

Study on the Interaction of Dioxovanadium(V) with Nitrilotriacetic Acid at Different Ionic Strengths by Using Extended Debye-Hückel Equation

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ABSTRACT

In this research complexation of dioxovanadium(V) with nitrilotriacetic acid (NTA) at different ionic strengths (0.1 to 1.0 mol dm⁻³) of sodium perchlorate as supporting electrolyte and pH range of 1.00-2.50 at 25 °C has been investigated by a combination of potentiometric and UV spectrophotometric measurements. Stability constants of two species, VO₂HL⁻ and VO₂H₂L have been calculated. Ionic strength dependence semi-empirical parameters for the dissociation and stability constants were derived on the basis of extended Debye-Hückel type equation.

Keywords: Complexation; Extended Debye-Hückel type Equation; NTA; Dioxovanadium(V)

INTRODUCTION

The present work measured the stability constants values of NTA complexes with dioxovanadium(V) at I = 0.1-1.0 mol dm⁻³ NaClO₄ and 25 °C by using extended Debye-Hückel theory. There are many papers about the ionic strength dependence of dissociation and stability constants [1-12] by using extended Debye-Hückel theory, but to our knowledge no reports of the ionic strength dependence of stability constants for the V(V) + NTA complex has been appeared. This work is performed in acidic medium and the complexes are characterized by a combination of potentiometric and spectrophotometric measurements.

Finally our results have been compared with the previously reported data on the similar complexes.

EXPERIMENTAL SECTION

Reagents. All chemicals were analytical reagent grade. Sodium perchlorate, perchloric acid, sodium hydroxide, sodium monovanadate and NTA were purchased from E. Merck and were used without further purification. Dilute perchloric acid solution was standardized against KHCO₃ [13]. In all experiments double-distilled water with specific conductance equal to (1.3 ± 0.1) μS.cm⁻¹ have been used.

MEASUREMENTS

All measurements were carried out at (25 ± 0.1) °C and different ionic strengths ranging from 0.1 to 1.0 mol dm⁻³ of sodium perchlorate. A Metrohm pH-meter, 744, was used for pH measurements.

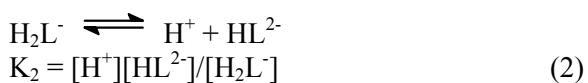
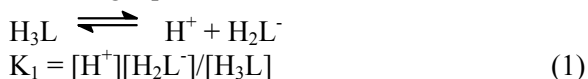
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The pH-meter has a sensitivity of 0.01 units. The hydrogenion concentration was measured with a Metrohm combination electrode, model 6.0228.000. A 0.01 mol dm⁻³ perchloric acid solution containing 0.09 mol dm⁻³ sodium perchlorate (for adjusting the 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 [13]. The calibration has been done for the whole pH (pH = -log[H⁺]) range used. Spectrophotometric measurements were performed with a Varian Cary 300 UV-Vis spectrophotometer with Pentium 4 computer between 245 nm and 280 nm 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

Complexation of Dioxovanadium(V) with NTA

According to our knowledge the dissociation equilibria of NTA have been studied in different kinds of background electrolytes [13,14]. Dissociation constants values have been gathered from the literature [8,10,12] on the basis of the following equilibria:



The values of dissociation constants are reported in Table 1 [8,10,12]. Stability constants were derived from the combination of dissociation and

Table 1. Dissociation constants, K_3 , K_2 and K_1 of NTA at different ionic strengths, I , of NaClO₄

$I / \text{mol dm}^{-3}$	$\log K_3$	$\log K_2$	$\log K_1$	experimental conditions	ref
0.1	1.98 ± 0.02	2.92 ± 0.05	10.00 ± 0.02		12
0.3	1.83 ± 0.04	2.84 ± 0.03	9.85 ± 0.01		12
0.5	1.76 ± 0.01	2.79 ± 0.02	9.70 ± 0.03		12
0.7	1.63 ± 0.02	2.61 ± 0.01	9.55 ± 0.02		12
1.0	1.55 ± 0.02	2.59 ± 0.04	9.25 ± 0.02		12
	2.05 ± 0.05	2.63 ± 0.02	9.17 ± 0.04	$I = 3.0 \text{ mol dm}^{-3} \text{ NaClO}_4, t = 25^\circ \text{C}$	13
			9.81 ± 0.10	$I = 0.15 \text{ mol dm}^{-3}, t = 25^\circ \text{C}$	15
	1.65	2.94	10.33	$t = 20^\circ \text{C}$	16

Acidic solutions of dioxovanadium (V) were titrated with basic solutions of NTA at different ionic strengths. The absorbance of the solution was measured after each addition and adjusting the pH. The pH range was 1.00-2.50. 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.

formation constants values. The absorbance data in the UV range (255 to 280 nm) were used for minimizing the error function on the basis of Gauss-Newton nonlinear least squares method in Microsoft Excel 2000 program according to the function $A=f(\text{pH})$. The error function is defined as the sum of the square of the difference between experimental and calculated absorbance data. A_{exp} values have been gathered from the UV spectrophotometric measurements. A_{cal}

values have been determined from the combination of the following mass-balance and Beer-Lambert laws ($L = \text{NTA}$):

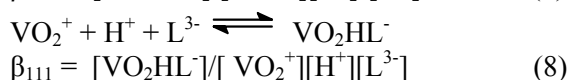
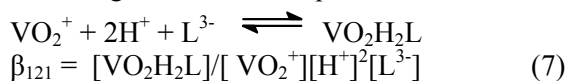
$$A = \varepsilon_{\text{VO}_2^+}[\text{VO}_2^+] + \varepsilon_{\text{VO}_2\text{HL}^-}[\text{VO}_2\text{HL}^-] + \varepsilon_{\text{VO}_2\text{H}_2\text{L}}[\text{VO}_2\text{H}_2\text{L}] \quad (4)$$

$$C_{\text{VO}_2^+} = [\text{VO}_2^+] + [\text{VO}_2\text{HL}^-] + [\text{VO}_2\text{H}_2\text{L}] \quad (5)$$

$$C_L = [\text{VO}_2\text{HL}^-] + [\text{VO}_2\text{H}_2\text{L}] + [\text{H}_3\text{L}] + [\text{H}_2\text{L}^-] + [\text{HL}^{2-}] \quad (6)$$

where $C_{\text{VO}_2^+}$ and C_L are the total concentration of VO_2^+ and the ligand respectively.

Different stoichiometric models were tested. Species having no significance effect on the statistical fit were neglected. Complexes with negligible concentrations over the entire range of experimental conditions are not taken into account in our proposed results. Finally the best fit and minimum error function were obtained with $\text{VO}_2\text{H}_2\text{L}$ and VO_2HL^- species on the basis of Gauss-Newton nonlinear least squares method. A_{exp} and A_{cal} values at 25°C , $I = 0.1 \text{ mol dm}^{-3}$ and 270 nm are shown in Fig. 1 which shows a very good graphical fit. Similar results were obtained for the other ionic strengths. The stability constants have been defined and calculated according to the combination of the following reactions and eqs 4-6:



The values of stability constants are shown in Fig. 2 versus the square root of ionic strength.

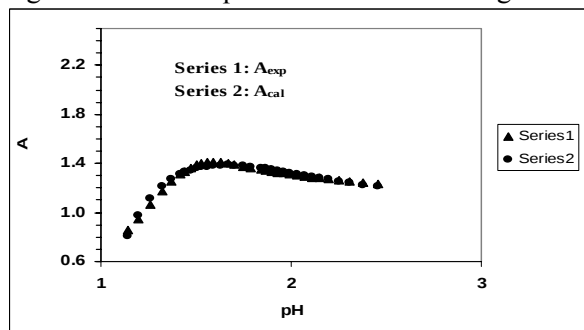


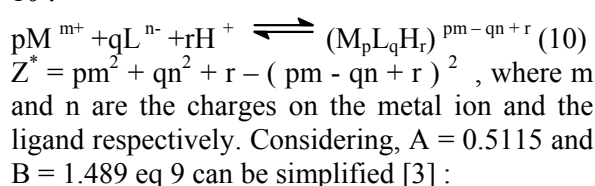
Fig.1. A_{exp} and A_{cal} values at 25°C , $I = 0.1 \text{ mol dm}^{-3}$ and 270 nm .

Ionic Strength Dependence of Dissociation and Stability Constants According to the Extended Debye-Hückel Model

The dependence of the dissociation and stability constants on the ionic strength can be described according to the previous works [1-12]:

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

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



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

where C and D are empirical coefficients and their values were obtained by minimizing the error squares sum, (U) , and the Gauss-Newton nonlinear least squares method in Excel 2000 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 one. The values of C and D are shown in Table 2. In this research, a_i is the experimental stability constant and b_i is the calculated one. The values of C and D have been inserted in eq 11, then the values of calculated stability constants have been determined according to the extended Debye-Hückel theory. The values of calculated stability constants are shown in Fig. 2 versus the square root of ionic strength. The values of C and D for the dissociation constants of NTA have been taken from the literature [12]. We have used $I_1 = 0.1 \text{ mol dm}^{-3}$ as the reference ionic strength in order to obtain better consistency between experimental and calculated stability constants. Therefore by using eq 11 and the values of C and D 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 on the basis of extended Debye-Hückel model.

Table 2. Parameters for the Dependence on the Ionic Strength of Dissociation and Stability Constants at 25 °C

species	C	D	Z*	ref
K_3	1.057	-0.864	6	12
K_2	0.803	-0.730	4	12
K_1	0.210	-0.775	2	12
$\text{VO}_2\text{H}_2\text{L}$	9.650	-8.465	12	this work
VO_2HL^-	2.395	-2.474	10	this work

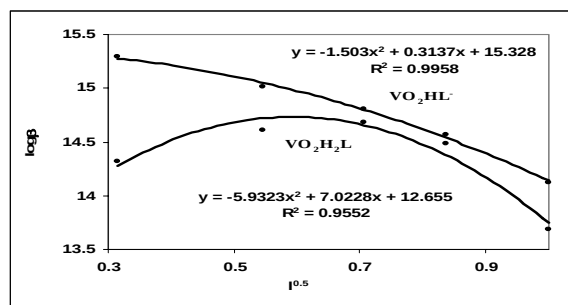


Fig. 2. Plot of $\log\beta_{121}$ and $\log\beta_{111}$ versus the square root of ionic strength on the basis of modified Debye-Hückel model.

CONCLUSIONS

The results on the basis of extended Debye-Hückel model are shown in Fig. 2 [7-12]. There is a descending pattern for the VO_2HL^- species, but $\text{VO}_2\text{H}_2\text{L}$ shows a maximum at $I = 0.5 \text{ mol dm}^{-3}$. NTA reacts with VO_2^+ as tetradentate ligand, so the stability constants are higher than methyliminodiacetic acid(MIDA) complexes with VO_2^+ [17]. The oxygen atoms in the VO_2^+ unit must be in the cis configuration for NTA to coordinate to VO_2^+ as a tetradentate ligand [17]. This conclusion is supported by the NMR studies of VO_2^+ - EDDA and related complexes [18]. The entropy term plays an important role in the formation of these aminopolycarboxylate complexes particularly for the VO_2^+ - NTA complex the enthalpy term barely contributes to the complex formation [18]. Finally it might be concluded that for $\text{VO}_2\text{H}_2\text{L}$ complex after $I = 0.5 \text{ mol dm}^{-3}$ attractive forces are more important and before $I = 0.5 \text{ mol dm}^{-3}$ it is vice versa.

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