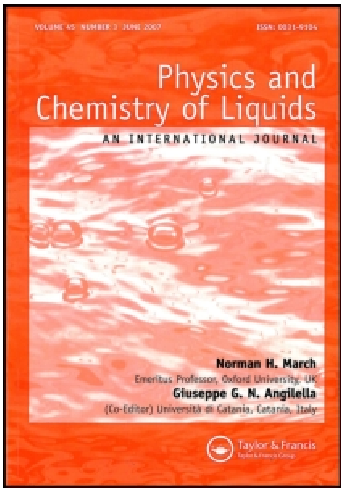

Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Determination and comparison of stability constants of tungsten(VI) and molybdenum(VI) with nitrilotriacetic acid and glutamic acid at different ionic strengths

Kavosh Majlesi[a]; Karim Zare[ab]
[a] Chemistry Department, Islamic Azad University, Science & Research Campus, Tehran, Hesarak, Iran
[b] Chemistry Department, Shahid Beheshti University, Tehran, Evin, Iran

To cite this Article Majlesi, Kavosh and Zare, Karim(2006) 'Determination and comparison of stability constants of tungsten(VI) and molybdenum(VI) with nitrilotriacetic acid and glutamic acid at different ionic strengths', Physics and Chemistry of Liquids, 44: 3, 257 — 268

To link to this Article: DOI: 10.1080/00319100500509645

URL: http://dx.doi.org/10.1080/00319100500509645

Physics and Chemistry of Liquids
Vol. 44, No. 3, June 2006, 257–268

Determination and comparison of stability constants of tungsten(VI) and molybdenum(VI) with nitrilotriacetic acid and glutamic acid at different ionic strengths

KAVOSH MAJLESI*† and KARIM ZARE†‡

†Chemistry Department, Islamic Azad University, Science & Research Campus, Tehran, Hesarak, Iran
‡Chemistry Department, Shahid Beheshti University, Tehran, Evin, Iran

(*Received 2 December 2005; revised 7 December 2005*)

The formation constants of species formed in the systems $H^+ + W(VI)$ + nitrilotriacetic acid (NTA) and H^+ + NTA have been determined in aqueous solution for pH = 4–9 at 25°C and different ionic strengths ranging from 0.1 to 1.0 mol dm^{-3} $NaClO_4$, using potentiometric and spectrophotometric techniques. It was shown that tungsten(VI) forms a mononuclear 1 : 1 complex with NTA of the type WO_3L^{3-} at pH = 7.5. The composition of the complex was determined by the continuous variations method. The complexation of molybdenum(VI) with glutamic acid was investigated in aqueous solution ranging in pH from 4 to 9, using polarimetric, potentiometric and spectrophotometric 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 glutamic acid of the type MoO_3L^{2-} at pH = 6.0. The dissociation constants of glutamic acid and the stability constants of the complex were determined at 25°C and at ionic strengths ranging from 0.1 to 1.0 mol dm^{-3} sodium perchlorate. In both complex formation reactions the dependence of the dissociation and stability constants on ionic strength is described by a Debye-Huckel type equation. Finally, a comparison has been made between the patterns of ionic strength dependence for the two complexes and the results have been compared with data previously reported.

Keywords: Ionic strength; Tungsten(VI); Molybdenum(VI); NTA; Glutamic acid; Stability constant

1. Introduction

By pursuing our systematic study on complexation of transitional metal ions by natural and biological ligands, we thought it interesting to investigate the complexation of W(VI) with nitrilotriacetic acid (NTA) and Mo(VI) with glutamic acid at different ionic strengths of sodium perchlorate. Desulphovibrio gigas formate dehydrogenase

---

*Corresponding author. Email: kavoshmajlesi@hotmail.com

Physics and Chemistry of Liquids
ISSN 0031-9104 print: ISSN 1029-0451 online
DOI: 10.1080/00319100500509645

is the first representative of a tungsten-containing enzyme from a mesophile that has been structurally characterized [1]. It is a heterodimer of 110 and 24 kDa subunits. The existence of a universal pterin dithiolene cofactor ligand for the molybdenum and tungsten oxotransferases supports a biological significance of the fundamental chemistry of mono and bis (dithiolene) complexes of these elements [2]. Tungsten(VI) also forms complexes with tryptophan [3] and porphyrin [4]. Molybdenum is capable of coordinating with an enormous variety of ligands and is present in cofactors of several enzymes. As a result, structural, thermodynamic and kinetic aspects of this metal have been the subject of several investigations.

Considerable number of studies have been performed on the stability constants of metals with α-aminoacids and aminopolycarboxylic acids, but to our knowledge only two works have been reported on the ionic strength dependence of stability constants of tungsten(VI) with NTA and molybdenum(VI) with glutamic acid [5,6]. Marcu [7] studied the radiochromatographic and electroradiochromatographic of sodium tungstate solutions under the action of NTA. Studies on the structural and bonding characteristics of various Mo(VI)–aminopolycarboxylic acid complexes has led to the evaluation of stability constants from proton nuclear magnetic resonance (NMR) data [8,9]. On the basis of these studies Kula [10] determined the stability constants of W(VI)–NTA complexes by potentiometric techniques. Collin [11] reported the stability constant of this system at 25°C and at an ionic strength of 0.5 mol dm^{-3} $NaClO_4$. Zare [12] studied this system and evaluated its stability constant at 25°C and at an ionic strength of 3 mol dm^{-3} $NaClO_4$ using the potentiometric technique. In a potentiometric study of molybdenum(VI) chelates with glutamic acid, Rabenstein [13] reported the stability constant at 25°C and at ionic strength of 0.2 mol dm^{-3} KNO_3. Raymond [14] has synthesized and proved the composition of the complex using the spectroscopic technique. Gharib [15] have proved the composition of glutamic acid complex and reported its stability constant, using the polarimetric and spectrophotometric techniques.

The present article describes the complexation of W(VI) with NTA and Mo(VI) with glutamic acid in an ionic strength range of 0.1 to 1.0 mol dm^{-3} sodium perchlorate at 25°C. The parameters that define the dependence on ionic strength were analyzed with the aim of obtaining further information regarding their variation as a function of the charges involved in the complex reaction. Moreover, we introduce a Debye-Huckel type equation for the dependence of dissociation and stability constants on ionic strength.

2. Experimental section

2.1. *Reagents*

Sodium perchlorate, perchloric acid, sodium hydroxide, sodium molybdate, sodium tungstate, L-glutamic acid, 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 specific conductance equal to $1.3 \pm 0.1\ \mu\Omega^{-1}\,cm^{-1}$ have been used.

2.2. *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 [12]. 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. 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.

3. Results and discussion

The dissociation equilibria of NTA 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 [5,6]. The following equilibria were studied:

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

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

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

where L^{3-} represents the fully dissociated ligand anion. The dissociation constants K_1, K_2 and K_3 have been determined using potentiometric techniques and calculated using a suitable computer program [16]. For the glutamic 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) with NTA*

Using the continuous variations method, we determined the absorbances of solutions of W(VI) and NTA of total concentration 0.006 mol dm^{-3} in the UV range 260–270 nm at a constant pH of 7.5. When solutions of tungstates are made weakly acid, polymeric anions are formed, but from more strongly acid solutions substances often called tungstic acid are obtained [17]. The behaviour of the tungstate systems is similar to that of the molybdate systems. Again the degree of aggregation in solution increases as the

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	Reference
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
	2.05 ± 0.05	2.63 ± 0.02	9.17 ± 0.04	$I = 3$ M $NaClO_4$, $t = 25°C$	[12]
	1.65	2.94	10.33	$t = 20°C$	[32]

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	Reference
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	$I = 0.15$ M $NaClO_4$, $t = 25°C$	[15]
	4.21	9.54	$I = 0.1$ M $NaNO_3$, $t = 25°C$	[33]
	4.05	9.46	$I = 0.1$ M $NaClO_4$, $t = 30°C$	[34]
	4.15	9.61	$I = 0.1$ M KNO_3, $t = 25°C$	[35]
	3.71	9.63	$I = 0.1$ M $NaClO_4$, $t = 30°C$	[36]

pH is lowered, and numerous tungstates have been crystallized from the solutions at different pHs [17].

It is now certain that WO_4^{2-} ion is tetrahedral in aqueous solution [17]. In the usual potentiometric method for evaluating metal–ligand stability constants, the competition between metal ion and hydrogen ion for the ligand is studied, and the pH region of interest is from about 1 to 5 [10]. In the W(VI) systems, however, the complication of metal polymerization is introduced in acidic solutions. Because the polymerization equilibria are not well understood, this pH region is not useful for stability determinations. In more alkaline solutions, on the other hand, a pH-dependent process involving the competition between tungstate formation and metal–ligand complexation i.e., a competition between OH^- and ligand for the metal ion can be utilized. This process was determined from the NMR studies to be important from about pH 6 to 9 and can be represented by [10]:

$$MO_3L^{x-} + OH^- \rightleftarrows MO_4^{2-} + HL^{1-x} \tag{4}$$

where M represents W and L represents the aminopolycarboxylic acid ligand. In the pH region above 6 no evidence was found for any Mo species containing fewer than three oxygen atoms—e.g., MoO_2^{2+}—as has been proposed for other systems [18]. The molybdenum coordinating species in all the aminopolycarboxylic acid systems above pH 6 is MoO_3, and by analogy we have assumed that the corresponding coordinating unit in the tungsten systems is WO_3.

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 [10]. 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 [10]. However, NMR studies show that tungsten chelates are significantly more labile with respect to individual metal–ligand bonds than are the molybdenum chelates. The slowness with which pH equilibrium was attained in the NTA chelates may be explained by the higher negative charge of this complex compared to the other complexes and the subsequently slower reaction with OH^-:

$$MO_3NTA^{3-} + OH^- \longrightarrow MO_4^{2-} + HNTA^{2-} \tag{5}$$

For NTA ligand system, NMR studies also indicate that only one metal–ligand species exists above pH 6, MO_3L^{x-} [10]. Thus, W(VI) will bond with this tridentate ligand as a 1 : 1 complex:

$$WO_4^{2-} + L^{3-} + 2H^+ \rightleftarrows WO_3L^{3-} + H_2O \tag{6}$$

with the stability constant, K_S, as:

$$K_S = \frac{[WO_3L^{3-}]}{[WO_4^{2-}][L^{3-}][H^+]^2} \tag{7}$$

The values of $\log K_S$ at different ionic strengths together with the values of literature are shown in table 7. These values have been calculated similar to the molybdenum(VI) complex.

3.2. *Complexation of molybdenum(VI) with glutamic acid*

3.2.1. Polarimetric studies. 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.

3.2.2. Spectrophotometric studies. Using the continuous variations 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 260–270 nm at a constant pH of 6.0. 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 [19]. At higher pH, the complex dissociates as a result of the competitive formation of MoO_4^{2-} [17]. The observed absorbances were corrected from equation (8) and are summarized in tables 3 and 4 and plotted in figures 1 and 2:

$$A_c = A_{obs} - \varepsilon_0[M] \tag{8}$$

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

Table 3. Continuous variations data for the W(VI) + NTA system at pH 7.5, an ionic strength of 0.1 M $NaClO_4$ and different wavelengths.

	A^a		
Mole fraction of W(VI)	260 nm	265 nm	270 nm
0.00	0.000	0.000	0.000
0.10	0.120	0.112	0.100
0.20	0.194	0.200	0.198
0.30	0.200	0.230	0.240
0.40	0.213	0.254	0.255
0.50	0.307	0.356	0.356
0.60	0.243	0.292	0.292
0.80	0.143	0.212	0.182
1.00	0.000	0.000	0.000

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

Table 4. Continuous variations data for the Mo(VI) + L-glutamic acid system at pH 6.0, wavelength 265 nm, and ionic strength 0.1 M $NaClO_4$.

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}.

fraction of Mo and W equal to 1 and are shown in tables 5 and 6. In figures 1 and 2(a) maximum at a mole fraction of Mo and W equal to 0.5 was obtained, indicating a 1 : 1 complex. The molar absorptivity of the complex, ε_1, were calculated from the linear part of the aforementioned plots at low mole fraction of the metal, where essentially all the metal ions were in the form of a complex, and are listed in tables 5 and 6. At the maximum point of the plot, the concentration of the complex is:

$$[\mathrm{C}] = \frac{A_c}{\varepsilon_1} \tag{9}$$

The molybdate anion MoO_4^{2-} maintains a tetrahedral configuration in neutral and alkaline solutions [17]. 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 [20] 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.

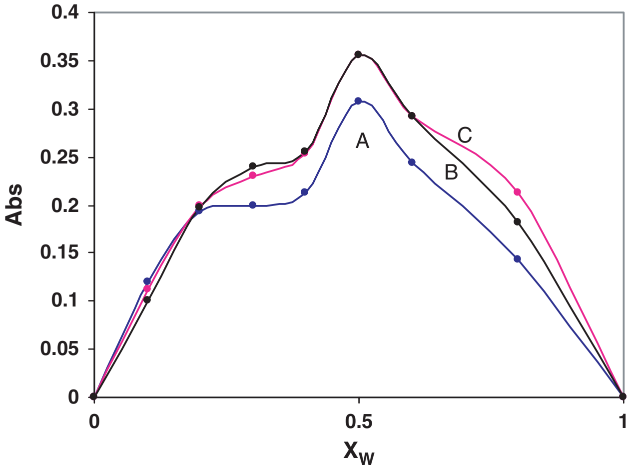

Figure 1. Continuous variations plots of the absorbances of WO_3NTA^{3-}, Abs, *vs.* the mole fraction of W(VI), X_W, at 25°C, an ionic strength of 0.1 mol dm^{-3} $NaClO_4$ and different wavelengths: (A) 260, (B) 265, and (C) 270 nm.

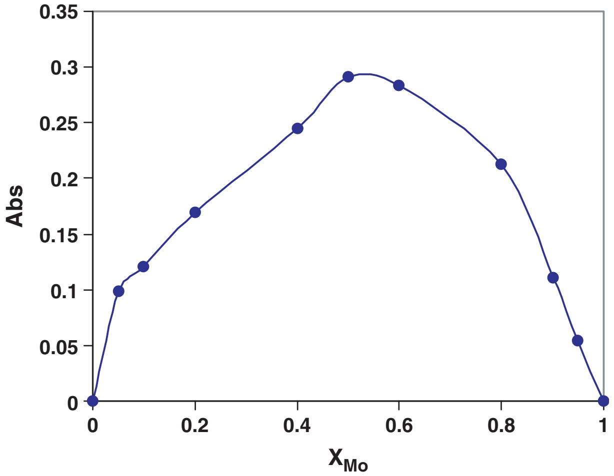

Figure 2. Continuous variations plots of the absorbances of MoO_3Glu^{2-}, Abs, *vs.* the mole fraction of Mo(VI), X_{Mo}, at 25°C, an ionic strength of 0.1 mol dm^{-3} $NaClO_4$ and wavelength 265 nm.

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. Raymond et al. [14] synthesized $Na[MoO_3(Glu)]H_2O$, among other molybdenum chelate complexes. The IR spectrum of this compound that was crystallized at pH = 6 shows the glutamate ion as a tridentate ligand coordinated to a *cis*-trioxo molybdenum core. A *cis*-dioxo molybdenum core was formed with tetradentate ligands, and, in the case of glycine, with two

Table 5. Molar absorptivities of W(VI), ε_0, and WO_3L^{3-}, ε_1, at pH 7.5, different wavelengths and various ionic strengths, *I*, of $NaClO_4$.

	ε_0			ε_1		
I (mol dm^{-3})	260 nm	265 nm	270 nm	260 nm	265 nm	270 nm
0.1	660.8	486.6	486.6	1116.6	1116.6	1116.6
0.3	527.5	365.0	246.1	1221.6	1268.3	1250.0
0.5	505.8	345.0	245.8	1533.3	1583.3	1716.6
0.7	478.3	320.0	224.1	716.6	750.0	766.6
1.0	522.5	355.0	251.6	2316.6	2350.0	2333.3

Table 6. Molar absorptivities of Mo(VI), ε_0, and MoO_3L^{2-}, ε_1, for the Mo(VI) + L-glutamic acid system at pH 6.0, different wavelengths and various ionic strengths, *I*, $NaClO_4$.

	ε_0		ε_1	
I (mol dm^{-3})	260 nm	265 nm	260 nm	265 nm
0.1	183.5	163.5	273.5	98.8
0.3	176.9	158.5	285.1	109.5
0.5	175.9	156.6	268.1	94.4
0.7	180.1	160.6	269.9	97.4
1.0	186.9	160.2	265.1	98.8

bidentate ligands. The formation of a *cis*-trioxo Mo(VI) core requires two hydrogen ions:

$$MoO_4^{2-} + 2H^+ \rightleftarrows MoO_3 + H_2O$$

whereas a *cis*-dioxo molybdenum(VI) species requires four:

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

If glutamic acid at a lower pH value has one of its ligating sites occupied by a hydrogen ion, it might be expected that a complex with two glutamic acid molecules per molybdate could be formed. However, Johansen and Jons [21] concluded that at pH 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 glutamic acid thus has Mo ligand proton equal to 1 : 1 : 2 stoichiometry as:

$$MoO_4^{2-} + L^{2-} + 2H^+ \rightleftarrows MoO_3L^{2-} + H_2O \qquad (10)$$

with the stability constant, K_S, as:

$$K_S = \frac{[MoO_3L^{2-}]}{[MoO_4^{2-}][L^{2-}][H^+]^2} \qquad (11)$$

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 figures 1 and 2:

$$C_M = [M] + [C] \qquad (12)$$

$$C_L = [L] + [C] \qquad (13)$$

Table 7. Average values of log K_S at pH 7.5 and different ionic strengths for the complexation of tungsten(VI) with NTA, $t = 25°C$.

I (mol dm^{-3})	log K_S	Experimental conditions	Reference
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	$I = 0.15$ M, $t = 25°C$	[10]
	19.10 ± 0.2	$I = 1.0$–2.5 M, $t = 35°C$	[10]
	17.75	$I = 0.5$ M NaClO$_4$, $t = 25°C$	[11]
	19.03 ± 0.15	$I = 3$ M NaClO$_4$, $t = 25°C$	[12]

Table 8. Average values of log K_S at pH 6 and different ionic strengths, for the complexation of molybdenum(VI) with L-glutamic acid, $t = 25°C$.

I (mol dm^{-3})	log K_S	Experimental conditions	Reference
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	$I = 0.2$ M NaClO$_4$, $t = 25°C$	[13]
	16.73	$I = 0.15$ M NaClO$_4$, $t = 25°C$	[15]

By substituting equations (9), (12) and (13) in equation (11) we can calculate the values of K_S. The values of log K_S at different ionic strengths together with the values of literature are shown in table 8.

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 [16,22–31]:

$$\log K_S(I) = \log K_S(I_1) - AZ^*\left(\frac{I^{0.5}}{1+BI^{0.5}} - \frac{I_1^{0.5}}{1+BI_1^{0.5}}\right) + C(I - I_1) + D(I^{1.5} - I_1^{1.5}) + E(I^2 - I_1^2) \tag{14}$$

where I and I_1 are the actual and reference ionic strengths, respectively and according to equation (15):

$$pM^{m+} + qL^{n-} + rH^+ \rightleftarrows (M_pL_qH_r)^{pm-qn+r} \tag{15}$$

$Z^* = pm^2 + qn^2 + r - (pm + qn + r)^2$, where m and n are the charges on the metal ion and the ligand respectively. Considering, $A = 0.5115$ and $B = 1.489$ equation (14) can be simplified:

$$\log K_S(I) = \log K_S(I_1) - Z^*\left(\frac{I^{0.5}}{2+3I^{0.5}} - \frac{I_1^{0.5}}{2+3I_1^{0.5}}\right) + C(I - I_1) + D(I^{1.5} - I_1^{1.5}) + E(I^2 - I_1^2) \tag{16}$$

Table 9. Parameters for the dependence on the ionic strength of dissociation and stability constants for the W(VI) + NTA system at 25°C.

Species	C	D	E	Z*
K_3	2.933	−4.807	2.161	6
K_2	4.860	−9.257	4.673	4
K_1	−0.292	0.280	−0.578	2
WO_3L^{3-}	−8.294	28.021	−18.886	6

Table 10. 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	E	Z*
K_2	−0.782	−0.453	0.702	2
K_1	−3.346	5.097	−2.241	4
MoO_3L^{2-}	−10.791	19.924	−9.911	6

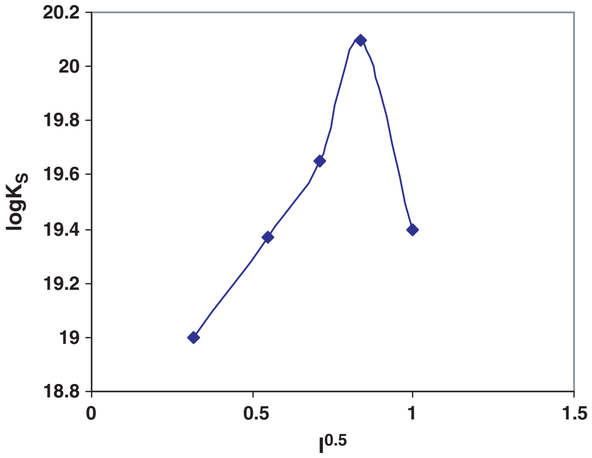

Figure 3. Plot of $\log K_S$ for WO_3NTA^{3-} *vs.* the square root of ionic strength.

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

$$U = \sum_i (a_i - b_i)^2 \quad (i = 1, 2, 3, \ldots) \tag{17}$$

where a is a quasi-experimental quantity and b_i is a calculated one. The values of C, D and E are shown in tables 9 and 10.

4. Conclusion

According to figures 3 and 4 it seems that the attraction forces are dominant before the minimum points and the systems are stabilized. The repulsive forces are more important

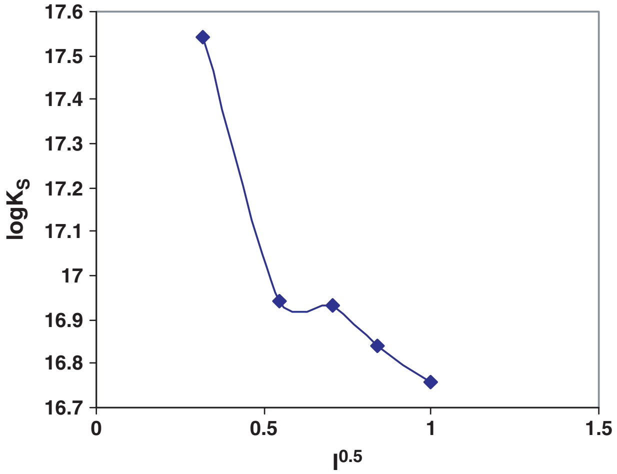

Figure 4. Plot of logK_S for MoO_3Glu^{2-} *vs.* the square root of ionic strength.

after the minimum points, therefore the stability of the systems are decreased. At the minimum points, attraction and repulsive forces between the ions are equal. Figure 3 shows that K_S has one maximum at $I = 0.7$. Figure 4 shows that the curve has a descending pattern. According to the obtained values of C, D, E and equation (16) it is very easy to calculate the values of stability constants for these complexes in the desired range of the ionic strength without any further experimental work. The dependence on ionic strength of log K_S is shown in tables 7 and 8 which are in good agreement with the results obtained in the previous papers [6,16,30]. We have used $I_1 = 0.1$ as the reference ionic strength in order to obtain better consistency between experimental and calculated stability constants.

References

[1] H. Raaijmakers, S. Macieira, J.M. Dias, S. Teixeira, S. Burasakov, R. Huber, J.J.G. Moura, I. Moura, M.J. Romo. *Structure*, **10**, 1261 (2002).
[2] C. Lorber, J.P. Donahue, C.A. Goddard, E. Nord, R.H. Holm. *J. Am. Chem. Soc.*, **120**, 8102 (1998).
[3] K. Gielzak, W. Wojciechowski. *Pol. J. Chem.*, **62**, 559 (1988).
[4] C.H. Yang, S.J. Dzugan, V.L. Goedken. *J. Chem. Soc. Chem. Commun.*, **20**, 1425 (1985).
[5] K. Majlesi, K. Zare, F. Teimouri. *J. Chem. Eng. Data*, **49**, 439 (2004).
[6] F. Gharib, K. Zare, K. Majlesi. *J. Chem. Eng. Data*, **45**, 833 (2000).
[7] G. Marcu, M. Tomus. *Ser. Chem*, **13**, 11 (1968).
[8] R.J. Kula. *Anal. Chem.*, **38**, 1382 (1966).
[9] R.J. Kula. *Anal. Chem.*, **38**, 1581 (1966).
[10] R.J. Kula, D.L. Rabenstein. *Anal. Chem.*, **38**, 1934 (1966).
[11] J.P. Collin, P. Lagrange. *Bull. Soc. Chim. France*, **9–10**, 1304 (1976).
[12] K. Zare, P. Lagrange, J. Lagrange. *J. Chem. Soc., Dalton Trans.*, 1372 (1979).
[13] D.L. Rabenstein, M.S. Greenberg, R. Saetre. *Inorg. Chem.*, **16**, 1241 (1977).
[14] J. Raymond, H. Butcher, J. Kipton, J. Powell. *J. Chem. Soc., Dalton Trans.*, 356 (1976).
[15] F. Gharib, S.A. Khorrami, S. Sharifi. *Proc. Indian Acad. Sci. (Chem. Sci.)*, **109**, 71 (1997).
[16] K. Majlesi, K. Zare, F. Teimouri. *J. Chem. Eng. Data*, **48**, 680 (2003).
[17] F.A. Cotton, G. Wilkinson. *Advanced Inorganic Chemistry*, 3rd Edn, Wiley-Interscience, New York (1972).

[18] G. Spengler, J. Gansheimer. *Angew. Chem.*, **69**, 523 (1957).
[19] S. Funahashi, Y. Kato, M. Nakayama, M. Tanaka. *Inorg. Chem.*, **20**, 1752 (1981).
[20] J.J. Cruywagen, E.F.C.H. Rohwer. *Inorg. Chem.*, **14**, 3136 (1975).
[21] E.S. Johansen, O. Jons. *Acta Chem. Scand*, **35**, 233 (1981).
[22] C. De Stefano, C. Foti, A. Gianguzza. *Talanta*, **41**, 1715 (1994).
[23] P.G. Daniele, C. Rigano, S. Sammartano, V. Zelano. *Talanta*, **41**, 1577 (1994).
[24] R. Gil, M.S. Corbillon, M.A. Olazabal, J.M. Madariaga. *Talanta*, **44**, 891 (1997).
[25] P.G. Daniele, C. Rigano, S. Sammartano. *Anal. Chem.*, **57**, 2956 (1985).
[26] A. De Robertis, C. Foti, A. Gianguzza. *J. Chem. Res.*, 288 (1995).
[27] A. De Robertis, C. De Stefano, S. Sammartano, C. Rigano. *Talanta*, **34**, 933 (1987).
[28] C. De Stefano, A. Gianguzza, D. Piazzese. *J. Chem. Eng. Data*, **45**, 876 (2000).
[29] P.G. Daniele, A. De Robertis, C. De Stefano, S. Sammartano, C. Rigano. *J. Chem. Soc.*, 2355 (1985).
[30] Majlesi, K., Zare, K. *Sixth Iranian Physical Chemistry Seminar*, Faculty of Science, Urmia University, 27–29 August 2002, Urmia, Iran.
[31] F. Gharib, K. Zare, K. Majlesi. *J. Chem. Res.*, 186 (2000).
[32] J.A. Dean. *Lange's Handbook of Chemistry*, 14th edn, McGraw Hill, New York (1992).
[33] W.E. Van Der Linden, C. Beers. *Anal. Chim. Acta*, **68**, 143 (1973).
[34] D.N. Shelke, D.V. Jahagirdar. *J. Inorg. Nucl. Chem.*, **41**, 1635 (1979).
[35] T. Sakurai, O. Yamauchi, A. Nakahara. *Bull. Chem. Soc. Jpn.*, **51**, 3203 (1978).
[36] D.N. Shelke, D.V. Jahagirdar. *Indian J. Chem.*, **16A**, 60 (1978).