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Thermodynamic Studies on Complexation of Glutamic Acid with Dioxovanadium(V) in Mixed Solvent Systems

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The stability constant on complexation of VO_2^+ with glutamic acid (Glu) in mixed solvent systems of methanol + water and free-energy changes have been determined spectro-photometrically with a temperature variation method in 0.2 mol dm^{-3} sodium perchlorate as ionic medium in the pH range (1.3−5), with high ligand-to-metal ratios. Linear relationships are observed when log *K* is plotted versus 1/*D*, where *K* and *D* represent stability and the dielectric constant of the system, respectively. The results are discussed in terms of the effect of solvent on protonation and complexation.

Introduction

Little is known about the complexation of pervanadyl ion in mixed solvent systems. The discovery of vanadium as a cofactor in bromoperoxidases[1] and nitrogenases[2] has increased the interest in the reactivity and complexation chemistry of vanadium(V). Vanadium(IV) and (V) are thought to be bound to the serum protein, transferrin, via an amino acid as a ligand. Oxovanadium(V) alkoxides of simple alcohols including methanol, ethanol, 2-propanol, and cyclohexanol are well-known;[3−5] also, more complex derivatives have recently been described for diol derivatives.[8] But few quantitative studies of the interaction between dioxovanadium(V) and alcohols in mixed solvent systems have been reported.[9]

The present paper describes the complexation of dioxovanadium(V) with Glu determined by a combination of potentiometric and spectrophotometric methods in mixed solvent systems of methanol + water with high ligand-to-metal ratios.

The pH range for our studies is 1.3 to 5 because (1) pervanadyl ion is represented as VO_2^+ in acidic solution[11] and (2) over a pH range from 5 to 8 the spectral change is attributable to the hydrolysis of the dioxovanadium complex.

$$VO_2Y^- + H_2O \rightleftharpoons VO_2(OH)Y^{2-} + H^+$$

At higher pH, $VO_2(OH)Y^{2-}$ dissociates to HVO_4^{2-} and VO_4^{3-}, and in aqueous solution vanadate will react with ethanol on a millisecond time scale to generate ethyle vanadate and diethylvanadate.[13]

Under these experimental conditions, hydrolysis of vanadium(V) ion was negligible. Thus, we are able to show how solvents and solvent mixtures with different dielectric constants affect formation of such complexes.

Experimental Section

Reagents. Sodium perchlorate, perchloric acid, methanol, and sodium hydroxide were supplied from E.merck; L-glutamic acid and sodium metavanadate were purchased from Aldrich Chemical and Riedel−De Haenayseelze−Hannover, respectively. Dilute perchloric acid solution was standardized against $KHCO_3$. A 50 mass % sodium hydroxide solution free from carbonate was prepared from analytical grade material, filtered through a G4 jena glass filter, and stored in a polyethylene bottle. Dilute solutions were prepared from double-distilled water, with conductivity equal to (1.3 ± 0.1) $\mu\Omega^{-1}$, and the stock solution was standardized against $HClO_4$. Vanadium(V) solutions were standardized titrimetrically against a standard iron(II) sulfate solution.[15]

Measurement. All measurements were carried out at (20, 25, 30 ± 0.1) °C. The ionic strength was maintained at 0.2 mol dm^{-3} with sodium perchlorate. An Horiba pH meter, D-14, was used for pH measurements. The hydrogen ion concentration was measured with an Ingold U03234 glass electrode and an Ingold U03236 calomel electrode. To determine hydrogen ion concentration in mixed solvent systems, it was necessary to calibrate the electrodes and pH meter for the various solvent mixtures with solutions of known hydrogen ion concentration and constant ionic strength.[10,16,17]

Spectrophotometric measurements were performed on a UV−vis shimadzu 2101 pc spectrophotometer with an Acermate 486SX/25D computer and using thermostated matched 10 mm quarts cells. The measurement cell was a flow type. A masterflex 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.

The dielectric constants of mixed solvent systems of methanol in water are measured by comparing the capacitances of a capacitor with and without the sample present (*C* and C_0), respectively, using $D = C/C_0$.[18] An Lutron-DM-

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Table 1. Absorbance, A, of Solution at Different pH Values and Wavelengths, in (x)Water + $(1 - x)$Methanol: $C_{\mathrm{VO_2^+}} = 10^{-4}$ M, $I = 0.2$ M, [Glu] = 10^{-2} M

	λ/nm =						λ/nm =				
pH	250	255	260	265	270	pH	250	255	260	265	270
					t = 25 °C						
					x = 1.000						
1.50	0.114	0.106	0.102	0.099	0.095	3.11	0.211	0.202	0.193	0.181	0.166
1.75	0.122	0.113	0.108	0.105	0.101	3.20	0.233	0.220	0.212	0.198	0.181
1.84	0.126	0.118	0.112	0.109	0.104	3.29	0.238	0.228	0.218	0.203	0.185
1.94	0.129	0.121	0.116	0.111	0.106	3.38	0.242	0.231	0.221	0.206	0.188
2.05	0.135	0.127	0.122	0.116	0.110	3.46	0.212	0.205	0.196	0.184	0.167
2.31	0.175	0.167	0.160	0.150	0.140	3.77	0.216	0.209	0.201	0.188	0.171
2.46	0.183	0.175	0.167	0.157	0.146	4.23	0.222	0.215	0.207	0.194	0.178
2.60	0.190	0.181	0.173	0.163	0.151	4.53	0.227	0.219	0.211	0.197	0.179
2.90	0.206	0.196	0.187	0.175	0.160	5.05	0.228	0.220	0.212	0.198	0.180
					x = 0.940						
1.55	0.155	0.107	0.101	0.098	0.095	3.05	0.202	0.191	0.181	0.170	0.156
1.60	0.121	0.112	0.107	0.103	0.100	3.20	0.211	0.200	0.190	0.178	0.163
1.70	0.127	0.118	0.112	0.108	0.104	3.46	0.228	0.218	0.206	0.193	0.177
1.90	0.143	0.134	0.127	0.122	0.115	3.65	0.235	0.224	0.212	0.198	0.182
2.10	0.156	0.148	0.140	0.133	0.125	3.70	0.237	0.226	0.215	0.201	0.184
2.30	0.165	0.156	0.148	0.140	0.131	3.91	0.243	0.232	0.221	0.206	0.188
2.45	0.174	0.164	0.156	0.148	0.137	4.17	0.248	0.238	0.226	0.212	0.194
2.60	0.180	0.171	0.162	0.153	0.142	4.31	0.249	0.239	0.228	0.214	0.196
2.85	0.189	0.180	0.170	0.160	0.148	4.61	0.251	0.241	0.230	0.216	0.199
					x = 0.870						
1.54	0.142	0.131	0.124	0.120	0.115	3.06	0.251	0.239	0.231	0.214	0.191
1.69	0.150	0.143	0.136	0.130	0.122	3.25	0.270	0.254	0.241	0.229	0.207
1.85	0.160	0.149	0.144	0.134	0.126	3.41	0.282	0.266	0.253	0.234	0.215
1.99	0.184	0.167	0.158	0.151	0.141	3.52	0.284	0.269	0.254	0.236	0.216
2.21	0.213	0.199	0.188	0.181	0.169	3.65	0.284	0.270	0.255	0.235	0.217
2.42	0.225	0.212	0.201	0.190	0.175	4.01	0.288	0.272	0.257	0.238	0.220
2.70	0.243	0.231	0.222	0.208	0.190	4.31	0.291	0.275	0.260	0.245	0.226
2.99	0.251	0.242	0.232	0.217	0.196	4.87	0.298	0.276	0.265	0.249	0.230
					x = 0.786						
1.60	0.178	0.164	0.157	0.149	0.140	3.00	0.287	0.272	0.257	0.238	0.218
1.70	0.190	0.178	0.169	0.160	0.151	3.25	0.293	0.262	0.277	0.243	0.220
1.82	0.210	0.196	0.187	0.177	0.164	3.40	0.304	0.271	0.287	0.251	0.228
2.00	0.224	0.212	0.201	0.190	0.176	3.50	0.310	0.275	0.293	0.255	0.232
2.20	0.239	0.226	0.216	0.202	0.187	3.64	0.317	0.281	0.299	0.260	0.236
2.40	0.240	0.241	0.229	0.214	0.197	3.80	0.324	0.287	0.305	0.265	0.241
2.60	0.262	0.248	0.235	0.220	0.202	4.02	0.314	0.279	0.296	0.258	0.236
2.83	0.276	0.261	0.248	0.231	0.211	4.48	0.324	0.290	0.306	0.270	0.248
					x = 0.687						
1.45	0.229	0.202	0.202	0.188	0.176	3.01	0.314	0.294	0.277	0.255	0.235
1.61	0.241	0.225	0.214	0.200	0.186	3.25	0.328	0.308	0.290	0.266	0.244
1.75	0.256	0.241	0.229	0.213	0.199	3.40	0.330	0.311	0.293	0.269	0.247
1.92	0.268	0.253	0.241	0.224	0.208	3.52	0.339	0.316	0.297	0.273	0.250
2.15	0.281	0.265	0.225	0.235	0.218	3.67	0.342	0.319	0.299	0.274	0.252
2.40	0.281	0.265	0.251	0.234	0.215	3.84	0.344	0.321	0.300	0.275	0.252
2.60	0.291	0.274	0.260	0.241	0.221	4.02	0.380	0.354	0.326	0.301	0.274
2.80	0.302	0.284	0.268	0.247	0.228	4.71	0.388	0.363	0.338	0.313	0.287
					t = 20 °C						
					x = 1.000						
1.50	0.113	0.104	0.100	0.099	0.095	3.06	0.175	0.116	0.159	0.151	0.142
1.58	0.116	0.104	0.102	0.099	0.097	3.25	0.190	0.181	0.175	0.165	0.154
1.75	0.126	0.114	0.111	0.107	0.103	3.50	0.206	0.198	0.191	0.181	0.167
1.95	0.129	0.118	0.115	0.109	0.105	3.80	0.216	0.207	0.202	0.191	0.178
2.19	0.134	0.124	0.119	0.115	0.110	3.95	0.219	0.211	0.206	0.193	0.179
2.44	0.141	0.131	0.126	0.119	0.113	4.30	0.220	0.212	0.207	0.196	0.180
2.69	0.150	0.138	0.132	0.125	0.119	4.56	0.222	0.216	0.209	0.198	0.182
2.80	0.150	0.138	0.133	0.125	0.119	4.81	0.222	0.216	0.210	0.199	0.184
2.92	0.151	0.140	0.134	0.126	0.120	5.14	0.220	0.216	0.210	0.198	0.185
					x = 0.786						
1.62	0.209	0.188	0.177	0.168	0.161	3.00	0.292	0.264	0.245	0.226	0.211
1.80	0.219	0.198	0.186	0.176	0.167	3.20	0.309	0.278	0.256	0.237	0.220
2.00	0.238	0.214	0.204	0.192	0.182	3.60	0.335	0.299	0.276	0.256	0.237
2.21	0.246	0.224	0.213	0.200	0.187	3.80	0.305	0.280	0.257	0.239	0.221
2.40	0.255	0.234	0.219	0.203	0.194	3.91	0.310	0.284	0.263	0.242	0.223
2.61	0.267	0.242	0.227	0.212	0.198	4.10	0.314	0.290	0.268	0.250	0.231
2.79	0.278	0.252	0.236	0.219	0.204	4.45	0.324	0.298	0.278	0.262	0.244
2.90	0.286	0.258	0.239	0.224	0.207	4.90	0.330	0.307	0.289	0.269	0.255

Table 1 (Continued)

	λ/nm =						λ/nm =				
pH	250	255	260	265	270	pH	250	255	260	265	270
						$t = 35$ °C $x = 0.940$					
1.64	0.128	0.114	0.108	0.106	0.103	3.00	0.194	0.176	0.166	0.155	0.145
1.70	0.128	0.114	0.108	0.104	0.101	3.09	0.201	0.184	0.171	0.161	0.151
1.80	0.131	0.117	0.110	0.107	0.104	3.19	0.207	0.191	0.178	0.166	0.154
1.95	0.133	0.120	0.114	0.109	0.106	3.29	0.212	0.195	0.181	0.169	0.157
2.10	0.141	0.128	0.119	0.116	0.110	3.40	0.222	0.205	0.189	0.177	0.165
2.25	0.147	0.134	0.126	0.121	0.116	3.49	0.226	0.210	0.194	0.182	0.168
2.40	0.157	0.142	0.133	0.129	0.123	3.55	0.221	0.206	0.196	0.183	0.167
2.55	0.165	0.149	0.141	0.133	0.127	3.65	0.227	0.214	0.201	0.187	0.172
2.70	0.172	0.157	0.146	0.139	0.131	3.90	0.237	0.223	0.210	0.199	0.181
2.80	0.179	0.163	0.153	0.143	0.135	4.20	0.241	0.228	0.215	0.206	0.188
2.90	0.186	0.171	0.159	0.150	0.141	4.80	0.294	0.233	0.223	0.211	0.194

9023 capacitance meter was used for dielectric constant measurements.

Results and Discussion

Prior to studing the metal−aminopolycarboxylate complex, we determined the stability constants of protonation equilibria of Glu in water and in the mixed solvent system of methanol + water. The protonation equilibria of Glu have been extensively studied in different kinds of background electrolyte in aqueous solutions, and the results were reported in the literature.[19−21] However, little is known about the protonation equilibria of Glu at different dielectric media. The following equilibria were studied:

$$H^+ + Y^{2-} \underset{}{\overset{K_{HY}}{\rightleftharpoons}} HY^- \qquad (1)$$

$$H^+ + HY^- \overset{K_{H_2Y}}{\rightleftharpoons} H_2Y \qquad (2)$$

$$H^+ + H_2Y \overset{K_{H_3Y}}{\rightleftharpoons} H_3Y^+ \qquad (3)$$

where Y^{2-} represents fully dissociated Glu anion.

The protonation constant has been determined using potentiometric techniques and calculated using a computer program which employs a nonlinear least-squares method.

In all cases in this work, the procedure was repeated at least three times and the resulting average values and corresponding standard deviations are shown in Table 3.

Complexation of Vanadium(V) with Glu

With the knowledge concerning the protonation of Glu in hand, we have studied the complexation equilibria of pervanadyl ion with glutamic acid. The method based on the relationship $A = f(\text{pH})$ was employed on account of the high stability of the complexes studied.[9,19]

Absorbance, A, and pH were measured for solutions containing V(V) (10^{-4} mol dm^{-3}) with a large excess of Glu (10^{-2} mol dm^{-3}) of pH ranging from (1.3−5) in various solvent systems. Under these experimental conditions, hydrolysis of vanadium(V) ion, VO_2^+, was negligible. Considering that the absorbance is a function of pH (Figure 1),[17] the values of the molar absorptivities of dioxovanadium(V), ϵ_0, at different wavelengths and various dielectric constants are shown in Table 2. The method of determining ϵ_0 was previously described.[9]

It seems very likely that Glu forms a 1:1 complex with dioxovanadium ion in the acidic solution where the concentration of Glu is in excess and is attributable to the equilibrium

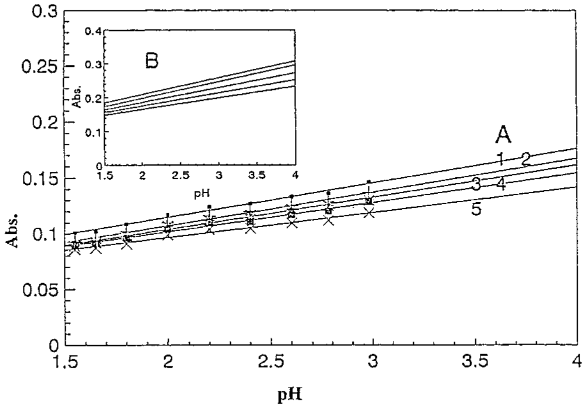

Figure 1. Absorbance versus pH for VO_2^+ at different wavelengths [(1) 250, (2) 255, (3) 260, (4) 265, (5) 270/nm] at 25 °C for (x)water + (1 − x)methanol: (A) $x = 1$; (B) $x = 0.687$.

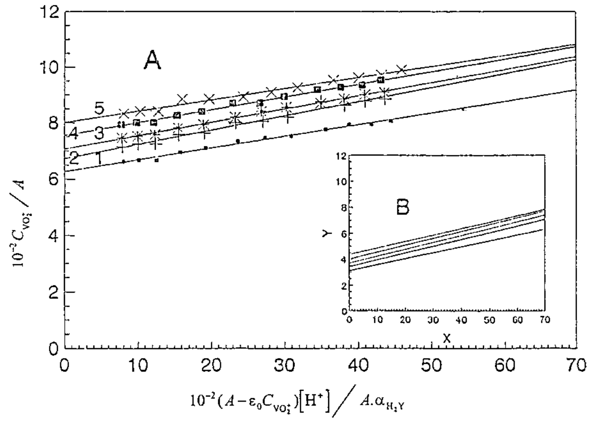

Figure 2. $C_{VO_2^+}/A$ versus $(A - \epsilon_0 C_{VO_2^+})[H^+]/A\alpha_{H_2Y}$ for (x)water + (1 − x)methanol at different wavelengths [(1) 250, (2) 255, (3) 260, (4) 265, (5) 270/nm] at 20 °C: (A) $x = 1$; (B) $x = 0.786$.

$$VO_2^+ + H_{2-m}Y^{m-} \rightleftharpoons VO_2H_{2-m-n}Y^{(m+n-1)-} + nH^+ \qquad (4)$$

It is evident from the values of the acid dissociation constants of Glu that H_2Y is the predominate species in the pH range of interest (pH < 3) for the complex formation. In this case, data were analyzed by using H_2Y ($m = 0$ in eq 4) as the reactant.

On the assumption of formation of a single complex in the pH range (1.3−3), the general equation of the complexation and the absorbance at wavelengths in the UV range is given by

$$VO_2^{\ +} + H_2Y \rightleftharpoons VO_2H_{2-n}Y^{(n-1)-} + nH^+ \tag{5}$$

$$A = \epsilon_0[V0_2^{\ +}] + \epsilon_1[VO_2H_{2-n}Y^{(n-1)-}] \tag{6}$$

where ϵ_1 is the molar absorptivity of the complex.

For the mass balance

$$VO_2^{\ +} = C_{VO_2^+} - [VO_2H_{2-n}Y^{(n-1)-}] \tag{7}$$

$$H_2Y = [C_Y - VO_2H_{2-n}Y^{(n-1)-}]\alpha_{H_2Y} \tag{8}$$

where $C_{VO_2^+}$ and $C_{Y^{-2}}$ are the total concentrations of VO_2^+ and Glu, respectively, and α_{H_2Y} is the mole fraction of H_2Y present as free ligand, given by

$$\alpha_{H_2Y} = \frac{K_{HY}[H^+]^2}{[H^+]^3 + K_{HY}[H^+]^2 + K_{HY}K_{H_2Y}[H^+] + K_{HY}K_{H_2Y}K_{H_3Y}}$$

Thus, the equilibrium constant for eq 5, K_{VO_2HY}, is given by

$$K_{VO_2HY} = \frac{[VO_2H_{2-n}Y^{(n-1)-}][H^+]^n}{[VO_2^{\ +}][H_2Y]} \tag{9}$$

Substituting eq 6 into eqs 7 and 8 and rearranging gives

$$[H_2Y] = \alpha_{H_2Y}C_Y - \frac{(A - \epsilon_0 C_{VO_2^+})}{\epsilon_1 - \epsilon_0}\alpha_{H_2Y} \tag{10}$$

$$[VO_2^{\ +}] = \frac{(\epsilon_1 C_{VO_2^+} - A)}{\epsilon_1 - \epsilon_0} \tag{11}$$

Substituting eqs 10 and 11 into eq 9 gives

$$K_{VO_2HY} = \frac{(A - \epsilon_0 C_{VO_2^+})[H^+]^n}{(\epsilon_1 C_{VO_2^+} - A)\left(C_Y - \dfrac{A - \epsilon_0 C_{VO_2^+}}{\epsilon_1 - \epsilon_0}\right)\alpha_{H_2Y}} \tag{12}$$

In the presence of a large excess of ligand, $C_{Y^{2-}} \gg C_{VO_2^+}$, the free concentration of H_2Y can be approximated by $C_Y\alpha_{H_2Y}$; therefore,

$$\frac{C_{VO_2^+}}{A} = \frac{1}{\epsilon_1} + \frac{1}{\epsilon_1\left(C_Y - \dfrac{A - \epsilon_0 C_{VO_2^+}}{\epsilon_1 - \epsilon_0}\right)K_{VO_2HY}} \frac{(A - \epsilon_0 C_{VO_2^+})[H^+]^n}{A\alpha_{H_2Y}} \tag{13}$$

The number of protons, *n*, was examined by applying eq 13, and the straight line plots of $C_{VO_2^+}/A$ against $(A - \epsilon_0 C_{VO_2^+})[H^+]^n/A\alpha_{H_2Y}$ with $n = 1$ confirmed the formation of a single complex with formula VO_2HY (see Figure 2).

The values of ϵ_1 and K_{VO_2HY} were determined from the intercept and slope of plots, respectively, and are listed in Tables 2 and 3, and the values of the absorbance, *A*, of VO_2HY at different pH values and wavelengths in methanol are shown in Table 1. Above pH = 3, a second increase in absorbance was observed; this was attributed to acid dissociation of the complex, VO_2HY, which is given by

Table 2. Values of Molar Absorptivities of Dioxovanadium(V) ($10^{-3}\epsilon_0$) and VO_2HY ($10^{-3}\epsilon_1$) and VO_2Y ($10^{-3}\epsilon_2$) in the Mixed Solvent System (*x*)Water + (1 − *x*)Methanol

x		$\lambda^a = 250$	$\lambda = 255$	$\lambda = 260$	$\lambda = 265$	$\lambda = 270$
$t = 20$ °C						
1.000	$\epsilon_0 =$	0.313	0.300	0.294	0.290	0.230
	$\epsilon_1 =$	1.488	1.483	1.406	1.352	1.249
	$\epsilon_2 =$	2.252	2.172	2.124	2.001	1.850
0.940	$\epsilon_0 =$	0.410	0.382	0.379	0.352	0.302
	$\epsilon_1 =$	2.429	2.248	2.112	1.960	1.788
	$\epsilon_2 =$	2.612	2.479	2.382	2.249	2.115
0.870	$\epsilon_0 =$	0.479	0.473	0.443	0.406	0.356
	$\epsilon_1 =$	2.841	2.630	2.457	2.252	2.052
	$\epsilon_2 =$	2.972	2.786	2.636	2.395	2.400
0.786	$\epsilon_0 =$	0.569	0.527	0.500	0.469	0.419
	$\epsilon_1 =$	3.218	2.932	2.723	2.502	2.269
	$\epsilon_2 =$	3.333	3.094	2.893	2.744	2.644
0.687	$\epsilon_0 =$	0.808	0.748	0.691	0.631	0.573
	$\epsilon_1 =$	3.630	3.313	3.052	2.756	2.501
	$\epsilon_2 =$	3.813	3.694	3.483	3.294	3.281
$t = 25$ °C						
1.000	$\epsilon_0 =$	0.305	0.300	0.287	0.262	0.225
	$\epsilon_1 =$	2.259	2.139	2.049	1.913	1.731
	$\epsilon_2 =$	2.302	2.205	2.104	1.930	1.870
0.940	$\epsilon_0 =$	0.390	0.385	0.369	0.364	0.334
	$\epsilon_1 =$	2.301	2.292	2.139	2.006	1.787
	$\epsilon_2 =$	2.571	2.456	2.368	2.199	2.064
0.870	$\epsilon_0 =$	0.431	0.389	0.383	0.375	0.358
	$\epsilon_1 =$	2.775	2.665	2.515	2.337	2.119
	$\epsilon_2 =$	2.991	2.838	2.695	2.519	2.332
0.786	$\epsilon_0 =$	0.482	0.436	0.411	0.380	0.359
	$\epsilon_1 =$	3.125	2.974	2.807	2.603	2.373
	$\epsilon_2 =$	3.301	3.136	2.957	2.745	2.533
0.687	$\epsilon_0 =$	0.539	0.493	0.464	0.394	0.368
	$\epsilon_1 =$	3.230	3.022	2.843	2.610	2.609
	$\epsilon_2 =$	3.921	3.669	2.425	3.189	2.952
$t = 35$ °C						
1.000	$\epsilon_0 =$	0.104	0.098	0.095	0.083	0.074
	$\epsilon_1 =$	1.879	1.811	1.713	1.572	1.448
	$\epsilon_2 =$	2.145	2.081	2.014	1.927	1.739
0.940	$\epsilon_0 =$	0.340	0.336	0.330	0.294	0.252
	$\epsilon_1 =$	2.003	1.889	1.752	1.618	1.503
	$\epsilon_2 =$	2.478	2.356	2.258	2.167	1.985
0.870	$\epsilon_0 =$	0.358	0.346	0.334	0.306	0.273
	$\epsilon_1 =$	2.326	2.163	1.988	1.847	1.696
	$\epsilon_2 =$	2.807	2.631	2.502	2.418	2.204
0.786	$\epsilon_0 =$	0.383	0.369	0.368	0.315	0.282
	$\epsilon_1 =$	2.623	2.346	2.168	1.957	1.791
	$\epsilon_2 =$	3.127	2.911	2.748	2.657	2.425
0.687	$\epsilon_0 =$	0.491	0.476	0.455	0.413	0.367
	$\epsilon_1 =$	3.003	2.690	2.402	2.146	1.986
	$\epsilon_2 =$	3.492	3.186	2.994	2.917	2.655

[a] All λ values are in nanometers.

$$VO_2HY \xrightleftharpoons{K^{H}_{VO_2HY}} H^+ + VO_2Y^- \tag{14}$$

The formation constant of the equilibrium reported in eq 14 was determined in the usual manner

$$\frac{C_{VO_2^+}}{A} = \frac{1}{\epsilon_2} + \frac{1}{K^{H}_{VO_2HY}\epsilon_2}\frac{(A - \epsilon_1 C_{VO_2^+})[H^+]}{A}$$

where $K^{H}_{VO_2HY}$ is the formation constant of eq 14 and ϵ_2 is the molar absorptivity of VO_2Y, which were calculated from the slope and intercept of the plot $C_{VO_2^+}/A$ versus (*A*

Table 3. Average Values of K_{VO_2HY} and $K^H_{VO_2HY}$ and log K_{VO_2Y} and the Protonation Constants for Glu with Standard Deviations (±0.01), in (x)Water + (1 − x)Methanol at Different Temperatures and I = 0.2 M

x	$1/D$	K_{VO_2HY}	$K^H_{VO_2HY}$	log K_{VO_2Y}	log K_{H_3Y}	log K_{H_2Y}	log K_{HY}
				$t = 20$ °C			
1.000	0.0124	309.74	9.8×10^{-4}	13.33	2.09	4.22	9.63
0.940	0.0133	501.20	1.5×10^{-3}	13.84	2.12	4.28	9.69
0.870	0.0143	654.65	2.3×10^{-3}	14.21	2.17	4.29	9.75
0.786	0.0154	516.42	3.9×10^{-5}	12.49	2.25	4.36	9.79
0.687	0.0171	699.84	5.8×10^{-5}	12.84	2.27	4.38	9.85
				$t = 25$ °C			
1.000	0.0126	380.19	1.56×10^{-5}	11.53	2.05	4.18	9.58
0.940	0.0136	213.80	8.74×10^{-5}	12.11	2.10	4.22	9.62
0.870	0.0147	524.81	3.41×10^{-5}	12.18	2.15	4.25	9.68
0.786	0.0157	575.44	5.21×10^{-5}	12.24	2.25	4.35	9.72
0.687	0.0175	1412.53	2.32×10^{-4}	13.69	2.26	4.37	9.80
				$t = 35$ °C			
1.000	0.0133	195.88	7.4×10^{-4}	12.79	2.01	4.15	9.48
0.940	0.0141	239.88	2.4×10^{-4}	12.47	2.03	4.16	9.53
0.870	0.0153	399.94	2.8×10^{-4}	12.83	2.03	4.20	9.59
0.786	0.0163	401.79	3.8×10^{-4}	13.07	2.06	4.25	9.63
0.687	0.0182	474.24	5.2×10^{-4}	13.43	2.11	4.32	9.71

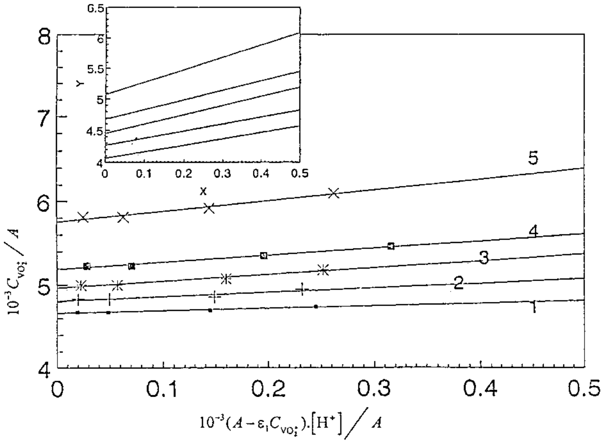

Figure 3. $C_{VO_2^+}/A$ versus $(A - \epsilon_1 C_{VO_2^+})[H^+]/A$ for (x)water + (1 − x)methanol at different wavelengths (1) 250, (2) 255, (3) 260, (4) 265, (5) 270/nm] at 35 °C: (A) $x = 1$; (B) $x = 0.940$.

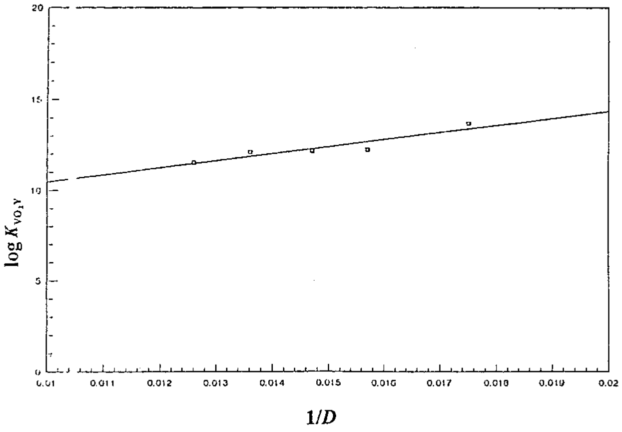

Figure 4. log K_{VO_2Y} versus $1/D$ for (x)water + (1 − x)methanol at 25 °C.

$- \epsilon_1 C_{VO_2^+}$). $[H^+]/A$ values for various mixed solvent systems (methanol + water) are shown in Table 2 (and Figure 3).

By combining these constants obtained above, the stability constant of the VO_2Y complex can be calculated from

$$K_{VO_2Y} = \frac{[VO_2Y^-]}{[VO_2^+][Y^{2-}]} = K_{VO_2HY} K^H_{VO_2HY} K_{HY} K_{H_2Y}$$

where the average values are shown in Table 3.

Table 4. Values of ΔG° and ΔH° and ΔS° of the Formation of the Pervanadyl Glu Complex in Aqueous and Mixed Solvent Systems for (x)Water + (1 − x)Methanol at Different Tempratures and I = 0.2 M

x	$\Delta G°$/J·mol^{-1}	$\Delta H°$/J·mol^{-1}	$\Delta S°$/J·mol^{-1}·K^{-1}
		$t = 20$ °C	
1.000	−74769	−3568	243.00
0.940	−77630	−3568	252.77
0.870	−79705	−3568	259.85
0.786	−70058	−3568	226.93
0.687	−72021	−3568	233.63
		$t = 25$ °C	
1.000	−65876	−3568	208.75
0.940	−69085	−3568	219.86
0.870	−69485	−3568	221.20
0.786	−69827	−3568	222.31
0.687	−78099	−3568	250.10
		$t = 35$ °C	
1.000	−75413	−3568	233.26
0.940	−73526	−3568	227.14
0.870	−75649	−3568	234.03
0.786	−77064	−3568	238.62
0.687	−79187	−3568	245.52

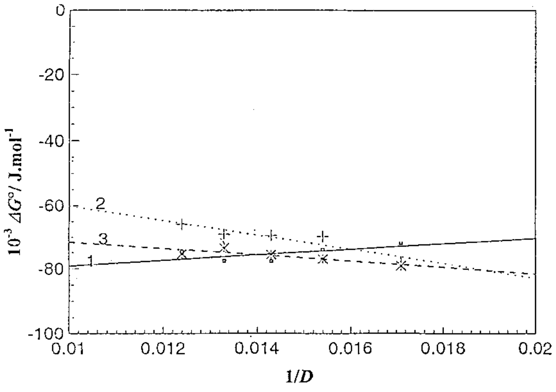

Figure 5. ΔG° versus $1/D$ for (x)water + (1 − x)methanol: (1) 20 °C; (2) 25 °C; (3) 35 °C.

Water, which has a higher dielectric constant, is substituted by methanol; therefore, the electrostatic force of attraction between two ions of opposite charge is considerably reduced. Adding an organic solvent decreases the dielectric constant of the solution, resulting in a greater attraction force and hence larger formation and protonation constants.

The $\Delta H°$ values were obtained from the slope of the plot ln k versus $1/T$. The linear relationship between log K_{VO_2Y} of Glu and $1/D$ of the solvent in the mehanol + water system is observed in Figure 4. It is noted that such a plot yields curves of different slope for each solvent system. The linear plots of the obtained values of free-energy changes as a function of 1/D show that our results agree with the above speculation (see Figure 5).

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