J. Chem. Eng. Data **1995**, *40*, 419−422

Comparison and Thermodynamic Studies on Complexation of Alanine with Vanadium(V) in Mixed Solvent Systems

Majid Monajjemi

Doctoral Department and Research Division of Islamic Azad University, Tehran, Iran

Karim Zare and Farrokh Gharib*

Chemistry Department, Shahid Beheshti University, Tehran, Evin, Iran

The stability constant on complexation of VO_2^+ with alanine in mixed solvent systems of methanol + water and ethanol + water have been determined spectrophotometrically at 25 ± 0.1 °C and $I = 1$ mol·dm^{-3} of sodium perchlorate as ionic medium in the pH range 1.3−2.3, 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 of the system, respectively. Also, the results are discussed in terms of the effect of solvent on protonation and complexation.

Introduction

We have recently reported the complexation of oxovanadium with some amino acids (*1*−*6*), and other authors (*7*−*10*) have reported the complexation in aqueous solution. There are very few quantitative studies on complexation of this oxometal with amino acids in nonaqueous solutions.

The present paper describes the formation of the complex of V(V) with DL-alanine by a spectrophotometric method in mixed solvent solution, to show how solvents and solvent mixtures with different dielectric constants affect formation of such a complex.

Experimental Section

Reagents. Sodium perchlorate, perchloric acid, ethanol, methanol, and sodium hydroxide were obtained from E. Merck; DL-alanine and sodium metavanadate were purchased from Aldrich Chemical and Riedel-De Haenag Seelze-Hannover, respectively, as analytical reagent grade materials 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 conductivity equal to 1.3 ± 0.1 $\mu\Omega^{-1}$, and this stock solution was standardized against $HClO_4$. Vanadium(V) solutions were standardized titrimetrically against a standard iron(II) sulfate solution (*11*).

Measurements. All measurements were carried out at 25 ± 0.1 °C. The ionic strength was maintained at 1.0 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 for the various solvent mixtures with solutions of known hydrogen ion concentration and constant ionic strength. 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.

Table 1. Values of log K_p for x Ethanol + (1 − x) Water at 25 °C

log K_p	x	log K_p	x
9.71	0.0	9.82	0.0522
9.73	0.0162	9.91	0.0947
9.78	0.0336	9.99	0.1728

Table 2. Values of log K_p for x Methanol + (1 − x) Water at 25 °C

log K_p	x	log K_p	x
9.71	0.0	9.76	0.0734
9.72	0.0230	9.78	0.1010
9.73	0.0476	9.82	0.1610

Table 3. Values of Molar Absorptivities of Vanadyl Ion at 25 °C

λ/nm	$10^{-2}\epsilon_0$	λ/nm	$10^{-2}\epsilon_0$
245	5.46	265	4.82
250	5.55	270	4.29
255	5.54	275	3.68
260	5.23	280	2.97

Results and Discussion

Protonation Equilibria of the Aminocarboxylic Acid. Prior to studying the metal−aminocarboxylate complex, we determined the stability constant of protonation equilibria of alanine in water and in mixed solvent systems of ethanol + water and methanol + water.

The different species present in an acidic medium of pH <2.3 were considered. The following equilibrium was studied:

$$H^+ + Y^- \rightleftharpoons HY \tag{1}$$

$$K_p = [HY]/[H^+][Y^-] \tag{2}$$

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

---

* Author to whom correspondence should be addressed.

0021-9568/95/1740-0419$09.00/0

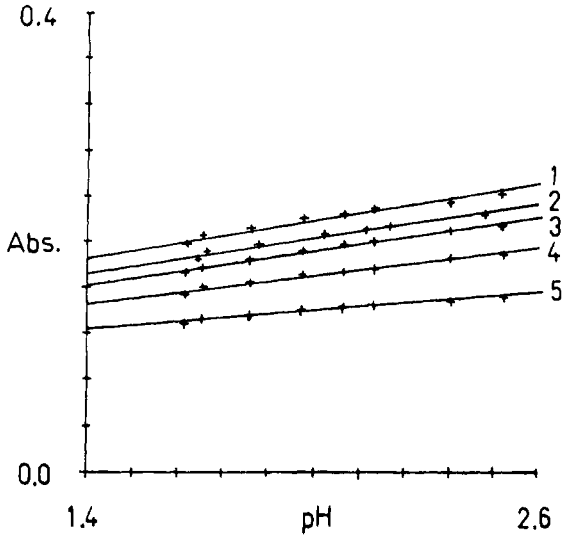

Figure 1. Absorbance versus pH for VO_2^+ at different wavelengths: (1) 245, (2) 250, (3) 260, (4) 270, (5) 280 nm.

Table 4. Values of Molar Absorptivities of VO_2Y in x Ethanol + $(1 - x)$ Water at 25 °C

	$10^{-3}\epsilon_1, x =$					
λ/nm	0.0	0.0162	0.0336	0.0522	0.0947	0.1728
245	1.24	1.25	1.28	1.30	1.32	1.58
250	1.06	1.08	1.12	1.12	1.14	1.39
255	0.99	1.01	1.03	1.08	1.10	1.30
260	0.95	0.98	1.00	1.04	1.06	1.26
265	0.94	0.96	0.98	1.00	1.05	1.20
270	0.90	0.95	0.97	0.97	0.99	1.19
275	0.84	0.90	0.93	0.93	0.97	1.12
280	0.81	0.84	0.87	0.88	0.91	1.08

Table 5. Values of Molar Absorptivities of VO_2Y in x Methanol + $(1 - x)$ Water at 25 °C

	$10^{-3}\epsilon_1, x =$					
λ/nm	0.0	0.0230	0.0476	0.0734	0.1010	0.1610
245	1.24	1.23	1.27	1.29	1.29	1.31
250	1.06	1.06	1.09	1.12	1.13	1.18
255	0.99	1.00	1.02	1.05	1.08	1.10
260	0.95	0.95	0.97	1.03	1.05	1.10
265	0.94	0.94	0.96	0.99	1.01	1.04
270	0.90	0.91	0.93	0.98	0.99	0.99
275	0.84	0.85	0.89	0.95	0.96	0.97
280	0.81	0.82	0.85	0.90	0.92	0.93

the results are shown in Tables 1 and 2. In this work, we have used the results reported by Gentile (*12*) for determining the dielectric constants of the systems ethanol + water and methanol + water.

Complexation of Vanadium(V) with Alanine. The equilibria involved in determination of stability constants of metal–aminocarboxylate are

$$H^+ + Y^- \rightleftharpoons HY \qquad (3)$$

$$HY + VO_2^+ \rightleftharpoons VO_2Y + H^+ \qquad (4)$$

where HY is alanine.

Considering the protonation constants of alanine, HY is the predominant species in the pH range of interest (pH <2.3) for complex formation. In acidic solution (pH <2.5), vanadium(V) exists as the VO_2^- ion (*13, 14*). This ion hydrolyzes in alkaline solutions (*15*) and polymerizes in moderately acidic solutions (*16*). However, in the presence of a large excess of a ligand at pH <7.5, both polymerization and hydrolysis of VO_2^+ were found to be negligible (*15*). In the pH range of interest (1.3–2.3), absorbance and pH were measured for solutions containing V(V), 10^{-4} mol·dm^{-3} with a large excess of alanine, 10^{-2} mol·dm^{-3} in various solvent systems of ethanol + water and methanol + water.

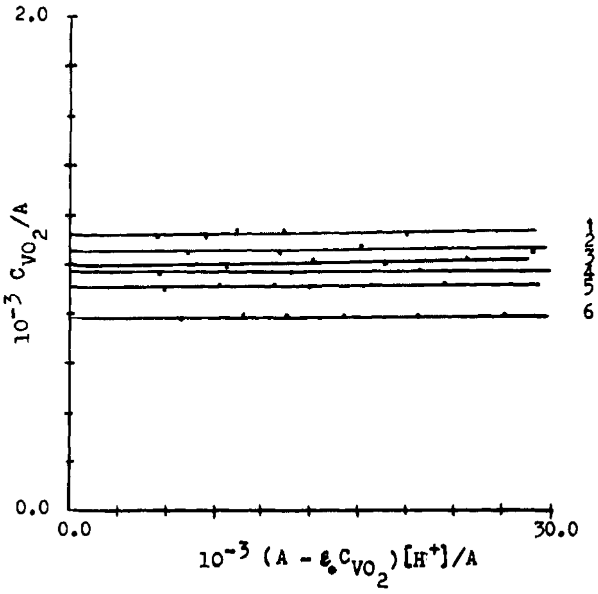

Figure 2. C_{VO_2}/A versus $(A - \epsilon_0 C_{VO_2})[H^+]/A$ for x ethanol + $(1 - x)$ water at different wavelengths: (1) 280, (2) 275, (3) 265, (4) 255, (5) 250, (5) 245 nm.

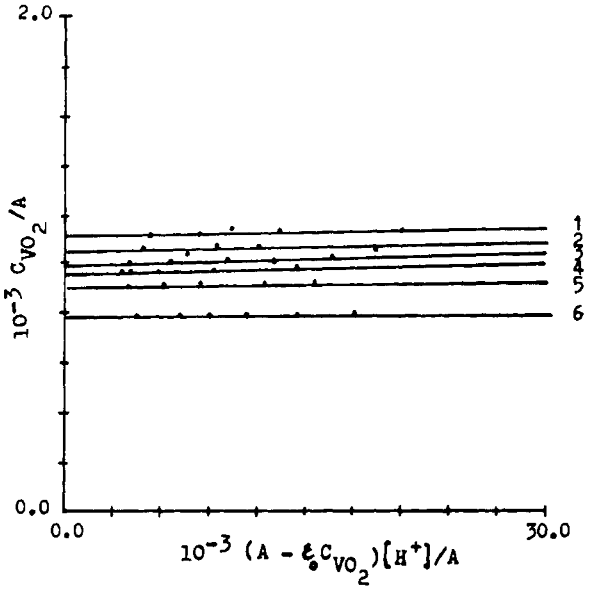

Figure 3. C_{VO_2}/A versus $(A - \epsilon_0 C_{VO_2})[H^+]/A$ for x methanol + $(1 - x)$ water at different wavelengths: (1) 280, (2) 275, (3) 265, (4) 255, (5) 250, (5) 245 nm.

The formation constant of eq 4, $K^H_{VO_2Y}$, and the overall stability constant of complexation, K_{VO_2Y}, can be expressed as follows:

$$K^H_{VO_2Y} = [VO_2Y][H^+]/[HY][VO_2^+] \qquad (5)$$

$$K_{VO_2Y} = [VO_2Y]/[VO_2^+][Y^-] \qquad (6)$$

The absorbance at a wavelength is given by

$$A = \epsilon_0[VO_2^+] + \epsilon_1[VO_2Y] \qquad (7)$$

where ϵ_0 and ϵ_1 are the molar absorptivities of the vanadyl ion and the complex VO_2Y, respectively. For the material balance

Table 6. Absorbance, A, of Solutions of Concentrations $C_{VO_2} = 10^{-4}$ M and $C_{HY} = 10^{-2}$ M, at Different pH Values and Wavelengths, in x Ethanol + (1 − x) Water at 25 °C

	A							
pH	245 nm	250 nm	255 nm	260 nm	265 nm	270 nm	275 nm	280 nm
$x = 0.0$								
2.09	0.119	0.102	0.095	0.091	0.089	0.088	0.081	0.079
1.94	0.118	0.101	0.094	0.091	0.088	0.086	0.081	0.079
1.78	0.119	0.102	0.094	0.091	0.089	0.088	0.082	0.080
1.56	0.119	0.100	0.094	0.090	0.087	0.087	0.082	0.078
$x = 0.0162$								
2.20	0.125	0.108	0.101	0.098	0.095	0.094	0.090	0.084
2.00	0.124	0.106	0.100	0.097	0.095	0.093	0.089	0.084
1.82	0.123	0.105	0.098	0.096	0.096	0.091	0.088	0.083
1.60	0.123	0.105	0.099	0.096	0.093	0.091	0.088	0.083
1.41	0.121	0.104	0.099	0.095	0.093	0.090	0.088	0.082
$x = 0.0336$								
2.01	0.125	0.109	0.101	0.097	0.097	0.095	0.091	0.086
1.80	0.126	0.108	0.100	0.096	0.096	0.094	0.090	0.081
1.63	0.125	0.106	0.099	0.097	0.096	0.092	0.089	0.084
1.40	0.124	0.106	0.098	0.096	0.096	0.092	0.088	0.083
$x = 0.0522$								
2.20	0.129	0.111	0.103	0.101	0.099	0.097	0.093	0.088
1.99	0.128	0.110	0.103	0.099	0.098	0.095	0.091	0.086
1.57	0.127	0.109	0.102	0.099	0.097	0.095	0.092	0.087
1.40	0.126	0.109	0.102	0.098	0.097	0.095	0.091	0.086

Table 7. Absorbance, A, of Solutions of Concentrations $C_{VO_2} = 10^{-4}$ M and $C_{HY} = 10^{-2}$ M, at Different pH Values and Wavelengths, in x Methanol + (1 − x) Water at 25 °C

	A							
pH	245 nm	250 nm	255 nm	260 nm	265 nm	270 nm	275 nm	280 nm
$x = 0.0$								
2.02	0.117	0.101	0.095	0.090	0.088	0.086	0.081	0.077
1.86	0.118	0.100	0.095	0.091	0.088	0.085	0.080	0.077
1.71	0.118	0.100	0.094	0.089	0.088	0.086	0.080	0.079
1.44	0.116	0.098	0.092	0.088	0.085	0.085	0.079	0.077
$x = 0.0230$								
2.15	0.118	0.102	0.094	0.091	0.093	0.091	0.084	0.081
2.00	0.114	0.100	0.092	0.088	0.087	0.086	0.081	0.079
1.92	0.114	0.098	0.092	0.088	0.087	0.085	0.082	0.079
1.72	0.115	0.098	0.091	0.087	0.086	0.085	0.081	0.078
1.43	0.113	0.096	0.091	0.085	0.084	0.084	0.080	0.077
$x = 0.0476$								
2.30	0.124	0.106	0.099	0.096	0.095	0.088	0.086	0.084
2.04	0.122	0.104	0.097	0.093	0.093	0.089	0.088	0.084
1.70	0.120	0.102	0.094	0.091	0.091	0.085	0.083	0.079
1.52	0.125	0.105	0.098	0.095	0.094	0.085	0.084	0.082
$x = 0.0734$								
2.10	0.128	0.110	0.103	0.100	0.99	0.096	0.095	0.089
1.80	0.126	0.109	0.101	0.097	0.097	0.095	0.092	0.087
1.72	0.127	0.110	0.103	0.100	0.098	0.095	0.093	0.088
1.54	0.127	0.109	0.102	0.100	0.096	0.095	0.094	0.088

Table 8. Average Values of log $K^{H}_{VO_2Y}$ and log K_{VO_2Y} in x Ethanol + (1 − x) Water at 25 °C

x	$1/D$	$\log K^{H}_{VO_2Y}$	$\log K_{VO_2Y}$
0.0	0.0127	1.61	11.32
0.0162	0.0128	1.64	11.37
0.0336	0.0132	1.72	11.50
0.0522	0.0137	1.80	11.62
0.0947	0.0150	1.93	11.84
0.1728	0.0173	1.99	11.98

$$[VO_2^+] = C_{VO_2} - [VO_2Y] \tag{8}$$

$$[HY] = C_{HY} - [VO_2Y] \tag{9}$$

where C_{VO_2} and C_{HY} are the total concentrations of VO_2^+ and alanine, respectively. Thus, the equilibrium constant of eq 5 can be expressed as follows (*1*):

$$\frac{C_{VO_2}}{A} = \frac{1}{\epsilon_1} + \frac{(\epsilon_1 - \epsilon_0)(A - \epsilon_0 C_{VO_2})[H^+]}{\epsilon_1 K^{H}_{VO_2Y}(\epsilon_1 C_{HY} - \epsilon_0 C_{HY} - A + \epsilon_0 C_{VO_2})A} \tag{10}$$

Table 9. Average Values of log $K^{H}_{VO_2Y}$ and log K_{VO_2Y} in x Methanol + (1 − x) Water at 25 °C

x	$1/D$	$\log K^{H}_{VO_2Y}$	$\log K_{VO_2Y}$
0.0	0.0127	1.61	11.32
0.0230	0.0130	1.68	11.40
0.0476	0.0134	1.76	11.50
0.0734	0.0139	1.81	11.57
0.1010	0.0143	1.85	11.63
0.1610	0.0152	1.93	11.75

Considering that A is a function of pH (*17*), the values of ϵ_0 are shown in Table 3 (from Figure 1). The values of ϵ_1 were determined from the intercept of the straight line plots of C_{VO_2}/A against $((A - \epsilon_0 C_{VO_2})[H^+])/A$ and are shown in Tables 4 and 5 (from Figures 2 and 3).

If we define $\bar{\epsilon}$ (*17*) as

$$\bar{\epsilon} = \frac{\epsilon_0[VO_2^+]}{[VO_2^+] + [VO_2Y]} + \frac{\epsilon_1[VO_2Y]}{[VO_2^+] + [VO_2Y]} \tag{11}$$

through the rearrangement of eq 11, the average ligand

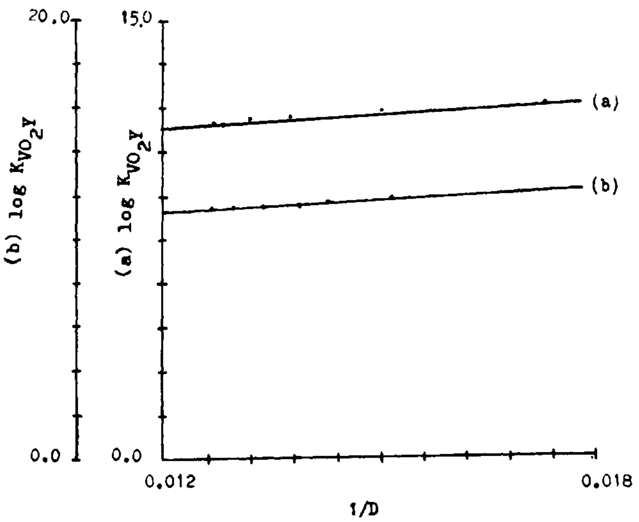

Figure 4. log K_{VO_2Y} versus $1/D$ for (a) x ethanol + $(1 - x)$ water and (b) x methanol + $(1 - x)$ water.

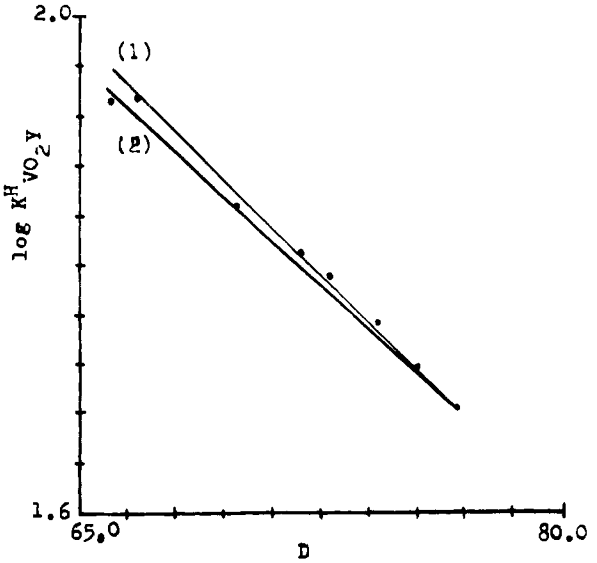

Figure 5. log $K^H_{VO_2Y}$ versus D for (1) x ethanol + $(1 - x)$ water and (2) x methanol + $(1 - x)$ water.

numbers, $\bar{n}$, can be calculated directly (*18*):

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

Calculations have shown $\bar{n} = 1$ for the complex; thus, the complex is a mononuclear 1:1 one, and $K^H_{VO_2Y}$ can be calculated from the slope of eq 10.

From Tables 6 and 7, the averages of log $K^H_{VO_2Y}$ and log K_{VO_2Y} are shown in Tables 8 and 9.

Water has a very 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 plots of the obtained values of log K_{VO_2Y} and log K_p, as a function of $1/D$, and log $K^H_{VO_2Y}$ versus D in methanol + water and ethanol + water systems (Figures 4 and 5) show that our results agree with above speculation.

Acknowledgment

We are indebted to Dr. H. R. Mozhdehi, Vice-President, Doctoral Department and Research Division of Islamic Azad University, for assistance with this work.

Literature Cited

(1) Gharib, F.; Khorrami, S. A.; Zare, K. *J. Sci. Isl. Azad Univ.* **1992**, *4–5*, 397.
(2) Gharib, F.; Zare, K.; Khorrami, S. A. *J. Chem. Eng. Data* **1993**, *38*, 602.
(3) Gharib, F.; Khorrami, S. A.; Zare, K. *J. Sci. Isl. Azad Univ.* **1992**, *4–5*, 535.
(4) Gharib, F.; Khorrami, S. A.; Zare, K. *Int. J. Chem.* **1994**, in press.
(5) Khorrami, S. A.; Gharib, F.; Zare, K.; Aghai, H. *Iran. J. Chem. Chem. Eng.* **1992**, *11*, 19.
(6) Gharib, F.; Zare, K.; Khorrami, S. A. *J. Sci. AlZahra Univ.* **1994**, 7–8.
(7) Costa Pessoa, J.; Marques, R. L.; Vilas Boas, L. F.; Gillard, R. D. *Polyhedron* **1990**, *9*, 81.
(8) Costa Pessoa, J.; Vilas Boas, F.; Gillard, R. D. *Polyhedron* **1989**, *8*, 1173.
(9) Tomiyasu, H.; Gordon, G. *Inorg. Chem.* **1976**, *15*, 870.
(10) Costa Pessoa, J.; Vilas Boas, F.; Gillard, R. D. *Polyhedron* **1988**, *14*, 1245.
(11) Charlot, G. *Les Methods de la Chimie Analytique, Analyse Quantitative Minerale*, 4th ed.; Masson et Cie: Paris, 1961.
(12) Gentile, P. S.; Dadgar, A. *J. Chem. Eng. Data* **1968**, *13*, 236.
(13) Cotten, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 3rd ed.; Wiley: New York, 1972.
(14) Rossotti, F. J. C.; Rossotti, H. *Acta Chem. Scand.* **1956**, *10*, 957.
(15) Zare, K.; Lagrange, P.; Lagrange, J. *J. Chem. Soc., Dalton Trans.* **1979**, 1372.
(16) Karadakov, B. P.; Venkova, P. I. *Talanta* **1970**, *17*, 878.
(17) Beck, M. T.; Nagypal, I. *Chemistry of Complex Equilibria*; Ellis Horwood: New York, 1990.

Received for review July 7, 1994. Accepted December 7, 1994.[⊗]

JE940128U

[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1995.