere of the metal completed by coordination to four or three donor atoms, respectively, it seems unlikely that complexes of 1:2 and 1:3 stoichiometry exist in aqueous solution. However, Johansen and Jons[18] 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 aspartic acid, thus, has Mo/ligand/proton equal to 1:1:2 stoichiometry as

$$MoO_4^{2-} + L^{2-} + 2H^+ \leftrightarrows MoO_3L^{2-} + H_2O \tag{5}$$

with the stability constant, K_S, as

$$K_S = \frac{[MoO_3L^{2-}]}{[MoO_4^{2-}][L^{2-}][H^+]^2} \tag{6}$$

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:

$$C_M = [Mo] + [C] \tag{7}$$

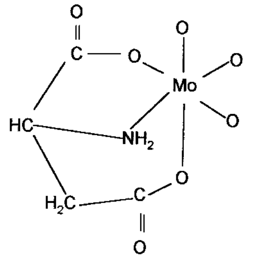
$$C_L = [L] + [C] \tag{8}$$

Combining eqs 4 and 7−8 in eq 6 and solving for K_S gives the stability constant of eq 5, and its values at different ionic strengths are shown in Table 3 together with the values reported in the literature.

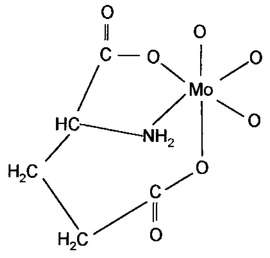
Table 3. Average Values of log K_S at pH 5.8 and Different Ionic Strengths, *I*, of $NaClO_4$

I/mol dm^{-3}	log K_S	experimental conditions	ref
0.1	18.7 ± 0.1		this work
0.2	18.5 ± 0.1		this work
0.4	17.8 ± 0.1		this work
0.6	18.1 ± 0.1		this work
0.8	18.3 ± 0.1		this work
	16.79	$I = 0.2$ M KNO_3, $t = 25$ °C	19
	18.2	$I = 0.15$ M $NaClO_4$, $t = 25$ °C	1

The structure of sodium molybdate is believed to be octahedral in solution,[17] with three positions to form its complexes with a tridentate ligand like aspartic or glutamic acid. These complexes usually have great stability constants to confirm this speculation (see Table 3). To specify which functional groups of the ligand are involved in complex formation, experiments were carried out with a simple amino acid at the same conditions as those for aspartic acid. No evidence for complex formation was found with L-alanine, which is potentially a bidentate ligand. An atomic model of aspartic acid shows that the tridentate structure **I** should be possible and suggests that the somewhat lower stability of Mo(VI) + L-glutamic acid, structure **II**, is due to a steric effect. The fact that the log K_S of Mo(VI) + glutamic acid is lower than that of Mo(VI) + aspartic acid (by about 1.2 log units[9]) indicates that aspartic acid probably coordinates with Mo(VI) as a six-membered ring between Mo(VI) and the β-carboxylic oxygen atom (more stable) and a seven-membered ring between Mo(VI) and the γ-carboxylic oxygen atom in the glutamic acid complex (less stable). The latter complex would probably be more strained and less favored, and a smaller log K_S value would be expected, that agrees with the present results.



structure I



Structure II

In our previous works,[8,9] complex formation of molybdenum(VI) and dioxovanadium(V) with glutamic acid and isoleucine was noted. The dependence of the protonation constants on ionic strength for the species H_jL can be described by a semiempirical equation

$$\log K_j(I) = \log K_j(I^*) - f(I) + CI \tag{9}$$

where

$$f(I) = z^* A I^{1/2}/(1 + B I^{1/2}) \tag{10}$$

and log $K_j(I)$ and log $K_j(I^*)$ are the protonation constants of the actual and the reference ionic strengths, respectively. *A* is the parameter of the extended Debye−Huckel equation ($A = 0.5115$ at 25 °C); $z^* = 1 + z_L^2 - jz_j$ (z_L and z_j are the charges on the anion and the species H_jL, respectively); *C* is an empirical parameter whose value is considered; and *B* is set[8] equal to 1.5 (a small error in fixing *B* is absorbed in the linear term *C*). If an approximate value of *C* is known† (†Under our conditions, a 10% error in *C* causes an error of 0.01 log units in the protonation constant.), the

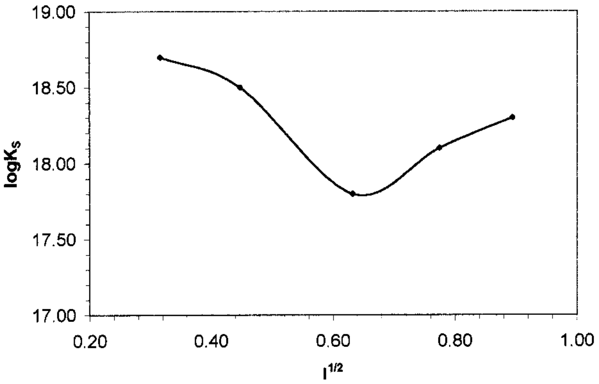


Figure 3. Plot of log K_S for MoO_3L^{-2} versus the square root of ionic strength.

Table 4. Parameters for the Dependence on Ionic Strength of the Protonation of Aspartic Acid and the Stability Constant of MoO_3L^{-2}

species	*C*	*D*	*z**
K_1	−2.70	2.63	4
K_2	−2.48	2.28	2
MoO_3L^{-2}	−5.89	6.21	6

protonation constants can be determined for the variation of ionic strength from I^* to I by the equation

$$\log K_j(I) = \log K_j(I^*) - f(I,I^*) + C(I - I^*) \quad (11)$$

where

$$f(I,I^*) = z^*A[I^{1/2}/(1 + 1.5I^{1/2}) - I^{*1/2}/(1 + 1.5I^{*1/2})] \quad (12)$$

where I or I^* is the ionic strength of the solution by $NaClO_4$.

The values of log K_j ($j = 1$ or 2 in our case) are reported in Table 1. The dependence of the protonation constants on ionic strength was then studied. A preliminary analysis of the data showed that if a fixed value is assigned to B, the fit with eq 9 is not always good over the whole range of ionic strength from 0.1 to 0.8 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 form $DI^{3/2}$ (D is another adjustable parameter). Therefore, the data were fitted to the equation

$$\log K_j(I) = \log K_j(I^*) - f(I,I^*) + C(I - I^*) + D(I^{3/2} - I^{*3/2}) \quad (13)$$

The values obtained for C and D are collected in Table 4. It is noticeable that the introduction of the term $D(I^{3/2} - I^{*3/2})$ very often improves the fit of the data. For example, for the protonation constant of aspartic acid, K_j ($j = 1$), from eq 13 we obtained two sets of values depending on whether we take into account the term in D:

$$C = -2.48\ \mathrm{mol^{-1}\,dm^3}, \quad D = 2.28\ (\mathrm{mol^{-1}\,dm^3})^{3/2}, \quad r = 0.99$$

$$C = -0.397\ \mathrm{mol^{-1}\,dm^3}, \quad D = 0.0, \quad r = 0.95$$

The correlation coefficients, r, show that there is a significant improvement in the fit when the D term is introduced.

We used the Gauss−Newton nonlinear least-squares method in a computer program[21] to refine the parameters C and D by minimizing the error squares sum from eq 14:

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

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

As can be seen from Table 4, the parameters which characterize the dependence of protonation constants on ionic strength show a regular trend and seem to be a function of the approximation of the z^* value.

The same procedure was applied for determining the dependence of the stability constant of the Mo(VI) + aspartic acid complex on ionic strength, where in this case $z^* = 2 + z_L^2 + z_M^2 - jz_c$, where z_M and z_c are the charges on the metal ion and the formed complex, respectively. The semiempirical parameters were determined as before and are shown in Table 4. The dependence of K_S is shown in Figure 3. This figure and Table 1 show that K_S and protonation constants have larger values at $I = 0.1$ and minima when the ionic strength approaches 0.4 for K_S and 0.6 mol dm^{-3} for protonation constants, which are in agreement with the results obtained for other species.

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