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Complexation of Dioxovanadium(V) with Methyliminodiacetic Acid in $NaClO_4$ Aqueous Solutions at Different Ionic Strengths by Using an Extended Debye−Hückel Equation, Specific Ion Interaction Theory, and Parabolic Equations

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This paper mainly deals with solution equilibria between dioxovanadium(V) and the ligand methyliminodiacetic acid (MIDA) at different ionic strengths ranging from (0.1 to 0.9) mol·dm^{-3} sodium perchlorate and a pH range of (1.00 to 2.50) at T = 298 K. VO_2HL and VO_2L^- were the main species which were obtained on the basis of the best fit at different ionic strengths. The application of a extended Debye−Hückel-type equation (EDH), specific ion interaction theory (SIT), and the parabolic model have been demonstrated for the representation of the ionic strength dependence of the stability and dissociation constants. Finally, the ionic strength dependence parameters were calculated on the basis of the aforementioned models, and the results were interpreted.

Introduction

Vanadium is a trace element with a widespread distribution in nature. Vanadium participation in biological systems has spawn considerable research, and it also has potential use in pharmaceutical therapeutics. Vanadium compounds show insulin-like effects which have been demonstrated both in vivo and in vitro.[1] The discovery of vanadium in active sites of biological systems such as nitrogenase[2] and bromoperoxidase[3] has increased interest in vanadium complexes with ligands bearing oxygen and nitrogen atoms that can mimic biological activity in natural systems. As an inorganic cofactor, vanadium possesses and promotes bioactivity, ranging from antitumorigenicity to mitogenicity and inhibition of metabolic enzymes such as phosphoglucomutases[4] and others.

Within a broad variety of applications, complexones have in common the regulation of metal concentrations in widely differing systems.[5] Uses of complexones span fields such as detergents, textile and paper processing, photographic developing solutions, scale solubilization in processing tanks, electroplating, control of the activity of metal-dependent polymerization, and so forth.[5]

In the past decade we have carried out several investigations dealing with the ionic strength dependence of stability constants of some transition metal complexes with complexones by using the extended Debye−Hückel-type equation (EDH) model,[6−14] and recently we have extended our studies to other models such as a specific ion interaction theory (SIT) and a parabolic model.[15−17] Therefore, we decided to study the stability of dioxovandium(V) complexes of methyliminodiacetic acid (MIDA) at different ionic strengths using the aforementioned models.

Experimental Section

Reagents. All chemicals were analytical reagent grade. Perchloric acid, sodium hydroxide, potassium hydrogen carbonate, sodium perchlorate, hydrochloric acid, sodium carbonate, and sodium monovanadate were purchased from Merck and MIDA from Aldrich and were used without further purification. The NaOH solutions were prepared from titrisol solutions, and their concentrations were 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 $KHCO_3$.[18] 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 small amounts still exist, 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 T = 298 K 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.[18] The calibration has been done for the whole pH (pH = −log [H$^+$]) range used. The change in liquid junction potential[18] was calculated from eq 1.

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

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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Table 1. Dissociation Constants K_2 and K_1 of MIDA at Different Ionic Strengths, I, of $NaClO_4$ and $T = 298$ K

I / $mol \cdot dm^{-3}$	I / $mol \cdot kg^{-1}$	log K_2(M)	log K_2(m)	log K_1(M)	log K_1(m)	ref
0.10	0.10	9.67 ± 0.10	9.68	2.54 ± 0.04	2.55	this work
0.30	0.30	9.47 ± 0.05	9.49	2.40 ± 0.07	2.42	this work
0.50	0.51	9.34 ± 0.07	9.37	2.34 ± 0.09	2.37	this work
0.70	0.72	9.43 ± 0.10	9.48	2.27 ± 0.05	2.32	this work
0.90	0.94	9.50 ± 0.12	9.56	2.35 ± 0.10	2.41	this work
1.00		9.48		2.36		21

Table 2. Experimental Values of Absorbance at Different pH and Wavelengths at $T = 298$ K and $I = 0.10\ mol \cdot kg^{-1}$

	λ/nm					
pH	255	260	265	270	275	280
1.05	0.9378	0.9113	0.8928	0.8704	0.8406	0.8038
1.13	0.8559	0.8298	0.8123	0.7912	0.7632	0.7300
1.19	0.8169	0.7908	0.7731	0.7526	0.7255	0.6925
1.24	0.7829	0.7572	0.7387	0.7182	0.6908	0.6596
1.29	0.7568	0.7293	0.7099	0.6886	0.6623	0.6306
1.35	0.7386	0.7097	0.6890	0.6660	0.6392	0.6080
1.40	0.7273	0.6957	0.6723	0.6483	0.6205	0.5887
1.44	0.7390	0.7048	0.6804	0.6555	0.6281	0.5967
1.47	0.7407	0.7037	0.6765	0.6490	0.6192	0.5863
1.51	0.7441	0.7038	0.6740	0.6448	0.6134	0.5803
1.54	0.7508	0.7078	0.6746	0.6434	0.6099	0.5761
1.58	0.7588	0.7125	0.6771	0.6430	0.6079	0.5729
1.61	0.7692	0.7190	0.6797	0.6436	0.6074	0.5707
1.68	0.7816	0.7273	0.6855	0.6461	0.6077	0.5701
1.75	0.7940	0.7357	0.6900	0.6488	0.6091	0.5694
1.84	0.8000	0.7403	0.6935	0.6509	0.6091	0.5696
1.90	0.8124	0.7481	0.6981	0.6534	0.6105	0.5697
2.01	0.8198	0.7552	0.7022	0.6560	0.6129	0.5712
2.12	0.8312	0.7649	0.7123	0.6661	0.6233	0.5823
2.23	0.8371	0.7690	0.7153	0.6684	0.6242	0.5832
2.34	0.8429	0.7732	0.7178	0.6696	0.6251	0.5834
2.47	0.8478	0.7767	0.7208	0.6703	0.6247	0.5824

ficient $NaClO_4$ to adjust the ionic media.[18] 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 that the pH and absorbance of the solution could be measured simultaneously.

Measurements have been done for different metal/ligand concentrations and ligand/metal molar ratios, but a good fit, the speciation pattern, and minimum error function have been obtained with $C_L = 5.18 \cdot 10^{-2}$ and $C_{VO_2} = 1.00 \cdot 10^{-3}\ mol \cdot dm^{-3}$. Therefore 50 cm^3 acidic solutions of dioxovanadium(V) ($1.00 \cdot 10^{-3}\ mol \cdot dm^{-3}$) were titrated with basic solutions of MIDA ($5.18 \cdot 10^{-2}\ mol \cdot dm^{-3}$) at different ionic strengths. The absorbance of the solution was measured after each addition and adjusting the pH. According to the literature,[18,19] in acidic solution (pH < 2.5) and in the presence of a large excess of ligand, vanadium(V) exists as the VO_2^+ ion. 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 MIDA. Theory and Calculation. Two values of dissociation constants of MIDA have been used in this research according to the following equilibria

$$H_2L \rightleftharpoons H^+ + HL^- \qquad K_1 = \frac{[H^+][HL^-]}{[H_2L]} \qquad (2)$$

$$HL^- \rightleftharpoons H^+ + L^{2-} \qquad K_2 = \frac{[H^+][L^{2-}]}{[HL^-]} \qquad (3)$$

The values of the dissociation constants which were obtained by using the potentiometric technique and the Microsoft Excel 2000 program[20] are gathered in Table 1 together with the literature values. Three titrations have been done for each ionic strength, and approximately 200 points have been used in the calculations at each ionic strength.[20] Stability constants were

Table 3. Experimental Values of Absorbance at Different pH and Wavelengths at $T = 298$ K and $I = 0.30\ mol \cdot kg^{-1}$

	λ/nm					
pH	255	260	265	270	275	280
1.06	0.9221	0.8953	0.8765	0.8545	0.8255	0.7884
1.13	0.8406	0.8147	0.7971	0.7755	0.7489	0.7142
1.19	0.8062	0.7802	0.7622	0.7408	0.7139	0.6812
1.24	0.7754	0.7487	0.7303	0.7088	0.6827	0.6500
1.29	0.7523	0.7250	0.7055	0.6839	0.6575	0.6258
1.33	0.7403	0.7116	0.6913	0.6688	0.6420	0.6103
1.37	0.7319	0.7022	0.6805	0.6572	0.6300	0.5978
1.40	0.7286	0.6969	0.6724	0.6481	0.6208	0.5889
1.45	0.7240	0.6907	0.6652	0.6397	0.6107	0.5780
1.50	0.7256	0.6899	0.6625	0.6352	0.6059	0.5723
1.56	0.7272	0.6900	0.6612	0.6336	0.6028	0.5689
1.61	0.7302	0.6916	0.6617	0.6329	0.6017	0.5679
1.67	0.7340	0.6932	0.6624	0.6324	0.6003	0.5659
1.72	0.7353	0.6937	0.6613	0.6301	0.5982	0.5643
1.77	0.7377	0.6945	0.6611	0.6290	0.5964	0.5605
1.83	0.7449	0.6990	0.6639	0.6309	0.5971	0.5617
1.89	0.7467	0.7003	0.6632	0.6293	0.5947	0.5586
1.95	0.7509	0.7024	0.6647	0.6292	0.5950	0.5562
2.01	0.7560	0.7062	0.6670	0.6360	0.5946	0.5574
2.09	0.7611	0.7099	0.6688	0.6314	0.5933	0.5557
2.16	0.7666	0.7130	0.6713	0.6320	0.5935	0.5549
2.23	0.7735	0.7187	0.6743	0.6347	0.5960	0.5573
2.29	0.7793	0.7224	0.6773	0.6358	0.5955	0.5552
2.35	0.7866	0.7273	0.6808	0.6382	0.5969	0.5564
2.41	0.7874	0.7274	0.6797	0.6362	0.5953	0.5544
2.47	0.7926	0.7311	0.6823	0.6390	0.5971	0.5555

Table 4. Experimental Values of Absorbance at Different pH and Wavelengths at $T = 298$ K and $I = 0.51\ mol \cdot kg^{-1}$

	λ/nm					
pH	255	260	265	270	275	280
1.18	0.9482	0.9222	0.9031	0.8802	0.8497	0.8105
1.25	0.8817	0.8527	0.8321	0.8088	0.7794	0.7424
1.30	0.8575	0.8237	0.8049	0.7804	0.7507	0.7139
1.36	0.8440	0.8094	0.7843	0.7569	0.7249	0.6876
1.42	0.8441	0.8047	0.7745	0.7445	0.7107	0.6727
1.46	0.8508	0.8076	0.7743	0.7415	0.7050	0.6655
1.50	0.8637	0.8148	0.7764	0.7408	0.7020	0.6612
1.54	0.8809	0.8277	0.7843	0.7441	0.7028	0.6599
1.58	0.8999	0.8405	0.7923	0.7490	0.7057	0.6613
1.62	0.9194	0.8541	0.8015	0.7547	0.7074	0.6611
1.66	0.9405	0.8694	0.8121	0.7601	0.7116	0.6631
1.70	0.9604	0.8843	0.8224	0.7672	0.7150	0.6647
1.75	0.9768	0.8961	0.8296	0.7714	0.7175	0.6658
1.77	0.9852	0.9020	0.8337	0.7742	0.7185	0.6657
1.79	0.9901	0.9060	0.8353	0.7750	0.7183	0.6645
1.81	0.9976	0.9103	0.8383	0.7763	0.7195	0.6647
1.86	1.0049	0.9154	0.8418	0.7779	0.7199	0.6654
1.91	1.0066	0.9161	0.8416	0.7778	0.7186	0.6628
1.99	1.0090	0.9172	0.8414	0.7769	0.7169	0.6618
2.07	1.0114	0.9181	0.8412	0.7756	0.7159	0.6599
2.16	1.0162	0.9216	0.8434	0.7763	0.7155	0.6597
2.25	1.0145	0.9189	0.8408	0.7731	0.7121	0.6557
2.33	1.0176	0.9220	0.8411	0.7733	0.7108	0.6546
2.42	1.0166	0.9200	0.8402	0.7715	0.7097	0.6534
2.51	1.0151	0.9184	0.8381	0.7690	0.7081	0.6509

Table 5. Experimental Values of Absorbance at Different pH and Wavelengths at T = 298 K and I = 0.72 mol·kg^{-1}

	λ/nm					
pH	255	260	265	270	275	280
1.25	0.9368	0.9100	0.8924	0.8703	0.8403	0.8019
1.32	0.8532	0.8291	0.8117	0.7910	0.7629	0.7283
1.37	0.8128	0.7881	0.7703	0.7494	0.7223	0.6894
1.41	0.7792	0.7543	0.7365	0.7159	0.6895	0.6566
1.47	0.7621	0.7361	0.7174	0.6964	0.6698	0.6375
1.50	0.7480	0.7214	0.7026	0.6810	0.6536	0.6215
1.56	0.7382	0.7094	0.6879	0.6660	0.6387	0.6072
1.62	0.7336	0.7034	0.6806	0.6566	0.6286	0.5959
1.69	0.7291	0.6966	0.6727	0.6481	0.6189	0.5856
1.76	0.7298	0.6953	0.6683	0.6413	0.6114	0.5777
1.85	0.7334	0.6950	0.6658	0.6378	0.6055	0.5717
1.92	0.7427	0.7002	0.6686	0.6369	0.6038	0.5679
1.99	0.7444	0.7018	0.6691	0.6362	0.6015	0.5655
2.07	0.7498	0.7049	0.6700	0.6363	0.6014	0.5650
2.13	0.7564	0.7096	0.6725	0.6375	0.6019	0.5646
2.19	0.7636	0.7140	0.6752	0.6392	0.6026	0.5641
2.27	0.7523	0.7016	0.6620	0.6247	0.5870	0.5488
2.34	0.7608	0.7075	0.6660	0.6275	0.5891	0.5496
2.40	0.7689	0.7134	0.6696	0.6291	0.5896	0.5496
2.46	0.7764	0.7182	0.6730	0.6310	0.5910	0.5498
2.54	0.7774	0.7198	0.6728	0.6303	0.5890	0.5477

Table 6. Experimental Values of Absorbance at Different pH and Wavelengths at T = 298 K and I = 0.94 mol·kg^{-1}

	λ/nm					
pH	255	260	265	270	275	280
0.84	0.9427	0.9164	0.8989	0.8766	0.8469	0.8096
0.99	0.8646	0.8400	0.8227	0.8016	0.7731	0.7385
1.14	0.8040	0.7795	0.7614	0.7405	0.7143	0.6817
1.28	0.7759	0.7495	0.7309	0.7103	0.6835	0.6514
1.40	0.7566	0.7293	0.7093	0.6875	0.6610	0.6281
1.49	0.7443	0.7149	0.6923	0.6685	0.6408	0.6089
1.58	0.7425	0.7097	0.6843	0.6592	0.6291	0.5960
1.67	0.7442	0.7081	0.6800	0.6521	0.6218	0.5883
1.79	0.7513	0.7125	0.6834	0.6522	0.6195	0.5831
1.88	0.7584	0.7151	0.6812	0.6494	0.6158	0.5804
1.97	0.7697	0.7242	0.6865	0.6510	0.6153	0.5781
2.06	0.7825	0.7313	0.6908	0.6540	0.6154	0.5774
2.15	0.7970	0.7431	0.6987	0.6587	0.6192	0.5794
2.24	0.8126	0.7544	0.7071	0.6641	0.6226	0.5812
2.34	0.8284	0.7658	0.7154	0.6695	0.6260	0.5830
2.42	0.8423	0.7763	0.7217	0.6724	0.6268	0.5828
2.52	0.8546	0.7844	0.7274	0.6758	0.6280	0.5827

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(pH). The error function is defined as[15,16]

$$U = \sum (A_{\mathrm{exp}} - A_{\mathrm{cal}})^2 \tag{4}$$

A_{exp} values have been gathered from the UV spectrophotometric measurements and are reported at different pH and wavelengths in Tables 2, 3, 4, 5, and 6. A_{cal} values have been obtained for the main model 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 was 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. Different stoichiometric models were tested as follows: (a) Although a good fit and speciation diagram were obtained by assuming only one unprotonated species, VO_2L^-, and even though the error function was lower than the main model (which will be discussed later), it was not preferred because of the fact that in our pH range of interest protonated species are more important.

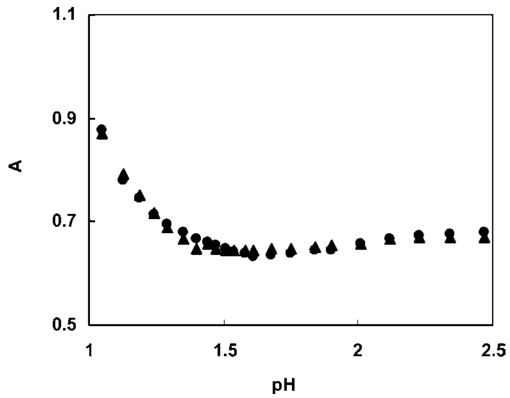

Figure 1. A_{exp} and A_{cal} values at T = 298 K, I = 0.10 mol·kg^{-1}, and 270 nm. ●, A_{cal}; ▲, A_{exp} for the model including VO_2HL and VO_2L^-.

$$\begin{array}{c} VO_2^{\;+} + H_2L \rightleftharpoons VO_2L^- + 2H^+ \\ H^+ + HL^- \rightleftharpoons H_2L \\ H^+ + L^{2-} \rightleftharpoons HL^- \\ \hline VO_2^{\;+} + L^{2-} \rightleftharpoons VO_2L^- \end{array} \tag{5}$$

$$\beta'_{101} = \frac{[VO_2L^-]}{[VO_2^{\;+}][L^{2-}]} \tag{6}$$

(b) We have assumed $VO_2H_2L^+$ and VO_2HL species on the basis of the following reactions and the ligand as H_2L

$$\begin{array}{c} VO_2^{\;+} + H_2L \rightleftharpoons VO_2H_2L^+ \\ H^+ + HL^- \rightleftharpoons H_2L \\ H^+ + L^{2-} \rightleftharpoons HL^- \\ \hline VO_2^{\;+} + 2H^+ + L^{2-} \rightleftharpoons VO_2H_2L^+ \end{array} \tag{7}$$

$$\beta_{121} = \frac{[VO_2H_2L^+]}{[VO_2^{\;+}][H^+]^2[L^{2-}]} \tag{8}$$

$$\begin{array}{c} VO_2^{\;+} + H_2L \rightleftharpoons VO_2H_2L^+ \\ VO_2H_2L^+ \rightleftharpoons VO_2HL + H^+ \\ H^+ + HL^- \rightleftharpoons H_2L \\ H^+ + L^{2-} \rightleftharpoons HL^- \\ \hline VO_2^{\;+} + H^+ + L^{2-} \rightleftharpoons VO_2HL \end{array} \tag{9}$$

$$\beta'_{111} = \frac{[VO_2HL]}{[VO_2^{\;+}][H^+][L^{2-}]} \tag{10}$$

The results for this model indicate that a good fit was obtained; however, the speciation was not suitable, and the mole fraction of the metal did not go to zero. The mole fractions of the species were also zero and never changed in the speciation diagram. Therefore, this model was not acceptable.

$$\begin{array}{c} VO_2^{\;+} + H_2L \rightleftharpoons VO_2H_2L^+ \\ VO_2H_2L^+ \rightleftharpoons VO_2HL + H^+ \\ VO_2HL \rightleftharpoons VO_2L^- + H^+ \end{array} \tag{c}$$

A good fit and speciation diagram were not obtained for this model.

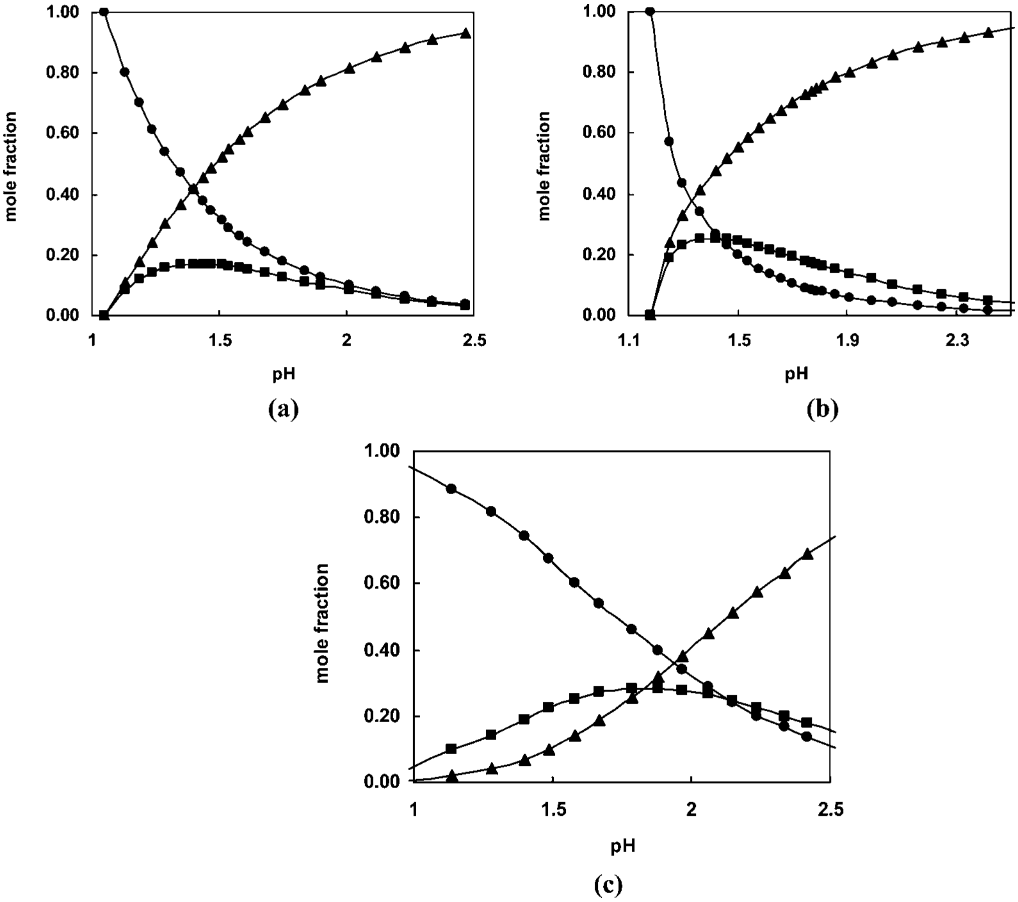

Figure 2. Speciation diagrams at $T = 298$ K, (a) $I = 0.10\ \text{mol}\cdot\text{kg}^{-1}$, (b) $I = 0.51\ \text{mol}\cdot\text{kg}^{-1}$, and (c) $I = 0.94\ \text{mol}\cdot\text{kg}^{-1}$ for the model including VO_2HL and VO_2L^-. $C_{VO_2^+} = 1.00\cdot10^{-3}$ and $C_L = 5.18\cdot10^{-2}\ \text{mol}\cdot\text{dm}^{-3}$. ●, VO_2^+; ▲, VO_2L^-; ■, VO_2HL.

Finally, the best fit and minimum error function were obtained with the VO_2HL and VO_2L^- species. A_{exp} and A_{cal} values at $T = 298$ K, $I = 0.1\ \text{mol}\cdot\text{kg}^{-1}$, and 270 nm are shown in Figure 1 which shows a very good graphical fit. Similar fits have been obtained for the other ionic strengths. The chosen model is also in close agreement with experimental data. The speciation diagrams are shown in Figure 2 for different ionic strengths. A_{cal} values have been determined from the combination of the following mass balance and Beer−Lambert laws for our accepted model (L = MIDA).

$$A = \varepsilon_0[VO_2^+] + \varepsilon_{VO_2HL}[VO_2HL] + \varepsilon_{VO_2L^-}[VO_2L^-] \tag{11}$$

$$C_{VO_2^+} = [VO_2^+] + [VO_2HL] + [VO_2L^-] \tag{12}$$

$$C_L = [VO_2HL] + [VO_2L^-] + [H_2L] + [HL^-] \tag{13}$$

and the formation constants

$$VO_2^+ + H_2L \rightleftharpoons VO_2HL + H^+ \qquad K_{VO_2HL} = \frac{[VO_2HL][H^+]}{[VO_2^+][H_2L]} \tag{14}$$

$$VO_2HL \rightleftharpoons VO_2L^- + H^+ \qquad K_{VO_2L^-} = \frac{[VO_2L^-][H^+]}{[VO_2HL]} \tag{15}$$

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

Table 7. Average Experimental and Calculated Values of log β_{111} at pH = 1.00 to 2.50 and Different Ionic Strengths for the Complexation of Dioxovanadium(V) with MIDA, with T = 298 K

I	I	log $\beta_{111}(M)$		log $\beta_{111}(m)$	
$\text{mol}\cdot\text{dm}^{-3}$	$\text{mol}\cdot\text{kg}^{-1}$	exptl	calcd	exptl	calcd
0.10	0.10	12.79 ± 0.15	12.79 ± 0.00	12.81	12.81 ± 0.00
0.30	0.30	11.96 ± 0.17	12.06 ± 0.46	11.99	12.10 ± 0.45
0.50	0.51	11.86 ± 0.25	11.76 ± 1.01	11.90	11.80 ± 0.98
0.70	0.72	11.71 ± 0.05	11.73 ± 1.61	11.77	11.78 ± 1.59
0.90	0.94	11.90 ± 0.10	11.91 ± 2.27	11.98	11.99 ± 2.27

Table 8. 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 MIDA, with T = 298 K

I	I	log $\beta_{101}(M)$		log $\beta_{101}(m)$	
$\text{mol}\cdot\text{dm}^{-3}$	$\text{mol}\cdot\text{kg}^{-1}$	exptl	calcd	exptl	calcd
0.10	0.10	11.74 ± 0.25	11.74 ± 0.00	11.75	11.75 ± 0.00
0.30	0.30	11.80 ± 0.30	11.83 ± 0.12	11.82	11.84 ± 0.08
0.50	0.51	11.56 ± 0.10	11.55 ± 0.27	11.59	11.58 ± 0.17
0.70	0.72	10.96 ± 0.20	10.94 ± 0.43	11.01	11.00 ± 0.28
0.90	0.94	10.05 ± 0.35	10.06 ± 0.61	10.11	10.12 ± 0.40

The combination of the reactions shown in eqs 5 and 9 have been used for the calculation of stability constants given in eqs 6 and 10. The average values of the experimental and calculated stability constants at various wavelengths are gathered in Tables 7 and 8. It is important to note that, according to the values of the dissociation constants of MIDA (Table 1), it is reasonable to assume protonated species for this complexation reaction.

Comparison with Literature Data. A literature survey showed that one value for the stability constant of this complexation reaction has been reported (L = MIDA),[21]

$$VO_2^{+} + L^{2-} \rightleftharpoons VO_2L^{-} \qquad \log \beta_{101} = 10.16 \pm 0.12$$
$$I = 1.0\ \mathrm{mol{\cdot}dm^{-3}}\ (NaClO_4)$$

but in our research two species, VO_2HL and VO_2L^-, have been obtained on the basis of a good fit and the speciation diagram, so this is the main reason for the difference with literature values. Yamada[21] assumed MIDA as H_2L but calculated the stability constant only for one species as VO_2L^- 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 using mathematical methods. Comparison of this work with the literature data is not easy with regard to the differences in experimental conditions (different ionic strengths, kinds of species) and methods of calculation. The difference between our method of calculation and the literature has been discussed previously.[15,16]

Ionic Strength Dependence of Dissociation and Stability Constants According to the SIT, Parabolic, and EDH Models. The activity coefficient γ_j of an ion j of charge z_j in a solution of ionic strength I may be described by[22−24]

$$\log \gamma_j = \frac{-z_j^2 0.509\sqrt{I}}{1 + 1.5\sqrt{I}} + \sum_k \varepsilon(j, k, I) m_k \qquad (16)$$

The summation in eq 16 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[25] for neutral species).[26] Their molality is denoted m_k. For a correct application of the SIT, concentrations should be reported in the molal concentration scale. Molar ionic strengths have been converted to the molal scale according to the literature.[27] The log β values were converted to the molal concentration scale according to the following equation[26]

$$\log \beta(m) = \log \beta(M) + \sum\nu \log(m/M) \qquad (17)$$

where m and M stand for molality and molarity, respectively. $\sum\nu$ is the sum of stoichiometric coefficients of the reaction species. Equation 16, which is the basis of the SIT, is a simplified version of the Pitzer ion-interaction approach, neglecting triple interactions which are important only in very concentrated solutions and the interactions between ions of the same sign. The first term in eq 16 shows the nonspecific long-range contribution of the electrostatic region, and the second reflects the contribution due to short-range ion−ion, ion−neutral, or neutral−neutral interactions, in accordance with the Bronsted postulate that $\varepsilon(j, k) = 0$ if ions have the same charge sign. 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 because of electrostatic repulsion. This holds to a lesser extent also for uncharged species.

There are many papers in the literature about the SIT.[28−38] Sammartano et al.[38] proposed a modified version of the SIT approach, in which the specific coefficients are expressed as a function of I

$$\varepsilon = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)(I + 1)^{-1} \qquad (18)$$

where ε_∞ is the value of ε for $I \rightarrow \infty$ and ε_0 is the value of ε for $I \rightarrow 0$. ε_∞ could be defined as follows

$$\varepsilon_\infty = \varepsilon_\infty^{(0)} + \varepsilon_\infty^{(1)} I \qquad (19)$$

Table 9. Parameters for the Dependence on the Ionic Strength of Dissociation and Stability Constants at T = 298 K

species	C kg·mol^{-1}	D kg$^{1.5}$·mol$^{-1.5}$	Z^*	ref
K_2	−1.11 ± 0.51	1.33 ± 0.52	4	thiswork
K_1	−0.80 ± 0.38	0.79 ± 0.39	2	thiswork
VO_2HL	−5.52 ± 1.30	4.95 ± 1.33	6	thiswork
VO_2L^-	6.23 ± 0.23	−7.38 ± 0.24	4	thiswork

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

		log β^0	$\Delta\varepsilon$	$\Delta\delta$	
species	model	m	kg·mol^{-1}	kg^2·mol^{-2}	R^2
VO_2HL	Debye−Hücke	13.15 ± 0.08			0.95
VO_2L^-	Debye−Hückel	11.60 ± 0.02			1.00
VO_2HL	SIT	13.22 ± 0.74	0.25 ± 1.24		0.12
VO_2L^-	SIT	12.72 ± 1.13	1.55 ± 1.90		0.69
VO_2HL	parabolic	13.68 ± 0.09	2.88 ± 0.10	−2.52 ± 0.12	0.88
VO_2L^-	parabolic	11.96 ± 0.02	−2.77 ± 0.04	4.14 ± 0.08	1.00

Table 11. Values of log K^0, $\Delta\varepsilon$, $\Delta\delta$, and R^2 according to Debye−Hückel, SIT, and Parabolic Models

		log K^0	$\Delta\varepsilon$	$\Delta\delta$	
species	model	m	kg·mol^{-1}	kg^2·mol^{-2}	R^2
K_1	Debye−Hückel	2.64 ± 0.02			0.97
K_2	Debye−Hückel	9.80 ± 0.03			0.93
K_1	SIT	2.73 ± 0.14	−0.02 ± 0.24		0.04
K_2	SIT	10.03 ± 0.21	−0.29 ± 0.36		0.69
K_1	parabolic	2.82 ± 0.03	0.47 ± 0.05	−0.47 ± 0.09	0.82
K_2	parabolic	10.16 ± 0.01	0.45 ± 0.03	−0.71 ± 0.06	0.95

Under our conditions and according to previous work,[15,16] it is often possible to simplify the summation in eq 16 so that only ion interaction coefficients between the participating ionic species and the ionic medium ions are included as shown in eqs 21 to 24.

For the formation of dioxovanadium(V)−MIDA complexes

$$pVO_2^{+} + qH^{+} + rL^{2-} \rightleftharpoons (VO_2)_pH_qL_r^{(p+q-2r)} \qquad (20)$$

the stability constant of $(VO_2)_pH_qL_r^{(p+q-2r)}$, $\beta_{p,q,r}$, determined in an ionic medium (1:1 salt $NaClO_4$) of ionic strength I, is related to the corresponding value at zero ionic strength, $\beta^0_{p,q,r}$, by eq 21

$$\log \beta_{p,q,r} - \Delta z^2 \mathrm{DH} = \log \beta^0_{p,q,r} - \Delta\varepsilon I \qquad (21)$$

where

$$\Delta z^2 = (p + q - 2r)^2 - (p + q + 4r) \qquad (22)$$

$$\mathrm{DH} = \frac{0.509\sqrt{I}}{1 + 1.5\sqrt{I}} \qquad (23)$$

$$\Delta\varepsilon = \varepsilon((VO_2)_pH_qL_r^{(p+q-2r)}, Na^{+}\ \text{or}\ ClO_4^{-}) - \varepsilon(VO_2^{+}, ClO_4^{-}) - q\varepsilon(H^{+}, ClO_4^{-}) - \varepsilon(L^{2-}, Na^{+}) \qquad (24)$$

Equilibria involving $H_2O(l)$ as a reactant or product require a correction for the activity of water.[22] 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.[22] According to eq 21 and $\Delta z^2 = -6$ or -4, the following formula were deduced for the extrapolation to zero ionic strength for VO_2HL and VO_2L^- complexes respectively[22,39]

$$\log \beta_{111} + 6\mathrm{DH} = \log \beta^0_{111} - \Delta\varepsilon I \qquad (25)$$

$$\log \beta_{101} + 4\mathrm{DH} = \log \beta^0_{101} - \Delta\varepsilon I \qquad (26)$$

The linear regressions were done on the basis of eqs 25 and 26, and the values of $\Delta\varepsilon$ = (0.25 ± 1.24 and 1.55 ± 1.90) kg·mol^{-1} have been obtained for VO_2HL and VO_2L^-, respectively. $\varepsilon(\mathrm{H^+}, \mathrm{ClO_4^-}) = 0.14 \pm 0.02\ \mathrm{kg \cdot mol^{-1}}$,[22] and thus, the following equations are valid[16]

$$\varepsilon(\mathrm{VO_2^+}, \mathrm{ClO_4^-}) + \varepsilon(\mathrm{L^{2-}}, \mathrm{Na^+}) = -0.39 \qquad (27)$$

$$\varepsilon(\mathrm{VO_2L^-}, \mathrm{Na^+}) - \varepsilon(\mathrm{VO_2^+}, \mathrm{ClO_4^-}) - \varepsilon(\mathrm{L^{2-}}, \mathrm{Na^+}) = 1.55 \qquad (28)$$

The values of $\log \beta^0{}_{111}$ and $\log \beta^0{}_{101}$ have been obtained: 13.22 ± 0.74 and 12.72 ± 1.13.

The parabolic model has also been applied to the dependence of metal complex formation and dissociation constants on ionic strength[28]

$$\log \beta_{p,q,r} - \Delta z^2 \mathrm{DH} = \log \beta^0{}_{p,q,r} - \Delta\varepsilon I - \Delta\delta_i I^2 \qquad (29)$$

The parabolic model with two coefficients is satisfactory for ionic strengths to $I = 14m$.[40] The parabolic model because of its advantages in mathematical simplicity and its less-parametrized nature is comparable to the Pitzer model in many cases.

The dependence of the dissociation and stability constants on ionic strength according to the EDH model can be described as follows[41−43]

$$\log \beta(I) = \log \beta(I_1) - Z^*\left(\frac{I^{0.5}}{1.955 + 2.91 I^{0.5}} - \frac{I_1{}^{0.5}}{1.955 + 2.91 I_1{}^{0.5}}\right) + C(I - I_1) + D(I^{1.5} - I_1{}^{1.5}) \qquad (30)$$

where I and I_1 are the actual and reference ionic strengths, respectively, and according to reaction 31

$$p\mathrm{M^{m+}} + q\mathrm{L^{n-}} + r\mathrm{H^+} \rightleftharpoons (\mathrm{M}_p\mathrm{L}_q\mathrm{H}_r)^{pm-qn+r} \qquad (31)$$

$Z^* = pm^2 + qn^2 + r - (pm - qn + r)^2$ 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, using the Gauss−Newton nonlinear least-squares method in the Excel 2000 program:

$$U = \sum_i (a_i - b_i)^2 (i = 1, 2, 3) \qquad (32)$$

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 9. The values of C and D have been inserted in eq 30, and then the values of the calculated stability constants have been determined according to EDH; their values are gathered in Tables 7 and 8. We have used $I_1 = 0.1$ as the reference ionic strength to obtain better consistency between experimental and calculated stability constants.

Values of $\log \beta^0$, $\log K^0$, $\Delta\varepsilon$, $\Delta\delta$, and R^2 on the basis of EDH, SIT, and parabolic models for the two species, $\mathrm{VO_2HL}$ and $\mathrm{VO_2L^-}$, and the dissociation constants are summarized in Tables 10 and 11. The results in Tables 10 and 11 show that fitting on the basis of the parabolic equation is better than the SIT model, as would be expected.

Conclusions

It was shown that large uncertainties exist for K_2 and K_1 on the basis of the C and D values in the EDH (Table 9). $\log K^0$ values obtained from EDH, SIT, and parabolic models are in close agreement with each other (Table 11) in contrast to $\log \beta^0$ values (Table 10). Uncertainties for $\log \beta^0$ and $\log K^0$ on the basis of the SIT model are greater than the other models. $\Delta\varepsilon$ values which were obtained on the basis of SIT and parabolic models are very different from each other. There are large uncertainties for $\Delta\varepsilon$ values on the basis of the SIT model in contrast to the parabolic model. The large value of C for $\mathrm{VO_2L^-}$ (Table 9) can be considered as a measure of the interactions between $\mathrm{VO_2L^-}$ and the other ions in the solution, mainly cations of the background salt. Finally it might be concluded that the EDH and parabolic models apply best for the $\mathrm{VO_2L^-}$ and $\mathrm{VO_2HL}$ species, respectively.

$\mathrm{VO_2HL}$ reaches a maximum of 17 % at $I = 0.10\ \mathrm{mol \cdot kg^{-1}}$, at pH = 1.47 (Figure 2a), but the maximum concentration of $\mathrm{VO_2HL}$ shifts to higher pH values (1.47 to 1.97) for the other ionic strengths and reaches a maximum of 28 % at $I = 0.94\ \mathrm{mol \cdot kg^{-1}}$ and pH = 1.97. This means that at higher ionic strengths the maximum formation percentage of the protonated species is shifted 0.5 pH units toward the more basic region than corresponding ones at $I = 0.10\ \mathrm{mol \cdot kg^{-1}}$.

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