Ionic Strength Dependence of Formation Constants, Protonation, and Complexation of Nitrilotriacetic Acid with Molybdenum(VI)

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The complexation of molybdenum(VI) with nitrilotriacetic acid (NTA) has been studied using potentiometric and spectrophotometric techniques. The temperature was kept constant at 25 °C, and the ionic strength was (0.1, 0.5, 0.7, and 1.0) mol dm^{-3} in $NaClO_4$. It was shown that molybdenum(VI) forms a mononuclear 1:1 complex with NTA of the type (MoO_3L^{3-}), where L^{3-} represents the fully dissociated NTA anion, at pH 6. The composition of the complex was determined by the continuous variations method. The protonation constants of NTA (using the potentiometric technique) and the stability constant of the complex (using the spectrophotometric technique) were determined at 25 °C and at different ionic strengths. The dependence on ionic strength of the protonation and stability constants was evaluated using a simple Debye−Huckel type equation.

Introduction

Molybdenum is present in cofactors of several enzymes. Some of them are involved in important biochemical processes such as nitrogen fixation. As a result, structural, thermodynamic, and kinetic studies of the complexation between molybdate and different chelating ligands have been the subject of several investigations.

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,[1−6] and little work has been carried for more stable complexes of α-amino acids with transition metal ions,[7−11] but according to the literature no work has been reported on the ionic strength dependence of formation constants, protonation, and complexation of molybdenum(VI) with nitrilotriacetic acid (NTA).

Chan[12] proved that a stable 1:1 molybdenum chelate is formed with NTA using the NMR technique. Raymond[13] confirmed the existence of a MoO_3 core for the complexation of Mo(VI) with the tridentate ligand NTA. Zare[14] has studied this system and reported its stability constant at 25 °C and at an ionic strength of 3 mol dm^{-3} $NaClO_4$ using the potentiometric technique. Funahashi[15] studied the reaction of molybdate(VI) with nitrilotriacetate spectrophotometrically in an aqueous solution of pH 6−8 at I = 1.00 M ($NaClO_4$) and 25 °C.

In the present work, we have studied the complexes of Mo(VI) with NTA in an ionic strength range of (0.1 to 1.0) mol dm^{-3} sodium perchlorate at 25 °C. A simple 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 for another ionic medium in the range ($0.1 < I < 1.0$) mol dm^{-3}.

Experimental Section

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

Measurements. A Horiba pH-meter, D-14, was used for pH measurements. The pH-meter has a sensitivity of 0.01 units. The hydrogen ion concentration was measured with a Horiba combination electrode, model S8720. 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.[14] The calibration has been done for the whole pH 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.

For each experiment, two solutions of Mo(VI) + NTA 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 or perchloric acid. The first solution was then titrated with the second one. 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, and the resulting average values and corresponding standard deviations are shown in the text and tables.

Results and Discussion

The dissociation equilibria of nitrilotriacetic acid have been studied in different kinds of background electrolytes, but there are no reports about the ionic strength depend-

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Table 1. Dissociation Constants K_3, K_2, and K_1 of NTA at Different Ionic Strengths, *I*, of $NaClO_4$

I/mol·dm^{-3}	log K_3	log K_2	log K_1	experimental conditions	ref
0.1	1.98 ± 0.02	2.92 ± 0.05	10.00 ± 0.02		this work
0.5	1.76 ± 0.01	2.79 ± 0.02	9.70 ± 0.03		this work
0.7	1.63 ± 0.02	2.61 ± 0.01	9.55 ± 0.02		this work
1.0	1.55 ± 0.02	2.59 ± 0.04	9.25 ± 0.02		this work
	2.05 ± 0.05	2.63 ± 0.02	9.17 ± 0.04	$I = 3$ M $NaClO_4$, $t = 25$ °C	14
	1.65	2.94	10.33	$t = 20$ °C	21

Table 2. Continuous Variations Data for the Mo(VI) + NTA System at pH 6, an Ionic Strength of 0.1 M $NaClO_4$, and Different Wavelengths

mole fraction of Mo(VI)	A^a for the following wavelengths		
	260 nm	265 nm	270 nm
0.00	0.000	0.000	0.000
0.10	0.229	0.207	0.185
0.20	0.310	0.283	0.290
0.30	0.380	0.343	0.305
0.40	0.406	0.365	0.315
0.50	0.441	0.398	0.347
0.60	0.404	0.364	0.315
0.80	0.329	0.297	0.250
1.00	0.000	0.000	0.000

[a] The corrected absorbance of [Mo(VI)] + [NTA] = 0.006 mol dm^{-3}.

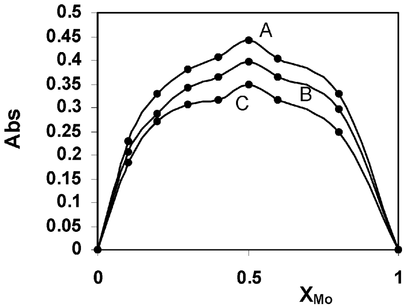

Figure 1. Continuous variations plots of the absorbances of MoO_3L^{3-}, Abs, versus the mole fraction of Mo(VI), X_{Mo}, at 25 °C, an ionic strength of 0.1 mol dm^{-3} $NaClO_4$, and different wavelengths: (A) 260, (B) 265, and (C) 270 nm.

ence of the dissociation constants of NTA. The following equilibria were studied:

$$H_3L \rightleftarrows H^+ + H_2L^- \qquad K_1 = [H^+][H_2L^-]/[H_3L] \tag{1}$$

$$H_2L^- \rightleftarrows H^+ + HL^{2-} \qquad K_2 = [H^+][HL^{2-}]/[H_2L^-] \tag{2}$$

$$HL^{2-} \rightleftarrows H^+ + L^{3-} \qquad K_3 = [H^+][L^{3-}]/[HL^{2-}] \tag{3}$$

where L^{3-} represents the fully dissociated NTA anion. The dissociation constants K_1, K_2, and K_3 have been determined using potentiometric techniques and calculated using a suitable computer program.[11] These values are listed in Table 1 together with the values reported in the literature, which are in good agreement.

Complexation of Molybdenum(VI) with NTA. Using the continuous variations method, we determined the absorbances of solutions of Mo(VI) and NTA of total concentration 0.006 mol dm^{-3} in the UV range (260 to 270 nm) at a constant pH of 6. Different sets of species have been proposed in order to assign the equilibria in molybdate solutions. The equilibria of molybdenum(VI) in acidified molybdate solutions are complex since various polynuclear species are formed.[15] At higher pH, the complex dissociates as a result of the competitive formation of MoO_4^{2-}.[16] The observed absorbances were corrected from eq 4 and are summarized in Table 2 and plotted in Figure 1:

Table 3. Molar Absorptivities of Mo(VI), ϵ_0, and MoO_3L^{3-}, ϵ_1, at pH 6, Different Wavelengths, and Various Ionic Strengths, *I*, of $NaClO_4$

	ϵ_0 for the following wavelengths			ϵ_1 for the following wavelengths		
I/mol·dm^{-3}	260 nm	265 nm	270 nm	260 nm	265 nm	270 nm
0.1	388.3	205.8	102.5	1928.3	1726.6	1533.3
0.5	380.0	199.2	95.8	3066.6	2916.6	2733.3
0.7	386.7	211.7	110.8	2346.6	2188.3	2000.0
1.0	402.5	223.3	120.3	1830.0	1710.0	1550.0

$$A_c = A_{obs} - \epsilon_0[Mo] \tag{4}$$

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

$$[C] = A_c/\epsilon_1 \tag{5}$$

The molybdate anion MoO_4^{2-} maintains a tetrahedral configuration in neutral and alkaline solutions.[16] Complexes of molybdate with chelating ligands have an octahedral configuration. The complex formation therefore will have to occur by an addition of the ligand to the molybdate ion, thereby increasing its coordination number from 4 to 6. It has been postulated that the monoprotonated species $HMoO_4^-$ exists in the form of an octahedral hydrate species in solution. From consideration of thermodynamic parameters for protonation of molybdate, Cruywagen and Rohwer[17] have suggested that it is the second protonation constant which is anomalous and that the change in coordination number occurs with addition of the second proton. Whichever of these viewpoints is correct, the diprotonated species H_2MoO_4 should be octahedral.

Although Mo(VI) forms complexes with the same chelating agents as most other metal ions, its chemistry is differentiated from that of other transition ions by its strong association with oxygen. Thus 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. An interesting consequence of this behavior is illustrated by the complex formed between Mo(VI) and ethylenediaminetetraacetic acid (EDTA) in which two Mo ions can coordinate with EDTA.[18] This is in distinct contrast to the normal metal−EDTA chelates in which only one metal ion coordinates with each ligand. Kula[19] concluded that for EDTA

Table 4. Average Values of log K_S at pH 6 and Different Ionic Strengths for the Complexation of Molybdenum(VI) with NTA, $t = 25$ °C

I/mol·dm^{-3}	log K_S	experimental conditions	ref
0.1	18.72 ± 0.20		this work
0.5	18.08 ± 0.30		this work
0.7	18.31 ± 0.20		this work
1.0	17.97 ± 0.10		this work
	18.60 ± 0.20	$I = 3$ M $NaClO_4$, $t = 25$ °C	14
	18.09 ± 0.04	$I = 1$ M $NaClO_4$, $t = 25$ °C	15

(between pH 9 and 5) two complexes with 1:1 and 2:1 metal−ligand ratios are formed. The structures which were proposed for the Mo_2−EDTA chelate led to speculation concerning the possibility of forming 1:1 Mo(VI) chelates with methyliminodiacetic acid (MIDA) and NTA, and proton NMR studies of these chelates confirmed that the predominate EDTA chelate does indeed contain two Mo ions and that stable 1:1 molybdenum chelates are formed with MIDA and NTA.[18,20] Thus, Mo(VI) will bond with this tridentate ligand as a 1:1 complex:

$$MoO_4^{2-} + L^{3-} + 2H^+ \rightleftarrows MoO_3L^{3-} + H_2O \qquad (6)$$

with the stability constant, K_S, as

$$K_S = [MoO_3L^{3-}]/[MoO_4^{2-}][L^{3-}][H^+]^2 \qquad (7)$$

The following equations are valid for the total concentration of molybdenum (C_M) and the total concentration of the ligand (C_L) at the maximum point on the plot of Figure 1:

$$C_M = [Mo] + [C] \qquad (8)$$

$$C_L = [L] + [C] \qquad (9)$$

By substituting eqs 5, 8, and 9 in eq 7, we can calculate the values of K_S according to reaction 6. The values of log K_S at different ionic strengths together with the values from the literature are shown in Table 4.

The dependence of the dissociation and stability constants on the ionic strength can be described according to the previous works:[7−11]

$$\log K_S(I) = \log K_S(I_1) - AZ^*\left(\frac{I^{0.5}}{1 + BI^{0.5}} - \frac{I_1^{\,0.5}}{1 + BI_1^{\,0.5}}\right) + C(I - I_1) + D(I^{1.5} - I_1^{\,1.5}) \quad (10)$$

where I and I_1 are the actual and reference ionic strengths, respectively, and according to eq 11,

$$pM^{m+} + qL^{n-} + rH^+ \rightleftarrows (M_pL_qH_r)^{pm-qn+r} \qquad (11)$$

$Z^* = pm^2 + qn^2 + r - (pm + qn + r)^2$, where m and n are the charges on the metal ion and the ligand, respectively. Considering that $A = 0.5115$ and $B = 1.489$, eq 10 can be simplified:

$$\log K_S(I) = \log K_S(I_1) - Z^*\left(\frac{I^{0.5}}{2 + 3I^{0.5}} - \frac{I_1^{\,0.5}}{2 + 3I_1^{\,0.5}}\right) + C(I - I_1) + D(I^{1.5} - I_1^{\,1.5}) \quad (12)$$

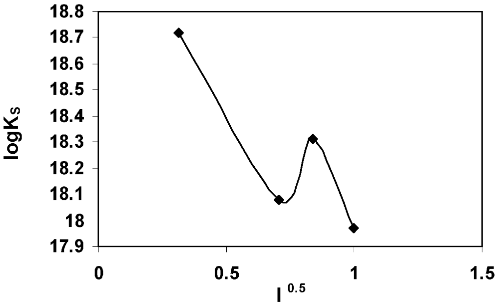

Figure 2. Plot of log K_S for MoO_3L^{3-} versus the square root of ionic strength.

Table 5. Parameters for the Dependence on the Ionic Strength of Dissociation and Stability Constants at 25 °C

species	C	D	Z^*	species	C	D	Z^*
K_3	0.993	−0.801	6	K_1	0.227	−0.791	2
K_2	0.648	−0.579	4	MoO_3L^{3-}	−0.519	0.338	6

where C and D are empirical coefficients and their values were obtained by minimizing the error squares sum, (U), and using the Gauss−Newton nonlinear least-squares method in a suitable computer program:

$$U = \sum_i (a_i - b_i)^2 \qquad (i = 1, 2, 3, ...) \qquad (13)$$

where a is a quasi-experimental quantity and b_i is a calculated one. The values of C and D are shown in Table 5.

The dependence on ionic strength of log K_S is shown in Table 4, and the values are in good agreement with the results obtained in the previous papers.[7−11] The dependence of K_S on the ionic strength is shown in Figure 2. This figure shows that K_S has one maximum at $I = 0.7$ and a minimum when the ionic strength approaches 0.5.

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