JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

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Investigation on the Complexation of Molybdenum(VI) with D-(−)-Quinic Acid at Different Ionic Strengths

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ABSTRACT: Potentiometric and UV spectroscopic measurements have been carried out to determine the stability constants for the complexation of the MoO_4^{2-} ion with D-(−)-quinic acid {(1*R*,3*R*,4*S*,5*R*)-(−)-1,3,4,5-tetrahydroxycyclohexane-1-carboxylic acid} in sodium chloride aqueous solutions for ionic strengths between (0.10 to 1.00) $\text{mol} \cdot \text{L}^{-1}$ of sodium chloride at $T = 298$ K. The Job method of continuous variations was applied for the determination of the metal-to-ligand ratio which was 1:1 at pH = 6.50. Extended Debye−Hückel type (EDH), specific ion interaction theory (SIT), and parabolic equations were investigated to derive the necessary ionic strength dependence parameters, and the results were justified.

INTRODUCTION

Molybdenum is required as a trace element by virtually all forms of life and is unique in being the only 4*d* transition metal utilized by biological systems.[1] The high concentration of Mo in seawater ($10^{-5}\ \text{g} \cdot \text{dm}^{-3}$) makes this element readily available for incorporation into biological systems, despite its relatively low terrestrial abundance.[1] Human metabolism involves several Mo enzymes, making Mo an essential trace element in our diet.[1] Because of the physiological relevance of molybdenum, its complexation behavior with organic ligands is of great interest for a better understanding of the interactions with biomolecules.

Quinic acid is an intermediate in the pathway of the synthesis of aromatic amino acids in plants and plays an important role in the regulation of energy metabolism in plants and belongs to the class of cyclitol.[2] The most important feature of cyclitol is that it is a chiral isomer, a key intermediate in the biosynthesis of aromatic compounds in living metabolism.

Several papers have been published regarding the stability constant determination for some transition metal complexes of aminopolycarboxylic acids and amino acids at different ionic strengths and in nonaqueous solutions in the past decade.[3−9] Therefore in this article the stability constants have been determined for the molybdenum(VI) complex with D-(−)-quinic acid at pH = 6.50, $T = 298$ K, and different ionic strengths of sodium chloride bearing in mind that there are no data about the above-mentioned stability constants.

EXPERIMENTAL SECTION

Reagents. Double-distilled water with a specific conductance equal to $(1.3 \pm 0.1)\ \mu\text{S} \cdot \text{cm}^{-1}$ was used to prepare the stock solutions. Sodium chloride, hydrochloric acid, sodium hydroxide, sodium molybdate, and sodium carbonate were purchased from Merck and D-(−)-quinic acid (Scheme 1) from Fluka and were used without further purification. All chemicals used were of analytical reagent grade. The NaOH solutions were prepared from titrisol solutions, and their concentration was determined by several titrations with standard HCl. The HCl solution was standardized with sodium carbonate solution.[9]

Measurements. All measurements were carried out at $T = 298$ K. A Metrohm pH meter, 827, was used for pH measurements. The hydrogen ion concentration was measured with a Metrohm combination electrode, model 6.0228.010. A 0.01 $\text{mol} \cdot \text{L}^{-1}$ hydrochloric acid solution containing 0.09 $\text{mol} \cdot \text{L}^{-1}$ sodium chloride (for adjusting the ionic strength to 0.10 $\text{mol} \cdot \text{L}^{-1}$) was used as a standard solution of hydrogen ion concentration. The same procedure was repeated for the other ionic strengths.[9] The calibration has been done for the whole pH ($\text{pH} = -\log[\text{H}^+]$) range used. The change in liquid junction potential[9] was calculated from eq 1

$$\text{pH(real)} = \text{pH(measured)} + a + b[\text{H}^+]\text{(measured)} \qquad (1)$$

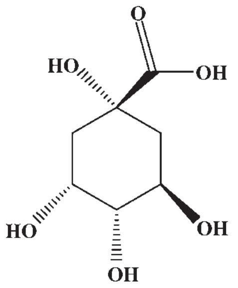
a and *b* were determined by the measurement of the hydrogen ion concentration for two different solutions of HCl with sufficient NaCl to adjust the ionic media.[9] Spectrophotometric measurements were performed with a Varian Cary 300 UV−vis spectrophotometer with a Pentium 4 computer between (245 and 280) nm in thermoregulated matched 10 mm quartz cells. The measurement cell was of the flow type. The circulation of the complex solution from the potentiometric cell to the spectrophotometric cell was possible by using a Masterflux pump. Therefore, the pH and absorbance of the solution could be measured simultaneously.

Measurements have been done for different metal−ligand concentrations and ligand−metal molar ratios, but the best results have been obtained with $C_L = 0.01$ and $C_M = 0.01\ \text{mol} \cdot \text{L}^{-1}$. A continuous variation method (Job method) has been used for solutions at different ionic strengths. It means that at first 11 solutions have been made (consist of metal + ligand + sodium chloride) for complex formation in which the mole fraction of Mo(VI) starts from 0 in the first solution and ends to 1 in the last solution. But all of these 11 solutions have the same ionic strength (for example $I = 0.1\ \text{mol} \cdot \text{L}^{-1}$, the ionic strength of these eleven solutions were maintained only with sodium chloride).

Received: March 18, 2011
Accepted: June 6, 2011
Published: June 21, 2011

dx.doi.org/10.1021/je2002754 | *J. Chem. Eng. Data* 2011, 56, 3194–3200

Scheme 1



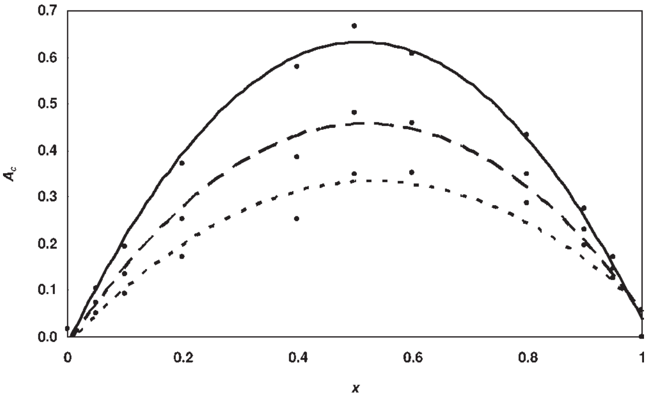


Figure 1. Corrected absorbance data, A_c, for MoO_3L^-, vs the mole fraction of Mo(VI), x, at T = 298 K, an ionic strength of 0.1 mol·kg^{-1} NaCl, and different wavelengths: solid line, 260 nm; long dashed line, 265 nm; and short dashed line, 270 nm. All of the lines have been obtained on the basis of the best fit to corrected absorbance data.

The concentration of Mo(VI) is different in each of these 11 solutions. Of course the concentration of Mo(VI) stock solution is constant in all of the experiments, and 11 solutions have been made from only one Mo(VI) stock solution. Then this experiment was repeated, but each time at different ionic strengths (0.1, 0.3, 0.5, 0.7, 1.0). So we have a series of solutions with different x_{metal} for each ionic strength. Also 11 other solutions have been prepared for adjusting the pH of the first 11 solutions which consist of metal + ligand + sodium hydroxide + sodium chloride, similar to the concentrations of the first 11 solutions. The ionic strength was maintained with sodium hydroxide + sodium chloride in these second 11 solutions. The pH of the first 11 solutions was adjusted with the second 11 solutions to 6.50. Using the continuous variations method, the corrected absorbances of the first 11 solutions of Mo(VI) + D-(−)-quinic acid complex at total concentration of 0.004 mol·L^{-1} in the UV range (260 to 270) nm at a constant pH = 6.50, and different ionic strengths have been calculated and gathered in Tables A1 to A5 in the Appendix and the plot in Figure 1 (for example, at I = 0.1 mol·kg^{-1}). In all cases, the procedure was repeated at least three times, and the resulting average values in the range of (260 to 265) nm and corresponding deviations from the average are shown in the text and tables.

RESULTS AND DISCUSSION

Dissociation Constants. One value of dissociation constant of D-(−)-quinic acid has been used in this research according to the following equilibrium

$$K = \frac{[H^+][L^-]}{[HL]} \quad HL \rightleftharpoons H^+ + L^- \tag{2}$$

Table 1. Dissociation Constants *K* of D-(−)-Quinic Acid at Different Ionic Strengths, *I*, of NaCl and *T* = 298 K

I mol·L^{-1}	I mol·kg^{-1}	log K (M)	log K (m)	ref
0.10	0.10	3.46 ± 0.03	3.47	this work
0.30	0.30	3.38 ± 0.04	3.40	this work
0.50	0.51	3.36 ± 0.01	3.39	this work
0.70	0.72	3.30 ± 0.04	3.35	this work
1.00	1.05	3.26 ± 0.01	3.33	this work
0.15		3.32		11[a]
		3.57		30

[a] NaCl.

The values of the dissociation constants which were obtained by using the potentiometric technique and the Microsoft Excel 2000 program[10] are gathered in Table 1 together with the literature values. Three titrations have been done for each ionic strength, and approximately 200 points have been used in the calculations at each ionic strength.[10]

Data Analysis. The equilibria of molybdenum(VI) in aqueous solution are complex, and various polynuclear species in addition to the monomeric species MoO_4^{2-}, $HMoO_4^-$, and H_2MoO_4 may exist in acidified molybdate solutions. The change in coordination number of molybdenum(VI) in monomeric molybdic acid has been discussed. An increase in the coordination number of Mo(VI) from 4 to 6 in the first step of the protonation of the molybdate ion has been pointed out. This conclusion was based on a slower recombination of H^+ with MoO_4^{2-} than expected for a diffusion-controlled reaction. On the other hand, from a consideration of the thermodynamic parameters for the protonation of molybdate, it has been suggested that only in the presence of a second proton are six-coordinate molybdate species to be expected. In most Mo(VI) complexes, MoO_2^{2+} or MoO_3 is the central coordinating unit, which with octahedral geometry, severely limits the number of coordination sites available to the ligands. The formation of a MoO_3 core requires two hydrogen ions:

$$MoO_4^{2-} + 2H^+ \rightleftharpoons MoO_3 + H_2O \tag{3}$$

but formation of the MoO_2^{2+} core requires four hydrogen ions:

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

MoO_4^{2-} will bind with D-(−)-quinic acid as a 1:1 complex on the basis of the literature,[2] and the results in Figure 1 in which we have maximum absorbance at the 1:1 metal-to-ligand ratio:

$$pMoO_4^{2-} + qH^+ + rL^- \rightleftharpoons MoO_3L^{(-2p+q-r)} + H_2O \tag{5}$$

$$\beta_{pqr} = \frac{[MoO_3L^{(-2p+q-r)}]}{[MoO_4^{2-}]^p[H^+]^q[L^-]^r} \tag{6}$$

For this complex formation reaction: p = 1, q = 2, and r = 1. Stability constants have been calculated at different ionic strengths by combination of the following equations according to our

Table 2. Average Experimental and Calculated Values of log β_{121} at pH = 6.50, 25 °C, and Different Ionic Strengths for the Complexation of Molybdenum(VI) with D-(−)-Quinic Acid

I	I	$\log \beta_{121}$ (M)		$\log \beta_{121}$ (m)	
$\text{mol}\cdot\text{L}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	exptl	calcd	exptl	calcd
0.10	0.10	16.45 ± 0.02	16.45 ± 0.00	16.48	16.48 ± 0.00
0.3	0.3	16.43 ± 0.03	16.36 ± 0.44	16.47	16.41 ± 0.43
0.50	0.51	16.26 ± 0.02	16.39 ± 0.97	16.32	16.45 ± 0.94
0.70	0.72	16.53 ± 0.06	16.44 ± 1.55	16.62	16.52 ± 1.53
1.00	1.05	16.50 ± 0.04	16.52 ± 2.52	16.63	16.65 ± 2.52

previous work[3,4,6]

$$A_c = A_{obs} - \varepsilon_0[\text{MoO}_4^{2-}] \tag{7}$$

$$[\text{MoO}_3\text{L}^{(-2p+q-r)}] = \frac{A_c}{\varepsilon_1} \tag{8}$$

$$C_M = [\text{MoO}_4^{2-}] + [\text{MoO}_3\text{L}^{(-2p+q-r)}] \tag{9}$$

$$C_L = [\text{ligand}] + [\text{MoO}_3\text{L}^{(-2p+q-r)}] \tag{10}$$

A_c, A_{obs}, and ε_0 are the corrected absorbance of the complex, the observed absorbance, and the molar absorptivity of MoO_4^{2-}, respectively. ε_0 values are calculated at $x_{metal} = 1.0$. The molar absorptivity values of the complex, ε_1, are calculated at a low mole fraction of the metal, where essentially all of the metal ions are in the form of a complex and $[\text{MoO}_3\text{L}^{(-2p+q-r)}]$ is the concentration of the complex.[3,4,6] $[\text{MoO}_3\text{L}^{(-2p+q-r)}]$ is calculated at $x_{metal} = 0.5$ where the maximum absorbance has been observed (for example at $I = 0.1$, Figure 1). Finally the values of $[\text{MoO}_3\text{L}^{(-2p+q-r)}]$, $[\text{MoO}_4^{2-}]$ and $[\text{L}^-]$ will be inserted in eq 6, and the stability constants are calculated; their values together with the literature values are shown in Table 2.

Comparison with Literature Data. Griffith prepared and characterized a 1:1 quinic acid compound with Mo(VI), and its structure was established by X-ray crystallography and ^{13}C- and ^{105}Mo-NMR spectroscopy.[2] There is an interaction between quinic acid and the metal ions[2,11] through the α-hydroxyacid group in C-1 and some stability constants are reported,[2,11] but the authors are not aware of any value for the stability constants of the complexation of the MoO_4^{2-} ion with D-(−)-quinic acid at different ionic strengths of sodium chloride in the literature. Therefore it is not possible to compare this work with the literature.

IONIC STRENGTH DEPENDENCE OF DISSOCIATION AND STABILITY CONSTANTS ACCORDING TO THE SIT, PARABOLIC, AND EDH MODELS

Many papers have been published in the literature about applications of the specific ion interaction theory (SIT) model for the ionic medium/ionic strength dependence of concentration equilibrium constants.[12−21] Sammartano et al.[20] proposed a modified version of the SIT approach, in which the specific coefficients are expressed as a function of I and formation of weak ion pairs have been taken into account; therefore the results were satisfactory in the whole range $0.1 < I/\text{mol}\cdot\text{kg}^{-1} < 6$.[22] Ciavatta[23] also proposed another expression for the ionic strength dependence of ε. Under our conditions $(0.10 < I/\text{mol}\cdot\text{kg}^{-1} < 1.05)$ only ion interaction coefficients between the participating ionic species and the ionic medium ions have been included. In this paper, the classic SIT model was used instead of the two parameter SIT model proposed in a previous paper by Sammartano et al.,[22] owing to the short ionic strength interval investigated here.[18] The activity coefficient γ_j of an ion j of charge z_j in a solution of ionic strength I may be described by the following equation on the basis of the classic SIT model[23,24]

$$\log \gamma_j = \frac{-z_j^2 0.509\sqrt{I}}{1 + 1.5\sqrt{I}} + \sum_k \varepsilon(j, k, I)m_k \tag{11}$$

The summation in eq 11 extends over all ions k present in solution at the molality m_k. All of the thermodynamic properties of an electrolyte solution can be calculated by establishing the activity coefficients of the electrolyte and their dependence on ionic medium, ionic strength, and temperature.[22] Therefore, the determination of the activity coefficients of aqueous electrolyte solutions is very important.[22] For correct application of the SIT, concentrations should be reported in the molal concentration scale. Molar ionic strengths have been converted to the molal scale according to the literature.[25] log β values were converted to the molal concentration scale according to the following equation[8]

$$\log \beta(m) = \log \beta(M) + \sum \nu \log(m/M) \tag{12}$$

where m and M stand for molality and molarity, respectively. $\sum \nu$ is the sum of stoichiometric coefficients of the reaction species. Equation 11, which is the basis of the SIT, is a simplified version of the Pitzer ion-interaction approach, neglecting triple interactions which are important only in very concentrated solutions and the interactions between ions of the same sign. The first term in eq 11 shows the nonspecific long-range contribution of the electrostatic region, and the second reflects the contribution due to short-range ion−ion, ion−neutral, or neutral−neutral interactions, in accordance with the Bronsted postulate that $\varepsilon\ (j, k) = 0$ if ions have the same charge sign. The rationale behind this is that ε, which describes specific short-range interactions, must be small for ions of the same charge since they are usually far from one another due to electrostatic repulsion. This holds to a lesser extent also for uncharged species.

The stability constant of $\text{MoO}_3\text{L}^{(-2p+q-r)}$, β_{pqr}, determined in an ionic medium (1:1 salt NaCl) of ionic strength I, is related to the corresponding value at zero ionic strength, β^0_{pqr}, by eq 13

$$\log \beta_{pqr} - \Delta z^2\text{DH} = \log \beta^0_{pqr} - \Delta\varepsilon I \tag{13}$$

where

$$\Delta z^2 = (-2p + q - r)^2 - (4p + q + r) \tag{14}$$

$$\text{DH} = \frac{0.509\sqrt{I}}{1 + 1.5\sqrt{I}} \tag{15}$$

$$\begin{aligned}\Delta\varepsilon = {} & \varepsilon(\text{MoO}_3\text{L}^{(-2p+q-r)}, \text{Na}^+ \text{ or } \text{Cl}^-) \\ & - \varepsilon(\text{MoO}_4^{2-}, \text{Na}^+) - q\varepsilon(\text{H}^+, \text{Cl}^-) - \varepsilon(\text{L}^-, \text{Na}^+)\end{aligned} \tag{16}$$

Equilibria involving $\text{H}_2\text{O(l)}$ as a reactant or product require a correction for the activity of water.[24] In the presence of an ionic medium NX in dominant concentration and by neglecting the

Table 3. Values of Osmotic Coefficients, φ, and Water Activities, a, at Different Ionic Strengths

I	I		
$\text{mol}\cdot\text{L}^{-1}$	$\text{mol}\cdot\text{kg}^{-1}$	φ	a
0.10	0.10	−0.59	1.00
0.30	0.30	0.14	1.00
0.50	0.51	0.37	0.99
0.70	0.72	0.48	0.99
1.00	1.05	0.60	0.98

contributions of all minor species, that is, the reacting ions, it is possible to calculate the activity of water for a 1:1 electrolyte of ionic strength $I_m \cong m_{\text{NX}}$:[24]

$$\log a_{\text{H}_2\text{O}} = \frac{-2m_{\text{NX}}\varphi}{(\ln 10)55.51} \qquad (17)$$

φ is the osmotic coefficient of the mixture. Values of osmotic coefficients for single electrolytes have been compiled by various authors. In the presence of an ionic medium $\text{N}_{\nu+}\text{X}_{\nu-}$ of a concentration much larger than those of the reacting ions, the osmotic coefficient can be calculated according to eq 18:[24]

$$1-\varphi = \frac{A(\ln 10)|z_+z_-|}{I_m(Ba_j)^3}\left[1+Ba_j\sqrt{I_m} - 2\log(1+Ba_j\sqrt{I_m}) - \frac{1}{1+Ba_j\sqrt{I_m}}\right] - (\ln 10)\varepsilon_{(\text{N,X})}m_{\text{NX}}\left(\frac{\nu_+\nu_-}{\nu_+ + \nu_-}\right) \qquad (18)$$

where ν_+ and ν_- are the number of cations and anions in the salt formula ($\nu_+z_+ = \nu_-z_-$). $\varepsilon_{(\text{N,X})} = 0.03 \pm 0.01$ for NaCl; $A = 0.509\ \text{kg}^{0.5}\cdot\text{mol}^{-0.5}$; $Ba_j = 1.5\ \text{kg}^{0.5}\cdot\text{mol}^{-0.5}$.[24] The activities of water at different ionic strengths have been obtained by inserting eq 18 into eq 17. The values of osmotic coefficients together with water activities at different ionic strengths have been gathered in Table 3. Therefore, according to Table 3, we can justify the approximation that in experimental studies of equilibria in dilute aqueous solutions, where an ionic medium is used in large excess with respect to the reactants, the activity of water is near constant and equal to 1.[24] According to eq 14, $\Delta z^2 = -6$ for the MoO_3L^-complex.[24] The linear regression (Figure 2) was done on the basis of eq 13, and the value of $\Delta\varepsilon = -0.78 \pm 0.43$ has been obtained for MoO_3L^-. $\varepsilon\ (\text{H}^+, \text{Cl}^-) = (0.12 \pm 0.01)\ \text{kg}\cdot\text{mol}^{-1}$;[24] thus, the following equation is valid[8]

$$\varepsilon(\text{MoO}_3\text{L}^-, \text{Na}^+) - \varepsilon(\text{MoO}_4{}^{2-}, \text{Na}^+) = -0.54 \pm 0.43 \quad (19)$$

The value of $\log \beta^0{}_{121} = 17.08 \pm 0.27$ has been obtained on the basis of Figure 2.

The parabolic model has also been applied to the dependence of metal complex formation and dissociation constants on ionic strength[3]

$$\log \beta_{pqr} - \Delta z^2 DH = \log \beta^0_{pqr} - \Delta\varepsilon I - \Delta\delta_i I^2 \qquad (20)$$

The parabolic model with two coefficients is satisfactory for ionic strengths to $I = 14\ m$.[26] The parabolic model because of its advantages in mathematical simplicity and its less-parametrized nature is comparable to the Pitzer model in many cases.

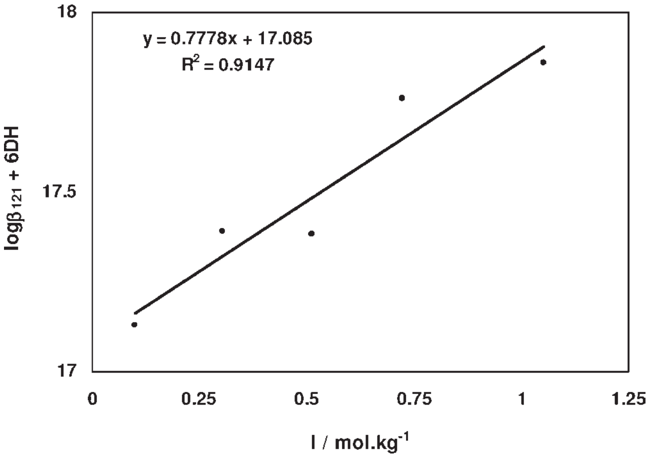


Figure 2. Plot of $\log \beta_{121} + 6\text{DH}$ for MoO_3L^- versus ionic strength on the basis of the SIT model.

Table 4. Parameters for the Dependence on the Ionic Strength of Dissociation and Stability Constants at 25 °C

	C	D		
species	$\text{kg}\cdot\text{mol}^{-1}$	$\text{kg}^{1.5}\cdot\text{mol}^{-1.5}$	Z^*	ref
K	0.22 ± 0.11	-0.15 ± 0.11	2	this work
MoO_3L^-	1.15 ± 1.27	-0.34 ± 1.25	6	this work

Table 5. Values of $\log \beta^0{}_{121}$, $\Delta\varepsilon$, $\Delta\delta$, and R^2 According to Debye−Hückel, SIT, and Parabolic Models

			$\Delta\varepsilon$	$\Delta\delta$	
species	model	$\log\beta^0{}_{121}\ (m)$	$\text{kg}\cdot\text{mol}^{-1}$	$\text{kg}^2\cdot\text{mol}^{-2}$	R^2
MoO_3L^-	Debye−Hückel	16.50 ± 0.10			0.49
MoO_3L^-	SIT	17.08 ± 0.27	-0.78 ± 0.43		0.92
MoO_3L^-	parabolic	17.04 ± 0.19	-1.03 ± 0.30	0.21 ± 0.10	0.92

The dependence of the dissociation and stability constants on ionic strength according to the extended Debye−Hückel-type equation (EDH) can be described as follows[27−29]

$$\log \beta(I) = \log \beta(I_1) - Z^*\left(\frac{I^{0.5}}{1.955 + 2.91I^{0.5}} - \frac{I_1{}^{0.5}}{1.955 + 2.91I_1{}^{0.5}}\right) + C(I - I_1) + D(I^{1.5} - I_1{}^{1.5}) \qquad (21)$$

where I and I_1 are the actual and reference ionic strengths, respectively, and according to reaction 3, $Z^* = 4p + q + r - (-2p + q - r)^2$. The classical Debye−Hückel model takes only into account electrostatic interactions between ions of opposite charge and is able to give a quantitative description of the variation of $\log \gamma_\pm$ versus $I^{0.5}$, as the ionic strength approaches zero. For $I < 2\ \text{mol}\cdot\text{L}^{-1}$ it was not necessary to include the EI^2 quadratic term in eq 21. C and D are empirical coefficients, and their values were obtained by minimizing the error squares sum (U) using the Gauss−Newton nonlinear least-squares method in

Table 6. Values of $\log K^0$, $\Delta\varepsilon$, $\Delta\delta$, and R^2 According to Debye−Hückel, SIT, and Parabolic Models

species	model	$\log K^0$ (m)	$\Delta\varepsilon$ $\text{kg}\cdot\text{mol}^{-1}$	$\Delta\delta$ $\text{kg}^2\cdot\text{mol}^{-2}$	R^2
K	Debye−Hückel	3.49 ± 0.01			0.98
K	SIT	3.70 ± 0.04	-0.05 ± 0.06		0.72
K	parabolic	3.68 ± 0.01	-0.15 ± 0.03	0.08 ± 0.04	0.90

the Excel 2000 program:

$$U = \sum_i (a_i - b_i)^2 \qquad (i = 1,\ 2,\ 3, \ldots) \tag{22}$$

where a_i is an empirical parameter and b_i is a calculated one. Sammartano et al. defined C as an empirical parameter that can be expressed as a function of ionic strength.[19] The values of C and D are shown in Table 4. The values of C and D have been inserted in eq 21, then the values of the calculated stability constants have been determined according to EDH, and their values are gathered in Table 2. We have used $I_1 = 0.1$ as the reference ionic strength to obtain better consistency between experimental and calculated stability constants.

Values of $\log \beta^0{}_{121}$, $\log K^0$, $\Delta\varepsilon$, $\Delta\delta$, and R^2 on the basis of EDH, SIT, and parabolic models for the MoO_3L^- and the dissociation constants are summarized in Tables 5 and 6.

CONCLUSIONS

One chelate (five-member) exists for the complexation of Mo(VI) with D-(−)-quinic acid according to the literature;[2] therefore, it seems that the stability constant values obtained in this work are reasonable. In our previous work on the complexation of Mo(VI) with methyliminodiacetic acid larger stability constants were obtained regarding the fact that two chelates (five-member) were formed.[3] In this research the stability constant values go through a minimum at $I = 0.5$, but we do not have significant changes between $I = 0.1$ and $I = 0.3$ and also between $I = 0.7$ and $I = 1.0$ $\text{mol}\cdot\text{L}^{-1}$ of sodium chloride. EDH, SIT, and parabolic models are the same expression of a more general polynomial function of $I^{0.5}$, where

$$\log \beta - \Delta z^2 \text{DH} = a + bx + cx^{1.5} + dx^2 \qquad a = \log \beta^0$$

$$\text{for EDH}: b = C,\ c = D,\ \text{and}\ d = E$$

$$\text{for SIT}: b = \Delta\varepsilon,\ c = d = 0$$

$$\text{for parabolic}: b = \Delta\varepsilon,\ d = \Delta\delta$$

So, in this work, considering $D = 0$ and refining E, EDH model is equal to parabolic. Analogously, for $D = E = 0$, EDH is equal to SIT.

In the light of the above considerations, EDH model gives, in this case, better results considering refining E instead of D. The medium dependence is described by ion-interaction coefficients in the SIT model. $\Delta\varepsilon$ values on the basis of SIT and parabolic models are more or less similar to each other. Values of C and D show the extent of the interaction between complex or ligand species and the other ions in the solution, mainly cations of the background salt. According to Table 4, the ligand and MoO_3L^- have different interactions with the background salt ions.

APPENDIX

Tables A1 to A5 are shown here.

Table A1. Corrected Absorbance, A_c, Data for the Mo(VI) + D-(−)-Quinic Acid System at T = 298 K, pH = 6.50, I = 0.10 $\text{mol}\cdot\text{kg}^{-1}$, and Different Wavelengths

mole fraction of Mo(VI)	A_c		
	260 nm	260 nm	270 nm
0.00	0.0181	0.0172	0.0165
0.05	0.1027	0.0723	0.0515
0.10	0.1942	0.1338	0.0921
0.20	0.3722	0.2532	0.1706
0.40	0.5782	0.3850	0.2518
0.50	0.6676	0.4812	0.3500
0.60	0.6077	0.4586	0.3520
0.80	0.4327	0.3492	0.2874
0.90	0.2765	0.2308	0.1956
0.95	0.1721	0.1465	0.1256
1.00	0.0000	0.0000	0.0000

Table A2. Corrected Absorbance, A_c, Data for the Mo(VI) + D-(−)-Quinic Acid System at T = 298 K, pH = 6.50, I = 0.30 $\text{mol}\cdot\text{kg}^{-1}$, and Different Wavelengths

mole fraction of Mo(VI)	A_c		
	260 nm	265 nm	270 nm
0.00	0.0133	0.0126	0.0114
0.05	0.0976	0.0686	0.0482
0.10	0.1838	0.1242	0.0837
0.20	0.3511	0.2339	0.1530
0.40	0.5331	0.3515	0.2264
0.50	0.6325	0.4519	0.3253
0.60	0.5700	0.4280	0.3269
0.80	0.3885	0.3132	0.2565
0.90	0.2634	0.2155	0.1794
0.95	0.1641	0.1384	0.1183
1.00	0.0000	0.0000	0.0000

Table A3. Corrected Absorbance, A_c, Data for the Mo(VI) + D-(−)-Quinic Acid System at T = 298 K, pH = 6.50, I = 0.51 $\text{mol}\cdot\text{kg}^{-1}$, and Different Wavelengths

mole fraction of Mo(VI)	A_c		
	260 nm	265 nm	270 nm
0.00	0.0225	0.0220	0.0209
0.05	0.1142	0.0853	0.0651
0.10	0.1970	0.1380	0.0973
0.20	0.3517	0.2353	0.1551
0.40	0.5527	0.3679	0.2406
0.50	0.6873	0.5040	0.3748
0.60	0.6657	0.5186	0.4105
0.80	0.4828	0.4014	0.3371
0.90	0.3302	0.2813	0.2414
0.95	0.2045	0.1785	0.1556
1.00	0.0000	0.0000	0.0000

Table A4. Corrected Absorbance, A_c, Data for the Mo(VI) + D-(−)-Quinic Acid System at T = 298 K, pH = 6.50, I = 0.72 $mol \cdot kg^{-1}$, and Different Wavelengths

mole fraction of Mo(VI)	A_c		
	260 nm	265 nm	270 nm
0.00	0.0194	0.0191	0.0177
0.05	0.1018	0.0722	0.0508
0.10	0.1888	0.1301	0.0893
0.20	0.3177	0.2139	0.1419
0.40	0.5866	0.3912	0.2564
0.50	0.6864	0.5018	0.3715
0.60	0.6381	0.4922	0.3857
0.80	0.4546	0.3772	0.3166
0.90	0.3177	0.2693	0.2304
0.95	0.1950	0.1686	0.1467
1.00	0.0000	0.0000	0.0000

Table A5. Corrected Absorbance, A_c, Data for the Mo(VI) + D-(−)-Quinic Acid System at T = 298 K, pH = 6.50, I = 1.05 $mol \cdot kg^{-1}$, and Different Wavelengths

mole fraction of Mo(VI)	A_c		
	260 nm	265 nm	270 nm
0.00	0.0190	0.0176	0.0156
0.05	0.0973	0.0686	0.0480
0.10	0.1831	0.1244	0.0835
0.20	0.3425	0.2274	0.1488
0.40	0.5423	0.3586	0.2328
0.50	0.6491	0.4674	0.3388
0.60	0.5853	0.4436	0.3410
0.80	0.3920	0.3184	0.2627
0.90	0.2644	0.2164	0.1798
0.95	0.1596	0.1333	0.1126
1.00	0.0000	0.0000	0.0000

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ACKNOWLEDGMENT

The authors gratefully acknowledge Prof. Paul L. Brown for providing information about the molarity to molality conversion in different ionic media.

REFERENCES

(1) Bertini, I.; Gray, H. B.; Stiefel, E. I.; Valentine, J. S. Biological Inorganic Chemistry. *Structure and Reactivity*, 1st ed.; University Science Books: Sausalito, CA, 2007.

(2) Dengel, A. C.; Griffith, W. P.; Powell, R. D.; Skapski, A. C. Studies on Transition-metal Peroxo Complexes. Part 7. Molybdenum(VI) and Tungsten(VI) Carboxylato Peroxo Complexes, and the *X*-ray Crystal Structure of $K_2[MoO(O_2)_2(glyc)] \cdot 2H_2O$. *J. Chem. Soc., Dalton Trans.* **1987**, 991–995.

(3) Majlesi, K.; Gholamhosseinzadeh, M.; Rezaienejad, S. Interaction of Molybdenum(VI) with Methyliminodiacetic Acid at Different Ionic Strengths by Using Parabolic, Extended Debye-Hückel and Specific Ion Interaction Models. *J. Solution Chem.* **2010**, *39*, 665–679.

(4) Majlesi, K.; Momeni, N. Complexation of Molybdenum(VI) with Ethylenediaminediacetic Acid in Different Water + Methanol Solutions. *J. Chem. Eng. Data* **2009**, *54*, 2479–2482.

(5) Majlesi, K.; Rezaienejad, S. Application of the Parabolic Model, Specific Ion Interaction, and Debye-Hückel Theories for the Complexation of Dioxovanadium(V) with Ethylenediamine-*N*,*N*′-diacetic Acid. *J. Chem. Eng. Data* **2009**, *54*, 1483–1492.

(6) Majlesi, K.; Rezaienejad, S. Application of Specific Ion Interaction Theory and Parabolic Models for the Molybdenum(VI) and Tungsten(VI) Complexes with NTA and IDA at Different Ionic Strengths. *Chin. Chem. Lett.* **2009**, *20*, 759–762.

(7) Majlesi, K.; Rezaienejad, S. Solvatochromic Effect Studies on the Stability of Dioxovanadium(V) Complexes with Ethylene glycol-bis(2-aminoethylether)-*N*,*N*,*N*′,*N*′-tetraacetic Acid in Different Water + Methanol Mixtures. *J. Chem. Eng. Data* **2010**, *55*, 4491–4498.

(8) Majlesi, K.; Rezaienejad, S. Complexation of Dioxovanadium(V) with Methyliminodiacetic Acid in $NaClO_4$ Aqueous Solutions at Different Ionic Strengths by Using an Extended Debye-Hückel Equation, Specific Ion Interaction Theory, and Parabolic Equations. *J. Chem. Eng. Data* **2010**, *55*, 882–888.

(9) Majlesi, K.; Rezaienejad, S.; Rouhzad, A. Ionic Strength Dependence of Dioxovanadium(V) Complexation with Ethylene Glycol-bis(2-aminoethylether)-*N*,*N*,*N*′,*N*′-tetraacetic Acid. *J. Chem. Eng. Data* **2011**, *56*, 541–550.

(10) Billo, J. E. *Excel for Chemists*, 2nd ed.; John Wiley & Sons: New York, 2001.

(11) Allegretti, Y.; Ferrer, E. G.; Gonzalez Baro, A. C.; Williams, P. A. M. Oxovanadium (IV) Complexes of Quinic Acid. Synthesis, Characterization and Potentiometric Study. *Polyhedron* **2000**, *19*, 2613–2619.

(12) Crea, P.; De Stefano, C.; Millero, F. J.; Sammartano, S.; Sharma, V. K. Dissociation Constants of Protonated Oxidized Glutathione in Seawater Media at Different Salinities. *Aquat. Geochem.* **2010**, *16*, 447–466.

(13) De Stefano, C.; Gianguzza, A.; Pettignano, A.; Sammartano, S.; Sciarrino, S. On the Complexation of Cu (II) and Cd (II) with Polycarboxyl Ligands. Potentiometric Studies with ISE-H^{+}, ISE-Cu^{2+}, and ISE-Cd^{2+}. *J. Chem. Eng. Data* **2010**, *55*, 714–722.

(14) Foti, C.; Sammartano, S. Ionic Strength Dependence of Protonation Constants of Carboxylate Ions in $NaCl_{aq}$ ($0 < I < 5.6$ $mol \cdot kg^{-1}$) and KCl_{aq} ($0 < I < 4.5$ $mol \cdot kg^{-1}$): Specific Ion Interaction Theory and Pitzer Parameters and the Correlation Between Them. *J. Chem. Eng. Data* **2010**, *55*, 904–911.

(15) Bretti, C.; De Stefano, C.; Manfredi, G.; Sammartano, S. Solubility, Activity Coefficients and Acid-Base Properties of three Naphthol Derivatives in $NaCl_{(aq)}$ at Different Ionic Strengths and at T = 298.15 K. *J. Mol. Liq.* **2011**, *158*, 50–56.

(16) Cigala, R. M.; Crea, F.; De Stefano, C.; Lando, G.; Milea, D.; Sammartano, S. Electrochemical Study on the Stability of Phytate Complexes with Cu^{2+}, Pb^{2+}, Zn^{2+}, and Ni^{2+}: A Comparison of Different Techniques. *J. Chem. Eng. Data* **2010**, *55*, 4757–4767.

(17) Bretti, C.; De Stefano, C.; Lando, G.; Sammartano, S. Activity Coefficients, Acid-Base Properties and Weak Na^{+} Ion Pair Formation of Some Resorcinol Derivatives. *Fluid. Phase Equilib.* **2010**, *292*, 71–79.

(18) Berto, S.; Crea, F.; Daniele, P. G.; De Stefano, C.; Prenesti, E.; Sammartano, S. Sequestering Ability of Dicarboxylic Ligands Towards Dioxouranium(VI) in NaCl and KNO_3 Aqueous Solutions at T = 298.15 K. *J. Solution Chem.* **2009**, *38*, 1343–1356.

(19) Bretti, C.; De Stefano, C.; Foti, C.; Giuffre, O.; Sammartano, S. Thermodynamic Protonation Parameters of Some Sulfur-Containing Anions in $NaCl_{aq}$ and $(CH_3)_4NCl_{aq}$ at t = 25 °C. *J. Solution Chem.* **2009**, *38*, 1225–1245.

(20) Bretti, C.; Foti, C.; Sammartano, S. Calculation of SIT Parameters: Part I. A New Approach in the Use of SIT in Determining the Dependence on Ionic Strength of Activity Coefficients, Application to Some Chloride Salts of Interest in the Speciation of Natural Fluids. *Chem. Spec. Bioavail.* **2004**, *16*, 105–110.

(21) Bretti, C.; De Stefano, C.; Foti, C.; Sammartano, S. Total and Specific Solubility and Activity Coefficients of Neutral Species of $(CH_2)_{2i\text{-}2}N_i(CH_2COOH)_{i+2}$ Complexons in Aqueous NaCl Solutions at Different Ionic Strengths, $(0 \leq I \leq 5)$ $\text{mol}\cdot\text{L}^{-1}$, and 298.15 K. *J. Chem. Eng. Data* **2011**, *56*, 437–443.

(22) Crea, F.; Foti, C.; De Stefano, C.; Sammartano, S. SIT Parameters for 1:2 Electrolytes and Correlation with Pitzer Coefficients. *Ann. Chim.* **2007**, *97*, 85–95.

(23) Ciavatta, L. The Specific Interaction Theory in Evaluating Ionic Equilibria. *Ann. Chim.* **1980**, *70*, 551–567.

(24) Grenthe, I.; Wanner, H. *TDB-2 Guidelines for the Extrapolation to Zero Ionic Strength*, Version 6; January 2000 (http://www.nea.fr/html/dbtdb/guidelines/tdb2.pdf).

(25) Brown, P. L.; Curti, E.; Gambrow, B. *Chemical Thermodynamics of Zirconium*, Vol. 8; Elsevier: New York, 2005; p 33.

(26) Mitting, D.; Choppin, G. R. *Actinide Speciation in High Ionic Strength Media*; Kluwer Academic/Plenum Publishers: New York, 1999.

(27) De Stefano, C.; Gianguzza, A.; Piazzese, D.; Sammartano, S. Polyacrylate Protonation in Various Aqueous Ionic Media at Different Temperatures and Ionic Strengths. *J. Chem. Eng. Data* **2000**, *45*, 876–881.

(28) Daniele, P. G.; Rigano, C.; Sammartano, S.; Zelano, V. Ionic Strength Dependence of Formation Constants — XVIII. The Hydrolysis of Iron (III) in Aqueous KNO_3 Solutions. *Talanta* **1994**, *41*, 1577–1582.

(29) Daniele, P. G.; Rigano, C.; Sammartano, S. Ionic Strength Dependence of Formation Constants. Alkali Metal Complexes of EDTA, NTA, Diphosphate and Tripolyphosphate in Aqueous Solution. *Anal. Chem.* **1985**, *57*, 2956–2960.

(30) El-Dossoki, F. Dissociation Constant of Quinic Acid and Association Constants of Some Quinates in Aqueous and in Aqueous-Alcoholic Mixed Solvents. *J. Chem. Eng. Data* **2010**, *55*, 2155–2163.