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Complexation of Leucine by Dioxovanadium(V) in Mixed Solvent Systems

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The stability constant on complexation of VO_2^+ with leucine in mixed solvent systems of methanol + water and dioxane + water have been determined spectrophotometrically at (25 ± 0.1) °C and $I = 0.15$ mol· dm^{-3} of sodium perchlorate as ionic medium in the pH range (1.20−10.20) 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 dielectric constants, respectively. The results are discussed in terms of the effect of solvent on protonation and complexation.

Introduction

A knowledge of the interaction between vanadium and amino acids is of possible significance of understanding of biological action of the metal. For example: (1) vanadium(IV) and (V) are thought to be bound to the serum protein, transferrin, via amino acid as a ligand, (2) the tunichromes are catechol derivetives thought to play an important role in the accumulation and storage of vanadium by marine organisms known as tunicats, (3) the interaction of vanadium with tyrosine is thought to be responsible for the insulin mimetic effects of vanadate, and (4) vanadium is known to have a function in various enzymes of plants and organisms (Butler and Carrano, 1991; Kendrick et al., 1992). Thus, interest in these systems has increased extensively over the past decade. Although some information is available concerning complex formation of some transition metals and amino acids in aqueous solution, little work has been done on complexation of dioxovanadium(V) with amino acids in nonaqueous solution (Monajjemi et al., 1995).

The work described here is a part of our systematic studies on transition metal ions and their complex formation with ligands that are present in natural and biological systems.

The present paper describes the complexation of dioxovanadium(V) with L-leucine determined by a combination of potentiometric and spectrophotometric methods in nonaqueous solvents with high ligand-to-metal ratios in the pH range (1.20−10.20), to show how solvents and solvent mixtures with different dielectric constants affect formation such a complexes.

Experimental Section

Reagents. Methanol and dioxane were obtained from E. Merck as analytical reagent grade materials and were used without further purification. Their refractive indices at 25 °C agreed closely with reported values (Bruno and Paris, 1989). Sodium perchlorate, perchloric acid, and sodium hydroxide were supplied from E. Merck; L-leucine and sodium metavanadate were obtained from Aldrich and Riedel-De Haenayseelze-Hannover, respectively, as analytical reagent grade material and were used without further purification. 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 specific conductance equal to (1.3 ± 0.1) $\mu\Omega^{-1}$ cm^{-1}, and this stock solution was standardized against $HClO_4$. Vanadium(V) solution was standardized titrimetrically against a standard iron(II) sulfate solution (Charlot, 1961).

Measurement. All measurements were carried out at (25 ± 0.1) °C. The ionic strength was maintained at 0.15 mol·dm^{-3} with sodium perchlorate. An Eyela pH meter PHM 2000 was used for pH measurements. The hydrogen ion concentration was measured with an Ingold UO 3234 glass electrode and an Ingold UO 3236 calomel electrode. To determine hydrogen ion concentration in mixed solvent systems, it was necessary to calibrate the electrodes and pH meter. Spectrophotometric measurements were performed on a UV−vis shimadzu 2100 spectrophotometer with a GDU-20 computer and using thermostated matched 10 mm quartz 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. For each experiment, two solutions of VO_2^+ + L-leucine had been prepared with the same concentration, but the ionic strength of the first was maintained with sodium perchlorate, and the second with sodium hydroxide or perchloric acid. The first solution was then titrated with the second one. The pH and absorbance were measured after addition of a few drops of titrant, and this procedure extended up to the required pH.

Calibration of the Glass Electrode. The term pH has significance only in aqueous medium (Bates, 1964). Retaining the terminology of Van Uitert (1953), all pH readings

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Table 1. Values of log *K* for *x* Methanol and Dioxane

x	1/*D*	log *K*
	MeOH + H_2O	
0.000	0.0127	9.51
0.059	0.0137	9.56
0.123	0.0149	9.61
0.194	0.0164	9.65
	Dioxane + H_2O	
0.000	0.0127	9.51
0.053	0.0167	9.62
0.128	0.0238	9.70
0.180	0.0302	9.74

taken in mixed solvents will hereafter be called *B* values. The *B* values obtained from the calibration solutions were converted to a quantity U_H, which is defined by

$$U_H = [\text{antilog}(-B)]/[H^+] \tag{1}$$

where $[H^+]$ is the known stiochiometric hydrogen ion concentration of the solutions, assuming 100% dissociation of the acid not only in aqueous solutions but also in partially aqueous solutions. U_H is then a conversion factor for obtaining the hydrogen ion concentration from the pH meter reading *B* according to eq 2

$$-\log[H^+] = B + \log U_H \tag{2}$$

and it is a function of ionic concentration and solvent composition.

Results and Discussion

Protonation Equilibrum of L-Leucine. Prior to studying the metal−amino carboxylate complex, we determined the stability constant of protonation equilibria of leucine in water and mixed solvent systems of methanol + water and dioxane + water. The following equilibrium was studied

$$H^+ + \rightleftharpoons L^- \; HL \tag{3}$$

$$K = [HL]/[H^+][L^-] \tag{4}$$

where L represents the fully dissociated amino acid anion. The protonation constant of amino acid, *K*, has been determined using potentiometric techniques and calculated using a computer program, Harvard graphics, which employs a nonlinear least-squares method; the results are shown in Table 1. 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 the text and tables.

In this work, we have used the results reported by Gentile et al. (1968) for determining the dielectric constants of the systems methanol + water and dioxane + water.

Complexation of Vanadium(V) with Leucine. The method based on the relationship $A = f(\text{pH})$ was employed (Gharib et al., 1993), on account of the high stability of the complex studied. Absorbance, *A*, and pH were measured for solutions containing V(V) (10^{-4} mol·dm^{-3}) with a large excess of ligand (10^{-2} mol·dm^{-3}) of pH ranging from (1.20 to 10.20) in various solvent systems, and the results are shown in Figure 1 and are listed in Table 2. Under this condition both polymerization and hydrolysis of dioxovanadium(V) were negligible (Gharib et al., 1995). From Figure 1 it seems very likely that a complex is formed in acidic solution (pH 3.0 to 4.2), and the general equation for the complexation is given by,

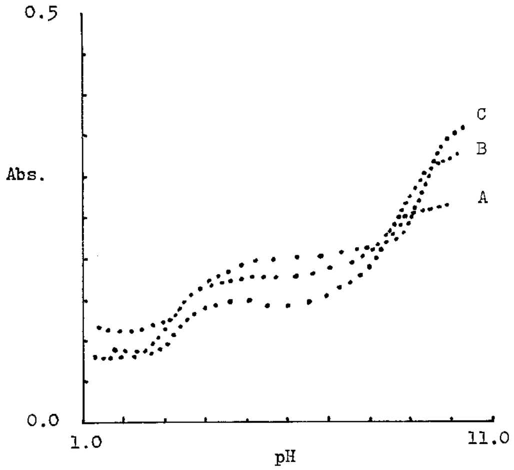

Figure 1. Absorbance versus pH for (A) $x_{\text{MeOH}} = 0.000$, (B) $x_{\text{MeOH}} = 0.194$, and (C) $x_{\text{dioxane}} = 0.128$ at (25 ± 0.1) °C, $I = 0.15$ mol·dm^{-3}, and $\lambda = 280$ nm.

$$VO_2^{\;+} + H_{1-m}L^{m-} \rightleftharpoons VO_2\,H_{1-m}\,L^{(m+n-1)-} + nH^+ \tag{5}$$

with the formation constant, $K^H{}_{VO2L}$, as

$$K^H{}_{VO2L} = \frac{[VO_2H_{1-m}L^{(m+n-1)}][H^+]^n}{[VO_2^{\;+}][H_{1-m}L^{m-1}]} \tag{6}$$

Considering the protonation constant of leucine, the predominant species in the pH range of (3.0 to 4.2) for complexation is HL. In this case, data were analyzed by using HL ($m = 0$ in eqs 5 and 6) as the reactant. It was assumed that only a single complex, VO_2L, was formed (Khorrami and Gharib, 1995). The absorbance of VO_2^+ + leucine at wavelengths in the UV range is given by

$$A = \epsilon_0[VO_2^{\;+}] + \epsilon_1[VO_2L] \tag{7}$$

where ϵ_0 and ϵ_1 are the molar absorptivities of dioxovanadium(V) and the complex, respectively. For the mass balance

$$[VO_2^{\;+}] = C_{VO2} - [VO_2L] \tag{8}$$

$$[HL] = C_{HL} - [VO_2\,L] \tag{9}$$

where C_{VO2} and C_{HL} are the total concentrations of VO_2^+ and leucin, respectively. Substituting eqs 7−9 into eq 6 and canceling like terms and rearranging gives

$$\frac{C_{VO2}}{A} = \frac{1}{\epsilon_1} + \frac{(\epsilon_1 - \epsilon_0)(A - \epsilon_0\,C_{VO2})[H^+]^n}{\epsilon_1 K^H{}_{VO2L}\,(\epsilon_1 C_{HL} - \epsilon_0 C_{HL} - A + \epsilon_0 C_{VO2})A} \tag{10}$$

The method of determining ϵ_0, was previously described (Gharib and Zare, 1992), and its values at different wavelengths and various dielectric constants are represented in Table 3. The number of protons, *n*, was examined by applying eq 10; the straight line plots of C_{VO2}/A against $(A - \epsilon_0 C_{VO2})[H]^n/A$ with $n = 1$ confirmed the formation of a single complex with the formula VO_2L. The values of ϵ_1

Table 2. Absorbance, *A*, of Solution at Different pH Values and Wavelengths, in Methanol and Dioxane

	A				*A*				*A*		
pH	$\lambda = 280$ nm	$\lambda = 275$ nm	$\lambda = 270$ nm	pH	$\lambda = 280$ nm	$\lambda = 275$ nm	$\lambda = 270$ nm	pH	$\lambda = 280$ nm	$\lambda = 275$ nm	$\lambda = 270$ nm
					x(MeOH) = 0.000						
1.96	0.091	0.098	0.100	4.36	0.145	0.165	0.187	8.23	0.219	0.258	0.291
2.15	0.089	0.096	0.099	4.65	0.147	0.167	0.189	8.45	0.228	0.265	0.303
2.41	0.088	0.095	0.098	5.17	0.147	0.168	0.190	8.76	0.247	0.290	0.327
2.77	0.081	0.084	0.092	6.57	0.150	0.171	0.194	8.92	0.251	0.297	0.334
2.96	0.083	0.087	0.094	6.93	0.154	0.175	0.199	9.04	0.255	0.304	0.340
3.31	0.094	0.102	0.113	7.16	0.158	0.180	0.204	9.19	0.257	0.306	0.344
3.43	0.108	0.115	0.129	7.42	0.166	0.189	0.215	9.35	0.263	0.312	0.351
3.53	0.119	0.132	0.147	7.63	0.173	0.200	0.227	9.50	0.262	0.311	0.352
3.67	0.129	0.145	0.164	7.86	0.185	0.213	0.241	9.65	0.264	0.314	0.354
3.87	0.139	0.156	0.177	8.08	0.203	0.237	0.267	10.00	0.267	0.318	0.359
4.11	0.144	0.162	0.184	8.19	0.209	0.246	0.276	10.16	0.265	0.315	0.356
					x(MeOH) = 0.059						
1.24	0.081	0.085	0.089	3.85	0.146	0.165	0.183	8.03	0.193	0.223	0.249
1.54	0.079	0.082	0.087	4.07	0.151	0.170	0.189	8.21	0.204	0.240	0.269
1.85	0.077	0.082	0.085	4.26	0.152	0.176	0.197	8.52	0.224	0.264	0.298
2.15	0.079	0.082	0.087	4.55	0.158	0.176	0.198	8.77	0.242	0.286	0.315
2.57	0.078	0.083	0.088	4.69	0.157	0.178	0.198	9.01	0.252	0.299	0.330
2.90	0.079	0.086	0.091	5.20	0.159	0.177	0.198	9.25	0.263	0.312	0.349
3.04	0.087	0.093	0.100	6.71	0.163	0.185	0.204	9.40	0.268	0.317	0.355
3.19	0.097	0.105	0.113	7.32	0.168	0.191	0.212	9.76	0.272	0.326	0.365
3.37	0.111	0.122	0.133	7.56	0.173	0.199	0.221	9.96	0.275	0.329	0.369
3.55	0.130	0.143	0.160	7.76	0.183	0.208	0.231	10.07	0.275	0.330	0.369
3.68	0.136	0.154	0.170								
					x(MeOH) = 0.123						
1.19	0.079	0.085	0.089	3.73	0.142	0.160	0.174	8.34	0.214	0.248	0.265
1.53	0.079	0.084	0.087	3.87	0.146	0.164	0.179	8.50	0.224	0.258	0.280
1.81	0.077	0.082	0.084	4.48	0.159	0.180	0.197	8.72	0.224	0.258	0.280
2.17	0.076	0.082	0.084	4.84	0.164	0.186	0.203	8.88	0.238	0.279	0.314
2.49	0.077	0.083	0.087	5.39	0.167	0.187	0.206	9.10	0.255	0.306	0.332
2.78	0.081	0.086	0.090	7.00	0.171	0.192	0.210	9.31	0.265	0.319	0.348
3.01	0.086	0.094	0.101	7.57	0.176	0.198	0.220	9.50	0.275	0.329	0.365
3.18	0.097	0.108	0.114	7.73	0.180	0.204	0.225	9.71	0.282	0.337	0.374
3.34	0.115	0.126	0.137	8.02	0.190	0.220	0.239	9.87	0.288	0.340	0.380
3.51	0.130	0.145	0.153	8.18	0.200	0.230	0.252	10.14	0.290	0.345	0.382
					x(dioxane) = 0.053						
1.36	0.045	0.048	0.055	4.62	0.108	0.117	0.130	8.62	0.201	0.229	0.257
1.70	0.042	0.047	0.054	4.82	0.123	0.136	0.148	8.82	0.220	0.246	0.281
2.10	0.043	0.047	0.054	5.02	0.136	0.151	0.165	8.99	0.229	0.263	0.288
2.44	0.047	0.051	0.056	5.42	0.143	0.156	0.171	9.19	0.247	0.285	0.313
2.70	0.048	0.054	0.059	6.43	0.148	0.161	0.172	9.40	0.260	0.300	0.333
3.40	0.054	0.054	0.058	7.11	0.148	0.162	0.172	9.60	0.273	0.316	0.349
3.71	0.062	0.062	0.068	7.53	0.148	0.167	0.178	9.84	0.283	0.328	0.365
3.89	0.066	0.067	0.071	7.75	0.150	0.172	0.183	9.98	0.289	0.334	0.372
4.11	0.072	0.073	0.078	7.97	0.156	0.181	0.192	9.98	0.289	0.334	0.372
4.11	0.072	0.073	0.078	7.97	0.156	0.181	0.192	10.21	0.294	0.341	0.380
4.29	0.085	0.086	0.095	8.21	0.165	0.192	0.210	10.40	0.299	0.347	0.388
4.47	0.094	0.102	0.113	8.39	0.182	0.206	0.222	10.62	0.303	0.353	0.395
					x(dioxane) = 0.180						
1.41	0.230	0.234	0.239	5.40	0.394	0.424	0.427	8.52	0.467	0.480	0.482
2.02	0.225	0.229	0.232	5.59	0.398	0.425	0.435	8.72	0.468	0.482	0.485
2.62	0.217	0.219	0.222	6.01	0.408	0.432	0.437	9.13	0.484	0.493	0.496
2.87	0.223	0.225	0.227	6.24	0.418	0.437	0.445	9.31	0.505	0.514	0.520
3.17	0.251	0.255	0.258	6.45	0.424	0.441	0.449	9.49	0.523	0.542	0.550
3.80	0.310	0.318	0.321	6.66	0.432	0.443	0.453	9.70	0.554	0.574	0.595
4.18	0-.347	0.356	0.356	7.20	0.442	0.458	0.462	9.91	0.574	0.598	0.614
4.40	0.362	0.373	0.375	7.46	0.451	0.463	0.467	10.12	0.588	0.617	0.632
4.65	0.372	0.403	0.406	7.75	0.460	0.472	0.476	10.30	0.600	0.632	0.648
5.00	0.388	0.405	0.404	8.10	0.462	0.475	0.477	10.53	0.613	0.642	0.659
5.21	0.391	0.413	0.415								

[a] $C_{\mathrm{VO2}} = 1 \times 10^{-4}$ mol·dm^{-3} and $C_{\mathrm{HL}} = 1 \times 10^{-2}$ mol·dm−3.

were determined from the intercept of the plots and are listed in Table 4 (from Figure 2). If we define $\bar{\epsilon}_1$ as in eq 11

$$\bar{\epsilon}_1 = \frac{\epsilon_0\,[\mathrm{VO_2}^+]}{[\mathrm{VO_2}^+] + [\mathrm{VO_2\,L}]} + \frac{\epsilon_1[\mathrm{VO_2L}]}{[\mathrm{VO_2}^+] + [\mathrm{VO_2L}]} \qquad (11)$$

through the rearrangement of eq 11, the average ligand number, $\bar{n}_1$, can be calculated directly

$$\bar{n}_1 = \frac{\bar{\epsilon}_1 - \epsilon_0}{\epsilon_1 - \epsilon_0} \qquad (12)$$

Calculation has shown that $\bar{n}_1$ equals 0.93, 0.97, and 0.94 for $x_{\mathrm{MeOH}} = 0.000$, $x_{\mathrm{MeOH}} = 0.194$, and $x_{\mathrm{dioxane}} = 0.128$,

Table 3. Values of Molar Absorptivities of Dioxovanadium(V) in *x* Methanol and Dioxane

	ϵ_0		
x	$\lambda = 280$ nm	$\lambda = 275$ nm	$\lambda = 270$ nm
	MeOH + H_2O		
0.000	288.02	352.39	399.85
0.059	304.30	348.96	426.17
0.123	310.22	392.38	395.73
0.194	381.77	441.94	533.85
	Dioxane + H_2O		
0.000	288.02	352.39	399.85
0.053	152.96	166.67	185.52
0.128	62.02	122.86	166.99
0.180	92.01	112.08	165.72

Table 4. Values of Molar Absorptivities of VO_2L in *x* Methanol and Dioxane

	ϵ_1		
x	$\lambda = 280$ nm	$\lambda = 275$ nm	$\lambda = 270$ nm
	MeOH + H_2O		
0.000	1843.68	2171.68	2559.18
0.059	1817.02	2159.96	2612.83
0.123	1870.89	2279.38	2288.68
0.194	1842.74	2037.00	2217.27
	Dioxane + H_2O		
0.000	1843.68	2171.68	2559.18
0.053	769.96	787.06	841.52
0.128	1829.72	1967.17	1993.52
0.180	3761.92	3873.54	3827.17

respectively. Thus, at this range of pH, leucine forms a mononuclear 1:1 complex with VO_2^+ and K^H_{VO2L} can be calculated from the slope of eq 10. The averages of them at different wavelengths are listed in Table 5.

Considering eq 13

$$VO_2^+ + L^- \rightleftharpoons VO_2L \tag{13}$$

the stability constant of the complex can be calculated from

$$K_{VO2L} = K^H_{VO2L} \cdot K \tag{14}$$

and the averages of them at different wavelengths are shown in Table 6.

From Figure 1 above pH 8.15 a second increase in absorbance was observed; this was attributed to formation of another species, which is given by,

$$VO_2L + HL \rightleftharpoons VO_2L_2^- + H^+ \tag{15}$$

The formation constant of eq 15 was determined in usual manner

$$\frac{C_{VO2}}{A} = \frac{1}{\epsilon_2} + \frac{(\epsilon_2 - \epsilon_1)(A - \epsilon_1 C_{VO2})[H^+]}{\epsilon_2 K^H_{VO2L2}(\epsilon_2 C_{HL} - \epsilon_1 C_{HL} - \epsilon_2 C_{VO2} + 2\epsilon_1 C_{VO2} - A)\,A} \tag{16}$$

where K^H_{VO2L2} is the formation constant of eq 15 and ϵ_2 is the molar absorptivity of VO_2L_2, which was calculated from the intercept of the plot C_{VO2}/A versus $(A - \epsilon_1 C_{VO2})[H^+]/A$, at different wavelengths and is shown in Table 7 (from Figure 3).

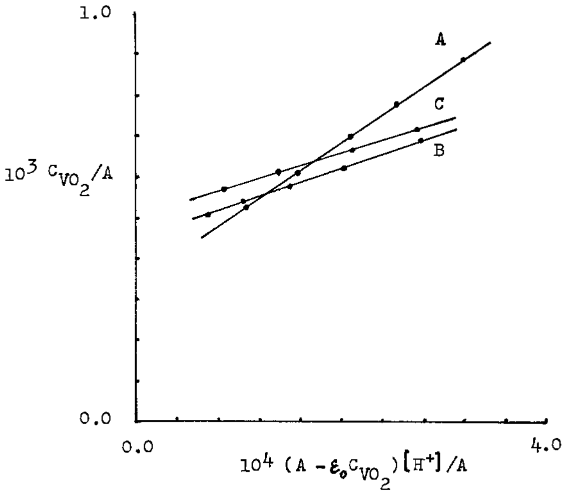

Figure 2. C_{VO2}/A versus $(A - \epsilon_0 C_{VO2})[H^+]/A$ for (A) $x_{MeOH} = 0.000$, (B) $x_{MeOH} = 0.194$, and (C) $x_{dioxane} = 0.128$ at (25 ± 0.1) °C, $I = 0.15$ mol·dm^{-3}, and $\lambda = 270$ nm.

Table 5. Average Values of $-\log K^H_{VO2L}$ in *x* Methanol and Dioxane

	$-\log K^H_{VO2L}$		
x	$\lambda = 280$ nm	$\lambda = 275$ nm	$\lambda = 270$ nm
	MeOH + H_2O		
0.000	1.43	1.52	1.57
0.059	1.29	1.39	1.51
0.123	1.28	1.32	1.34
0.194	1.19	1.24	1.28
	Dioxane + H_2O		
0.000	1.43	1.52	1.57
0.053	1.18	1.23	1.22
0.128	1.12	1.18	1.17
0.180	1.10	1.11	1.04

Table 6. Average Values of $\log K_{VO2L}$ in *x* Methanol and Dioxane

	$\log K_{VO2L}$		
x	$\lambda = 280$ nm	$\lambda = 275$ nm	$\lambda = 270$ nm
	MeOH + H_2O		
0.000	8.08	7.99	7.94
0.059	8.27	8.17	8.05
0.123	8.33	8.29	8.27
0.194	8.46	8.41	8.37
	Dioxane + H_2O		
0.000	8.08	7.99	7.94
0.053	8.44	8.39	8.40
0.128	8.58	8.52	8.53
0.180	8.64	8.63	8.70

Through the rearrangement of eq 11 for the species VO_2L_2, the average ligand number, $\bar{n}_2$ (at pH range of 8.15 to 9.20), can be calculated directly from eq 17

$$\bar{n}_2 = \frac{\bar{\epsilon}_2 + \epsilon_2 - 2\epsilon_1}{\epsilon_2 - \epsilon_1} \tag{17}$$

where $\bar{\epsilon}_2$ is similar to $\bar{\epsilon}_1$ but for the species VO_2L_2. Calculation has shown that $\bar{n}_2$ equals 1.90, 1.99, and 1.88 for $x_{MeOH} = 0.000$, $x_{MeOH} = 0.194$, and $x_{dioxane} = 0.128$, respectively. Thus, at this range of pH leucine forms a mononuclear 1: 2 complex with VO_2^+ and K^H_{VO2L2} can be calculated from the slope of eq 16. The averages of them at different wavelengths are listed in Table 8.

Considering eq18

$$VO_2^+ + 2\,L^- \rightleftharpoons VO_2L_2^- \tag{18}$$

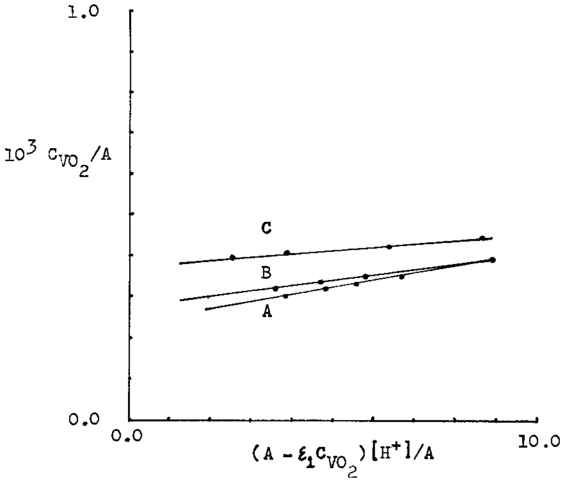

Figure 3. C_{VO2}/A versus $(A - \epsilon_1 C_{VO2})[H^+]/A$ for (A) $x_{MeOH} = 0.000$, (B) $x_{MeOH} = 0.194$, and (C) $x_{dioxane} = 0.128$ at (25 ± 0.1)°C, $I = 0.15$ mol·dm^{-3}, and $\lambda = 270$ nm.

Table 7. Values of Molar Absorptivities of VO_2L_2 in x Methanol and Dioxane

x	ϵ_2		
	$\lambda = 280$ nm	$\lambda = 275$ nm	$\lambda = 270$ nm
	MeOH + H_2O		
0.000	3010.12	3639.92	4214.64
0.059	2822.46	3411.96	3775.04
0.123	2615.43	3196.31	3801.48
0.194	2757.21	3263.03	3668.97
	Dioxane + H_2O		
0.000	3010.12	3639.92	4214.64
0.053	2523.37	2731.53	3351.84
0.128	2402.05	2500.67	2595.90
0.180	4714.79	4859.26	4894.68

Table 8. Average Values of $-\log K^H_{VO2L2}$ in x Methanol and Dioxane

x	$-\log K^H_{VO2L2}$		
	$\lambda = 280$ nm	$\lambda = 275$ nm	$\lambda = 270$ nm
	MeOH + H_2O		
0.000	6.68	6.74	6.86
0.059	6.62	6.70	6.84
0.123	6.55	6.66	6.77
0.194	6.52	6.60	6.68
	Dioxane + H_2O		
0.000	6.68	6.74	6.86
0.053	6.20	6.07	6.27
0.128	5.93	6.00	6.20
0.180	5.22	5.29	5.35

the stability constant of VO_2L_2 can be calculated from

$$K_{VO2L2} = K^H{}_{VO2L2} \cdot K^H{}_{VO2L} \cdot K^2 \tag{19}$$

and the averages of them at different wavelengths are shown in Table 9.

Leucine is potentially a bidentate ligand toward metal ions, with two donor sites on the terminal amino and carboxyl groups. Dioxovanadium(V) ion has a octahedral configuration with four positions to form its complexes. Thus, at higher pH, it is likely that two leucine molecules each as a bidentate ligand coordinate to each metal ion to form a mononuclear 1:2 complex, while at acidic pH a mononuclear 1:1 species will be formed.

Table 9. Average Values of log K_{VO2L2} in x Methanol and Dioxane

x	log K_{VO2L2}		
	$\lambda = 280$ nm	$\lambda = 275$ nm	$\lambda = 270$ nm
	MeOH + H_2O		
0.000	10.91	10.76	10.59
0.059	11.21	11.03	10.77
0.123	11.39	11.24	11.11
0.194	11.59	11.46	11.34
	Dioxane + H_2O		
0.000	10.91	10.76	10.59
0.053	11.86	11.94	11.75
0.128	12.35	12.22	12.03
0.180	13.16	13.08	13.09

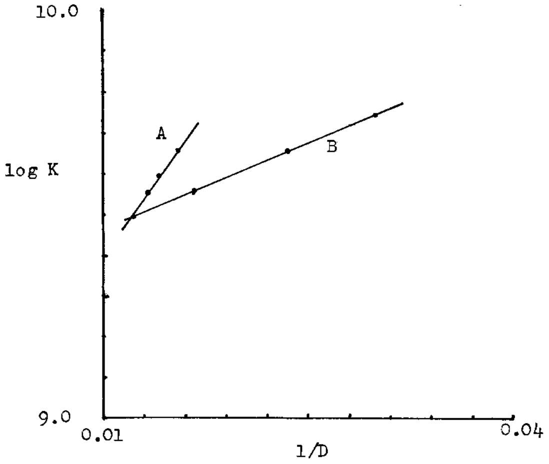

Figure 4. Log K of L-leucine versus $1/D$ for (A) methanol + water and (B) dioxane + water at (25 ± 0.1) °C, $I = 0.15$ mol·dm^{-3}, and $\lambda = 270$ nm.

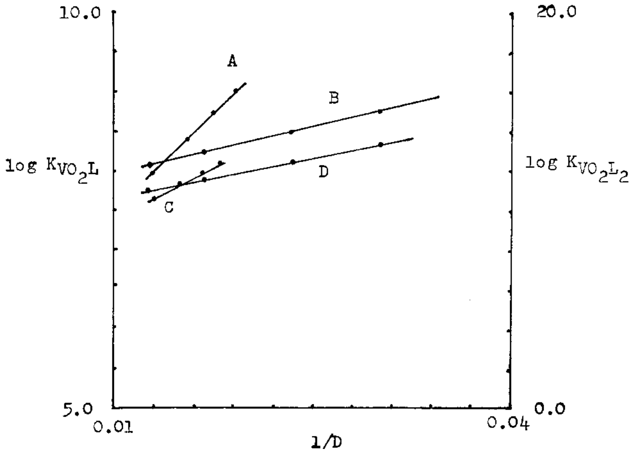

Figure 5. Log K $_{VO2L}$ versus 1/D for (A) methanol + water and (B) dioxan + water and Log K_{VO2L2} versus 1/D for (C) methanol + water and (D) dioxan + water at (25 ± 0.1) °C, I = 0.15 mol. dm $^{-3}$ and $\lambda = 270$ nm at (25 ± 0.1) °C, I = 0.15 mol. dm $^{-3}$ and $\lambda = 270$ nm.

Water has a high dielectric constant of about 80 D, so 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 linear relationship between log K of leucine and $1/D$ of solvent in methanol + water and dioxane + water systems 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 value of log K_{VO2L} and log K_{VO2L2} as a function of $1/D$ resolve all the data to a single linear relationship for values of D between 80 and 30 (Figure 5). The obtained values show that our results agree with above speculation.

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