A modified equation for the calculation of the stability constants of W(VI)–NTA, Mo(VI)–NTA and Mo(VI)–glutamic acid complexes at different ionic strengths

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Abstract

The equilibria between molybdenum(VI) and tungsten(VI) with nitrilotriacetic acid (NTA) and glutamic acid are studied in aqueous solution at 25 °C and different ionic strengths ranging from (0.1 to 1.0) mol dm^{-3} (NaClO$_4$). Stoichiometry and stability of the complexes formed are determined from a combination of potentiometric, polarimetric and spectrophotometric measurements. Tungsten(VI) forms a mononuclear complex with NTA of the type (WO$_3$L^{3-}) at pH = 7.5. The complexation of molybdenum(VI) with nitrilotriacetic acid and glutamic acid occurs at pH = 6.0.

By introducing two empirical parameters C and D in these three complex formation reactions the dependence of the dissociation and stability constants on ionic strength is described by a Debye–Hückel type equation. Finally a comparison has been made between the calculated and experimental values of stability constants.
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Keywords: Ionic strength; Nitrilotriacetic acid; Glutamic acid; Tungsten(VI); Molybdenum(VI)

1. Introduction

The biological importance of tungsten has been fully proved in the last decade due to the isolation of a number of tungsten containing enzymes from hyperthermophilic archaea. Tungsten was previously considered only as an antagonist of molybdenum, because the replacement of molybdenum by tungsten (due to their chemical similarity) leads to inactivation of molybdenum containing enzymes. In addition to the "true W enzymes" in which tungsten can not be replaced by molybdenum, recently some enzymes have been isolated which can use either molybdenum or tungsten in the catalytic process.

Considerable studies have been performed on the stability constants of metals with α-aminoacids and aminopolycarboxylic acids, but only little work has been reported on the ionic strength dependence of stability constants of tungsten(VI) and molybdenum(VI) with nitrilotriacetic acid and glutamic

acid [1–3]. Marcu and Tomus [4] studied the radiochromatographic and electroradiochromatographic characteristics of various tungstate solutions under the action of NTA. Studies on the structural and bonding characteristics of various Mo(VI)-aminopolycarboxylic acid complexes have led to the evaluation of stability constants from proton nuclear magnetic resonance (NMR) data [5,6]. On the basis of these studies Kula and Rabenstein [7] determined the stability constants of W(VI)–NTA complexes by potentiometric techniques. Collin and Lagrange [8] reported the stability constant of this system at 25 °C and at an ionic strength of 0.5 mol dm^{-3} NaClO$_4$. Zare et al. [9] studied the W(VI)–NTA and Mo(VI)–NTA systems and evaluated their stability constants at 25 °C and at an ionic strength of 3 mol dm^{-3} NaClO$_4$ using the potentiometric technique. Chan et al. [10] proved that stable one to one molybdenum chelate is formed with NTA using the NMR technique. Raymond et al. [11] confirmed the existence of a MoO$_3$ core for the complexation of Mo(VI) with the tridentate ligand NTA. Funahashi et al. [12] studied the reaction of molybdate(VI) with nitrilotriacetate spectrophotometrically in aqueous solu-

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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}	logK_3	logK_2	logK_1	Experimental conditions	Ref
0.1	1.98±0.02	2.92±0.05	10.00±0.02		This work
0.3	1.83±0.04	2.84±0.03	9.85±0.01		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
			9.81±0.10	I=0.15 mol dm^{-3}, t=25 °C	[7]
	2.05±0.05	2.63±0.02	9.17±0.04	I=3 mol dm^{-3} NaClO$_4$, t=25 °C	[9]
	1.65	2.94	10.33	t=20 °C	[29]

tion of pH 6–8 at I=1.00 M (NaClO$_4$) and 25 °C. In a potentiometric study of molybdenum(VI) chelates with glutamic acid, Rabenstein et al. [13] reported the stability constant at 25 °C and at ionic strength of 0.2 mol dm^{-3} KNO$_3$. Raymond et al. [11] have synthesized and proved the composition of the complex using the spectroscopic technique. Gharib et al. [14] have proved the composition of glutamic acid complex and reported its stability constant, using the polarimetric and spectrophotometric techniques.

In this investigation we have calculated the stability constants of tungsten(VI)–NTA, molybdenum(VI)–NTA and molybdenum(VI)–glutamic acid complexes in an ionic strength range of (0.1 to 1.0) mol dm^{-3} sodium perchlorate at 25 °C by introducing two empirical parameters and using the Debye–Hückel type equation.

2. Experimental

2.1. Materials

Sodium perchlorate, perchloric acid, sodium hydroxide, sodium tungstate, sodium molybdate, nitrilotriacetic acid and

Table 2
Dissociation constants K_2 and K_1 of L-glutamic acid at different ionic strengths, I, of NaClO$_4$

I/mol dm^{-3}	logK_2	logK_1	Experimental conditions	Ref
0.1	4.24±0.05	9.64±0.05		This work
0.3	4.03±0.05	9.27±0.05		This work
0.5	3.76±0.05	9.19±0.05		This work
0.7	3.74±0.05	9.04±0.05		This work
1.0	3.60±0.05	8.98±0.05		This work
	4.15	9.49	I=0.15 mol dm^{-3} NaClO$_4$, t=25 °C	[14]
	4.21	9.54	I=0.1 mol dm^{-3} NaNO$_3$, t=25 °C	[30]
	4.05	9.46	I=0.1 mol dm^{-3} NaClO$_4$, t=30 °C	[31]
	4.15	9.61	I=0.1 mol dm^{-3} KNO$_3$, t=25 °C	[32]
	3.71	9.63	I=0.1 mol dm^{-3} NaClO$_4$, t=30 °C	[33]

Table 3
Continuous variations data for the W(VI)+NTA system at pH 7.5, Mo(VI)+NTA system at pH 6, an ionic strength of 0.1 mol dm^{-3} NaClO$_4$ and 265 nm

Mole fraction of metal	A^a	
	W(VI)+NTA	Mo(VI)+NTA
0.00	0.000	0.000
0.10	0.112	0.207
0.20	0.200	0.283
0.30	0.222	0.343
0.40	0.254	0.365
0.50	0.356	0.398
0.60	0.292	0.364
0.70	0.212	0.297
1.00	0.000	0.000

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

glutamic 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 specific conductance equal to $(1.3±0.1)$ µs cm^{-1} has been used.

2.2. Methods

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 [9]. 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. Polarimetric measurements were performed 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 two solutions of metal+ligand 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

Table 4
Continuous variations data for the Mo(VI)+L-glutamic acid system at pH 6.0, wavelength 265 nm, an ionic strength of 0.1 mol dm^{-3} NaClO$_4$

Mole fraction of Mo(VI)	A^a	Mole fraction of Mo(VI)	A^a
0.00	0.000	0.60	0.284
0.05	0.099	0.80	0.213
0.10	0.121	0.90	0.111
0.20	0.169	0.95	0.054
0.40	0.245	1.0	0.000
0.50	0.291		

^{a} The corrected absorbance of [Mo(VI)]+[L-glutamic acid]=0.02 mol dm^{-3}
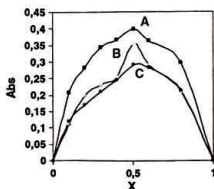
Fig. 1. Continuous variation plots of the absorbances of (A) MoO₃NTA³⁻, (B) WO₃NTA³⁻, (C) MoO₃Glu²⁻ Abs, versus the mole fractions of W(VI) and Mo(VI), X, at 25 °C, an ionic strength of 0.1 mol dm⁻³ NaClO₄ and 265 nm.

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 + HClO₄. The absorbance of the first solution was measured after adjusting the 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.

3. Results and discussion

The dissociation equilibria of nitrilotriacetic acid and glutamic acid have been studied in different kinds of background electrolytes but there are no reports about the ionic strength dependence of the dissociation constants of NTA and glutamic acid [1–3]. The following equilibria were studied:

$$H_3L \rightleftharpoons H^+ + H_2L^- \quad K_1 = [H^+][H_2L^-]/[H_3L] \quad (1)$$

$$H_2L^- \rightleftharpoons H^+ + HL^{2-} \quad K_2 = [H^+][HL^{2-}]/[H_2L^-] \quad (2)$$

$$HL^{2-} \rightleftharpoons H^+ + L^{3-} \quad K_3 = [H^+][L^{3-}]/[HL^{2-}] \quad (3)$$
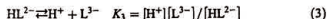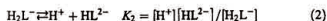
Where L^{3-} represents the fully dissociated ligand anion. The dissociation constants K_1, K_2 and K_3 were determined using potentiometric techniques and calculated using a suitable computer program [15–18]. For the glutamic

Table 5
Average values of logK_s at pH 7.5 and different ionic strengths for the complexation of tungsten(VI) with NTA, $t = 25$ °C

I/mol dm⁻³	logK_s	Experimental conditions	Ref
0.1	19.00 ± 0.30		This work
0.3	19.37 ± 0.10		This work
0.5	19.65 ± 0.25		This work
0.7	20.10 ± 0.10		This work
1.0	19.40 ± 0.20		This work
	18.86 ± 0.05	$I = 0.15$ mol dm⁻³, $t = 25$ °C	[7]
	19.10 ± 0.2	$I = 1.0 – 2.5$ mol dm⁻³, $t = 35$ °C	[7]
	17.75	$I = 0.5$ mol dm⁻³ NaClO₄, $t = 25$ °C	[8]
	19.03 ± 0.15	$I = 3$ mol dm⁻³ NaClO₄, $t = 25$ °C	[9]

Table 6
Average values of logK_s at pH 6.0 and different ionic strengths, for the complexation of molybdenum(VI) with NTA, $t = 25$ °C

I/mol dm⁻³	logK_s	Experimental conditions	Ref
0.1	18.72 ± 0.20		This work
0.3	19.36 ± 0.10		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	$I = 3$ mol dm⁻³ NaClO₄, $t = 25$ °C	[9]
	18.09 ± 0.04	$I = 1$ mol dm⁻³ NaClO₄, $t = 25$ °C	[12]

acid only K_1 and K_2 have been determined. These values are listed in Tables 1 and 2 together with the values reported in the literature, which are in good agreement with those reported before.

3.1. Complexation of tungsten(VI) and molybdenum(VI) with NTA

3.1.1. Theory and calculation

Using the continuous variation method, we determined the absorbances of solutions of complexes of W(VI) and Mo(VI) with NTA of total concentration 0.006 mol dm⁻³ in the UV range (260 to 265 nm) at a constant pH of 7.5. When solutions of tungstate are made into weak acid, polymeric anions are formed, but for stronger acid solutions, substances often called tungstic acid are obtained [19]. The behavior of the tungstate systems is similar to that of the molybdate systems. Again the degree of aggregation in solution increases as the pH is lowered, and numerous tungstate have been crystallized from the solutions at different pHs [19].

Using the potentiometric technique, results obtained for simple one to one metal–ligand chelates are more precise than for higher complexes, such as those formed with EDTA. In fact, for the multicomplex systems the NMR data are probably more reliable than the potentiometric data as indicated by the range of calculated values for the EDTA systems [7]. A comparison of the formation constants shows that within experimental error there is essentially no difference between the stabilities of the corresponding Mo(VI) and W(VI) chelates. This does not seem too surprising in view of the similarities of the two ions and their nearly equal ionic radii [7]. However, NMR studies show that tungsten chelates are significantly more labile with respect to individual metal–ligand bonds than are the molybdenum chelates [7].

Table 7
Average values of logK_s at pH 6.0 and different ionic strengths, for the complexation of molybdenum(VI) with L-glutamic acid, $t = 25$ °C

I/mol dm⁻³	logK_s	Experimental conditions	Ref
0.1	17.54 ± 0.30		This work
0.3	16.94 ± 0.40		This work
0.5	16.93 ± 0.50		This work
0.7	16.84 ± 0.35		This work
1.0	16.76 ± 0.40		This work
	16.78	$I = 0.2$ mol dm⁻³ NaClO₄, $t = 25$ °C	[13]
	16.73	$I = 0.15$ mol dm⁻³ NaClO₄, $t = 25$ °C	[14]

Table 8
Parameters for the dependence on the ionic strength of dissociation and stability constants for the W(VI)+NTA and Mo(VI)+NTA systems at 25 °C

Species	C	D	Z^*
K_3	1.057	−0.864	6
K_2	0.803	−0.730	4
K_1	0.210	−0.775	2
WO_3NTA^{3-}	8.099	−6.439	6
MoO_3NTA^{3-}	3.225	−3.294	6

For the NTA ligand system, NMR studies also indicate that only one metal–ligand species exists above pH 6, MoL^{x-} [7]. Thus, W(VI) will bond with this tridentate ligand as a 1:1 complex:

$$WO_4^{2-} + NTA^{3-} + 2H^+ \rightleftharpoons WO_3NTA^{3-} + H_2O \qquad (4)$$

with the stability constant, K_s, as:

$$K_s = [WO_3NTA^{3-}] / [WO_4^{2-}][NTA^{3-}][H^+]^2. \qquad (5)$$

The observed absorbances were corrected from Eq. (6) and are summarized in Tables 3 and 4 for the W(VI)–NTA and Mo(VI)–NTA systems and plotted in Fig. 1:

$$A_c = A_{obs} - \varepsilon_0[Metal]. \qquad (6)$$

A_c, A_{obs}, and ε_0 are the absorbance of the complex, the observed absorbance and the molar absorptivity of the metal, respectively. ε_0 values were calculated at the mole fraction of the metal equal to 1. In Fig. 1 a maximum at a mole fraction of the metal 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 aforementioned plot at low mole fraction of the metal, where essentially all metal ions were in the form of a complex. At the maximum point of the plot, the concentration of the complex is:

$$[C] = A_c / \varepsilon_1. \qquad (7)$$

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

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

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

The structures which were proposed for the Mo_2-EDTA chelate led to speculation concerning the possibility of forming one to one Mo(VI) chelates with methyliminodiacetic acid
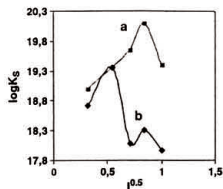
Table 9
Parameters for the dependence on the ionic strength of dissociation and stability constants for the Mo(VI)+L-glutamic acid system at 25 °C

Species	C	D	Z^*
K_2	−1.392	0.829	2
K_1	−1.401	1.008	4
MoO_3Glu^{2-}	−2.188	1.840	6

Fig. 2. Plot of $\log K_s$ versus the square root of ionic strength for (a) WO_3NTA^{3-}, (b) MoO_3NTA^{3-}.

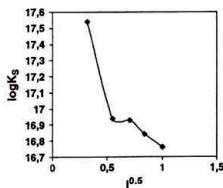Fig. 3. Plot of $\log K_s$ versus the square root of ionic strength for MoO_3Glu^{2-}.

(MIDA) and nitrilotriacetic acid (NTA) and proton NMR studies of these chelates confirmed that the predominate EDTA chelate does indeed contain two Mo ions and that stable one to one molybdenum chelates are formed with MIDA and NTA [5]. Thus, Mo(VI) will bond with this tridentate ligand (NTA) as a 1:1 complex:

$$MoO_4^{2-} + NTA^{3-} + 2H^+ \rightleftharpoons MoO_3NTA^{3-} + H_2O \qquad (10)$$

with the stability constant, K_s, as:

$$K_s = [MoO_3NTA^{3-}] / [MoO_4^{2-}][NTA^{3-}][H^+]^2. \qquad (11)$$

By substituting Eqs. (7) (8) and (9) in Eqs. (5), (11) and (12) we can calculate the values of K_s. We did not take into account the hydrolysis constants of the metals. The values of $\log K_s$ at

Table 10
Calculated values of $\log K_s$ at pH 7.5 and different ionic strengths for the complexation of tungsten(VI) and molybdenum(VI) with NTA, t=25 °C

I/mol dm^{-3}	W(VI)+NTA	Mo(VI)+NTA
0.1	19.00	18.72
0.3	19.51	18.67
0.5	19.78	18.56
0.7	19.82	18.36
1.0	19.50	17.87

different ionic strengths together with the values of literature are shown in Tables 5 and 6.

3.2. Complexation of molybdenum(VI) with glutamic acid

The effect of pH on the optical activity of glutamic acid and its complex with molybdenum(VI) shows the difference of optical rotation for the ligand and the complex. This difference reaches a maximum in the pH range 5.0–6.0, which means that we have the largest amount of complex formation in this pH range.

Using the continuous variation method, we determined the absorbances of solutions of Mo(VI) and glutamic acid of total concentration 0.02 mol dm^{-3} in the UV range (260 to 265 nm) at a constant pH of 6.0. In Fig. 1 a rather sharp maximum at a mole fraction of Mo equal to 0.5 was obtained indicating a 1:1 complex.

Although Mo(VI) forms complexes with the same chelating agents as most other metal ions, its chemistry is differentiated from 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. For the glutamic acid the species is MoO_3Glu^{2-} [3] with the stability constant as:

$$K_s = [MoO_3Glu^{2-}]/[MoO_4{}^{2-}][Glu^{2-}][H^+]^2. \quad (12)$$

The values of logK_s for the glutamic acid complex together with the values of the literature are shown in Table 7.

3.3. Ionic strength dependence of dissociation and stability constants

The dependence of the dissociation and stability constants on the ionic strength can be described according to the previous works [1,16–18,20–28]:

$$\log K_s(I) = \log K_s(I_1) - AZ^* \left(\frac{I^{0.5}}{1 + BI^{0.5}} - \frac{I_1{}^{0.5}}{1 + BI_1{}^{0.5}} \right) \\ + C(I - I_1) + D(I^{1.5} - I_1{}^{1.5}) \quad (13)$$

where I and I_1 are the actual and reference ionic strengths, respectively and according to Eq. (14):

$$pM^{m+} + qL^{n-} + rH^+ \rightleftharpoons (M_pL_qH_r)^{pm-qn+r} \quad (14)$$

$Z^* = pm^2 + qn^2 + r - (pm + qn + r)^2$, where m and n are the charges on the metal ion and the ligand, respectively. Considering, $A = 0.5115$ and $B = 1.489$ Eq. (13) can be simplified:

$$\log K_s(I) = \log K_s(I_1) - Z^* \left(\frac{I^{0.5}}{2 + 3I^{0.5}} - \frac{I_1{}^{0.5}}{2 + 3I_1{}^{0.5}} \right) \\ + C(I - I_1) + D(I^{1.5} - I_1{}^{1.5}) \quad (15)$$

where C and D are empirical parameters and their values were obtained by minimizing the error squares sum, (U), and the

Table 11
Calculated values of logK_s at pH 6.0 and different ionic strengths for the complexation of molybdenum(VI) with glutamic acid, $t = 25$ °C

I/mol dm^{-3}	logK_s
0.1	17.54
0.3	17.09
0.5	16.87
0.7	16.78
1.0	16.80

Gauss–Newton nonlinear least squares method in a suitable computer program:

$$U = \sum_i (a_i - b_i)^2 \quad (i = 1, 2, 3, \ldots) \quad (16)$$

where a is a quasi-experimental quantity and b_i is a calculated one. The values of C and D are shown in Tables 8 and 9.

4. Conclusions

According to Fig. 2 there are two maximums ($I = 0.3$ and $I = 0.7$) in the Mo(VI)+NTA complex, but there is only one maximum in the W(VI)+NTA complex. For the Mo(VI)+glutamic acid system, at first we have a deep decrease and then after $I = 0.5$ this decrease continues with a milder slope, so we can not detect any maximum. Anyway it seems that at the minimum points attractive and repulsive forces are equal but before the minimum points attractive forces are dominant and after the minimum points repulsive forces are more important (Fig. 3).

Finally we can insert the obtained values of C and D in Eq. (15) and then it is very easy to calculate the values of stability constants in the desired range of the ionic strength without any further experimental work (Tables 10 and 11). Comparison of the experimental and calculated stability constants shows a very good agreement.

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