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IONIC STRENGTH DEPENDENCE OF STABILITY CONSTANTS, COMPLEXATION OF W(VI) WITH IMINODIACETIC ACID

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Поступила в редакцию 27.07.2006 г.

The equilibria between tungsten(VI) and iminodiacetic acid (IDA) have been studied in aqueous solution. Stoichiometry and stability constants of the complexes formed are determined from a combination of potentiometric and UV spectroscopic measurements. All measurements have been carried out at 25°C, pH 7.5 and different ionic strengths ranging from (0.1 to 1.0) mol dm⁻³ (NaClO₄). According to these results tungsten(VI) forms a mononuclear complex with IDA of the type (WO₄L)²⁻. By introducing two empirical parameters C and D in the complex formation reaction between tungsten(VI) and IDA the dependence of the dissociation and stability constants on ionic strength is described by amended Debye-Huckel type equation. Finally a pattern for the ionic strength dependence has been obtained.

1. INTRODUCTION

Tungsten is the third row transition element which is found in a mononuclear form in the active site of a diverse group of enzymes. This group of enzymes catalyzes, in general, the transfer of an oxygen atom in reactions that imply a net exchange of two electrons between enzyme and substrate and in which the metal ion cycles between the redox states IV and VI, with the Mo(VI)/W(VI) ion being paramagnetic. These proteins may also have other redox cofactors such as iron-sulfur centers, which participate in electron transfer processes and also are paramagnetic in certain redox states [1]. Although these centers are separated by large distances, they often interact through weak magnetic couplings. Studies of the magnetic properties of the redox centers and the analysis of the intercenter magnetic interactions enable one to determine structural aspects which are necessary to understand the mechanism of action of these enzymes [1].

In most of eukaryotes and prokaryotes tungsten is an antagonist of molybdenum and during growth of organisms the latter is easily replaced by tungsten due to their chemical similarity. The biological importance of tungsten has been fully proved in the last decade due to isolation of a number of tungsten containing enzymes from hyperthermophilic archaea [2]. In recent years, tungsten was reported to be able to cause hyperexpression of the structural gene of some other enzymes; for example, tungsten inhibited anaerobic growth of *Escherichia coli* on glycerol-dimethylsulfoxide medium, and this inhibition was partly compensated by hypersynthesis of dimethylsulfoxide reductase [2].

Although there are some investigations about the complexes of tungsten(VI) with aminopolycarboxylic acids (IDA, MIDA, NTA, EDTA) [3–6] according to our knowledge there is only one paper on the ionic

strength dependence of the stability constants of W(VI) with NTA [7]. Zare [3] studied W(VI)-IDA complex and evaluated its stability constant at 25°C and at an ionic strength of 3 mol dm⁻³ NaClO₄ using the potentiometric technique. Kula [4] determined the stability constant of this system by potentiometric technique at an ionic strength of 0.15 mol dm⁻³.

The present paper describes the complexation of tungsten(VI) with iminodiacetic acid. All metal-ligand equilibria were studied at 25°C with 0.1, 0.3, 0.5, 0.7 and 1.0 mol dm⁻³ sodium perchlorate as ionic medium. Comparisons are made of chelate stability constants at different ionic strengths. These results and a modified Debye-Huckel equation allows us to predict the values of stability constants in the desired range of ionic strengths.

2. EXPERIMENTAL PROCEDURES

2.1. Reagents. Sodium perchlorate, perchloric acid, sodium hydroxide, sodium tungstate and iminodiacetic acid were obtained from E. Merck 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 have been used.

2.2. 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 concentration. The

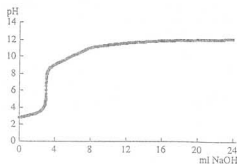


Fig 1. Titration of Iminodiacetic Acid with Sodium Hydroxide at $I = 0.1 \text{ mol dm}^{-3}$ of NaClO_4 and 25°C .

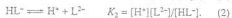
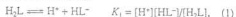
same procedure was performed for the other ionic strengths [3]. The calibration has been done for the whole $\text{pH}(\text{pH} = -\log[\text{H}^+])$ range used. Spectrophotometric measurements were performed on a UV-vis Shimadzu 2101 spectrophotometer with an Acer Mate 486 SX/250 computer using thermostated, 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 $\text{W(VI)} + \text{IDA}$ 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.

3. RESULTS AND DISCUSSION

The dissociation equilibria of iminodiacetic 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 IDA. The following equilibria were studied:



Where L^{2-} represents the fully dissociated iminodiacetic acid anion. Three titrations have been done for each ionic strength. The dissociation constants K_1 and K_2 have been determined using potentiometric technique and calculated using the Solver, Microsoft Excel 2000 powerful optimization package, to perform non-linear least-squares curve fitting [7–9]. 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 Tungsten (VI) with IDA

By use of the continuous variations method, the absorbances of solutions of W(VI) and IDA of total concentration $0.003 \text{ mol dm}^{-3}$ in the UV range (260 to 270 nm) at a constant pH of 7.5 were determined. 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 [10]. The degree of aggregation in solution increases as the pH is lowered, and numerous tungstates have been crystallized from the solutions at different pHs [10]. Tungsten(VI) and the complex both have absorbances at the specified wavelengths, so the absorbance of the tungsten should be eliminated from the

Table 1. Dissociation Constants K_2 and K_1 of IDA at Different Ionic Strengths, I , of NaClO_4

$I/\text{mol dm}^{-3}$	$\log K_2$	$\log K_1$	Experimental conditions	Ref
0.1	9.50 ± 0.01	2.86 ± 0.04		this work
0.3	9.46 ± 0.03	2.75 ± 0.01		this work
0.5	9.27 ± 0.05	2.63 ± 0.03		this work
0.7	9.32 ± 0.02	2.67 ± 0.05		this work
1.0	9.40 ± 0.01	2.74 ± 0.01		this work
	9.68 ± 0.05	2.77 ± 0.03	$I = 3 \text{ mol dm}^{-3} \text{ NaClO}_4, t = 25^\circ\text{C}$	[3]
	9.52 ± 0.02		$I = 0.15 \text{ mol dm}^{-3}, t = 25^\circ\text{C}$	[4]
	9.12	2.57	$I = 0.5 \text{ mol dm}^{-3} \text{ NaClO}_4$	[21]
	9.29	2.58	$I = 1 \text{ mol dm}^{-3} \text{ NaClO}_4$	[22]

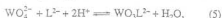
total absorbance (A_{obs}). The observed absorbances were corrected from eq 3 and are plotted in Figure 2:

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

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 Figure 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 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:

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

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 [11]. 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 system is WO_3 [3]. W (VI) will bond with this tridentate ligand as a 1 : 1 complex [3]:



with the stability constant, β_{112} , as:

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

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 Figure 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 in eqn 6 we can calculate the values of β_{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 values of literature are shown in Table 3.

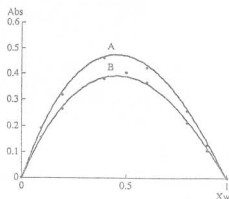


Fig. 2. Continuous variations plots of the absorbances of WO_3L^{2-} . Abs, versus the mole fraction of W(VI), X_w , at 25°C, an ionic strength of 0.1 mol dm^{-3} NaClO_4 and different wavelengths: (A) 260 nm, (B) 270 nm.

The dependence of the dissociation and stability constants on the ionic strength can be described according to the previous works [7, 8, 12–20]:

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

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.

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	260.0	131.7	74.0	660.0	633.3	546.0
0.3	242.0	122.7	60.3	591.3	570.7	512.7
0.5	226.0	110.7	50.7	514.0	489.3	456.0
0.7	201.0	116.0	50.7	485.3	410.7	362.7
1.0	238.7	120.7	59.0	541.3	526.0	494.0

Table 3. Average Values of $\log \beta_{112}$ at pH 7.5 and Different Ionic Strengths for the Complexation of Tungsten (VI) with IDA, $t = 25^\circ\text{C}$

$I/\text{mol dm}^{-3}$	$\log \beta_{112}$	Experimental conditions	Ref
0.1	20.14 ± 0.02	$I = 3 \text{ mol dm}^{-3} \text{ NaClO}_4$, $t = 25^\circ\text{C}$	this work
0.3	20.05 ± 0.03		this work
0.5	19.84 ± 0.03		this work
0.7	19.83 ± 0.04		this work
1.0	19.97 ± 0.01		this work
	18.14 ± 0.10	$I = 0.15 \text{ mol dm}^{-3}$, $t = 25^\circ\text{C}$	[3]
	18.5 ± 0.2		[4]

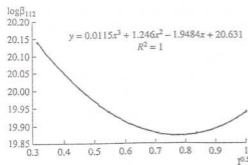
Table 4. Parameters for the Dependence on the Ionic Strength of Dissociation and Stability Constants at 25°C

Species	C	D	Z^*
K_2	0.023	0.242	4
K_1	-0.891	0.893	2
WO_3L^{2-}	0.085	0.291	6

tively. Considering, $A = 0.5115$ and $B = 1.489$ eq 9 can be simplified:

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

where C and D are empirical coefficients and their values were obtained by minimizing the error squares

Fig. 3. Plot of $\log \beta_{112}$ for WO_3L^{2-} versus the square root of ionic strength.

sum, (U), and the Gauss-Newton nonlinear least squares method in a suitable computer program:

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

where a_i is a quasi-experimental quantity and b_i is a calculated one. 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.

4. CONCLUSION

We have used $I_1 = 0.1$ as the reference ionic strength in order to obtain better consistency between experimental and calculated stability constants. The calculated stability constants are shown in Figure 3. Values of C and D have been inserted in eq 11 and then the values of calculated stability constants have been obtained.

For both Mo(VI) and W(VI) with IDA, MIDA and EDTA the reaction of complex with the added base was fairly rapid. For the Mo(VI) and W(VI)-NTA systems, however more time is required to achieve equilibrium after each addition of base [7, 8]. The stability constants of EDTA complexes are of the same order of magnitude as for the corresponding IDA complexes (molybdenum) or as for the corresponding EDTA complexes (vanadium and tungsten) [3]. The stability of complexes of multidentate ligands increases with the number of chelate rings formed and, for the same number of rings formed with the number of nitrogens bound to the metal [3].

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