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Ionic Strength Dependence of Formation Constants: Complexation of Cysteine with Molybdenum(VI)

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The formation constants of the species formed in the systems H^+ + Mo(VI) + cysteine and H^+ + cysteine have been determined in aqueous solution in the range $4 \le pH \le 8$ at 25 °C and different ionic strengths ranging from (0.1 to 1.0) 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 cysteine of the type MoO_3L^{2-} at $-\log [H^+] = 5.8$. The dependence of protonation and the stability constants of cysteine and its complex on ionic strength are described by a Debye−Huckel type equation, and finally the results have been compared with data previously reported and interpreted.

Introduction

Special attention has been devoted to complexes of molybdenum(VI) and molybdenum(V) in aqueous solution because of their important role in enzymatic redox reactions. The redox enzyme xanthine oxidase is a thiolo enzyme which is thought to involve molybdenum−sulfur bonding.[1] The molybdoprotein constituent of nitrogenase is also a sulfur-containing enzyme, and it is tentatively presumed to contain molybdenum−sulfur linkages, although with much less compelling evidence than in the xanthine oxidase case.[2]

The equilibria of Mo(VI) in aqueous solution are complex, and various polynuclear species are formed in acidic solution ($pH < 4$).[3] In basic solution, little or no complex is formed[4] due to the exceedingly high stability of MoO_4^{2-}. The stability constants of the complexes formed by Mo(VI) with some amino acids in aqueous solution have been determined by various authors using different techniques, but according to the literature, no work has been reported on the ionic strength dependence of the Mo(VI) + cysteine system.

On the ionic strength dependence of formation constants for some stable complexes of amino acids by some metal ions, we have recently reported some interesting features of the function $\log K = f(I)$,[5−13] where K and I refer to the formation constant and ionic media, respectively. In particular, all the formation constants seem to follow the same trend as a function of ionic strength, if allowance is made for different types of reaction stoichiometry and different charges of reactants and products. In determining a formation constant at a fixed ionic strength, in all cases, some uncertainties are always present. This fact is mainly due to the uncertainties in numerical values of stability constants. For example, the 0.7 log unit difference in the stability constants determined at 0.1 and 0.7 mol·dm^{-3} should be the result of the uncertainties in the numerical values.

The present work deals with the study of the Mo(VI) + L-cysteine system in an ionic strength range of (0.1−1.0) mol·dm^{-3} sodium perchlorate. 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 reaction. Moreover, a Debye−Huckel type equation was established for the dependence of the formation constant on ionic strength. This equation gives the possibility of estimating a stability constant in a fixed ionic strength when its value is known for another ionic medium in the range $0.1 \le I \le 1.0$ mol·dm^{-3} and therefore may give a significant contribution of solving many analytical and speciation problems.

Experimental Section

Reagents. L-Cysteine (E. Merck, analytical reagent grade) was recrystallized from hot water, washed with ethanol, and dried over P_2O_5, and the concentration of its solution was checked by several titrations against standard alkalis. The NaOH solution was prepared from titrisol solution (E. Merck), and its concentration was determined by titration with standard HCl. Perchloric acid, sodium perchlorate, and sodium molybdate were supplied from E. Merck as analytical reagent grade materials and were used without further purification. Dilute perchloric acid solution was standardized against standard NaOH solution. All dilute solutions were prepared from double-distilled water with specific conductance equal to (1.3 ± 0.1) $\mu\Omega^{-1}\cdot cm^{-1}$.

Measurements. All measurements were performed at (25 ± 0.1) °C. The ionic strength was maintained from (0.1 to 1.0) mol·dm^{-3} with sodium perchlorate. An Eyela pH-meter, PHM 2000, was used for $-\log [H^+]$ measurements. A purified nitrogen atmosphere was maintained in the vessel during the titrations. The hydrogen ion concentration was measured with an Ingold UO 3234 glass electrode and an Ingold UO 3236 calomel electrode. The pH-meter was calibrated for the relevant H^+ concentration with a solution of 1.00×10^{-2} mol·dm^{-3} perchloric acid solution containing 0.09 mol·dm^{-3} sodium perchlorate (for adjusting the ionic strength on 0.1 mol·dm^{-3}). The same procedure was performed for the other ionic strengths. For these standard solutions, we set $-\log [H^+] = 2.00$.[14] Spectrophotometric measurements were performed on a UV−vis Shimadzu 2100 spectrophotometer with a GDU-20 com-

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Table 1. Protonation Constants of the Carboxylic, K_1, Sulfydryl, K_2, and Amino, K_3, Groups of L-Cysteine at 25 °C and Different Ionic Strengths, I, of $NaClO_4$

I/mol·dm^{-3}	log K_1	log K_2	log K_3	experimental condition	ref
0.1	1.79 ± 0.05	8.33 ± 0.10	10.47 ± 0.12		this work
0.3	1.65 ± 0.03	8.19 ± 0.10	10.29 ± 0.13		this work
0.5	1.48 ± 0.04	8.02 ± 0.09	9.92 ± 0.11		this work
0.7	1.32 ± 0.05	7.84 ± 0.08	9.75 ± 0.10		this work
1.0	1.59 ± 0.04	8.25 ± 0.09	10.10 ± 0.12		this work
		7.91	10.36	I = 0.1 M $NaClO_4$, t = 50 °C	16
		8.27	10.46	I = 0.15 M $NaClO_4$, t = 37 °C	17
		8.24	10.55	I = 0.1 M KNO_3, t = 25 °C	18

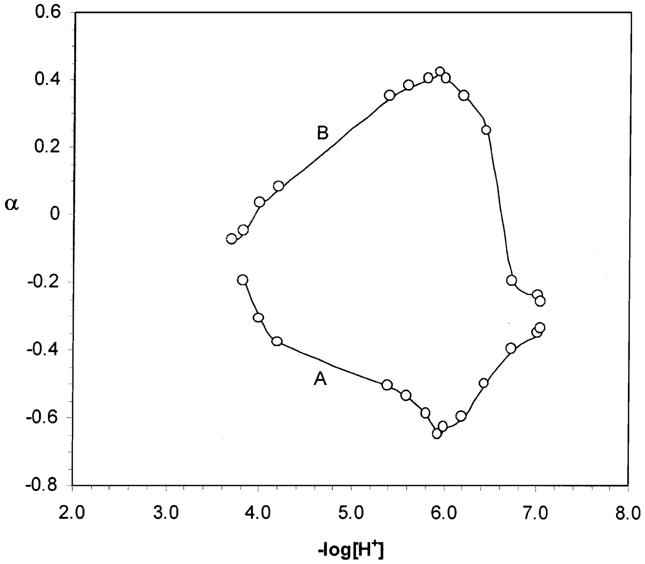


Figure 1. Effect of −log [H$^+$] on optical rotation, α, of (A) [Mo(VI)+] (5.0 × 10^{-2} mol·dm^{-3}) + [L-cysteine] (5.0 × 10^{-2} mol·dm^{-3}) and (B) [L-cysteine] (5.0 × 10^{-2} mol·dm^{-3}), at 25 °C and an ionic strength of 0.1 mol·dm^{-3} $NaClO_4$.

puter and 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 −log [H$^+$] of the solution could be measured simultaneously. Polarimetric measurements were made 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 spectrophotometric and polarimetric methods), two solutions of Mo(VI) + L-cysteine were prepared with the same concentration, but the ionic strength of the first was maintained with sodium perchlorate, and that of the second, with sodium hydroxide, perchloric acid, or sodium perchlorate. The first solution was then titrated with the second. The −log [H$^+$] and absorbance or optical activity 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

The following species of cysteine may exist in solution at different log [H$^+$]: L^{2-}, HL^-, H_2L, and H_3L^+, where L^{2-} represents the fully dissociated amino acid anion. The protonation constants of cysteine have been extensively studied in different kinds of background electrolytes, and the results are reported in the literature. In this work, the protonation constants of cysteine have been determined using the potentiometric technique[5] under the same condition of temperature and ionic media as mentioned before and calculated using a computer program which employs a least-squares method.[15] The protonation constant values, expressed in log units, are collected in Table 1 together with the values reported in the literature, which are in good agreement with those reported before.[16−18]

Complexation of Molybdenum(VI)

Polarimetric Studies. Assuming that the optical activity of L-cysteine 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-cysteine, as well as those of L-cysteine alone with the same concentration but at different −log [H$^+$]. The effect of −log [H$^+$] on the optical rotation of such solutions is shown in Figure 1. As Figure 1 shows, when the −log [H$^+$] is less than 7, the optical rotation of the Mo(VI) + cysteine solution becomes increasingly different from that of cysteine alone, indicating complexation by Mo(VI). The difference reaches a maximum between −log [H$^+$] of 5.5 and 6.2 and decreases as the −log [H$^+$] is decreased below 5, indicating the largest amount of complex is formed in the −log [H$^+$] range 5.5−6.2. At higher −log [H$^+$], the complex dissociates as a result of the competitive formation of MoO_4^{2-},[19] while at low −log [H$^+$] values, isopolymolybdates are formed.[3] Almost similar results were obtained for Mo(VI) + glutamic and aspartic acids as well as with histidine systems in our previous studies.[5−7]

Spectrophotometric Studies. Using the continuous variations method, we determined the absorbances of solutions of Mo(VI) and cysteine of total concentration 8.0 × 10^{-3} mol·dm^{-3} in the UV range (260−275 nm) at a constant −log [H$^+$] of 5.8. The observed absorbances were corrected for unreacted Mo from eq 1 and are listed in Table 2 and plotted in Figure 2.

$$A_C = A_{obs} - \epsilon_0[\mathrm{Mo(VI)}] \tag{1}$$

where A_C, A_{obs}, and ϵ_M are the absorbance of the complex, the observed absorbance, and the molar absorptivity of Mo(VI), respectively. Values of ϵ_M were calculated at the mole fraction of Mo(VI) equal to 1. In Figure 2, a rather sharp maximum at a mole fraction of Mo(VI) equal to 0.5 was obtained, indicating a 1:1 complex formation. The molar absorptivity of the complex, ϵ_C, 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

$$[\mathrm{C}] = A_C/\epsilon_C \tag{2}$$

Raymond et al.[20] synthesized $Na[MoO_3(L)]H_2O$, among other molybdenum chelate complexes, where L refers to a tridentate amino acid as ligand. The IR spectrum of those compounds that were crystallized at −log [H$^+$] = 6 shows

Table 2. Continuous Variations Data for the Mo(VI) + L-Cysteine System at $-\log [H^+] = 5.8$, Different Wavelengths, and Various Ionic Strengths, *I*, of $NaClO_4$

mole fraction of Mo(VI)	A^a at the following wavelengths 260 nm	265 nm	270 nm	275 nm
	$I = 0.3$ mol·dm^{-3}			
0.10	0.349	0.210	0.128	0.086
0.20	0.571	0.350	0.220	0.155
0.25	0.669	0.400	0.258	0.181
0.50	0.936	0.535	0.338	0.238
0.75	0.677	0.341	0.224	0.160
0.90	0.319	0.157	0.114	0.073
	$I = 0.5$ mol·dm^{-3}			
0.10	0.357	0.213	0.127	0.088
0.20	0.601	0.340	0.211	0.140
0.25	0.680	0.400	0.260	0.170
0.50	0.881	0.510	0.331	0.232
0.75	0.692	0.359	0.236	0.158
0.90	0.308	0.143	0.098	0.073
	$I = 0.7$ mol·dm^{-3}			
0.10	0.358	0.218	0.134	0.093
0.20	0.531	0.319	0.210	0.148
0.25	0.600	0.350	0.236	0.166
0.50	0.744	0.406	0.283	0.206
0.75	0.610	0.351	0.240	0.170
0.90	0.370	0.222	0.150	0.100
	$I = 1.0$ mol·dm^{-3}			
0.10	0.365	0.202	0.136	0.093
0.20	0.581	0.303	0.231	0.166
0.25	0.701	0.351	0.281	0.202
0.50	1.053	0.433	0.399	0.283
0.75	0.750	0.352	0.290	0.201
0.90	0.401	0.201	0.140	0.100

[a] The corrected absorbance of [Mo(VI)] + [L-cysteine] = 8.0×10^{-3} mol·dm^{-3}.

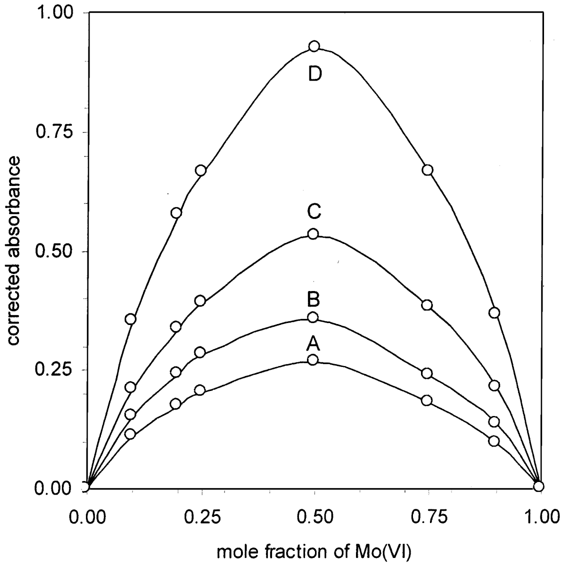


Figure 2. Continuous variations plots of corrected absorbances of MoO_3L^{2-} versus mole fraction of Mo(VI) at 25 °C, an ionic strength of 0.1 mol·dm^{-3} $NaClO_4$, and different wavelengths: (A) 260, (B) 265, (C) 270, and (D) 275 nm.

Table 3. Average Values of log K_S at Various Wavelengths at $-\log [H^+] = 5.8$ and Different Ionic Strengths, *I*, of $NaClO_4$

I/mol·dm^{-3}	log K_S	experimental conditions	ref
0.1	21.4 ± 0.1		this work
0.3	21.1 ± 0.1		this work
0.5	20.9 ± 0.2		this work
0.7	20.7 ± 0.1		this work
1.0	21.2 ± 0.1		this work
	17.54	glutamic acid + Mo(VI), $I = 0.1$ M $NaClO_4$, 25 °C	5
	18.7	aspartic acid + Mo(VI), $I = 0.1$ M $NaClO_4$, 25 °C	6
	18.37	histidine + Mo(VI), $I = 0.1$ M NaClO4, 25 °C	7

that the tridentate ligands 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, Johanson and Jones[3] concluded that at $-\log [H^+] = 5.8$, 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 cysteine, thus, has Mo/ligand/proton equal to 1:1:2 stoichiometry as

$$MoO_4^{2-} + L^{2-} + 2H^+ \leftrightarrows MoO_3L^{2-} + H_2O \tag{3}$$

with the stability constant, K_S, as

$$K_S = [MoO_3L^{2-}]/[MoO_4^{2-}][L^{2-}][H^+]^2 \tag{4}$$

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

$$C_M = [Mo] + [C] \tag{5}$$

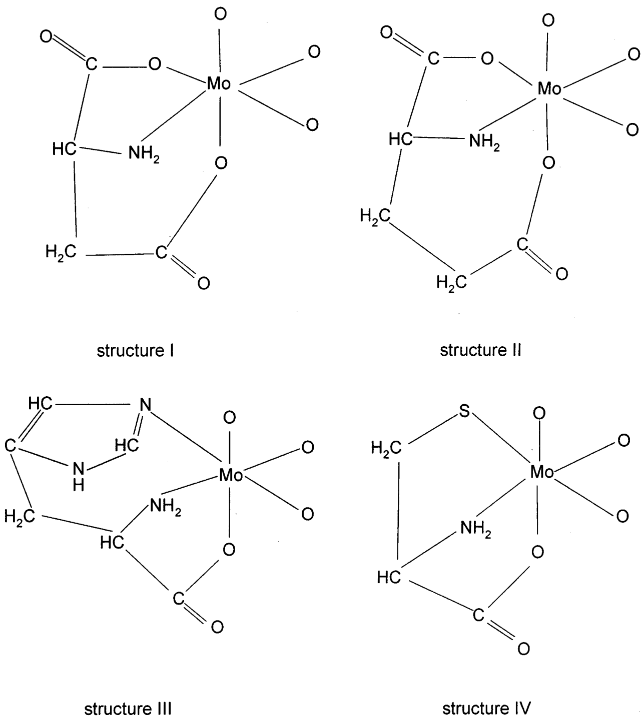
$$C_L = [L] + [C] \tag{6}$$

Combining eqs 2 and 5−6 in eq 4 and solving for K_S gives the stability constant of eq 3, and its average values at different wavelengths and at various ionic strengths are shown in Table 3 together with the values reported in the literature.

The structure of sodium molybdate is believed to be octahedral in solution,[19] with three positions to form its complexes with a tridentate ligand like aspartic or glutamic acid, histidine, and cysteine. These complexes usually have great stability constants to confirm this speculation (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 cysteine. No evidence for complex formation was found with L-alanine, which is potentially a bidentate ligand.

Values of log K_S obtained for Mo(VI) + glutamic acid, histidine, and aspartic acid systems (Table 3) are lower than that of the Mo(VI) + cysteine system in the order of their stability constants: glutamic acid < histidine < aspartic acid < cysteine. Assuming that these amino acids are all tridentate ligands in their molybdenum(VI) complexes,[5−7] the differences can be readily explained by considering the size of chelate rings involved in their atomic models (Chart 1): five and seven for Mo(VI) + glutamic acid (structure I), five and six for Mo(VI) + aspartic acid (structure II), eight and five for Mo(VI) + histidine (structure III), and finally five and five for the species of Mo(VI) + cysteine (structure IV). The log K_S values of the complexes obtained in our previous works[5−7] and this work strongly support the above argument. The higher log K_S value for the Mo(VI) + cysteine system shows that the two five-membered chelate rings in the complex make it more stable than the five- and six-membered rings in the case

Chart 1



structure I

structure II

structure III

structure IV

of Mo(VI) + aspartic acid, and the Mo(VI) + aspartic acid system is in turn more stable than the one that has five- and eight-membered rings, that is, Mo(VI) + histidine, and the same order for Mo(VI) + glutamic acid.

The dependence of the protonation constant on ionic strength for the species H_jL can be described by a semi-empirical equation,[21−22]

$$\log K_j(I) = \log K_j(I^*) - f(I) + CI \tag{7}$$

where $f(I) = Z^*AI^{1/2}/(1 + BI^{1/2})$, and $K_j(I)$ and $K_j(I^*)$ are the protonation constants of the actual and the reference ionic media, respectively. A is the parameter of the Debye−Huckel equation ($A = 0.5115$ at 25 °C), $Z^* = 1 + Z_L^2 - Z_j$ (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 equal to 1.5[22] (a small error in fixing B is absorbed in the linear term C[6]). If an approximate value of C is known, the protonation constant can be determined for the variation of ionic strength from I^* to I by the equation

$$\log K_j(I) = \log K_j(I^*) - f(I,I^*) + C(I - I^*) \tag{8}$$

where

$$f(I,I^*) = Z^*A[I^{1/2}/(1 + 1.5I^{1/2}) - I^{*1/2}/(1 + 1.5I^{*1/2})] \tag{9}$$

I and I^* are the ionic strength of the solution by $NaClO_4$. A preliminary analysis of the data showed that if a fixed value is assigned to C, the fit with eq 8 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 further terms of $DI^{3/2}$ and EI^2 (D and E are other adjustable parameters). Therefore the data were fitted to eq 10.

$$\log K_j(I) = \log K_j(I^*) - f(I,I^*) + C(I - I^*) + D(I^{3/2} - I^{*3/2}) + E(I^2 - I^{*2}) \tag{10}$$

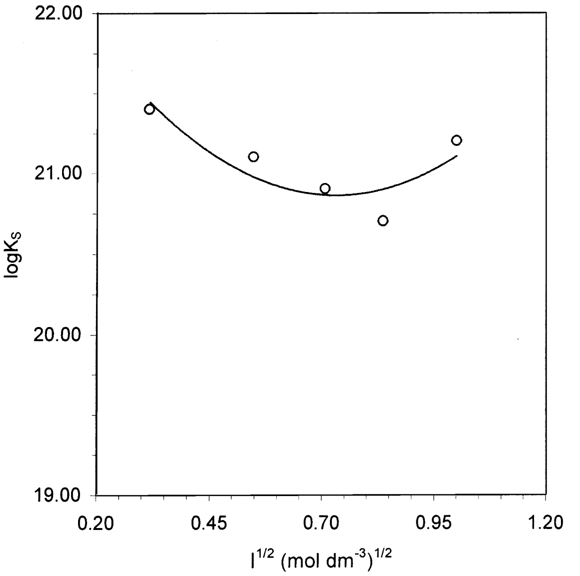


Figure 3. Plot of log K_S versus the square root of the ionic strength at 25 °C.

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

species	C	D	E	Z^*	U
K_1	5.53	−14.87	9.31	0	1×10^{-3}
K_2	8.78	−21.19	12.84	2	3×10^{-3}
K_3	11.55	−27.29	16.20	4	3×10^{-4}
MoO_3L^{2-}	9.06	−21.84	13.48	6	5.8×10^{-4}

The values obtained for C, D, and E are collected in Table 4. 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 fit of the data. For example, for the protonation constant of the amino group of L-cysteine, from eq 10 we obtained three sets of values depending on whether we take into account the term in D and E:

$$C = -0.26 \quad D = 0.0 \quad E = 0.0 \quad U = 0.15$$

$$C = -2.51 \quad D = -2.27 \quad E = 0.0 \quad U = 0.06$$

$$C = 11.55 \quad D = -27.29 \quad E = 16.20 \quad U = 3.0 \times 10^{-4}$$

The squares sum, U, shows that there is a significant improvement in the fit when the D and E terms are introduced. We used the Gauss−Newton nonlinear least-squares method in the computer program[15] to refine the parameters C, D, and E by minimizing the squares sum from eq 11,

$$U = \sum (a_i - b_i)^2 \qquad i = 1, 2, 3, ... \tag{11}$$

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 the protonation constant on ionic strength show a regular trend and seem to be a function of the Z^* value. The same procedure was applied for determining the dependence of the stability constants of the Mo(VI) + cysteine complex on ionic strength, where in this case $Z^* = Z_M^2 + Z_L^2 - Z_C^2 + 2$, where Z_M and Z_C are the charges on the metal ion and MoO_3L^{2-}, respectively. The semiempirical parameters were determined as before and are shown in Table 4. The dependence of protonation and stability constant values with ionic strength is shown in Figure 3. This figure and Tables 1 and 3 show that the protonation and the stability constants have larger values at $I = 0.1$ and a minimum when the ionic strength approaches 0.7 mol·dm^{-3} sodium perchlorate, which are in good agreement with the results obtained for other species.[5−13,21−23]

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