

# Determination of the Stability Constants of the Mo(VI) Complex with Ethylenediaminediacetic Acid at Different Ionic Strengths

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The solution equilibrium of the molybdenum(VI) complex formed by ethylenediaminediacetic acid (EDDA) has been investigated potentiometrically and spectrophotometrically at 25 °C, pH 6.0, and different ionic strengths ranging from (0.1 to 1.0) mol dm<sup>-3</sup> of sodium perchlorate. Molybdenum(VI) forms a mononuclear complex with EDDA of type (MoO<sub>3</sub>L<sup>2-</sup>). The dependence of dissociation and stability constants on the ionic strength is described by a modified Debye–Huckel equation and by introducing two empirical parameters. Finally, a comparison has been made between the calculated and experimental values of stability constants.

## Introduction

Because molybdenum is widely available to biological systems, the coordination chemistry of Mo(VI) has aroused considerable interest in view of its biochemical significance.<sup>1,2</sup> For example, dioxomolybdenum(VI) complexes are studied as models for oxidized forms of molybdoenzymes (e.g., aldehyde oxidase and sulfite oxidase, which are supposed to contain *cis*-MoX<sub>2</sub> units (X = O, S) coordinated to sulfur, nitrogen, and oxygen donor atoms of the protein structure<sup>3</sup>). The present view of these enzymes indicates that the formal oxidation state of molybdenum cycles between 4+ and 6+ in reactions with substrate and oxidant. The two-electron oxygen atom transfer seems to be the relevant mechanism in understanding the chemical role of enzymatic reactions.

There have been many studies of the complexes of molybdenum(VI) with  $\alpha$ -amino acids<sup>4–7</sup> and some aminopolycarboxylic acids (NTA, EDTA, MIDA, IDA),<sup>4,8–14</sup> but to our knowledge, no reports of the ionic strength dependence of the complexes of Mo(VI)–EDDA have appeared. Chan<sup>8</sup> reported the proton nuclear magnetic resonance spectra and structures of ethylenediaminetetraacetic acid, methyliminodiacetic acid, and nitrilotriacetic acid chelates of molybdenum(VI). Kula studied the solution equilibria and structures of molybdenum chelates, (ethylenedinitrilo) tetraacetic acid,<sup>9</sup> and *N*-methyliminodiacetic acid<sup>10</sup> and determined structural and bonding characteristics in the molybdenum(VI)–iminodiacetate system by infrared and proton nuclear magnetic resonance techniques.<sup>12</sup> Kula<sup>11</sup> reported the stability constants of molybdenum(VI) chelates, IDA, MIDA, NTA, and EDTA at 25 °C and at an ionic strength of 0.15 mol dm<sup>-3</sup> by the potentiometric technique. Zare<sup>14</sup> determined the stability constant of the Mo(VI)–EDDA complex at 25 °C and at an ionic strength of 3 mol dm<sup>-3</sup> sodium perchlorate using the potentiometric technique.

The present work deals with the complexation of molybdenum(VI) with EDDA in an ionic strength range of (0.1

to 1.0) mol dm<sup>-3</sup> sodium perchlorate at 25 °C. Finally, we have used a modified Debye–Huckel equation for the calculation of stability constants at different ionic strengths.

## Experimental Section

**Reagents.** Sodium perchlorate, perchloric acid, sodium hydroxide, and sodium molybdate were obtained from E. Merck and ethylenediaminediacetic acid was obtained from Fluka as analytical reagent-grade materials and were used without further purification. Dilute perchloric acid solution was standardized against KHCO<sub>3</sub>. In all experiments, double-distilled water with a specific conductance equal to (1.3  $\pm$  0.1)  $\mu$ S·cm<sup>-1</sup> has been used.

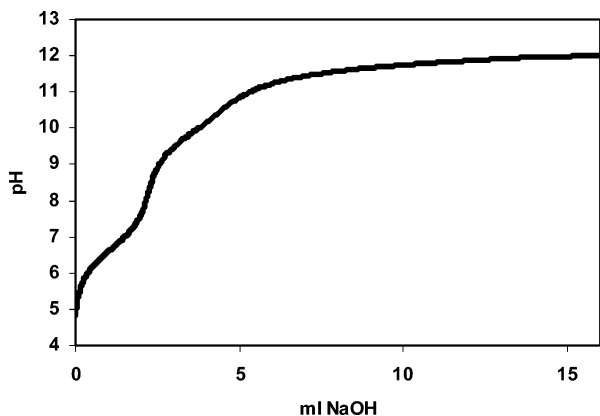
**Measurements.** All measurements were carried out at (25  $\pm$  0.1) °C. A Horiba D-14 pH meter was used for pH measurements. The pH meter has a sensitivity of 0.01 units. The hydrogen ion concentration was measured with a Horiba combination electrode, model S8720. A 0.01 mol dm<sup>-3</sup> perchloric acid solution containing 0.09 mol dm<sup>-3</sup> sodium perchlorate (for adjusting the ionic strength to 0.1 mol dm<sup>-3</sup>) was employed as a standard solution of hydrogen ion concentration. The same procedure was performed for the other ionic strengths.<sup>14</sup> The calibration has been done for the whole pH (pH =  $-\log[H^+]$ ) 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. The measurement cell was of the flow type. A Masterflux pump allowed circulation of the solution under study from the potentiometric cell to the spectrophotometric cell so that the absorbance and pH of the solution could be measured simultaneously.

For each experiment two solutions of Mo(VI) + EDDA 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 pH of the first solution was adjusted with the second one. The second solution consists of metal + ligand + NaOH for increasing pH, while for decreasing pH the second one consists of metal + ligand + HClO<sub>4</sub>. The absorbance of the first solution was measured after adjusting the pH.

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**Figure 1.** Titration of ethylenediaminediacetic acid with sodium hydroxide at  $I = 0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$  and  $25^\circ\text{C}$ .

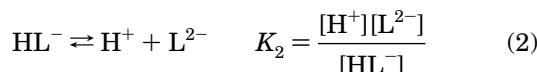
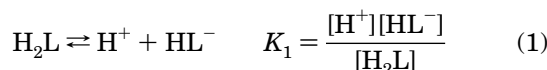
**Table 1.** Dissociation Constants  $K_2$  and  $K_1$  of EDDA at Different Ionic Strengths,  $I$ , of  $\text{NaClO}_4$

$I/\text{mol dm}^{-3}$	$\log K_2$	$\log K_1$	experimental conditions	ref
0.1	$10.10 \pm 0.02$	$8.12 \pm 0.01$		this work
0.3	$9.80 \pm 0.01$	$8.10 \pm 0.04$		this work
0.5	$9.65 \pm 0.01$	$8.00 \pm 0.02$		this work
0.7	$9.40 \pm 0.04$	$7.75 \pm 0.03$		this work
1.0	$9.30 \pm 0.03$	$7.50 \pm 0.05$		this work
	$10.06 \pm 0.06$	$7.18 \pm 0.05$	$I = 3.0 \text{ mol dm}^{-3}$ , $t = 25^\circ\text{C}$	14

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 ethylenediaminediacetic acid have been studied in different kinds of background electrolytes, but there are no reports of the ionic strength dependence of the dissociation constants of EDDA. The following equilibria were studied:



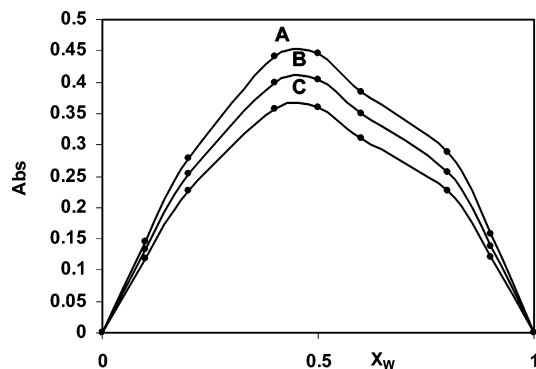
where  $\text{L}^{2-}$  represents the fully dissociated ethylenediaminediacetic acid anion. Three titrations have been done for each ionic strength, and 389 points have been used for calculations at each ionic strength. The dissociation constants  $K_1$  and  $K_2$  have been determined using potentiometric techniques and calculated using the Microsoft Excel 2000 program.<sup>13,15</sup>

The titration curve is shown in Figure 1. Dissociation constants are given in Table 1, together with the values reported in the literature, which are in good agreement with those reported before.

## Complexation of Molybdenum(VI) with EDDA

The absorbances of the solution of Mo(VI) and EDDA at a total concentration of  $0.006 \text{ mol dm}^{-3}$  in the UV range (260 to 270 nm) at a constant pH of 6.0 were determined. The observed absorbances were corrected from eq 3 and are shown in Figure 2:

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



**Figure 2.** Continuous variation plots of the absorbance of  $\text{MoO}_3\text{L}^{2-}$ , Abs, vs the mole fraction of Mo(VI),  $X_{\text{Mo}}$ , at  $25^\circ\text{C}$ , an ionic strength of  $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$ , and different wavelengths: (A) 260 nm, (B) 265 nm, and (C) 270 nm.

**Table 2.** Molar Absorptivities of Mo(VI),  $\epsilon_0$ , and  $\text{MoO}_3\text{L}^{2-}$ ,  $\epsilon_1$ , at pH 6.0, Different Wavelengths, and Various Ionic Strengths,  $I$ , of  $\text{NaClO}_4$

$I/\text{mol dm}^{-3}$	$\epsilon_0$			$\epsilon_1$		
	260 nm	265 nm	270 nm	260 nm	265 nm	270 nm
0.1	340.0	179.3	86.7	1173.3	1066.7	960.0
0.3	348.0	180.0	84.0	1052.0	966.7	876.0
0.5	343.3	180.0	88.7	1016.0	926.7	857.3
0.7	348.7	186.0	94.7	997.3	906.7	800.0
1.0	349.3	186.7	96.0	797.3	746.7	666.7

$A_c$ ,  $A_{\text{obs}}$ , and  $\epsilon_0$  are the absorbance of the complex and the observed absorbance and the molar absorptivity of Mo, respectively.  $\epsilon_0$  values were calculated at a mole fraction of Mo equal to 1 and are shown in Table 2. In Figure 2, a maximum at a mole fraction of Mo equal to 0.5 was obtained, indicating a 1:1 complex. The molar absorptivity of the complex,  $\epsilon_1$ , was calculated from the linear part of the aforementioned plot at a low mole fraction of Mo, where essentially all of the metal ions were in the form of a complex and are listed in Table 2. At the maximum point of the plot, the concentration of the complex is

$$[\text{C}] = \frac{A_c}{\epsilon_1} \quad (4)$$

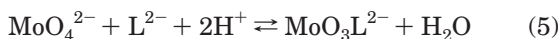
One advantage of using potentiometric methods is that the solution ionic strength may be kept constant. It should be noted that because of the high concentrations that must be employed for the NMR studies (minimum of 0.1 M in metal and ligand), the ionic strength of the solutions will continuously change as the pH changes.<sup>10,11</sup> This behavior is an unfortunate and unavoidable consequence of using NMR for equilibrium studies but is compensated somewhat by the additional information that is gained about the structural bonding and kinetic aspects of the complexes.<sup>10,11</sup>

The equilibria of molybdenum(VI) in aqueous solution are complex, and various polynuclear species in addition to the monomeric species  $\text{MoO}_4^{2-}$ ,  $\text{HMoO}_4^-$ , and  $\text{H}_2\text{MoO}_4$  may exist in acidified molybdate solutions.<sup>16,17</sup> The change in coordination number of molybdenum(VI) in monomeric molybdic acid has been discussed. Honig and Kustin<sup>18</sup> pointed out an increase in the coordination number of Mo(VI) from 4 to 6 in the first step of the protonation of the molybdate ion. Their conclusion was based on a slower recombination of  $\text{H}^+$  with  $\text{MoO}_4^{2-}$  than expected for a diffusion-controlled reaction. However, from a consideration of the thermodynamic parameters for the protonation of molybdate, Cruywagen and Rohwer<sup>19</sup> have suggested that only in the presence of a second proton are six-coordinate molybdate species to be expected.

**Table 3.** Average Values of  $\log \beta_{112}$  at pH 6.0 and Different Ionic Strengths for the Complexation of Molybdenum(VI) with EDDA at  $t = 25^\circ\text{C}$ 

$I/\text{mol dm}^{-3}$	$\log \beta_{112}$	experimental conditions	ref
0.1	$21.66 \pm 0.01$		this work
0.3	$21.27 \pm 0.03$		this work
0.5	$21.09 \pm 0.03$		this work
0.7	$20.60 \pm 0.01$		this work
1.0	$20.04 \pm 0.04$		this work
	$19.69 \pm 0.05$	$I = 3.0 \text{ mol dm}^{-3}$ , $t = 25^\circ\text{C}$	14

The three coordination sites of the  $\text{MoO}_3$  or  $\text{WO}_3$  central metal coordinating unit are occupied by one nitrogen and two acetate oxygen atoms of IDA, NTA, or EDTA and by two nitrogen atoms and one acetate oxygen atom of EDDA.<sup>14</sup> The first three complexes have analogous structures and therefore constants of formation of the same order of magnitude (except the  $\text{W(VI)}\text{-EDTA}$  complex).<sup>14</sup> All four ligands should be tridentate when coordinated to  $\text{MoO}_3$  and  $\text{WO}_3$ .<sup>14</sup> For NTA and EDDA, one acetate group is not bonded to the metal. For EDTA, two acetate groups and one amine group are not bonded to the metal; the end of the ligand not coordinated to  $\text{Mo(VI)}$  or  $\text{W(VI)}$  behaves much like an iminodiacetate group that can complex another  $\text{MoO}_3$  or  $\text{WO}_3$  central metal coordination unit.<sup>14</sup> Thus,  $\text{Mo(VI)}$  will bond with this tridentate ligand as a 1:1 complex<sup>14</sup>



with the stability constant  $\beta_{112}$  as

$$\beta_{112} = \frac{[\text{MoO}_3\text{L}^{2-}]}{[\text{MoO}_4^{2-}][\text{L}^{2-}][\text{H}^+]^2} \quad (6)$$

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 2:

$$C_M = [\text{Mo}] + [\text{C}] \quad (7)$$

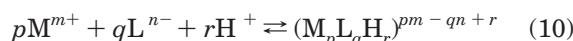
$$C_L = [\text{L}] + [\text{C}] \quad (8)$$

$[\text{C}]$  is the concentration of the complex. By substituting eqs 4, 7, and 8 in eq 6, we can calculate the values of  $\beta_{112}$  according to reaction 5. Stability constants have been calculated by the combination of spectrophotometric and potentiometric data. The values of  $\log \beta_{112}$  at different ionic strengths together with the literature values are shown in Table 3.

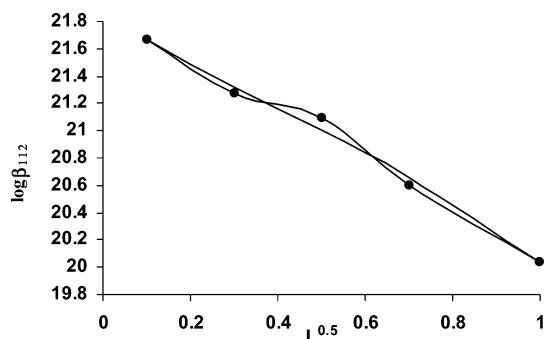
The dependence of the dissociation and stability constants on the ionic strength can be described according to previous work<sup>4-7,20-26</sup>

$$\log \beta_{112}(I) = \log \beta_{112}(I_1) - AZ^* \left( \frac{I^{0.5}}{1 + BI^{0.5}} - \frac{I_1^{0.5}}{1 + BI_1^{0.5}} \right) + C(I - I_1) + D(I^{1.5} - I_1^{1.5}) \quad (9)$$

where  $I$  and  $I_1$  are the actual and reference ionic strengths, respectively, and according to eq 10



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

**Figure 3.** Plot of  $\log \beta_{112}$  for  $\text{MoO}_3\text{L}^{2-}$  vs the square root of ionic strength.**Table 4.** Parameters for the Dependence on the Ionic Strength of Dissociation and Stability Constants at  $25^\circ\text{C}$ 

species	$C$	$D$	$Z^*$
$K_2$	$-0.895 \pm 0.100$	$0.372 \pm 0.004$	4
$K_1$	$1.292 \pm 0.005$	$-1.671 \pm 0.001$	2
$\text{MoO}_3\text{L}^{2-}$	$0.883 \pm 0.160$	$-1.928 \pm 0.008$	6

Considering  $A = 0.5115$  and  $B = 1.489$ , we can simplify eq 9:

$$\log \beta_{112}(I) = \log \beta_{112}(I_1) - Z^* \left( \frac{I^{0.5}}{2 + 3I^{0.5}} - \frac{I_1^{0.5}}{2 + 3I_1^{0.5}} \right) + C(I - I_1) + D(I^{1.5} - I_1^{1.5}) \quad (11)$$

where  $C$  and  $D$  are empirical coefficients and their values were obtained by minimizing the sum of the squares of the errors ( $U$ ) and the Gauss-Newton nonlinear least-squares method with a suitable computer program:

$$U = \sum_i (a_i - b_i)^2 \quad i = 1, 2, 3, \dots \quad (12)$$

where  $a$  is a quasi-experimental quantity and  $b_i$  is a calculated quantity. The values of  $C$  and  $D$  are shown in Table 4. In this research,  $a_i$  is the experimental stability constant and  $b_i$  is the calculated one.

The structure of  $\text{Mo(VI)}$ -aminopolycarboxylic acid complexes has been determined by Kula,<sup>9-12</sup> but we are looking for a correlation between ionic strength dependence patterns and the structures of the complexes, if there is one. Therefore, after more experimental work that is in progress, we will determine whether there is any correlation. The dependence on ionic strength of  $\log \beta_{112}$  is shown in Table 3, which is in good agreement with the results obtained in the previous papers.<sup>4-7,20-22</sup> In Figure 3, the dotted and continuous curves show the experimental and calculated stability constants, respectively. This Figure shows that no definite maximum or minimum can be detected. We can see only a mild decrease in the values of stability constants. Finally, we have inserted the values of  $C$  and  $D$  in eq 11, and then the values of calculated stability constants have been obtained. We have used  $I_1 = 0.1$  as the reference ionic strength in order to obtain better consistency between experimental and calculated stability constants. Therefore, by using eq 11 and the values of  $C$  and  $D$  it is very easy to calculate the values of stability constants for this complex in the desired range of the ionic strength without any further experimental work.

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