

Complexation of Dioxovanadium(V) with Nitrilotriacetic Acid at Different Ionic Strengths by Using Specific Ion Interaction and Debye–Hückel Theories

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This research has been undertaken to show the application of specific ion interaction theory (SIT) for the complexation of dioxovanadium(V) with nitrilotriacetic acid (NTA) at different ionic strengths of (0.1 to 1.0) mol·dm⁻³ sodium perchlorate as supporting electrolyte and pH range of 1.00 to 2.50 at 25 °C. Two species, VO₂HL⁻ and VO₂H₂L, have been detected according to curve fitting, which enables us to calculate the values of stability constants. Ionic strength dependence semiempirical parameters for the dissociation and stability constants were derived on the basis of an extended Debye–Hückel-type equation. The SIT model successfully described the ionic strength dependencies of the stability constant values.

Introduction

Research in vanadium chemistry has gained new attention in recent years. Vanadium complexes are known to exhibit antitumor activity namely by inhibition of cellular PTPases and activation of tyrosine phosphorylases. Some of these compounds may also induce oxidative stress and DNA fragmentation and act as potential antimetastatic agents.¹ Diabetes Mellitus (DM) is growing in importance everyday, and there is still no simple solution to restore glucose homeostasis permanently, particularly for noninsulin-dependent diabetes which accounts for 90 % of cases.² Vanadium insulin-mimetic properties are well-known, and several complexes were shown to be active for therapy of both DM types. The therapeutic use of vanadium complexes is thus promising. On the other hand, polyaminocarboxylic acids are involved in many areas; for example, they are used as contrast agents in computer tomography.³

The present work measured the stability constant values of NTA complexes with dioxovanadium(V) at ionic strengths of (0.1 to 1.0) mol·dm⁻³ NaClO₄ and 25 °C by using SIT. There is a project on the IUPAC Web site about the ionic strength corrections for stability constants using SIT which has been completed in 2005, but to our knowledge no reports of the ionic strength dependence of stability constants for the V(V) + NTA complex using SIT have appeared. This work is performed in an acidic medium in order to suppress hydrolysis of the dioxovanadium(V), and the complexes are characterized by a combination of potentiometric and spectrophotometric measurements. Finally, SIT results have been compared with the results on the basis of an extended Debye–Hückel-type equation.

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 KHCO₃.⁴ A stock solution of vanadium(V) was prepared by dissolution of an anhydrous sodium monovanadate in perchloric acid solution affecting the destruction of the decavanadate. The solution stood overnight before use to obtain only the VO₂⁺ ion, and isopolyvanadates will not be formed. 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 has been used.

Measurements. All measurements were carried out at (25 ± 0.1) °C and from ionic strengths of (0.1 to 1.0) mol·dm⁻³ sodium perchlorate. A Metrohm pH-meter, 744, was used for pH measurements. The pH-meter has 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.⁴ 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 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.

Acidic solutions (50 cm³) of dioxovanadium(V) (5·10⁻³ mol·dm⁻³) were titrated with basic solutions of NTA (6·10⁻³ mol·dm⁻³) at different ionic strengths. The absorbance of the solution was measured after each addition and adjusting the pH. 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.

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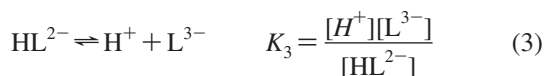
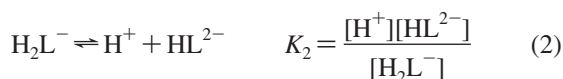
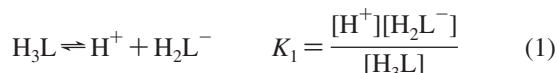
[‡] Shahid Beheshti University.

Table 1. Dissociation Constants K_3 , K_2 , and K_1 of NTA at Different Ionic Strengths, I , of NaClO₄

$I/\text{mol}\cdot\text{dm}^{-3}$	$\log K_3$	$\log K_2$	$\log K_1$	experimental conditions	ref
0.1	1.98 ± 0.02	2.92 ± 0.05	10.00 ± 0.02		6
0.3	1.83 ± 0.04	2.84 ± 0.03	9.85 ± 0.01		6
0.5	1.76 ± 0.01	2.79 ± 0.02	9.70 ± 0.03		6
0.7	1.63 ± 0.02	2.61 ± 0.01	9.55 ± 0.02		6
1.0	1.55 ± 0.02	2.59 ± 0.04	9.25 ± 0.02		6
	2.05 ± 0.05	2.63 ± 0.02	9.17 ± 0.04	$I = 3.0 \text{ mol}\cdot\text{dm}^{-3} \text{ NaClO}_4, t = 25^\circ\text{C}$	4
			9.81 ± 0.10	$I = 0.15 \text{ mol}\cdot\text{dm}^{-3}, t = 25^\circ\text{C}$	8
	1.65	2.94	10.33	$t = 20^\circ\text{C}$	9

Results and Discussion

Complexation of Dioxovanadium(V) with NTA. Theory and Calculation. According to our knowledge, the dissociation equilibria of NTA have been studied in different kinds of background electrolytes.^{4,5} Dissociation constant values have been gathered from the literature^{6,7} on the basis of the following equilibria



The values of dissociation constants are reported in Table 1.^{4,6,8,9} 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 the 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

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

A_{exp} values have been gathered from the UV spectrophotometric measurements and are reported at different pH values and wavelengths in Tables 2 to 6. A_{cal} values have been determined from the combination of the following mass-balance and Beer–Lambert laws (L = NTA)

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

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

$$C_L = [\text{VO}_2\text{HL}^-] + [\text{VO}_2\text{H}_2\text{L}] + [\text{H}_3\text{L}] + [\text{H}_2\text{L}^-] + [\text{HL}^{2-}] \quad (7)$$

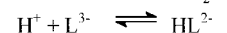
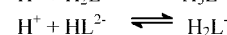
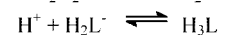
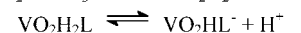
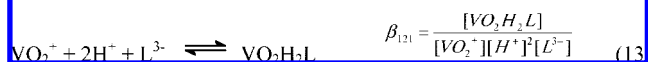
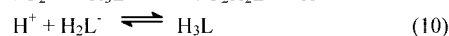
and formation constants

$$\text{VO}_2^+ + \text{H}_3\text{L} \rightleftharpoons \text{VO}_2\text{H}_2\text{L} + \text{H}^+ \quad K_{\text{VO}_2\text{H}_2\text{L}} = \frac{[\text{VO}_2\text{H}_2\text{L}][\text{H}^+]}{[\text{VO}_2^+][\text{H}_3\text{L}]} \quad (8)$$

$$\text{VO}_2\text{H}_2\text{L} \rightleftharpoons \text{VO}_2\text{HL}^- + \text{H}^+ \quad K_{\text{VO}_2\text{HL}^-} = \frac{[\text{VO}_2\text{HL}^-][\text{H}^+]}{[\text{VO}_2\text{H}_2\text{L}]} \quad (9)$$

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

Different stoichiometric models were tested. Species having no significance 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 $\text{VO}_2\text{H}_2\text{L}$ and VO_2HL^- species. The chosen model is also in close agreement with experimental data. A_{exp} and A_{cal} values at 25°C , $I = 0.1 \text{ mol}\cdot\text{dm}^{-3}$, 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 distribution of species is shown in Figure 2 for 270 nm and different ionic strengths. Figure 2a shows the maximum concentration of $\text{VO}_2\text{H}_2\text{L}$ at $I = 0.1 \text{ mol}\cdot\text{dm}^{-3}$, and 270 nm is reached at $\text{pH} = 1.70$. Similar results were obtained for the other ionic strengths. The combination of the following reactions have been used for the calculation of stability constants



The average values of experimental stability constants at various wavelengths are gathered in Table 7.

Comparison with Literature Data. A literature survey shows that two values for the stability constants of this complexation reaction have been reported (L = NTA)^{4,10}

$$\text{VO}_2^+ + \text{L}^{3-} \rightleftharpoons \text{VO}_2\text{L}^{2-} \quad \log \beta_{110} = 13.8 \pm 0.4 \quad I = 1.0 \text{ mol}\cdot\text{dm}^{-3} (\text{NaClO}_4)$$

$$\text{VO}_2^+ + \text{L}^{3-} \rightleftharpoons \text{VO}_2\text{L}^{2-} \quad \log \beta_{110} = 13.8 \pm 0.2 \quad I = 3.0 \text{ mol}\cdot\text{dm}^{-3} (\text{NaClO}_4)$$

but in our research only two species VO_2HL^- and $\text{VO}_2\text{H}_2\text{L}$ have been obtained on the basis of curve fitting, so it is the main reason for the difference with literature values. With regard to the difference in experimental conditions (ionic strength, investigated pH range), comparison of this work with the literature is not easy.

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

pH	λ/nm					
	255	260	265	270	275	280
1.14	0.9216	0.8946	0.8766	0.8560	0.8277	0.7913
1.20	1.0961	1.0355	0.9894	0.9469	0.9028	0.8540
1.26	1.3074	1.2071	1.1275	1.0606	0.9979	0.9351
1.32	1.5234	1.3824	1.2694	1.1767	1.0962	1.0191
1.37	1.6560	1.4901	1.3579	1.2498	1.1577	1.0723
1.42	1.7751	1.5866	1.4333	1.3121	1.2106	1.1170
1.44	1.8235	1.6221	1.4627	1.3361	1.2305	1.1344
1.47	1.8629	1.6563	1.4888	1.3575	1.2479	1.1497
1.50	1.9163	1.7012	1.5269	1.3896	1.2779	1.1769
1.53	1.9425	1.7202	1.5418	1.4011	1.2867	1.1847
1.56	1.9598	1.7316	1.5494	1.4073	1.2901	1.1867
1.59	1.9685	1.7370	1.5526	1.4070	1.2899	1.1858
1.63	1.9691	1.7373	1.5496	1.4037	1.2865	1.1827
1.67	1.9664	1.7318	1.5445	1.3972	1.2799	1.1760
1.70	1.9570	1.7234	1.5346	1.3877	1.2707	1.1675
1.75	1.9479	1.7121	1.5236	1.3766	1.2598	1.1590
1.79	1.9312	1.6976	1.5098	1.3638	1.2485	1.1476
1.84	1.9148	1.6816	1.4937	1.3489	1.2343	1.1348
1.87	1.9039	1.6715	1.4849	1.3411	1.2279	1.1283
1.90	1.8952	1.6635	1.4774	1.3341	1.2210	1.1228
1.93	1.8859	1.6546	1.4690	1.3266	1.2136	1.1164
1.96	1.8757	1.6452	1.4603	1.3185	1.2062	1.1089
1.99	1.8668	1.6368	1.4529	1.3105	1.1992	1.1028
2.03	1.8553	1.6267	1.4431	1.3023	1.1915	1.0957
2.07	1.8436	1.6154	1.4338	1.2943	1.1842	1.0900
2.11	1.8345	1.6082	1.4261	1.2860	1.1772	1.0832
2.15	1.8238	1.5985	1.4170	1.2780	1.1689	1.0759
2.20	1.8130	1.5884	1.4083	1.2697	1.1622	1.0695
2.25	1.8014	1.5783	1.3995	1.2621	1.1555	1.0632
2.31	1.7908	1.5696	1.3901	1.2540	1.1475	1.0555
2.38	1.7802	1.5595	1.3812	1.2464	1.1406	1.0501
2.46	1.7691	1.5493	1.3725	1.2376	1.1329	1.0433

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

pH	λ/nm					
	255	260	265	270	275	280
1.01	0.9208	0.8947	0.8760	0.8554	0.8278	0.7924
1.10	1.2969	1.1998	1.1230	1.0579	0.9979	0.9361
1.17	1.5351	1.3938	1.2807	1.1891	1.1082	1.0314
1.21	1.6806	1.5115	1.3762	1.2680	1.1753	1.0889
1.26	1.8081	1.6155	1.4600	1.3368	1.2337	1.1389
1.31	1.9085	1.6959	1.5242	1.3886	1.2778	1.1776
1.34	1.9420	1.7219	1.5439	1.4030	1.2900	1.1871
1.37	1.9690	1.7424	1.5598	1.4160	1.2996	1.1956
1.40	1.9880	1.7560	1.5695	1.4238	1.3054	1.2002
1.43	1.9972	1.7629	1.5726	1.4251	1.3062	1.2004
1.46	1.9997	1.7632	1.5714	1.4217	1.3020	1.1967
1.50	1.9966	1.7581	1.5660	1.4158	1.2963	1.1914
1.53	1.9900	1.7506	1.5577	1.4075	1.2888	1.1845
1.57	1.9761	1.7376	1.5454	1.3958	1.2774	1.1734
1.61	1.9591	1.7220	1.5294	1.3813	1.2634	1.1607
1.63	1.9609	1.7226	1.5307	1.3834	1.2668	1.1638
1.65	1.9457	1.7092	1.5179	1.3703	1.2542	1.1528
1.68	1.9324	1.6970	1.5052	1.3597	1.2435	1.1421
1.70	1.9246	1.6889	1.4996	1.3537	1.2384	1.1373
1.72	1.9155	1.6812	1.4916	1.3463	1.2320	1.1318
1.75	1.9063	1.6731	1.4842	1.3396	1.2251	1.1265
1.78	1.8951	1.6628	1.4748	1.3309	1.2175	1.1186
1.81	1.8851	1.6637	1.4662	1.3233	1.2109	1.1130
1.84	1.8966	1.6653	1.4783	1.3356	1.2222	1.1250
1.86	1.8874	1.6562	1.4706	1.3276	1.2150	1.1186
1.90	1.8757	1.6459	1.4609	1.3186	1.2073	1.1112
1.94	1.8638	1.6353	1.4507	1.3096	1.1988	1.1033
1.98	1.8495	1.6217	1.4387	1.2983	1.1884	1.0932
2.01	1.8366	1.6118	1.4286	1.2895	1.1802	1.0857
2.05	1.7903	1.5700	1.3922	1.2558	1.1493	1.0581
2.12	1.7775	1.5576	1.3805	1.2452	1.1404	1.0493
2.22	1.7657	1.5472	1.3706	1.2360	1.1314	1.0419
2.36	1.7550	1.5373	1.3622	1.2286	1.1251	1.0357

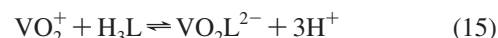
Careful examination of the literature data yields disputed results with various complex stoichiometries reported.^{8,11}

Zare⁴ studied the NTA complex with VO_2^+ assuming that there is only a 1:1 stoichiometry (VO_2L^{2-}) on the basis of the Sillen

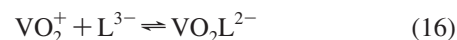
Table 4. Experimental Values of Absorbance at Different pH and Wavelengths at 25 °C, $I = 0.5 \text{ mol} \cdot \text{dm}^{-3}$

pH	λ/nm					
	255	260	265	270	275	280
1.04	0.9216	0.8953	0.8773	0.8563	0.8272	0.7914
1.07	1.1507	1.0815	1.0278	0.9799	0.9312	0.8787
1.12	1.4013	1.2860	1.1939	1.1167	1.0474	0.9789
1.16	1.5659	1.4196	1.3029	1.2067	1.1231	1.0440
1.20	1.7165	1.5424	1.4014	1.2880	1.1922	1.1027
1.24	1.8439	1.6456	1.4842	1.3557	1.2488	1.1519
1.26	1.8941	1.6857	1.5163	1.3822	1.2701	1.1708
1.29	1.9367	1.7186	1.5425	1.4031	1.2880	1.1851
1.32	1.9678	1.7444	1.5617	1.4184	1.3003	1.1957
1.34	1.9916	1.7618	1.5750	1.4271	1.3078	1.2018
1.37	2.0048	1.7712	1.5804	1.4311	1.3100	1.2033
1.40	2.0099	1.7717	1.5802	1.4291	1.3077	1.2004
1.43	2.0076	1.7688	1.5751	1.4241	1.3017	1.1951
1.46	1.9998	1.7599	1.5661	1.4145	1.2926	1.1870
1.50	1.9861	1.7472	1.5533	1.4026	1.2818	1.1771
1.54	1.9708	1.7323	1.5395	1.3899	1.2695	1.1652
1.58	1.9497	1.7123	1.5217	1.3731	1.2550	1.1515
1.62	1.9305	1.6949	1.5052	1.3567	1.2399	1.1378
1.67	1.9088	1.6747	1.4860	1.3403	1.2244	1.1239
1.70	1.8963	1.6651	1.4775	1.3320	1.2164	1.1167
1.73	1.8867	1.6545	1.4681	1.3235	1.2086	1.1099
1.76	1.8746	1.6443	1.4580	1.3151	1.2018	1.1036
1.79	1.8633	1.6354	1.4506	1.3071	1.1937	1.0958
1.82	1.8531	1.6245	1.4407	1.2986	1.1861	1.0889
1.86	1.8414	1.6143	1.4312	1.2898	1.1781	1.0814
1.90	1.8293	1.6040	1.4233	1.2826	1.1703	1.0744
1.94	1.8192	1.5941	1.4129	1.2735	1.1632	1.0681
1.98	1.8072	1.5849	1.4047	1.2665	1.1572	1.0627
2.03	1.7970	1.5743	1.3946	1.2566	1.1477	1.0542
2.09	1.7844	1.5640	1.3859	1.2487	1.1406	1.0477
2.15	1.7743	1.5537	1.3766	1.2404	1.1335	1.0405
2.21	1.7629	1.5445	1.3680	1.2324	1.1252	1.0339
2.29	1.7591	1.5405	1.3642	1.2289	1.1225	1.0311
2.39	1.7485	1.5317	1.3570	1.2211	1.1157	1.0250

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. In our pH range of interest (1.00 to 2.50), protonated species have been assumed which are in agreement with dissociation constant values of NTA,⁶ but in the previous works,^{4,10} no protonated species were used in the fitting methods. According to Table 1, we are sure that at least at $\text{pH} < 1.55$ for $I = 1.0$ NTA exists as H_3L , and as we go to lower ionic strengths, $\text{pH} = 1.55$ will be shifted to higher pH values; so, it is very reasonable that protonated complexes of NTA exist in our pH region of interest. Therefore, we assumed two species, $\text{VO}_2\text{H}_2\text{L}$ and VO_2HL^- , simultaneously. If we assume only one species (VO_2L^{2-}), then the values of stability constants will change. So, the VO_2L^{2-} complex was also studied as one of our models, and the results are gathered in Table 8 which are in closer agreement with previous results in the literature;^{4,10} however, there is no definite ionic strength dependence pattern of stability constants for the VO_2L^{2-} complex. Of course, we have calculated stability constants (Table 8) for VO_2L^{2-} species on the basis of the following reaction and reactions 10 to 12



but Zare⁴ only used the following reaction for the formation of VO_2L^{2-} species



We also used reaction 16 as another model for stability constant calculation without any use of reactions (10 to 12); however, a good fit was not obtained, and the error functions were not minimized. Although the basis of the LETAGROP-SPEFO

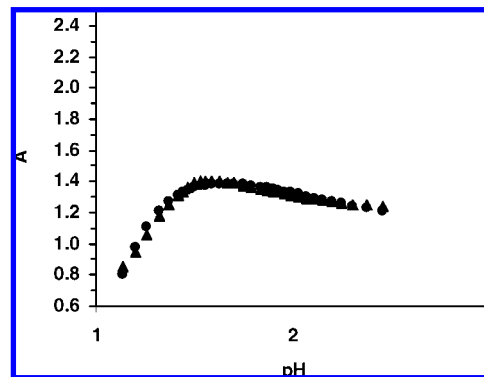
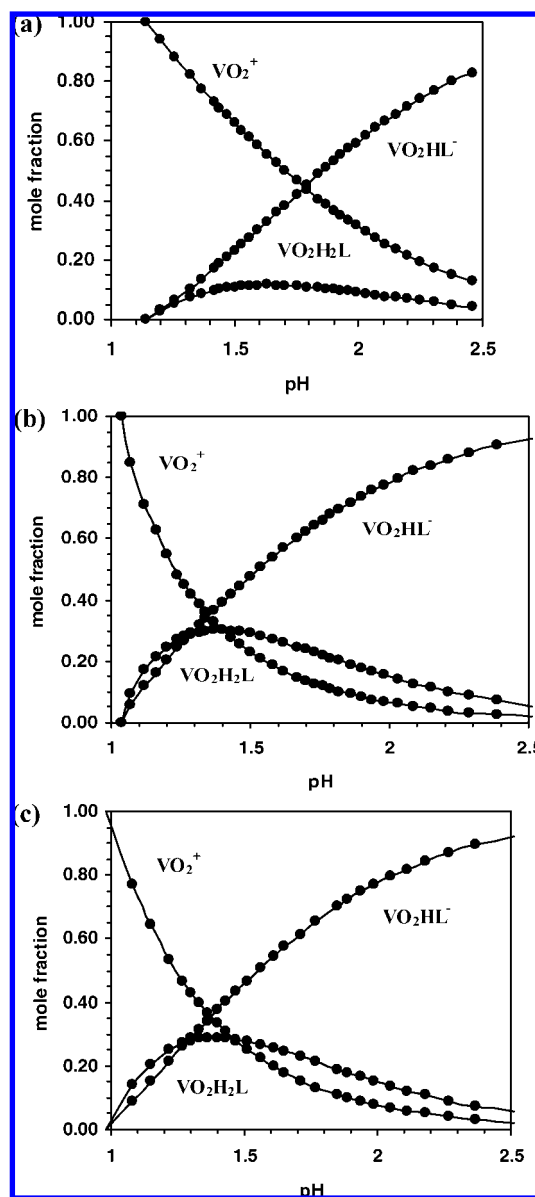
Table 5. Experimental Values of Absorbance at Different pH and Wavelengths at 25 °C, $I = 0.7 \text{ mol} \cdot \text{dm}^{-3}$

pH	λ/nm					
	255	260	265	270	275	280
1.02	0.9174	0.8911	0.8734	0.8528	0.8255	0.7899
1.09	1.2858	1.1908	1.1148	1.0504	0.9905	0.9290
1.13	1.4893	1.3554	1.2483	1.1598	1.0826	1.0074
1.16	1.6078	1.4513	1.3251	1.2222	1.1344	1.0519
1.20	1.7083	1.5315	1.3882	1.2743	1.1782	1.0884
1.21	1.7498	1.5651	1.4158	1.2958	1.1957	1.1027
1.23	1.7847	1.5936	1.4377	1.3136	1.2103	1.1151
1.25	1.8169	1.6183	1.4564	1.3283	1.2223	1.1251
1.27	1.8391	1.6361	1.4706	1.3387	1.2298	1.1309
1.29	1.8586	1.6496	1.4802	1.3458	1.2355	1.1354
1.30	1.8705	1.6583	1.4861	1.3493	1.2373	1.1365
1.32	1.8783	1.6639	1.4877	1.3509	1.2380	1.1369
1.33	1.8823	1.6643	1.4881	1.3488	1.2354	1.1342
1.35	1.8822	1.6606	1.4840	1.3439	1.2307	1.1283
1.37	1.8772	1.6560	1.4776	1.3376	1.2238	1.1219
1.39	1.8693	1.6481	1.4704	1.3298	1.2158	1.1157
1.40	1.8598	1.6409	1.4615	1.3202	1.2076	1.1070
1.42	1.8468	1.6276	1.4494	1.3105	1.1985	1.0984
1.46	1.8245	1.6057	1.4297	1.2918	1.1815	1.0839
1.50	1.7783	1.5738	1.4001	1.2656	1.1565	1.0601
1.54	1.7503	1.5388	1.3674	1.2347	1.1274	1.0335
1.58	1.7169	1.5092	1.3405	1.2105	1.1059	1.0142
1.63	1.6753	1.4714	1.3062	1.1787	1.0771	0.9871
1.68	1.6363	1.4362	1.2747	1.1492	1.0495	0.9630
1.70	1.6184	1.4198	1.2599	1.1360	1.0382	0.9521
1.73	1.5998	1.4040	1.2460	1.1237	1.0266	0.9416
1.76	1.5813	1.3872	1.2306	1.1090	1.0130	0.9296
1.79	1.5645	1.3730	1.2175	1.0984	1.0028	0.9207
1.82	1.5624	1.3713	1.2178	1.0997	1.0067	0.9255
1.87	1.5338	1.3458	1.1945	1.0767	0.9843	0.9035
1.89	1.5166	1.3313	1.1804	1.0631	0.9722	0.8919
1.97	1.4826	1.2994	1.1520	1.0394	0.9496	0.8719
2.05	1.4503	1.2713	1.1266	1.0155	0.9283	0.8530
2.16	1.4184	1.2434	1.1014	0.9933	0.9076	0.8338
2.28	1.3902	1.2175	1.0785	0.9715	0.8877	0.8161
2.44	1.3548	1.1853	1.0492	0.9459	0.8642	0.7945

Table 6. Experimental Values of Absorbance at Different pH and Wavelengths at 25 °C, $I = 1.0 \text{ mol} \cdot \text{dm}^{-3}$

pH	λ/nm					
	255	260	265	270	275	280
0.98	0.9193	0.8931	0.8759	0.8552	0.8272	0.7915
1.08	1.3394	1.2364	1.1545	1.0849	1.0210	0.9558
1.15	1.6083	1.4568	1.3346	1.2345	1.1471	1.0641
1.22	1.8430	1.6481	1.4898	1.3623	1.2557	1.1578
1.27	1.9595	1.7424	1.5649	1.4253	1.3081	1.2016
1.30	2.0033	1.7771	1.5937	1.4470	1.3264	1.2178
1.33	2.0377	1.8045	1.6137	1.4623	1.3389	1.2288
1.36	2.0608	1.8211	1.6262	1.4729	1.3470	1.2349
1.40	2.0718	1.8281	1.6315	1.4749	1.3481	1.2360
1.43	2.0728	1.8287	1.6288	1.4716	1.3441	1.2321
1.47	2.0686	1.8222	1.6222	1.4644	1.3374	1.2251
1.51	2.0573	1.8109	1.6100	1.4531	1.3264	1.2156
1.56	2.0391	1.7948	1.5951	1.4381	1.3132	1.2034
1.61	2.0206	1.7769	1.5774	1.4234	1.2990	1.1897
1.65	2.0027	1.7601	1.5638	1.4100	1.2859	1.1785
1.71	1.9795	1.7396	1.5446	1.3919	1.2700	1.1640
1.77	1.9552	1.7176	1.5243	1.3732	1.2524	1.1486
1.85	1.9326	1.6952	1.5053	1.3565	1.2370	1.1343
1.89	1.9202	1.6854	1.4956	1.3475	1.2292	1.1267
1.94	1.9079	1.6744	1.4859	1.3375	1.2205	1.1189
1.99	1.8977	1.6642	1.4758	1.3300	1.2137	1.1117
2.05	1.8852	1.6533	1.4664	1.3211	1.2053	1.1052
2.11	1.8737	1.6439	1.4569	1.3132	1.1981	1.0981
2.18	1.8619	1.6335	1.4486	1.3042	1.1901	1.0908
2.27	1.8513	1.6230	1.4394	1.2955	1.1827	1.0844
2.37	1.8388	1.6121	1.4288	1.2866	1.1742	1.0769

program is similar to the Excel program, there are some points that require attention. At first, we used the Mathematica program to obtain some relationships between formation constants and

**Figure 1.** A_{exp} and A_{cal} values at 25 °C, $I = 0.1 \text{ mol} \cdot \text{dm}^{-3}$ and 270 nm. ●, A_{cal} ; ▲, A_{exp} .**Figure 2.** Distribution of species at 25 °C, 270 nm. (a) $I = 0.1 \text{ mol} \cdot \text{dm}^{-3}$. (b) $I = 0.5 \text{ mol} \cdot \text{dm}^{-3}$. (c) $I = 1.0 \text{ mol} \cdot \text{dm}^{-3}$.

species concentration. We used the Mathematica output in the Excel program to obtain A_{cal} and finally the error function (eq 4). 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.

Table 7. Average Experimental Values of $\log \beta_{121}$ and $\log \beta_{111}$ at pH = 1.00 to 2.50 and Different Ionic Strengths for the Complexation of Dioxovanadium(V) with NTA, $t = 25^\circ\text{C}$

$I/\text{mol}\cdot\text{dm}^{-3}$	$\log \beta_{121}$	$\log \beta_{111}$
0.1	16.30 ± 0.15	14.99 ± 0.20
0.3	16.47 ± 0.45	15.16 ± 0.01
0.5	16.35 ± 0.20	15.07 ± 0.10
0.7	15.77 ± 0.05	14.52 ± 0.04
1.0	15.44 ± 0.01	14.16 ± 0.01

Table 8. Average Experimental Values of $\log \beta'_{101}$ at pH = 1.00 to 2.50 and Different Ionic Strengths for the Complexation of Dioxovanadium(V) with NTA, $t = 25^\circ\text{C}$

$I/\text{mol}\cdot\text{dm}^{-3}$	$\log \beta'_{101}$
0.1	14.41 ± 0.15
0.3	14.07 ± 0.07
0.5	14.32 ± 0.12
0.7	13.51 ± 0.10
1.0	14.00 ± 0.50

Table 9. 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	6
K_2	0.803	-0.730	4	6
K_1	0.210	-0.775	2	6
$\text{VO}_2\text{H}_2\text{L}$	6.673	-6.034	12	this work
VO_2HL^-	6.183	-5.728	10	this work

Table 10. Calculated Values of $\log \beta_{121}$ and $\log \beta_{111}$ at Different Ionic Strengths for the Complexation of Dioxovanadium(V) with NTA, $t = 25^\circ\text{C}$

$I/\text{mol}\cdot\text{dm}^{-3}$	$\log \beta_{121}$	$\log \beta_{111}$
0.1	16.30	14.99
0.3	16.32	15.03
0.5	16.25	14.97
0.7	16.02	14.74
1.0	15.35	14.08

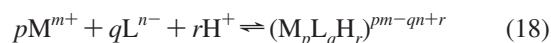
It is important to note that the computer programs are solely based on mathematics and numerical analysis, but we should also take into account chemical facts. According to the dissociation constants of NTA, it is reasonable to assume the protonated complex species instead of the VO_2L^{2-} species. For example, at $I = 0.1$, the first proton of NTA will be released at pH = 1.98 and the second proton at pH = 2.92. Of course, according to Table 1, these protons are released at lower pH values as we go to higher ionic strengths. These protons will be released more easily in the presence of a metal. So, although the error function of calculation for only one species (VO_2L^{2-}) is less than the corresponding function for $\text{VO}_2\text{H}_2\text{L}$ and VO_2HL^- species, protonated complex species are preferred from the chemical viewpoint. Correia¹² also proved and calculated stability constants for protonated complex species of VO_2^+ . Lagrange¹³ 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 ML and ML_2 species according to the best fit for dioxovanadium(V) complexes with glycine. Zare⁴ did not use any chemical methods like NMR for proving the existence of the VO_2L^{2-} species and calculated the stability constants solely on the basis of experimental UV absorbance data as a function of pH (pH < 2) at ionic strength of $3.0 \text{ mol}\cdot\text{dm}^{-3}$ sodium perchlorate and using the LETAGROP-SPEFO program. The other report in the literature¹⁰ is also only on the basis of experimental UV absorbance data as a function of pH (pH < 3) at ionic strength of $1.0 \text{ mol}\cdot\text{dm}^{-3}$ sodium perchlorate. Yamada¹⁰ also only assumed VO_2L^{2-} species on the basis of mathematical methods.

Therefore, it seems that we can conclude our results are not in contrast to the literature values, and the main differences are due to different ionic strengths, kinds of species, and methods of calculation.

Ionic Strength Dependence of Dissociation and Stability Constants According to the Extended Debye–Hückel and SIT Models. The dependence of the dissociation and stability constants on the ionic strength can be described according to previous work^{14–21}

$$\log \beta(I) = \log \beta(I_1) - AZ^* \left(\frac{I^{0.5}}{1 + BI^{0.5}} - \frac{I_1^{0.5}}{1 + BI_1^{0.5}} \right) + C(I - I_1) + D(I^{1.5} - I_1^{1.5}) \quad (17)$$

where I and I_1 are the actual and reference ionic strengths, respectively, and according to reaction 18



$Z^* = pm^2 + qn^2 + r - (pm - qn + r)^2$, where m and n are the charges on the metal ion and the ligand, respectively. Considering, $A = 0.5115$ and $B = 1.489$ ^{19–21} at 25°C , eq 17 can be simplified

$$\log \beta(I) = \log \beta(I_1) - Z^* \left(\frac{I^{0.5}}{1.955 + 2.91I^{0.5}} - \frac{I_1^{0.5}}{1.955 + 2.91I_1^{0.5}} \right) + C(I - I_1) + D(I^{1.5} - I_1^{1.5}) \quad (19)$$

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 the Excel 2000 program

$$U = \sum_i (a_i - b_i)^2 \quad (i = 1, 2, 3, \dots) \quad (20)$$

where a is a quasiexperimental quantity and b_i is a calculated one. The values of C and D are shown in Table 9. 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 19. Then, the values of the calculated stability constants have been determined according to the extended Debye–Hückel theory, and their values are gathered in Table 10. The values of C and D for the dissociation constants of NTA have been taken from the literature.⁶ We have used $I_1 = 0.1$ as the reference ionic strength to obtain better consistency between experimental and calculated stability constants. Therefore, by using eq 19 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 the extended Debye–Hückel model. The results on the basis of the extended Debye–Hückel model are shown in Figure 3.^{14–21} It should be mentioned that the current pattern for ionic strength dependence of the $\text{V(V)} + \text{NTA}$ system is in agreement with our previous published paper about tungsten(VI) complex with NTA.⁶

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. In investigations of systems where complex formation takes place, a method of constant ionic

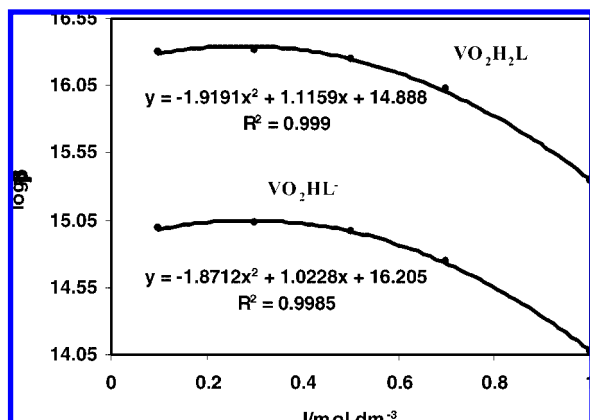


Figure 3. Plot of $\log \beta_{121}$ and $\log \beta_{111}$ versus ionic strength on the basis of the extended Debye–Hückel model.

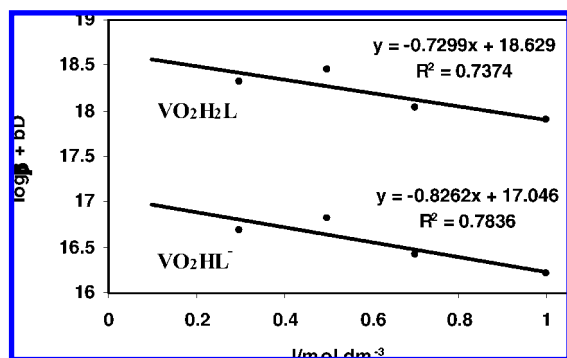


Figure 4. Plot of $\log \beta + bD$ ($b = 12$ and 10 for $\text{VO}_2\text{H}_2\text{L}$ and VO_2HL^- , respectively) versus ionic strength on the basis of the SIT model.

medium is usually adopted. There are difficulties in determination of activity coefficients of reaction species in a constant ionic medium. Usually only a value of equilibrium constant in a certain medium can be determined, and the number of equilibrium constants obtained is generally small. Second, the accuracy of the equilibrium constants is relatively low in comparison with that of mean activity coefficients and osmotic coefficients. Accordingly, owing to these two facts, it is sensible to use an activity model with fewer parameters when dealing with experimental equilibrium constants, as it is often impractical to determine more than one or two empirical parameters from a small number of such constants with limited accuracy. Grenthe²² concluded that the less-parametrized SIT model gives quite reasonable estimations of equilibrium constants in different media at various ionic strengths, provided that the necessary interaction coefficients are known. There are many papers about SIT.^{23–34} The SIT model, because of its advantages in mathematical simplicity and its less-parametrized nature, may find applications when the experimental data are less extensive, or the accuracy provided by the SIT model is deemed to be satisfactory, or in systems where complex formation occurs. This is especially true in cases in treatment of equilibrium constants. Consequently, the SIT model has the potential to become a useful method to estimate medium effects on equilibrium constants in concentrated solution in high-temperature aqueous geochemistry and chemistry.

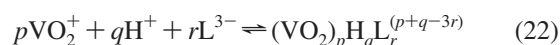
The two basic assumptions in the specific ion interaction theory (SIT) are as follows:³⁵

(a) The activity coefficient γ_j of an ion j of charge z_j in the solution of the ionic strength I may be described by^{36,37}

$$\log \gamma_j = -\frac{z_j^2 0.509 \sqrt{I}}{1 + 1.5 \sqrt{I}} + \sum_k \varepsilon(j, k, I) m_k \quad (21)$$

The summation in eq 21 extends over all ions k present in solution. Their molality is denoted m_k . The concentrations of the ions of the ionic medium are often much larger than those of the reacting species. Hence, the ionic medium ions will make the main contribution to the value of $\log \gamma_j$ for the reacting ions. This fact often makes it possible to simplify the summation in eq 21 so that only ion interaction coefficients between the participating ionic species and the ionic medium ions are included as shown in eqs 23 to 26.

(b) The ion interaction coefficients $\varepsilon(j, k, I)$ are zero for ions of the same charge sign and for uncharged species.³⁵ 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)–NTA complexes



The stability constant of $(\text{VO}_2)_p\text{H}_q\text{L}_r^{(p+q-3r)}$, $\beta_{p,q,r}$, determined in an ionic medium (1:1 salt NaClO_4) of the ionic strength I , is related to the corresponding value at zero ionic strength, $\beta_{p,q,r}^0$, by eq 23

$$\log \beta_{p,q,r} - \Delta z^2 D = \log \beta_{p,q,r}^0 - \Delta \varepsilon I \quad (23)$$

where

$$\Delta z^2 = (p + q - 3r)^2 - (p + q + 9r) \quad (24)$$

$$D = \frac{0.509 \sqrt{I}}{1 + 1.5 \sqrt{I}} \quad (25)$$

$$\Delta \varepsilon = \varepsilon((\text{VO}_2)_p\text{H}_q\text{L}_r^{(p+q-3r)}, \text{Na}^+ \text{ or } \text{ClO}_4^-) -$$

$$\varepsilon(\text{VO}_2^+, \text{ClO}_4^-) - q\varepsilon(\text{H}^+, \text{ClO}_4^-) - \varepsilon(\text{L}^{3-}, \text{Na}^+) \quad (26)$$

Equilibria involving $\text{H}_2\text{O}(l)$ as a reactant or product require a correction for the activity of water.³⁵ 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 1.³⁵ According to eq 23 and $\Delta z^2 = -12, -10$, the following formulas were deduced for the extrapolation to zero ionic strength for the $\text{VO}_2\text{H}_2\text{L}$ and VO_2HL^- complexes, respectively^{35,38}

$$\log \beta_{121} + 12D = \log \beta_{121}^0 - \Delta \varepsilon I \quad (27)$$

$$\log \beta_{111} + 10D = \log \beta_{111}^0 - \Delta \varepsilon I \quad (28)$$

The linear regressions were done (Figure 4) on the basis of eqs 27 and 28, and the values of $\Delta \varepsilon = 0.7299$ and 0.8262 have been obtained for $\text{VO}_2\text{H}_2\text{L}$ and VO_2HL^- , respectively. $\varepsilon(\text{H}^+, \text{ClO}_4^-) = 0.14$,³⁵ thus, the following equations are valid¹⁷

$$\varepsilon(\text{VO}_2^+, \text{ClO}_4^-) + \varepsilon(\text{L}^{3-}, \text{Na}^+) = -1.0099 \quad (29)$$

$$\varepsilon(\text{VO}_2\text{HL}^-, \text{Na}^+) - \varepsilon(\text{VO}_2^+, \text{ClO}_4^-) - \varepsilon(\text{L}^{3-}, \text{Na}^+) = 0.9662 \quad (30)$$

According to Figure 4, the values of $\log \beta_{121}$ and $\log \beta_{111}$ at $I = 0$ have been obtained: 18.629 and 17.046, respectively. Comparison of Figures 3 and 4 shows that the Debye–Hückel model applies better for NTA complex formation with

dioxovanadium(V). According to the difference between interaction coefficients ($\Delta\epsilon$ values), it might be concluded that $\text{VO}_2\text{H}_2\text{L}$ interaction with ionic medium ions is weaker than summation of interaction between VO_2^+ , NTA, and H^+ with ionic medium ions, and it is vice versa for VO_2HL^- interaction.

Conclusions

The dependence of constants on ionic strength is not very significant, although there are some significant changes such as for example (Table 7): $\log \beta_{121} (I = 0.5) - \log \beta_{121} (I = 0.7) = 0.58$ or $\log \beta_{111} (I = 0.5) - \log \beta_{111} (I = 0.7) = 0.55$. It seems that we can explain the insignificant differences according to the parameters. The infinite sum of the most divergent terms generates the Debye–Hückel screened coulomb potential, and of course, also the limiting law forms for the thermodynamic properties of the electrolyte solution with the characteristic $m^{1/2}$ concentration dependence. Electrostatic Coulombic interactions are shown by the $AI^{1/2}$ term in eq 17. These interactions are screened by the ionic atmosphere. Disturbances in ion–solvent interactions are included in the BI term. At high ionic strengths, ionic charges will be screened by the ionic atmosphere, and Debye length will decrease. Therefore, dipole–dipole or multipole–multipole interactions between the ions are dominant and affect the values of C and D in eq 17 (or 19), but at low ionic strengths, $AI^{1/2}$ and BI terms are more important. The obtained values of C and D in Table 9 are small or in some cases have approximately equal values with opposite signs. On the other hand, the stability or dissociation constants in eq 17 (or 19) vary as a function of C and D , so it seems that we can conclude for the desired range of ionic strengths in this research the values of C and D do not have important contributions in eq 17 (or 19). Maybe this is the main reason that dependence of constants on ionic strength is not very significant. It can be estimated that the contribution of C and D will be more important at ionic strengths higher than $1 \text{ mol} \cdot \text{dm}^{-3} \text{ NaClO}_4$. Of course, this point should be studied. On the other hand, the slopes of the SIT figures (-0.7299 and -0.8262 for $\text{VO}_2\text{H}_2\text{L}$ and VO_2HL^- , respectively) are small negative values, and it means that stability constants change as a function of ionic strength with a mild decrease. In other words, it might be concluded that changes in stability constants versus ionic strength are not very significant. According to Figure 2, $\text{VO}_2\text{H}_2\text{L}$ reaches the maximum of 12 % at $\text{pH} = 1.70$ at $I = 0.1 \text{ mol} \cdot \text{dm}^{-3}$ and 270 nm but at other ionic strengths reaches the maximum of (25 to 30) % at lower pH values, $\text{pH} < 1.53$.

Acknowledgment

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