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## STABILITY OF TUNGSTEN(VI) COMPLEX WITH IMINODIACETIC ACID AT DIFFERENT IONIC STRENGTHS

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Stability of tungsten(VI) complex formed by iminodiacetic acid (IDA) has been studied at 25 °C, pH = 7.5 and different ionic strengths ranging from (0.1 to 1.0) mol dm<sup>-3</sup> of sodium perchlorate. A combination of potentiometric and spectrophotometric techniques have been used based on the continuous variations method. According to our investigations the metal to ligand ratio is 1:1.<sup>(1-4)</sup>

The Solver, Microsoft Excel 2000 powerful optimization package, has been used to perform non-linear least-squares curve fitting. In order to obtain better consistency between the experimental and calculated results, three empirical parameters have been introduced in a Debye-Huckel type equation. This equation enable us to calculate the values of stability constants in the desired range of ionic strength without any further experimental work. Finally an ionic strength dependence pattern has been obtained.<sup>(1-5)</sup>

### Introduction

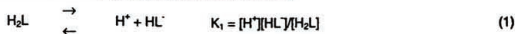
Although there are some investigations about the complexes of tungsten(VI) with aminopolycarboxylic acids (IDA, MIDA, NTA, EDTA) according to our knowledge there is only one paper on the ionic strength dependence of the stability constants of W(VI) with NTA.<sup>2</sup> The present paper describes the 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<sup>-3</sup> 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.

### Experimental Section

**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 KHCO<sub>3</sub>. In all experiments double-distilled water with specific conductance equal to (1.3 ± 0.1) µS.cm<sup>-1</sup> have 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<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>3</sup> The calibration has been done for the whole pH (pH = -log[H<sup>+</sup>]) 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.

**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<sup>2-</sup> represents the fully dissociated iminodiacetic acid anion. Three titrations have been done for each ionic strength. The dissociation constants K<sub>1</sub> and K<sub>2</sub> 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.<sup>(1-5)</sup>

### 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. The observed absorbances were corrected from eq 3:

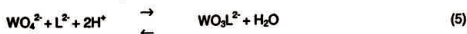
$$A_c = A_{\text{obs}} - \epsilon_0[W] \quad (3)$$

$A_c$ ,  $A_{\text{obs}}$ , and  $\epsilon_0$  are the absorbance of the complex, the observed absorbance and the molar absorptivity of W, respectively.  $\epsilon_0$  values were calculated at the mole fraction of W equal to

1. 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,  $\epsilon_1$ , were calculated at low mole fraction of W, where essentially all the metal ions were in the form of a complex. At the maximum point of the plot, the concentration of the complex is:

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

W (VI) will bond with this tridentate ligand as a 1:1 complex: <sup>(1-5)</sup>



with the stability constant,  $K_s$ , as:

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

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 absorbance:

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

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

By substituting eqs 4, 7 and 8 in eqn 6 we can calculate the values of  $K_s$  according to reaction 5. Stability constants have been calculated by the combination of spectrophotometric and potentiometric data. The values of  $\log K_s$  at different ionic strengths are shown in Figure 1.

The dependence of the dissociation and stability constants on the ionic strength can be described according to the previous works: <sup>(1-5)</sup>

$$\log K_s(I) = \log K_s(I_1) - AZ^* \left( \frac{I^{0.5}}{1 + BI^{0.5}} - \frac{I_1^{0.5}}{1 + BI_1^{0.5}} \right) + C(I - I_1) + D(I^{1.5} - I_1^{1.5}) + E(I^2 - I_1^2) \quad (9)$$

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

$$pM^{m+} + qL^{n-} + rH^+ \rightleftharpoons (M_pL_qH_r)^{pm - qn + r} \quad (10)$$

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

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

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:

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

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

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

species	C	D	E	Z*
$K_2$	4.592	-9.362	5.263	4
$K_1$	0.366	-1.749	1.448	2
$\text{WO}_3\text{L}^{2-}$	6.819	-13.864	7.758	6

We have used  $I_1 = 0.1$  as the reference ionic strength in order to obtain better consistency between experimental and calculated stability constants. Values of  $C$ ,  $D$  and  $E$  have been inserted in eq 11 and then the values of calculated stability constants have been obtained. Figure 3(calculated stability constants) shows that there is a minimum at  $I = 0.7$ .

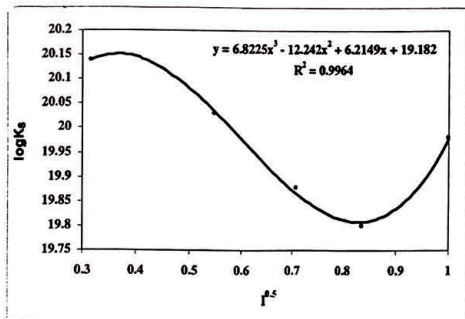


Figure 1. Plot of  $\log K_S$  for  $\text{WO}_3\text{L}^{2-}$  versus the square root of ionic strength.

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### SOLID-LIQUID EQUILIBRIA IN THE QUATERNARY SYSTEM $\text{NaCl-KCl-NH}_4\text{Cl-H}_2\text{O}$

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The mixing parameters pertaining to  $\text{NH}_4\text{Cl}+\text{KCl}+\text{H}_2\text{O}$  mixtures were indirectly obtained by fitting the mole-fraction based equations of Pitzer-Simonson-Clegg to the experimental solubilities of  $\text{NaCl}$ , from 293 to 333K, in the quaternary system  $\text{NaCl}+\text{KCl}+\text{NH}_4\text{Cl}+\text{H}_2\text{O}$ . The fitted parameters and the SLE data of  $\text{NH}_4\text{Cl}$  and  $\text{KCl}$  were used to calculate the activity coefficients of  $\text{KCl}$  and  $\text{NH}_4\text{Cl}$  in the solid solutions, in systems with and without  $\text{NaCl}$ , thus allowing the calculation of the eutonic points for the  $\text{KCl}+\text{NH}_4\text{Cl}$  aqueous system.

**Experimental Procedures.** Binary invariant data defining the crystallization fields of the three electrolytes were first determined, in the temperature range 293 to 333 K, by equilibrating excess amounts of salts of each chloride pair in the presence of different contents of the third electrolyte in the solution. The compositions of the co-saturated solutions were described by empirical equations from which the coordinates of the quaternary invariant point, at each temperature studied, were estimated. After defining the boundaries of the three crystallization domains, as shown in Figure 1, the solubilities of  $\text{NaCl}$ ,  $\text{KCl}$  and  $\text{NH}_4\text{Cl}$  in the quaternary system were obtained for different ratios of the admixtures, using the polythermal visual method.

For each of the crystallization fields, equilibrium at a given temperature was also approached through precipitation of the solid phase, with equilibration times of about 96 hours, at constant temperature and under continuous stirring. At the end of the runs, the slurries were filtrated and the solid phases washed with ethanol and air-dried. The solid and liquid phases thus obtained were analyzed for the contents of sodium, ammonium and potassium, in order to determine the influence of the admixtures on the type of solid phase. The contents of sodium and potassium were obtained by atomic absorption spectroscopy, while the concentration of ammonium was analyzed by the Kjeldahl method.