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Application of the Parabolic Model, Specific Ion Interaction, and Debye−Hückel Theories for the Complexation of Dioxovanadium(V) with Ethylenediamine-*N*,*N*′-diacetic Acid[†]

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Interaction between dioxovanadium(V) and ethylenediamine-*N*,*N*′-diacetic acid (EDDA) has been investigated by potentiometric and UV spectrophotometric measurements in an aqueous solution of pH = 1.00 to 2.50 at I = (0.1 to 0.9) mol·dm^{-3} ($NaClO_4$) and 25 °C. Different speciation models were used to detect the species, but the model that best fits the experimental data takes into account the formation of two species, $VO_2H_2L^+$ and VO_2HL. Distribution diagrams for the main species at different ionic strengths have been calculated as a function of pH. The dependence on ionic strength of the stability and dissociation constants was studied by using the extended Debye−Hückel-type equation (EDH), specific ion interaction theory (SIT), and the parabolic model. All of these approaches gave comparable and satisfactory results. Literature data were also considered and compared.

Introduction

Vanadium is an essential element well-known as a metabolic regulator, as a mitogenic activator, and for reversing drug resistance. It is essential for several organisms and, in particular, is implicated in the synthesis of chlorophyll in green plants and in the normal growth of some animals.[1,2] In recent decades, in vivo and in vitro studies of the biological effects of this metal have revealed other important effects. These include the ability to inhibit certain enzymes, the possibility of mimicking the effects of insulin, the capacity to reduce cholesterol biosynthesis,[3] in addition to antitumorigenic properties.[4,5] At present, the use of vanadium compounds as therapeutic agents is limited by the narrow range between beneficial and toxic effects. Thus V(IV) and V(V) complexes containing adequate ligands have been synthesized searching for properties to improve their pharmacological action, such as hydrolytic stability, water solubility, neutral charge, and/or lipophilicity, low toxicity, and antidiabetic or anticancer activity.[2] On the other hand, an important aspect of the aqueous solution chemistry of polyaminocarboxylic acids concerns their structure, which makes them useful models in speciation studies of naturally occurring aminocarboxylic ligands, such as humic substances in aquatic environments.[6]

We have previously reported the effect of ionic strength on the stability of the Mo(VI) + EDDA[7] system by using EDH and the V(V) + NTA system[8] by using the SIT and EDH models. According to our knowledge, there is no report about the effect of ionic strength on the stability of the V(V) + EDDA system in the literature. Therefore, in this study we have applied the SIT and parabolic models to investigate the ionic strength effects on the complexation of dioxovanadium(V) with EDDA. Finally, the results have been compared with the EDH model.

Experimental Section

Reagents. All chemicals were analytical reagent grade. Sodium perchlorate, perchloric acid, sodium hydroxide, hydrochloric acid, sodium monovanadate, potassium hydrogen carbonate, and sodium carbonate were purchased from Merck and EDDA from Fluka and were used without further purification. The NaOH solutions were prepared from titrisol solutions, and their concentration was determined by several titrations with standard HCl. The HCl solution was standardized with sodium carbonate solution (Na_2CO_3). Dilute perchloric acid solution was standardized against $KHCO_3$.[9] A stock solution of vanadium(V) was prepared by dissolution of anhydrous sodium monovanadate in perchloric acid solution affecting the destruction of the decavanadate. The solution stood overnight before use to obtain only the VO_2^+ ion. Isopolyvanadates will not be formed, or if little amounts of isopolyvanadates still exist, then they will be decomposed. In all experiments double-distilled water with a specific conductance equal to (1.3 ± 0.1) μS·cm^{-1} was used.

Measurements

All measurements were carried out at (25 ± 0.1) °C and an ionic strength of (0.1 to 0.9) mol·dm^{-3} sodium perchlorate. A Metrohm pH-meter, 744, was used for pH measurements. The pH-meter had a sensitivity of 0.01 units. The hydrogen ion 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.[9] The calibration has been done for the whole pH (pH = $-\log[H^+]$) range used. The change in liquid junction potential[9] was calculated from eq 1

$$\text{pH (real)} = \text{pH (measured)} + a + b[H^+] \text{ (measured)} \quad (1)$$

a and b were determined by measurement of the hydrogen ion concentration for two different solutions of $HClO_4$ with suf-

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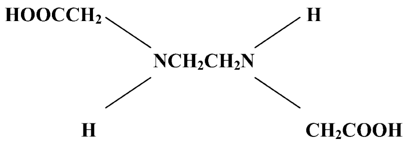
ficient $NaClO_4$ to adjust the ionic media.[9] Spectrophotometric measurements were performed with a Varian Cary 300 UV−vis spectrophotometer with a Pentium 4 computer between (245 and 280) nm in thermoregulated matched 10 mm quartz cells. The measurement cell was of the flow type. A Masterflux pump 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.

Measurements have been done for different metal, ligand concentrations and ligand/metal molar ratios, such as $C_L = (4.20 \cdot 10^{-3}, 6.00 \cdot 10^{-3}, 2.00 \cdot 10^{-2}, 2.34 \cdot 10^{-2}, \text{and } 2.58 \cdot 10^{-2})$ $mol \cdot dm^{-3}$ and $C_{VO2^+} = (1.00 \cdot 10^{-4}, 5.00 \cdot 10^{-4}, \text{and } 1.00 \cdot 10^{-3})$ $mol \cdot dm^{-3}$, but a good fit and the speciation pattern and minimum error function have been obtained with $C_L = 2.34 \cdot 10^{-2}$ $mol \cdot dm^{-3}$ and $C_{VO2^+} = 1.00 \cdot 10^{-3}$ $mol \cdot dm^{-3}$. Therefore, 50 cm^3 acidic solutions of dioxovanadium(V) ($1 \cdot 10^{-3}$ $mol \cdot dm^{-3}$) were titrated with basic solutions of EDDA ($2.34 \cdot 10^{-2}$ $mol \cdot dm^{-3}$) at different ionic strengths. The absorbance of the solution was measured after each addition and adjusting the pH. According to the literature,[9,14] in acidic solution (pH < 2.5) vanadium(V) exists as the $[VO_2]^+$ ion. This ion hydrolyzes to $[H_2VO_4]^-$, $[HVO_4]^{2-}$, $[VO_4]^{3-}$, $[V_3O_9]^{3-}$, and $[HV_2O_7]^{3-}$ in alkaline solutions and polymerizes in moderately acidic solutions giving an instability range.[9,14] However, in the presence of a large excess of ligand at pH < 7.5, both polymerization and hydrolysis of $[VO_2]^+$ were found to be negligible.[9,14] Therefore the pH range was 1.00 to 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.

Results and Discussion

Complexation of Dioxovanadium(V) with EDDA. Theory and Calculation. The chemical structure of EDDA is shown below:



Three values of dissociation constants are necessary for our calculations according to the following equilibria

$$H_3L^+ \rightleftharpoons H^+ + H_2L \qquad K_1 = \frac{[H^+][H_2L]}{[H_3L^+]} \tag{2}$$

$$H_2L \rightleftharpoons H^+ + HL^- \qquad K_2 = \frac{[H^+][HL^-]}{[H_2L]} \tag{3}$$

$$HL^- \rightleftharpoons H^+ + L^{2-} \qquad K_3 = \frac{[H^+][L^{2-}]}{[HL^-]} \tag{4}$$

We had previously assumed EDDA as a ligand with two protons (H_2L) for its complexation with Mo(VI), and two values of dissociation constants at different ionic strengths had been reported.[7] These two values had been denoted by K_1 and K_2, but in this research the notation has been changed and only the first dissociation constant, and the values at $I = 0.9$ $mol \cdot dm^{-3}$ ($NaClO_4$), have been determined. The second and third dissociation constants have been taken from our previous paper (denoted by K_1 and K_2, but in this paper they are K_2 and K_3).[7] Three titrations have been done for each ionic strength, and 389 points have been used for calculations at each ionic strength.[7] The dissociation constants have been determined by using the potentiometric technique and the Microsoft Excel 2000 program.[7,10] The values of the dissociation constants together with literature values are reported in Table 1. Stability constants were derived from the summation of dissociation and formation constant values. The absorbance data in the UV range (255 to 280) nm were used for minimizing the error function on the basis of a Gauss−Newton nonlinear least-squares method in the Microsoft Excel 2000 program according to the function $A = f(\text{pH})$. The error function is defined as below

Table 1. Dissociation Constants K_3, K_2, and K_1 of EDDA at Different Ionic Strengths, I, of $NaClO_4$

$I/mol \cdot dm^{-3}$	log K_3	log K_2	log K_1	t	ref
0.1	10.10 ± 0.02	8.12 ± 0.01	2.55 ± 0.05	25 °C	7
0.3	9.80 ± 0.01	8.10 ± 0.04	2.44 ± 0.06	25 °C	7
0.5	9.65 ± 0.01	8.00 ± 0.02	2.30 ± 0.07	25 °C	7
0.9	9.78 ± 0.10	7.63 ± 0.05	2.32 ± 0.03	25 °C	this work
3.0	10.06	7.18	2.98	25 °C	9, 55
1.0	9.64	6.71	2.37	25 °C	55
0.1	9.60	6.55	2.36	25 °C	55
0.15	9.54	6.48	2.30	37 °C	55

Table 2. Experimental Values of Absorbance at Different pH and Wavelengths at 25 °C and $I = 0.1$ $mol \cdot dm^{-3}$

	λ/nm					
pH	255	260	265	270	275	280
1.06	0.8767	0.8500	0.8331	0.8121	0.7833	0.7486
1.15	0.8219	0.7963	0.7795	0.7600	0.7333	0.6989
1.23	0.7758	0.7508	0.7350	0.7159	0.6899	0.6577
1.29	0.7484	0.7239	0.7079	0.6889	0.6632	0.6323
1.35	0.7227	0.6993	0.6837	0.6645	0.6396	0.6088
1.43	0.7033	0.6796	0.6632	0.6442	0.6192	0.5886
1.51	0.6888	0.6651	0.6472	0.6281	0.6027	0.5722
1.60	0.6865	0.6609	0.6410	0.6199	0.5922	0.5611
1.65	0.6906	0.6621	0.6413	0.6183	0.5898	0.5584
1.70	0.7037	0.6727	0.6488	0.6237	0.5935	0.5600
1.75	0.7267	0.6913	0.6641	0.6350	0.6017	0.5648
1.81	0.7677	0.7263	0.6931	0.6585	0.6205	0.5798
1.87	0.8309	0.7806	0.7392	0.6973	0.6517	0.6044
1.94	0.9243	0.8620	0.8088	0.7561	0.7007	0.6449
2.01	1.0502	0.9713	0.9037	0.8365	0.7674	0.6999
2.09	1.2073	1.1089	1.0207	0.9355	0.8510	0.7694
2.17	1.3803	1.2596	1.1516	1.0478	0.9441	0.8472
2.26	1.5474	1.4063	1.2774	1.1550	1.0345	0.9215
2.38	1.6826	1.5238	1.3799	1.2414	1.1062	0.9809
2.51	1.7735	1.6033	1.4477	1.2979	1.1534	1.0194

$$U = \sum (A_{\text{exp}} - A_{\text{cal}})^2 \tag{5}$$

A_{exp} values have been gathered from the UV spectrophotometric measurements and are reported at different pH and wavelengths in Tables 2 to 4 and in the Appendix, Table A1. A_{cal} values have been determined from the combination of the following mass-balance and Beer−Lambert laws (L = EDDA)

$$A = \varepsilon_0[VO_2^+] + \varepsilon_{VO_2H_2L^+}[VO_2H_2L^+] + \varepsilon_{VO_2HL}[VO_2HL] \tag{6}$$

$$C_{VO_2^+} = [VO_2^+] + [VO_2H_2L^+] + [VO_2HL] \tag{7}$$

$$C_L = [VO_2H_2L^+] + [VO_2HL] + [H_3L^+] + [H_2L] + [HL^-] \tag{8}$$

and the formation constants

$$VO_2^+ + H_3L^+ \rightleftharpoons VO_2H_2L^+ + H^+$$

$$K_{VO_2H_2L^+} = \frac{[VO_2H_2L^+][H^+]}{[VO_2^+][H_3L^+]} \tag{9}$$

$$\mathrm{VO_2H_2L^+} \rightleftharpoons \mathrm{VO_2HL + H^+} \qquad K_{\mathrm{VO_2HL}} = \frac{[\mathrm{VO_2HL}][\mathrm{H^+}]}{[\mathrm{VO_2H_2L^+}]} \tag{10}$$

where $C_{VO_2^+}$ and C_L are the total concentration of VO_2^+ and the ligand, respectively.

Different stoichiometric models were tested which will be discussed later. Species having no significant effect on the statistical fit were neglected. The concentration of the complexes contributing to the general species distribution in our experimental conditions may be calculated by the Microsoft Excel 2000 program. 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 the $VO_2H_2L^+$ and VO_2HL species. The chosen model is also in close agreement with experimental data. A_{exp} and A_{cal} values at 25 °C, $I = 0.1$ mol·dm^{-3}, and 270 nm are shown in Figures 1 and 3 for two different models which show a very good graphical fit. Similar fits have been obtained for the other ionic strengths. The distribution of species is shown in Figures 2 and 4 for 270 nm and different ionic strengths and two models. Figure 2(a) shows that the maximum concentration of $VO_2H_2L^+$ at $I = 0.1$ mol·dm^{-3} and 270 nm is reached at pH = 1.87 to 2.09. Similar

Table 3. Experimental Values of Absorbance at Different pH and Wavelengths at 25 °C and $I = 0.5$ mol·dm^{-3}

	λ/nm					
pH	255	260	265	270	275	280
0.94	0.9217	0.8959	0.8774	0.8562	0.8278	0.7913
1.06	0.8374	0.8126	0.7958	0.7760	0.7495	0.7160
1.16	0.7962	0.7722	0.7556	0.7362	0.7108	0.6793
1.23	0.7732	0.7495	0.7326	0.7139	0.6883	0.6570
1.32	0.7553	0.7318	0.7144	0.6948	0.6697	0.6382
1.40	0.7456	0.7203	0.7021	0.6810	0.6554	0.6244
1.50	0.7536	0.7254	0.7042	0.6800	0.6516	0.6184
1.56	0.7706	0.7392	0.7146	0.6879	0.6573	0.6216
1.62	0.8032	0.7671	0.7378	0.7071	0.6720	0.6335
1.69	0.8570	0.8135	0.7757	0.7385	0.6977	0.6534
1.76	0.9391	0.8839	0.8366	0.7892	0.7388	0.6866
1.84	1.0621	0.9907	0.9282	0.8666	0.8029	0.7393
1.87	1.1316	1.0521	0.9812	0.9107	0.8395	0.7692
1.92	1.2148	1.1240	1.0432	0.9632	0.8835	0.8053
1.96	1.3069	1.2041	1.1117	1.0216	0.9323	0.8457
2.01	1.3993	1.2851	1.1818	1.0809	0.9824	0.8869
2.05	1.4959	1.3699	1.2545	1.1434	1.0336	0.9299
2.10	1.5877	1.4498	1.3243	1.2015	1.0831	0.9706
2.16	1.6756	1.5265	1.3902	1.2580	1.1301	1.0097
2.22	1.7536	1.5960	1.4492	1.3092	1.1719	1.0448
2.29	1.8171	1.6525	1.4984	1.3513	1.2074	1.0752
2.36	1.8697	1.6977	1.5375	1.3834	1.2342	1.0956
2.44	1.9064	1.7270	1.5627	1.4047	1.2518	1.1100

Table 4. Experimental Values of Absorbance at Different pH and Wavelengths at 25 °C and $I = 0.9$ mol·dm^{-3}

	λ/nm					
pH	255	260	265	270	275	280
0.85	0.9262	0.8993	0.8815	0.8604	0.8317	0.7950
1.00	0.8345	0.8096	0.7931	0.7731	0.7463	0.7117
1.15	0.7696	0.7449	0.7281	0.7092	0.6836	0.6514
1.26	0.7387	0.7151	0.6979	0.6786	0.6532	0.6220
1.40	0.7270	0.7009	0.6820	0.6607	0.6343	0.6029
1.51	0.7430	0.7130	0.6897	0.6646	0.6356	0.6012
1.57	0.7661	0.7320	0.7053	0.6773	0.6441	0.6070
1.63	0.8105	0.7701	0.7372	0.7027	0.6648	0.6232
1.70	0.8785	0.8294	0.7881	0.7458	0.7005	0.6521
1.74	0.9226	0.8672	0.8195	0.7718	0.7216	0.6690
1.78	0.9806	0.9182	0.8635	0.8091	0.7529	0.6948
1.81	1.0448	0.9739	0.9112	0.8495	0.7861	0.7211
1.85	1.1148	1.0343	0.9636	0.8938	0.8229	0.7525
1.90	1.1979	1.1073	1.0261	0.9471	0.8680	0.7891
1.94	1.2871	1.1855	1.0934	1.0041	0.9158	0.8290
1.98	1.3783	1.2656	1.1627	1.0635	0.9657	0.8712
2.03	1.4753	1.3506	1.2367	1.1266	1.0178	0.9144
2.09	1.5701	1.4341	1.3091	1.1877	1.0696	0.9566
2.14	1.6548	1.5073	1.3712	1.2408	1.1134	0.9924
2.21	1.7389	1.5808	1.4351	1.2943	1.1578	1.0303
2.28	1.8010	1.6348	1.4812	1.3330	1.1900	1.0572
2.36	1.8571	1.6841	1.5239	1.3699	1.2202	1.0821
2.45	1.8969	1.7176	1.5527	1.3943	1.2399	1.0980

Table 5. Average Experimental and Calculated Values of log β_{121} and log β_{111} at pH = 1.00 to 2.50 and Different Ionic Strengths for the Complexation of Dioxovanadium(V) with EDDA, $t = 25$ °C

I	log β_{121}		log β_{111}	
mol·dm^{-3}	exptl	calcd	exptl	calcd
0.1	18.37 ± 0.10	18.37 ± 0.00	16.52 ± 0.15	16.52 ± 0.00
0.3	18.18 ± 0.01	18.16 ± 0.09	16.42 ± 0.01	16.41 ± 0.06
0.5	18.01 ± 0.10	18.03 ± 0.19	16.36 ± 0.20	16.37 ± 0.12
0.9	17.75 ± 0.10	17.75 ± 0.43	16.29 ± 0.10	16.29 ± 0.28

Table 6. Average Experimental and Calculated Values of log β_{101} at pH = 1.00 to 2.50 and Different Ionic Strengths for the Complexation of Dioxovanadium(V) with EDDA, $t = 25$ °C

I	log β_{101}	
mol·dm^{-3}	exptl	calcd
0.1	16.54 ± 0.02	16.54 ± 0.00
0.3	16.44 ± 0.10	16.36 ± 0.37
0.5	16.16 ± 0.20	16.23 ± 0.80
0.9	15.98 ± 0.13	15.97 ± 1.80

Table 7. Different Speciation Models and F-values Versus the Accepted Model for 95 % Confidence Level

model	reaction	F-value
Accepted	$VO_2^+ + H_3L^+ \rightleftharpoons VO_2H_2L^+ + H^+$	-
	$VO_2H_2L^+ \rightleftharpoons VO_2HL + H^+$	-
(a)	$VO_2^+ + H_3L^+ \rightleftharpoons VO_2L^- + 3H^+$	versus $VO_2H_2L^+$: $1.06 \cdot 10^{-10}$
		versus VO_2HL: $1.21 \cdot 10^{-4}$
(b)	$VO_2^+ + H_2L \rightleftharpoons VO_2HL + H^+$	$5.00 \cdot 10^{-1}$
	$VO_2HL \rightleftharpoons VO_2L^- + H^+$	$5.00 \cdot 10^{-1}$
(c)	$VO_2^+ + H_3L^+ \rightleftharpoons VO_2H_2L^+ + H^+$	$7.74 \cdot 10^{-5}$
	$VO_2H_2L^+ \rightleftharpoons VO_2HL + H^+$	$2.22 \cdot 10^{-4}$
	$VO_2HL \rightleftharpoons VO_2L^- + H^+$	versus $VO_2H_2L^+$: $2.25 \cdot 10^{-1}$
		versus VO_2HL: $3.02 \cdot 10^{-6}$
(d)	$VO_2^+ + L^{3-} \rightleftharpoons VO_2L^{2-}$	versus $VO_2H_2L^+$: $1.14 \cdot 10^{-1}$
		versus VO_2HL: $6.78 \cdot 10^{-6}$

Table 8. Parameters for the Dependence on the Ionic Strength of Dissociation and Stability Constants at 25 °C

species	C	D	Z^*	ref
K_3	−2.16 ± 0.28	2.14 ± 0.28	4	this work
K_2	1.57 ± 0.08	−1.91 ± 0.08	2	this work
K_1	−1.50 ± 0.45	1.17 ± 0.46	0	this work
$VO_2H_2L^+$	0.90 ± 0.26	−0.99 ± 0.27	6	this work
VO_2HL	1.38 ± 0.17	−0.98 ± 0.18	6	this work
VO_2L^-	0.35 ± 1.10	−0.61 ± 1.13	4	this work

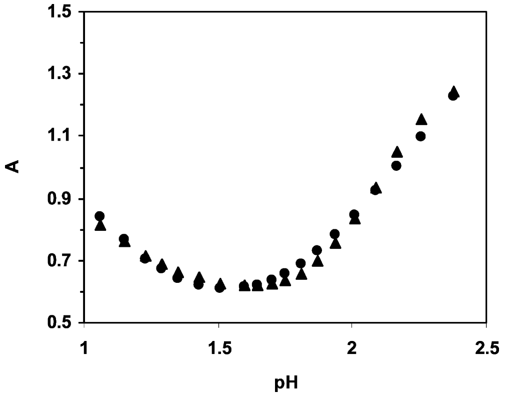


Figure 1. A_{exp} and A_{cal} values at 25 °C, $I = 0.1$ mol·dm^{-3}, and 270 nm. ●, A_{cal}; ▲, A_{exp} for the model including $VO_2H_2L^+$ and VO_2HL.

Table 9. Values of log β^0, $\Delta\varepsilon$, $\Delta\delta$, and R^2 According to SIT, Parabolic, and Debye−Hückel Models

species	model	log β^0	$\Delta\varepsilon$	$\Delta\delta$	R^2
$VO_2H_2L^+$	SIT	19.09 ± 0.04	0.13 ± 0.08	-	0.43
VO_2HL	SIT	17.19 ± 0.04	−0.36 ± 0.08	-	0.86
VO_2L^-	SIT	17.05 ± 0.05	0.30 ± 0.10	-	0.74
$VO_2H_2L^+$	Parabolic	18.99 ± 0.03	−0.48 ± 0.07	0.59 ± 0.09	0.93
VO_2HL	Parabolic	17.08 ± 0.02	−0.97 ± 0.05	0.60 ± 0.08	0.99
VO_2L^-	Parabolic	17.02 ± 0.04	0.12 ± 0.09	0.18 ± 0.10	0.76
$VO_2H_2L^+$	Debye−Hückel	18.48 ± 0.02	-	-	1.00
VO_2HL	Debye−Hückel	16.57 ± 0.01	-	-	1.00
VO_2L^-	Debye−Hückel	16.67 ± 0.08	-	-	0.96

Table 10. Values of log K^0, $\Delta\varepsilon$, $\Delta\delta$, and R^2 According to SIT, Parabolic, and Debye−Hückel Models

species	model	log K^0	$\Delta\varepsilon$	$\Delta\delta$	R^2
K_1	SIT	2.53 ± 0.05	0.28 ± 0.10	-	0.70
K_2	SIT	8.48 ± 0.07	0.43 ± 0.14	-	0.73
K_3	SIT	10.43 ± 0.08	−0.08 ± 0.16	-	0.06
K_1	Parabolic	2.66 ± 0.02	1.04 ± 0.05	−0.73 ± 0.09	0.97
K_2	Parabolic	8.29 ± 0.01	−0.69 ± 0.04	1.08 ± 0.07	1.00
K_3	Parabolic	10.65 ± 0.01	1.23 ± 0.05	−1.27 ± 0.08	0.99
K_1	Debye−Hückel	2.66 ± 0.03	-	-	0.97
K_2	Debye−Hückel	8.11 ± 0.01	-	-	1.00
K_3	Debye−Hückel	10.30 ± 0.02	-	-	1.00

results were obtained for the other ionic strengths. The combination of the following reactions has been used for the calculation of stability constants

$$\begin{array}{l} \mathrm{VO_2}^+ + \mathrm{H_3L}^+ \rightleftharpoons \mathrm{VO_2H_2L}^+ + \mathrm{H}^+ \\ \mathrm{H}^+ + \mathrm{H_2L} \rightleftharpoons \mathrm{H_3L}^+ \\ \mathrm{H}^+ + \mathrm{HL}^- \rightleftharpoons \mathrm{H_2L} \\ \mathrm{H}^+ + \mathrm{L}^{2-} \rightleftharpoons \mathrm{HL}^- \\ \hline \mathrm{VO_2}^+ + 2\mathrm{H}^+ + \mathrm{L}^{2-} \rightleftharpoons \mathrm{VO_2H_2L}^+ \end{array} \qquad \beta_{121} = \frac{[\mathrm{VO_2H_2L}^+]}{[\mathrm{VO_2}^+][\mathrm{H}^+]^2[\mathrm{L}^{2-}]} \tag{11}$$

$$\begin{array}{l} \mathrm{VO_2}^+ + \mathrm{H_3L}^+ \rightleftharpoons \mathrm{VO_2H_2L}^+ + \mathrm{H}^+ \\ \mathrm{VO_2H_2L}^+ \rightleftharpoons \mathrm{VO_2HL} + \mathrm{H}^+ \\ \mathrm{H}^+ + \mathrm{H_2L} \rightleftharpoons \mathrm{H_3L}^+ \\ \mathrm{H}^+ + \mathrm{HL}^- \rightleftharpoons \mathrm{H_2L} \\ \mathrm{H}^+ + \mathrm{L}^{2-} \rightleftharpoons \mathrm{HL}^- \\ \hline \mathrm{VO_2}^+ + \mathrm{H}^+ + \mathrm{L}^{2-} \rightleftharpoons \mathrm{VO_2HL} \end{array} \qquad \beta_{111} = \frac{[\mathrm{VO_2HL}]}{[\mathrm{VO_2}^+][\mathrm{H}^+][\mathrm{L}^{2-}]} \tag{12}$$

The average values of the experimental and calculated stability constants at various wavelengths are gathered in Table 5. It is important to note that according to the values of the dissociation constants of EDDA (Table 1) it is reasonable to assume protonated species for this complexation reaction. Yamada[11] assumed EDDA as H_2L but calculated the stability constant only for one species as VO_2L^-.

Comparison with Literature Data. A literature survey shows that two values for the stability constants of this complexation reaction have been reported (L = EDDA)[9,11]

$$\mathrm{VO_2}^+ + \mathrm{L}^{2-} \rightleftharpoons \mathrm{VO_2L}^- \qquad \log \beta_{101} = 15.98 \pm 0.14 \quad I = 3.0\ \mathrm{mol \cdot dm^{-3}}\ (\mathrm{NaClO_4})$$

$$\mathrm{VO_2}^+ + \mathrm{L}^{2-} \rightleftharpoons \mathrm{VO_2L}^- \qquad \log \beta_{101} = 14.5 \pm 0.3 \quad I = 1.0\ \mathrm{mol \cdot dm^{-3}}\ (\mathrm{NaClO_4})$$

but in our research two species $VO_2H_2L^+$ and VO_2HL have been obtained on the basis of a good fit and the speciation pattern, so it is the main reason for the difference with literature values. We have also assumed the models (a) to (d).

(a) We have calculated stability constants (Table 6) for VO_2L^- species on the basis of the following reactions and assuming the ligand as H_3L^+

$$\begin{array}{l} \mathrm{VO_2}^+ + \mathrm{H_3L}^+ \rightleftharpoons \mathrm{VO_2L}^- + 3\mathrm{H}^+ \\ \mathrm{H}^+ + \mathrm{H_2L} \rightleftharpoons \mathrm{H_3L}^+ \\ \mathrm{H}^+ + \mathrm{HL}^- \rightleftharpoons \mathrm{H_2L} \\ \mathrm{H}^+ + \mathrm{L}^{2-} \rightleftharpoons \mathrm{HL}^- \\ \hline \mathrm{VO_2}^+ + \mathrm{L}^{2-} \rightleftharpoons \mathrm{VO_2L}^- \end{array} \tag{13}$$

$$\beta_{101} = \frac{[\mathrm{VO_2L}^-]}{[\mathrm{VO_2}^+][\mathrm{L}^{2-}]} \tag{14}$$

In this case a good fit and speciation pattern were obtained (Figures 3 and 4), but as was mentioned above, we asummed two species $VO_2H_2L^+$ and VO_2HL (Table 5) because in the pH range of interest (1.00 to 2.50) it is not very reasonable to assume VO_2L^- according to the values of the dissociation constants (Table 1). So although the error function of calculation for only one species (VO_2L^-) is less than the corresponding function for the $VO_2H_2L^+$ and VO_2HL species, the protonated complex species are preferred from a chemical viewpoint in addition to the existence of VO_2L^-.[12]

(b) The stability constant data in this model are exactly equal to our accepted model ($VO_2H_2L^+$, VO_2HL), but the difference is in the number of protons because we have assumed EDDA as H_2L in this model. Therefore, we have two species, VO_2HL and VO_2L^-, according to the following reactions

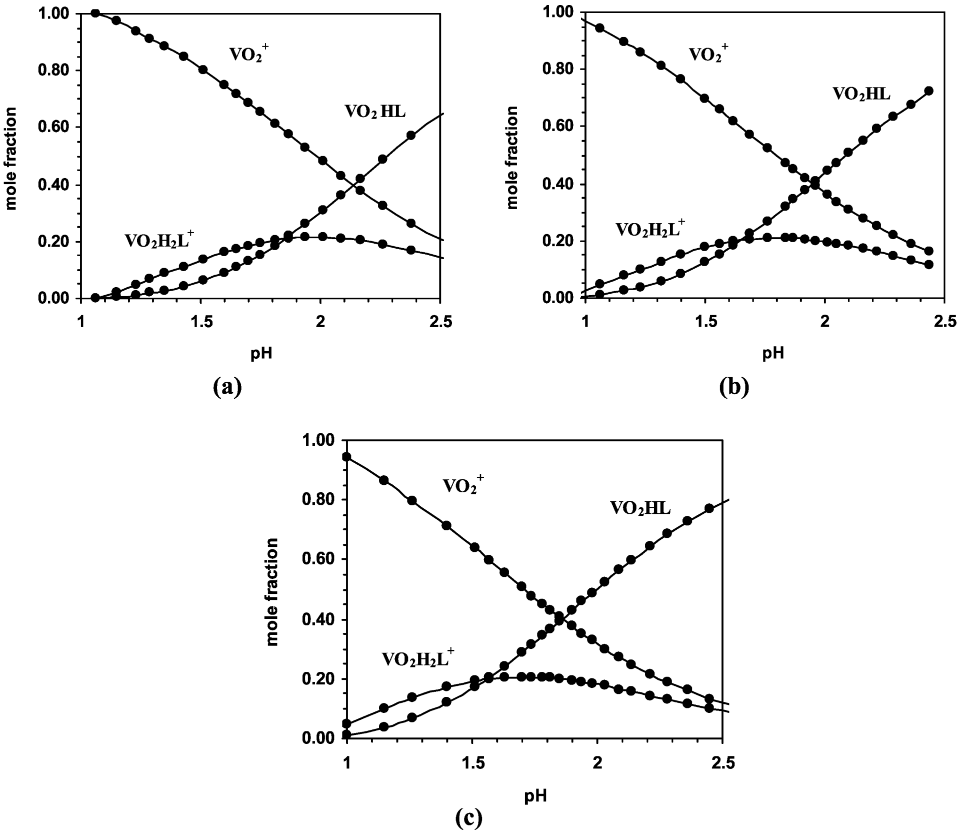
$$\begin{array}{l} \mathrm{VO_2}^+ + \mathrm{H_2L} \rightleftharpoons \mathrm{VO_2HL} + \mathrm{H}^+ \\ \mathrm{H}^+ + \mathrm{HL}^- \rightleftharpoons \mathrm{H_2L} \\ \mathrm{H}^+ + \mathrm{L}^{2-} \rightleftharpoons \mathrm{HL}^- \\ \hline \mathrm{VO_2}^+ + \mathrm{H}^+ + \mathrm{L}^{2-} \rightleftharpoons \mathrm{VO_2HL} \end{array} \tag{15}$$

$$\beta'_{111} = \frac{[\mathrm{VO_2HL}]}{[\mathrm{VO_2}^+][\mathrm{H}^+][\mathrm{L}^{2-}]} \tag{16}$$

$$\begin{array}{l} \mathrm{VO_2}^+ + \mathrm{H_2L} \rightleftharpoons \mathrm{VO_2HL} + \mathrm{H}^+ \\ \mathrm{VO_2HL} \rightleftharpoons \mathrm{VO_2L}^- + \mathrm{H}^+ \\ \mathrm{H}^+ + \mathrm{HL}^- \rightleftharpoons \mathrm{H_2L} \\ \mathrm{H}^+ + \mathrm{L}^{2-} \rightleftharpoons \mathrm{HL}^- \\ \hline \mathrm{VO_2}^+ + \mathrm{L}^{2-} \rightleftharpoons \mathrm{VO_2L}^- \end{array} \tag{17}$$

$$\beta'_{101} = \frac{[\mathrm{VO_2L}^-]}{[\mathrm{VO_2}^+][\mathrm{L}^{2-}]} \tag{18}$$

It should be mentioned that although in both of these cases, models (a) and (b), a good fit and speciation pattern were



(a) (b) (c)

Figure 2. Distribution of species at 25 °C, 270 nm, (a) $I = 0.1$ mol·dm^{-3}, (b) $I = 0.5$ mol·dm^{-3}, and (c) $I = 0.9$ mol·dm^{-3} for the model including $VO_2H_2L^+$ and VO_2HL. $C_{VO2^+} = 1\cdot10^{-3}$ and $C_L = 2.34\cdot10^{-2}$.

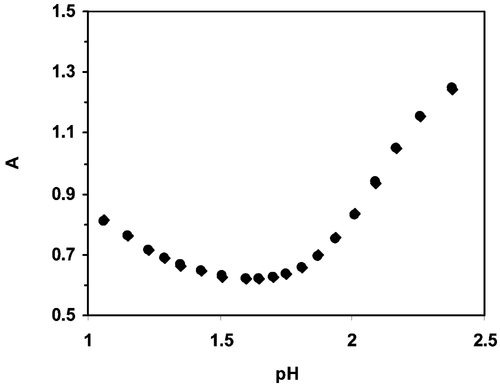


Figure 3. A_{exp} and A_{cal} values at 25 °C, $I = 0.1$ mol·dm^{-3}, and 270 nm. ●, A_{cal}; ▲, A_{exp} for the model including only VO_2L^-.

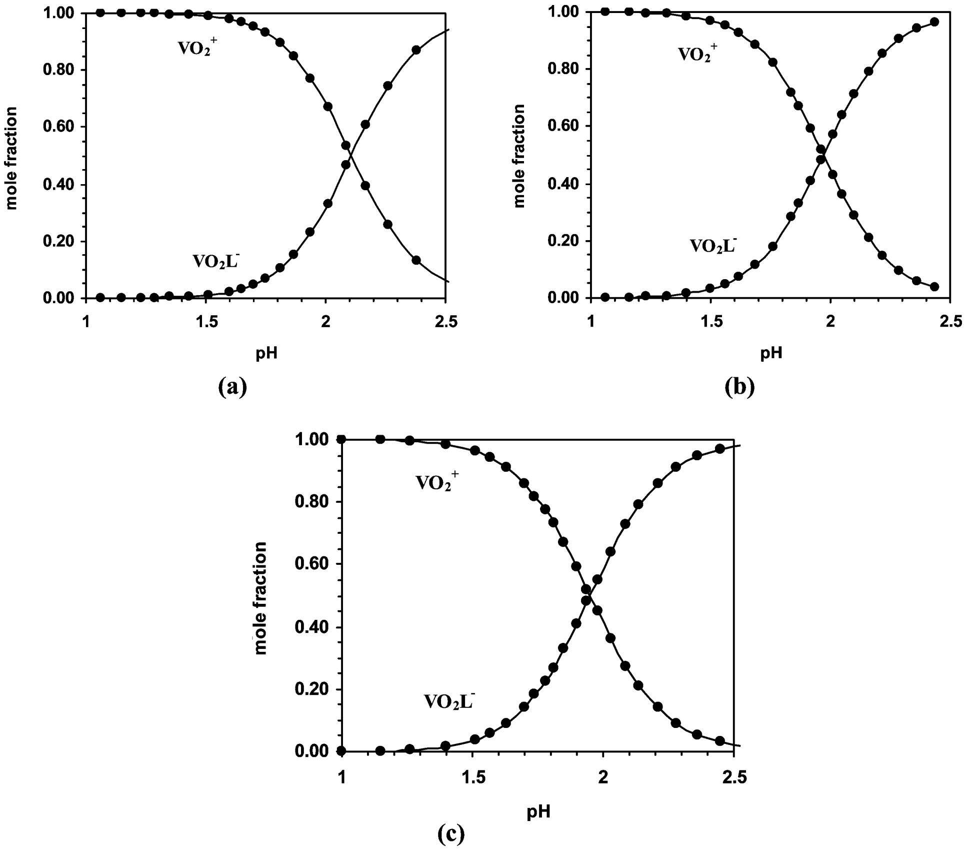
obtained the fitting (Figure 3) and speciation (Figure 4) were better for model (a). The fitting and speciation for model (b) are exactly similar to our accepted model (Figures 1 and 2). Also in Table 7 the F-values were obtained equal to 0.5 for model (b) which shows that there is not a significant difference between model (b) and the accepted model.

(c) Existence of three simultaneous species, $VO_2H_2L^+$, VO_2HL, and VO_2L^-, was also tested, but a good fit was not obtained and the speciation diagram was not suitable.

(d) The following model was also rejected on the basis of curve fitting and the speciation diagram

$$VO_2^+ + L^{3-} \rightleftharpoons VO_2L^{2-} \qquad (19)$$

All of these models are gathered in Table 7 together with their F-values versus the accepted model. Since all of the F-values are less than 0.05 (except for model (b), which was discussed above), according to the F-test for a 95 % probability, the null hypothesis is rejected, and it is concluded that there is a significant difference between these models. Also a p-value $= 2.44\cdot10^{-4}$ was obtained for a single factor ANOVA (Analysis of Variance) which again with the null hypothesis will be rejected. Therefore all of the models (a, c, and d) in Table 7 were rejected. Zare[9] studied the EDDA complex with VO_2^+ assuming that there is only a 1:1 stoichiometry (VO_2L^-) on the basis of the Sillen generalized least-squares method and using the LETAGROP-SPEFO program for calculation of stability constants that is different from the method described in this paper. Although the basis of the LETAGROP-SPEFO program is similar to the Excel program, there are some points that require attention. At first we used the Mathematica program to obtain relationships between formation constants and species concentration. We used the Mathematica output in the Excel program to obtain A_{cal} and finally the error function (eq 5). Then the error functions were minimized on the basis of the Gauss−Newton nonlinear least-squares method, and formation constants and molar extinction coefficients were obtained. Lagrange[13,14] considered MHL, MH_2L_2, MHL_2, ML, and ML_2 species only on the basis of the Sillen generalized least-squares method and the LETAGROP-SPEFO program but chose only the ML and ML_2 species according to the best fit for dioxovanadium(V) complexes with glycine. Zare[9] did not use any chemical methods like NMR for proving the existence of the VO_2L^- species and calculated the stability constants solely on the basis of experimental UV absorbance data as a function of pH (pH < 2) at an ionic strength of 3.0 mol·dm^{-3} sodium perchlorate and using the LETAGROP-SPEFO program. The other report in the literature[11] is also only on the basis of experimental UV absorbance data as a function of pH (pH < 3) at an ionic strength of 1.0 mol·dm^{-3} sodium perchlorate.



(a)

(b)

(c)

Figure 4. Distribution of species at 25 °C, 270 nm, (a) $I = 0.1$ mol·dm^{-3}, (b) $I = 0.5$ mol·dm^{-3}, and (c) $I = 0.9$ mol·dm^{-3} for the model including only VO_2L^-. $C_{VO2^+} = 1 \cdot 10^{-3}$ and $C_L = 2.34 \cdot 10^{-2}$.

Yamada[11] also only assumed the VO_2L^- species on the basis of mathematical methods. Therefore, it seems that comparison of this work with literature is not easy with regard to the differences in experimental conditions (different ionic strengths, kinds of species) and methods of calculation.

Ionic Strength Dependence of Dissociation and Stability Constants According to the SIT and Extended Debye−Hückel Models

Two types of methods can be used to describe the ionic medium dependence of equilibrium constants. One type of method takes into account the individual characteristics of the ionic media by using a medium dependent expression for the activity coefficients of the species involved in the equilibrium reactions. The medium dependence is described by virial or ion interaction coefficients as used in the Pitzer equations and in the specific ion interaction theory (SIT). The other type of method uses an extended Debye−Hückel expression in which the activity coefficients of reactants and products depend only on the ionic charge and the ionic strength but accounts for medium specific properties by introducing ionic pairing between the medium ions and the species involved in the equilibrium reactions. The activity factor estimates are thus based on the use of Debye−Hückel-type equations. The extended Debye−Hückel equations are either in the form of specific ion interaction methods or the Davies equation. However, the Davies equation should in general not be used at ionic strengths larger than 0.1 mol·kg^{-1}. Three forms of specific ion interaction methods have been described in the literature: (1) The Bronsted−Guggenheim−Scatchard approach, (2) the Pitzer and Brewer "B-method", and (3) the Pitzer virial coefficient method. Methods (1) and (2) are equivalent and differ only in the form of the denominator in the Debye−Hückel term. Method (3) requires more parameters for the description of the activity factors. These parameters are not available in many cases. This is generally the case for complex formation reactions. The specific ion interaction methods are reliable for intercomparison of experimental data in a given concentration range. Consequently, the SIT model has the potential to become a useful method to estimate medium effects on equilibrium constants in concentrated aqueous solution chemistry and has gained new attention in recent years.[15−36] The IUPAC Analytical Chemistry Division has also recommended the SIT model for correction of stability constants at different ionic strengths.[8]

The two basic assumptions in the specific ion interaction theory (SIT) are as follows:[37]

(a) The activity coefficient γ_j of an ion j of charge z_j in a solution of ionic strength I may be described by[38,39]

$$\log \gamma_j = \frac{-z_j^2 0.509\sqrt{I}}{1 + 1.5\sqrt{I}} + \sum_k \varepsilon(j, k, I) m_k \qquad (20)$$

The summation in eq 20 extends over all ions k present of opposite sign and neutral species in solution (the latter modification is included for consistency with the Setschenow equation[26] for neutral species). Their molality is denoted m_k. In the experimental determination of solution equilibrium constants, it is usual to keep the ionic strength of the solution constant by using a monovalent background electrolyte, at a concentration much higher than that of the reacting species. Under these conditions, it is reasonable to assume that the activity coefficient of a species will depend only on its interaction with the background electrolyte. This fact often makes it possible to simplify the summation in eq 20 so that only ion interaction

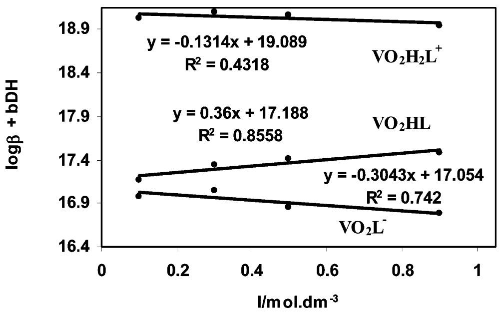


Figure 5. Plot of log $\beta + b$DH ($b = 6, 6, 4$ for $\mathrm{VO_2H_2L^+}$, $\mathrm{VO_2HL}$, and $\mathrm{VO_2L^-}$, respectively) versus ionic strength on the basis of the SIT model.

coefficients between the participating ionic species and the ionic medium ions are included as shown in eqs 22 to eq 25.

(b) The ion interaction coefficients $\varepsilon(j, k, I)$ are zero for ions of the same charge sign and for uncharged species.[37] The rationale behind this is that ε, which describes specific short-range interactions, must be small for ions of the same charge since they are usually far from one another due to electrostatic repulsion. This holds to a lesser extent also for uncharged species.

For the formation of dioxovanadium(V)−EDDA complexes

$$p\mathrm{VO_2}^{+} + q\mathrm{H}^{+} + r\mathrm{L}^{2-} \rightleftharpoons (\mathrm{VO_2})_p\mathrm{H}_q\mathrm{L}_r^{(p+q-2r)} \qquad (21)$$

The stability constant of $(\mathrm{VO_2})_p\mathrm{H}_q\mathrm{L}_r^{(p+q-2r)}$, $\beta_{p,q,r}$, determined in an ionic medium (1:1 salt $\mathrm{NaClO_4}$) of ionic strength I, is related to the corresponding value at zero ionic strength, $\beta^0_{p,q,r}$, by eq 22

$$\log \beta_{p,q,r} - \Delta z^2\mathrm{DH} = \log \beta^0_{p,q,r} - \Delta\varepsilon I \qquad (22)$$

where

$$\Delta z^2 = (p + q - 2r)^2 - (p + q + 4r) \qquad (23)$$

$$\mathrm{DH} = \frac{0.509\sqrt{I}}{1 + 1.5\sqrt{I}} \qquad (24)$$

$$\Delta\varepsilon = \varepsilon((\mathrm{VO_2})_p\mathrm{H}_q\mathrm{L}_r^{(p+q-2r)}, \mathrm{Na}^+ \text{ or } \mathrm{ClO_4}^-) - \varepsilon(\mathrm{VO_2}^+, \mathrm{ClO_4}^-) - q\varepsilon(\mathrm{H}^+, \mathrm{ClO_4}^-) - \varepsilon(\mathrm{L}^{2-}, \mathrm{Na}^+) \qquad (25)$$

Equilibria involving $\mathrm{H_2O(l)}$ as a reactant or product require a correction for the activity of water.[37] 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.[37] According to eq 22 and $\Delta z^2 = -6$, the following formulas were deduced for the extrapolation to zero ionic strength for $\mathrm{VO_2H_2L^+}$ and $\mathrm{VO_2HL}$ complexes, respectively[37,40]

$$\log \beta_{121} + 6\mathrm{DH} = \log \beta^0_{121} - \Delta\varepsilon I \qquad (26)$$

$$\log \beta_{111} + 6\mathrm{DH} = \log \beta^0_{111} - \Delta\varepsilon I \qquad (27)$$

The linear regressions were done (Figure 5) on the basis of eqs 26 and 27, and the values of $\Delta\varepsilon = 0.13 \pm 0.08$ and -0.36 ± 0.08 have been obtained for $\mathrm{VO_2H_2L^+}$ and $\mathrm{VO_2HL}$, respectively. $\varepsilon(\mathrm{H}^+, \mathrm{ClO_4}^-) = 0.14 \pm 0.02$, thus the following equations are valid[8,41]

$$\varepsilon(\mathrm{VO_2H_2L}^+, \mathrm{ClO_4}^-) - \varepsilon(\mathrm{VO_2}^+, \mathrm{ClO_4}^-) - \varepsilon(\mathrm{L}^{2-}, \mathrm{Na}^+) = 0.41 \qquad (28)$$

$$\varepsilon(\mathrm{VO_2}^+, \mathrm{ClO_4}^-) + \varepsilon(\mathrm{L}^{2-}, \mathrm{Na}^+) = 0.22 \qquad (29)$$

The values of $\log \beta_{121}$ and $\log \beta_{111}$ at $I = 0$ have been obtained: 19.09 ± 0.04 and 17.19 ± 0.04 according to Figure 5.

The stability constants at different ionic strengths were also fitted to the parabolic model, an extension of the SIT model.[36] The parabolic model has the form

$$\log \beta_{p,q,r} - \Delta z^2\mathrm{DH} = \log \beta^0_{p,q,r} - \Delta\varepsilon I - \Delta\delta_{\mathrm{i}} I^2 \qquad (30)$$

It has been shown that the parabolic model with two coefficients is satisfactory for ionic strengths to $I = 14$ m.[41] Although the Pitzer model[42] is more successful in calculating the interaction parameters, a large number of parameters are necessary even for simple systems. However, in many cases the Pitzer model is comparable to the parabolic model.[36] The advantage of the parabolic model in comparison to the Pitzer formalism is that it has fewer unknown parameters, and the fit is feasible with less experimental data. The results on the basis of the parabolic model are shown in Figure 6. It can be concluded from Figure 6 that fitting is better than the SIT model, as would be expected.

The dependence of the dissociation and stability constants on the ionic strength according to the EDH model can be described as follows[8,43−54]

$$\log \beta(I) = \log \beta(I_1) - Z^*\left(\frac{I^{0.5}}{1.955 + 2.91I^{0.5}} - \frac{I_1^{0.5}}{1.955 + 2.91I_1^{0.5}}\right) + C(I - I_1) + D(I^{1.5} - I_1^{1.5}) \qquad (31)$$

where I and I_1 are the actual and reference ionic strengths, respectively, and according to reaction 32

$$p\mathrm{M}^{m+} + q\mathrm{L}^{n-} + r\mathrm{H}^+ \rightleftharpoons (\mathrm{M}_p\mathrm{L}_q\mathrm{H}_r)^{pm-qn+r} \qquad (32)$$

$Z^* = pm^2 + qn^2 + r - (pm - qn + r)^2$, where m and n are the charges on the metal ion and the ligand, respectively. 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 the Excel 2000 program

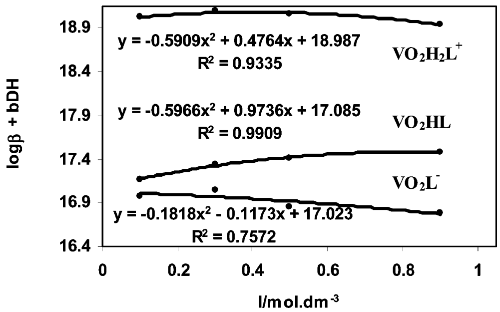


Figure 6. Plot of log $\beta + b$DH ($b = 6, 6, 4$ for $\mathrm{VO_2H_2L^+}$, $\mathrm{VO_2HL}$, and $\mathrm{VO_2L^-}$, respectively) versus ionic strength on the basis of the parabolic model.

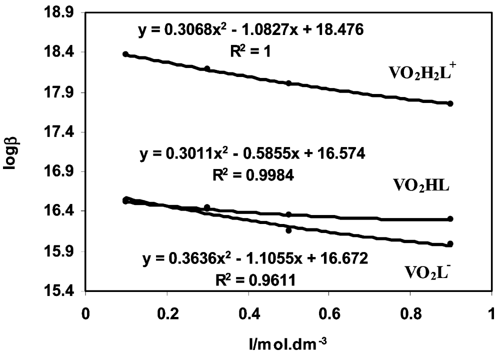


Figure 7. Plot of log β versus ionic strength on the basis of the extended Debye−Hückel model.

$$U = \sum_i (a_i - b_i)^2 \quad (i = 1, 2, 3, ...) \qquad (33)$$

where a is a quasi-experimental quantity and b_i is a calculated one. The values of C and D are shown in Table 8. The values of C and D have been inserted in eq 31, then the values of the calculated stability constants have been determined according to EDH, and their values are gathered in Tables 5 and 6. We have used $I_1 = 0.1$ as the reference ionic strength to obtain better consistency between experimental and calculated stability constants. The results on the basis of EDH are shown in Figure 7. The Debye–Hückel term which is the dominant term in the expression for the activity coefficients in dilute solution accounts for electrostatic, nonspecific, long-range interactions. At higher concentrations, short-range, nonelectrostatic interactions have to be taken into account.

If we assume the complex only as VO_2L^- (as was discussed previously in model (a)), similar calculations can be done on the basis of the SIT, Parabolic, and Debye–Hückel models. Values of log β^0, log K^0, $\Delta\varepsilon$, $\Delta\delta$, and R^2 according to the SIT, Parabolic, and Debye–Hückel models for different species, $VO_2H_2L^+$, VO_2HL, and VO_2L^-, and dissociation constants have been calculated from Figures 5 to 10 and are summarized in Tables 9 and 10.

Conclusions

Figure 2(a) shows that $VO_2H_2L^+$ at $I = 0.1$ mol·dm^{-3}, 270 nm, and pH = 1.87 to 2.09 reaches a maximum of 21 %, but this occurs at pH < 1.87 for the other ionic strengths. According to Figure 4(a), the maximum concentration of VO_2L^- at $I = 0.1$ mol·dm^{-3}, 270 nm, and pH = 2.51 is 94 %. It can be concluded from Figure 4 that VO_2^+ and VO_2L^- concentrations (at pH = 2.44 to 2.55 and 270 nm) fluctuate between 0.01 to 0.06 and 0.94 to 0.99, respectively, for different ionic strengths. In the SIT model on the basis of the difference between interaction coefficients ($\Delta\varepsilon$ values), it might be concluded that $VO_2H_2L^+$ interaction with ionic medium ions is stronger than the summation of interaction between VO_2^+, EDDA, and H^+ with ionic medium ions, and a similar situation exists for VO_2L^-. Stability constants change as a function of ionic strength with a mild decrease for $VO_2H_2L^+$ and VO_2L^- and vice versa for VO_2HL according to the slopes of the SIT figures. There was a large difference between $\Delta\varepsilon$ values which were obtained in the SIT and parabolic models. There is a good agreement between the SIT and parabolic models for log β^0 values, but the results on the basis of the Debye–Hückel model are different from the aforementioned models. log K^0 values obtained from the three models are in good agreement with each other. It is possible to place the complex species interaction with the other ions according to the Debye–Hückel model in the order: $VO_2HL > VO_2H_2L^+ > VO_2L^-$ on the basis of C values and $VO_2L^- > VO_2HL > VO_2H_2L^+$ on the basis of D values. Table 9 shows that data fit with the parabolic model follows the order $VO_2HL > VO_2H_2L^+ > VO_2L^-$ and for the SIT model $VO_2HL > VO_2L^- > VO_2H_2L^+$, but data fit with the parabolic model are better than the SIT model. The obtained values of C and D in Table 8 show that there are large uncertainties for VO_2L^- in contrast to small uncertainties for K_2. The data fit with the Debye–Hückel model on the basis of the errors for C and D is $VO_2HL > VO_2H_2L^+ > VO_2L^-$ and for dissociation constants is $K_2 > K_3 > K_1$. On the basis of errors for C and D in EDH (Table 8), SIT, and parabolic parameters (Tables 9 and 10), it might be concluded that the Debye–Hückel model applies best for these complex formation reactions and also for dissociation constants. The Parabolic and SIT models are in the second and third place, respectively, for the aforementioned reactions. Also R^2 values confirm this order.

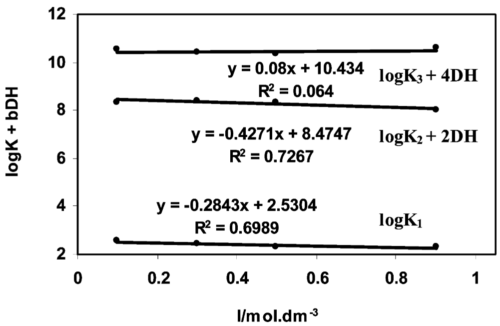


Figure 8. Plot of log K + bDH (b = 0, 2, 4 for K_1, K_2, and K_3, respectively) versus ionic strength on the basis of the SIT model.

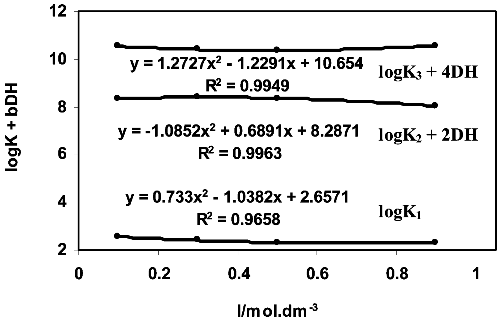


Figure 9. Plot of log K + bDH (b = 0, 2, 4 for K_1, K_2, and K_3, respectively) versus ionic strength on the basis of the parabolic model.

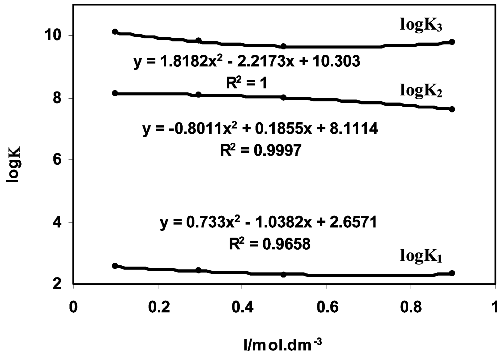


Figure 10. Plot of log K versus ionic strength on the basis of the extended Debye–Hückel model.

Appendix

Table A1. Experimental Values of Absorbance at Different pH and Wavelengths at 25 °C, and I = 0.3 mol·dm^{-3}

	λ/nm					
pH	255	260	265	270	275	280
1.25	0.9318	0.9053	0.8873	0.8661	0.8366	0.8000
1.35	0.8636	0.8376	0.8196	0.7971	0.7862	0.7334
1.43	0.8323	0.8062	0.7871	0.7644	0.7353	0.7003
1.51	0.8190	0.7917	0.7716	0.7483	0.7180	0.6832
1.54	0.8162	0.7883	0.7674	0.7425	0.7119	0.6761
1.61	0.8269	0.7952	0.7710	0.7423	0.7090	0.6714
1.66	0.8467	0.8120	0.7841	0.7523	0.7163	0.6759
1.72	0.8828	0.8428	0.8092	0.7728	0.7319	0.6871
1.78	0.9498	0.9004	0.8589	0.8133	0.7648	0.7137
1.86	1.0587	0.9951	0.9393	0.8818	0.8214	0.7604
1.94	1.2193	1.1352	1.0597	0.9841	0.9067	0.8306
2.02	1.4261	1.3157	1.2159	1.1166	1.0175	0.9229
2.12	1.6643	1.5238	1.3954	1.2694	1.1460	1.0293
2.24	1.8794	1.7132	1.5579	1.4077	1.2620	1.1254
2.39	2.0309	1.8445	1.6708	1.5035	1.3409	1.1908

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