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Comparison of the Application of Debye–Huckel and Specific Ion Interaction Theories for the Complexation of Tungsten(VI) with Ethylenediaminediacetic Acid

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Abstract—Equilibrium of the reaction of tungsten(VI) with ethylenediaminediacetic acid (EDDA) has been investigated in aqueous solution of pH 7.5 and 25°C. All measurements have been carried out at different ionic strengths ranging from (0.1 to 1.0) mol dm⁻³ (NaClO₄). According to our results the metal to ligand ratio is 1 : 1. Stability constants and stoichiometry of the complex have been determined from a combination of potentiometric and UV spectroscopic measurements. In this semi-empirical model, two parameters have been introduced in a Debye–Huckel type equation based on the Gauss–Newton nonlinear least-squares method and minimizing the sum of the squares of the errors. Comparison of the ionic strength effect on these complex formation reactions has been made using a Debye–Huckel type equation and Bronsted–Guggenheim–Scatchard specific ion interaction theory (SIT).

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Data obtained so far indicate a very important biological role of tungsten in various metabolic processes and the participation of this microelement in enzymes catalyzing these processes [1]. W enzymes catalyze oxidation-reduction reactions at much lower redox potentials than their Mo analogs [1]. Thus, one can conclude that hyperthermophilic bacteria and archaea with anaerobic metabolism synthesize W enzymes [1]. It is supposed that before the appearance of molecular oxygen formed during photosynthesis, molybdenum and tungsten were present on the Earth as sulfides (MoS and WS) rather than oxyanions (MoO and WO). Since tungsten sulfide is better soluble in water than molybdenum sulfide, it is supposed that in the pre oxygen epoch tungsten could be more available to organisms than molybdenum. Although Chan [2] and Kula [3–6] studied on the structure and stability constants of molybdenum(VI) and tungsten(VI) complexes with some aminopolycarboxylic acids (NTA, EDTA, MIDA, IDA), according to our knowledge there is no report about the ionic strength dependence of the stability constants of W(VI) with EDDA. Zare [7] studied W(VI)-EDDA complex and evaluated its stability constant at 25°C and at an ionic strength of 3 mol dm⁻³ NaClO₄ using the potentiometric technique and recently reported a primary investigation about the ionic strength dependence of this complex [8]. In this study, the complexation between tungsten(VI) and EDDA was studied at 25°C with (0.1, 0.3,

0.5, 0.7 and 1.0) mol dm⁻³ sodium perchlorate as ionic medium. These results and a modified Debye–Huckel equation allows us to predict the values of stability constants in the desired range of ionic strengths. Finally SIT and Debye–Huckel models have been compared for the study of ionic strength effects.

EXPERIMENTAL PROCEDURES

Reagents

Sodium perchlorate, perchloric acid, sodium hydroxide, sodium tungstate were obtained from E. Merck and ethylenediaminediacetic acid from Fluka as analytical reagent grade materials and were used without further purification. Dilute perchloric acid solution was standardized against KHCO₃. In all experiments double-distilled water with specific conductance equal to (1.3 ± 0.1) μS cm⁻¹ has been used.

Measurements

All measurements were carried out at (25 ± 0.1)°C. 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 con-

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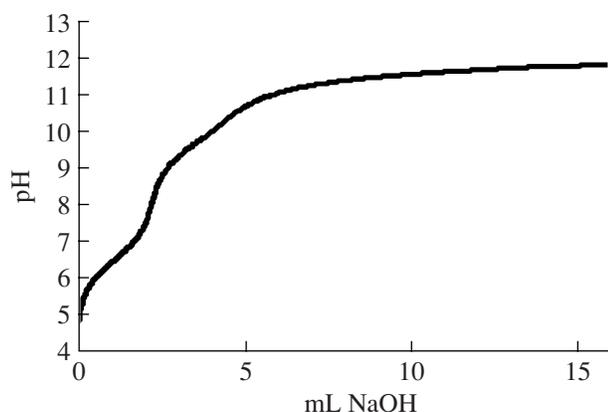


Fig. 1. Titration of ethylenediaminediacetic acid with sodium hydroxide at $I = 0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$ and 25°C .

centration. For this standard solution, we set $-\log[\text{H}^+] = 2.00$. Junction potential was taken into account from:

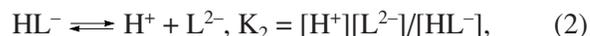
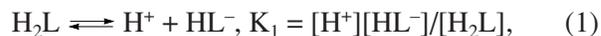
$\text{pH}(\text{real}) = \text{pH}(\text{measured}) + a + b[\text{H}^+](\text{measured})$. a and b were determined by measuring the hydrogen ion concentration for two different solutions of HClO_4 with sufficient NaClO_4 to adjust the ionic strength. The same procedure was performed for the other ionic strengths [7, 9]. The calibration has been done for the whole pH ($\text{pH} = -\log[\text{H}^+]$) 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 the absorbance and pH of the solution could be measured simultaneously. For each experiment two solutions of $\text{W(VI)} + \text{EDDA}$ 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_4 . 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.

RESULTS AND DISCUSSION

Dissociation Constants

The dissociation equilibria of ethylenediaminediacetic acid have been studied in different kinds of background electrolytes but according to our knowledge there are no reports about the ionic strength dependence of the dissociation constants of EDDA except our previous work [10]. The following equilibria were studied:



where 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 Microsoft Excel 2000 program [10, 11]. Titration curve is shown in Fig. 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 Tungsten(VI) with EDDA

The absorbances of solution of W(VI) and EDDA of total concentration of $0.003 \text{ mol dm}^{-3}$ in the UV range (260 to 270 nm) at a constant pH of 7.5 were determined. The observed absorbances were corrected from Eq. (3) and are shown in Fig. 2:

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

A_c , A_{obs} , and ϵ_0 are the absorbance of the complex, the observed absorbance and the molar absorptivity of W , respectively. ϵ_0 values were calculated at the mole fraction of W equal to 1 and are shown in Table 2. In Fig. 2 a maximum at a mole fraction of 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 plot at low mole fraction of W , where essentially all of the metal ions were in the

Table 1. Dissociation constants K_2 and K_1 of EDDA at different ionic strengths, I , of NaClO_4

$I, \text{ mol dm}^{-3}$	$\log K_2$	$\log K_1$	Experimental conditions	Ref
0.1	10.10 ± 0.02	8.12 ± 0.01		This work
0.3	9.80 ± 0.01	8.10 ± 0.04		This work
0.5	9.65 ± 0.01	8.00 ± 0.02		This work
0.7	9.40 ± 0.04	7.75 ± 0.03		This work
1.0	9.30 ± 0.03	7.50 ± 0.05		This work
	10.06 ± 0.06	7.18 ± 0.05	$I = 3.0 \text{ mol dm}^{-3} \text{ NaClO}_4, T = 25^\circ\text{C}$	7

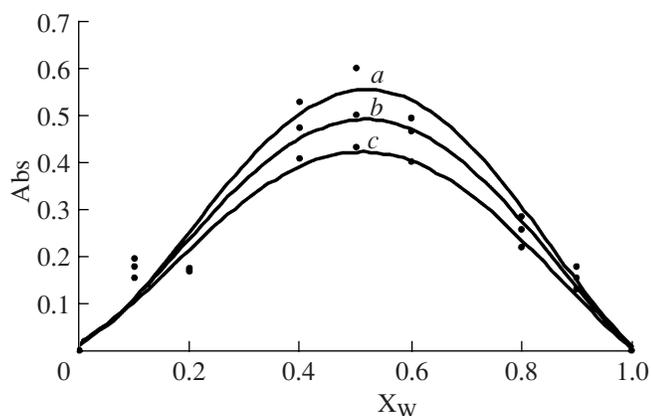
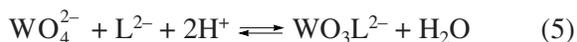


Fig. 2. Continuous variations plots of the absorbances of WO_3L^{2-} , Abs, vs the mole fraction of W(VI), X_W , at 25°C , an ionic strength of 0.1 mol dm^{-3} NaClO_4 , and different wavelengths: (a) 260 nm, (b) 265 nm, and (c) 270 nm.

form of a complex and are listed in Table 2. At the maximum point of the plot, the concentration of the complex is:

$$[C] = A_c/\epsilon_1. \quad (4)$$

W(VI) will bond with this tridentate ligand as a 1 : 1 complex [7]:



with the stability constant β_{112} as:

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

The following equations are valid for the total concentration of tungsten (C_M) and the total concentration of the ligand (C_L) at the maximum point on the plot of Fig. 2:

$$C_M = [W] + [C], \quad (7)$$

$$C_L = [L] + [C], \quad (8)$$

[C] is the concentration of the complex. By substituting Eqs. (4, 7, and 8) into Eq. (6), we can calculate the values of β_{112} according to reaction 5. Stability constants have been calculated by the combination of spectropho-

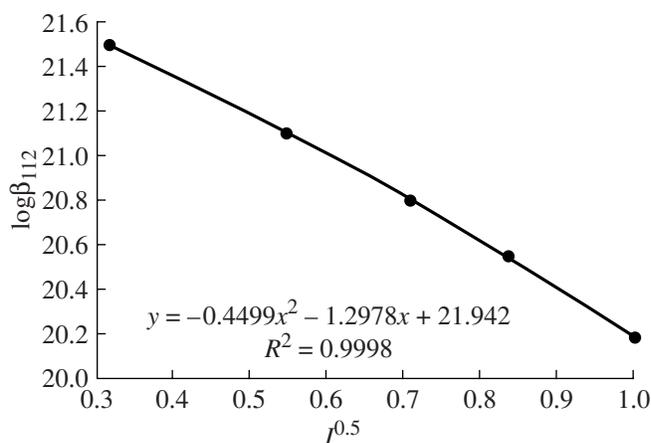


Fig. 3. Plot of $\log \beta_{112}$ for WO_3L^{2-} vs the square root of ionic strength according to the extended Debye–Huckel theory.

tometric and potentiometric data. The values of experimental $\log \beta_{112}$ at different ionic strengths together with the values of literature are shown in Table 3.

Ionic Strength Dependence of Dissociation and Stability Constants According to Debye–Huckel and Specific Ion Interaction Theories

The dependence of the dissociation and stability constants on the ionic strength can be described according to the previous works [10, 12–30]:

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

where I and I_1 are the actual and reference ionic strengths, respectively and according to Eq. (10):

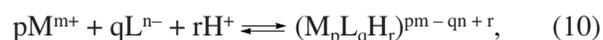


Table 2. Molar absorptivities of W(VI), ϵ_0 , and WO_3L^{2-} , ϵ_1 , at pH 7.5, different wavelengths, and various ionic strengths, I , of NaClO_4

$I, \text{ mol dm}^{-3}$	ϵ_0			ϵ_1		
	260 nm	265 nm	270 nm	260 nm	265 nm	270 nm
0.1	235.3	114.0	50.0	713.3	660.0	580.0
0.3	878.3	204.7	122.0	373.3	293.3	253.3
0.5	29.0	16.0	8.66	126.6	106.6	93.3
0.7	25.33	14.33	8.00	106.6	93.3	80.0
1.0	30.6	18.0	10.0	100.0	100.0	100.0

Table 3. Average values of $\log \beta_{112}$ at pH 7.5 and different ionic strengths for the complexation of tungsten(VI) with EDDA, $T = 25^\circ\text{C}$

I , mol dm^{-3}	$\log \beta_{112}$	Experimental conditions	Ref
0.1	21.49 ± 0.10	$I = 3.0 \text{ mol dm}^{-3}$ NaClO_4 , $t = 25^\circ\text{C}$	This work
0.3	21.10 ± 0.04		This work
0.5	20.69 ± 0.07		This work
0.7	20.69 ± 0.02		This work
1.0	20.16 ± 0.10		This work
	19.62 ± 0.12		7

Table 4. Parameters for the dependence on the ionic strength of dissociation and stability constants at 25°C

Species	C	D	Z^*
K_2	-0.895	0.372	4
K_1	1.292	-1.671	2
WO_3L^{2-}	-0.504	-0.291	6

$Z^* = pm^2 + qn^2 + r - (pm - qn + r)^2$, where m and n are the charges on the metal ion and the ligand respectively. Considering, $A = 0.5115$ and $B = 1.489$ Eq. (9) can be simplified:

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

where C and D are empirical parameters and their values were obtained by minimizing the sum of the squares of the errors (U) and the Gauss—Newton non-linear 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.

According to SIT, the activity coefficient of an ion j of charge z_j in the solution of the ionic strength, I , may be described by [31–33]:

$$\log \gamma_j = \frac{-z_j^2 0.509 \sqrt{I}}{1 + 1.5 \sqrt{I}} + \sum_k \varepsilon(j, k, I) m_k, \quad (13)$$

the ion interaction coefficients $\varepsilon(j, k, I)$ are zero for ions of the same charge sign and for uncharged species [31]. The concentration dependence of the ion interaction

coefficients can often be neglected [34]. For a general case of a complex formation reaction (charges are omitted for simplicity):



The stability constant of $M_m L_n (\text{OH})_p$, $\beta_{n,p,m}$, determined in an ionic medium (1 : 1 salt NX) of the ionic strength I , is related to the corresponding value at zero ionic strength, $\beta_{n,p,m}^0$, by Eq. (15) [31]:

$$\log \beta_{n,p,m} - \Delta z^2 D - p \log a_{\text{H}_2\text{O}} = \log \beta_{n,p,m}^0 - \Delta \varepsilon I \quad (15)$$

where:

$$\Delta z^2 = (mz_M - nz_L - p)^2 + p - mz_M^2 - nz_L^2, \quad (16)$$

$$D = \frac{0.509 \sqrt{I}}{1 + 1.5 \sqrt{I}}, \quad (17)$$

$$\Delta \varepsilon = \varepsilon_{(n,p,m,N \text{ or } X)} + p\varepsilon_{(H,X)} - n\varepsilon_{(N,L)} - m\varepsilon_{(M,X)}. \quad (18)$$

Equilibria involving $\text{H}_2\text{O}(l)$ as a reactant or product require a correction for the activity of water [31]. In most experimental studies of equilibria in dilute aqueous solutions, where an ionic medium is used in large excess with respect to the reactants, the activity of water is near constant and equal to 1 [31]. According to Eq. (15), the following formula is deduced for the extrapolation to zero ionic strength [31, 35]:

$$\log \beta_{110} + 6D = \log \beta_{110}^0 - \Delta \varepsilon I. \quad (19)$$

The linear regression is done and the results are shown in Fig. 4.

CONCLUSIONS

By pursuing our systematic study on complexation of molybdenum(VI) with EDDA [10], we thought it interesting to investigate the dissociation and complexation of EDDA with W(VI) at different ionic strengths of sodium perchlorate. A comparison of the stability constants shows that there is little difference between the stabilities of the corresponding Mo(VI) and W(VI) complexes of EDDA [10] and at higher ionic strengths this difference approaches zero. The results at $I = 3 \text{ mol dm}^{-3}$ NaClO_4 for these two complexes also confirm the above conclusion [7]. The equation on Fig. 3 has been obtained by Excel program after regression and choosing a polynomial that fits the data. Stability constants which have been used in Fig. 3 are calculated stability constants. Calculated stability constants have been obtained by Excel program after minimizing the error function, Eq. (12). After minimization the value of error function was equal to 0.033. So it can be observed that the equation on Fig. 3 is very similar to Eq. (11). According to SIT, the value of $\Delta \varepsilon = 0.7643$ has been obtained. From Figs. 3 and 4 it seems that we can conclude, data for the EDDA complex fit better in the Debye–Huckel model in comparison to the SIT model.

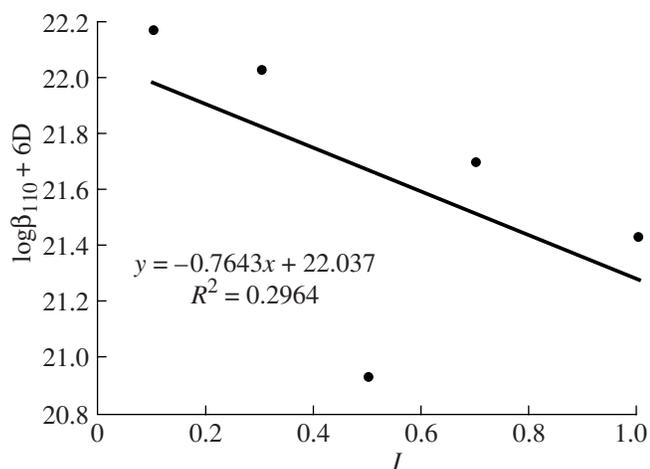


Fig. 4. Plot of $\log\beta_{110} + 6D$ versus I on the basis of SIT model for WO_3L^{2-} .

The structure of Mo(VI)-aminopolycarboxylic acid complexes has been determined by Kula [3–6] but we are looking for a correlation between ionic strength dependence patterns and structures of these complexes if there is one. It seems that ligand plays a dominant role in the ionic strength dependence pattern in comparison to the metal. For example in the W(VI) + NTA system a combination of ascending and descending pattern with a maximum at $I = 0.7 \text{ mol dm}^{-3} \text{ NaClO}_4$ had been obtained [15] although the metal is the same as in the current complex.

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