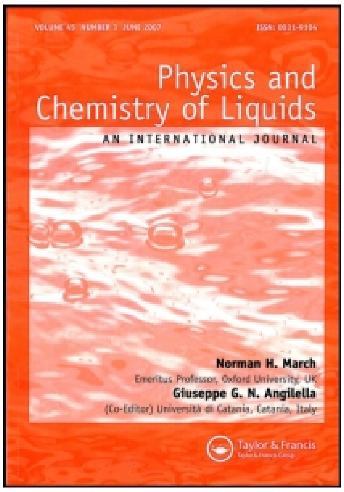

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

On The Effect of Dielectric Constant on Formation and Stability Constants of Vanadium(v) with Leucine in Mixed Solvent of Methanol Water at 298.15 K

H. Iloukhani[a]; M. Mollaie[a]; F. Gharib[b]
[a] Department of Chemistry, Faculty of Sciences, Bu-Ali-Sina University, Hamadan, Iran [b] Department of Chemistry, Shahid Beheshti University, Tehran, Evin, Iran

To cite this Article Iloukhani, H. , Mollaie, M. and Gharib, F.(2000) 'On The Effect of Dielectric Constant on Formation and Stability Constants of Vanadium(v) with Leucine in Mixed Solvent of Methanol Water at 298.15 K', Physics and Chemistry of Liquids, 38: 5, 607 — 613

To link to this Article: DOI: 10.1080/00319100008030307

URL: http://dx.doi.org/10.1080/00319100008030307

Phys. Chem. Liq., 2000, Vol. 38, pp. 607–613
Reprints available directly from the publisher
Photocopying permitted by license only

ON THE EFFECT OF DIELECTRIC CONSTANT ON FORMATION AND STABILITY CONSTANTS OF VANADIUM(V) WITH LEUCINE IN MIXED SOLVENT OF METHANOL + WATER AT 298.15 K

H. ILOUKHANI[a,*], M. MOLLAIE[a] and F. GHARIB[b]

[a]*Department of Chemistry, Faculty of Sciences, Bu-Ali-Sina University, Hamadan-Iran;* [b]*Department of Chemistry, Shahid Beheshti University, Tehran, Evin, Iran*

(Received 30 January 1999)

Equilibria in aqueous solutions in the system leucine + VO_2^+ has been studied by a combination of potentiometric and spectrophotometric methods, in the pH range 3–4.4 with high ligand-to-metal ratios. An equilibrium model, MY, is assumed, where M and Y represent the metal ion and fully dissociated amino acid anion, respectively. The results showed that formation and stability constants of complex system increased with decrease of dielectric constants. Linear relationships were observed when $\log K_P$ was plotted *vs.* 1/D, where K_P and D represent stability and dielectric constants of the system, respectively.

Keywords: Stability constant; dielectric constant; leucine; methanol

1. INTRODUCTION

This paper taken further work on the measurement of thermodynamic properties of solutions [1–3]. The biochemistry of vanadium has attracted increasing interest [4–7], particularly in studies related to its accumulation in certain tunicates [8–11], and in the mush-room

---

*Corresponding author. e-mail: iloukhani@basu.ac.ir

amanita [12–16]. Although knowledge of the system amino acid + dioxovanadium(V) is relevant to understanding its possible interaction with likely biological ligands, few reliable data exist. The equilibria in aqueous solution containing vanadium with amino acids have been reviewed recently [17]. Several experimental methods have been used, and the isolation of solids has also been claimed [18].

The present paper describes the formation of the complex dioxovanadium(V) with leucine by a spectrophotometric method. The effects of dielectric constant are also examined on the mixed system of methanol + water. These metal-ligand equilibria have been studied in mixed solvent system of methanol + water at 298 ± 0.1 K with $0.15\,\mathrm{mol \cdot dm^{-3}}$ sodium perchlorate as the ionic medium.

2. EXPERIMENTAL SECTION

2.1. Materials

Sodium perchlorate, perchloric acid, and sodium hydroxide were obtained from E. Merck. L – leucine, methanol were from E. Merck and sodium metavanadate was from Riedel – De Haenag Seelze – Hanover as analytical reagent grade materials. All four 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 $1.3 \pm 0.1\,\mu\Omega^{-1}$, and this stock solutions was standardized against $HClO_4$. Vanadium (V) solutions were standardized titrimetrically against a standard iron (II) sulfate solution [19].

2.2. Measurements

All measurements were carried out at 298 ± 0.1 K. The ionic strength was maintained at $0.15\,\mathrm{mol \cdot dm^{-3}}$ with sodium perchlorate. An Eyela pH meter, pHM 2000 was used for pH measurement. The hydrogen ion concentration was measured with an Ingold UO 3234 glass electrode and an Ingold UO 3236 calomel electrode. Spectrophotometric measurements were performed on an UV-*vis* shimadzu 2100 spectrophotometer with a GDU−20 C computer and using thermostated matched 10 mm quartz cells. The measurement cell was a flow type. A masterflen pump allowed circulation of the solution under study from the potentiometric cell to the spectrophotometric cell so the absorbance and pH of the solutions could be measured simultaneously.

For each experiment two solutions of VO_2^+ with leucine have been prepared with the same concentration. But the ionic strength of the first is maintained with sodium perchlorate, and the second with perchloric acid. The first solution is then titrated with the second one. The pH and absorbance is measured after addition of a few drops, and this procedure extends up to the pH of interest.

3. RESULT AND DISCUSSION

3.1. Protonation Equilibria of Aminocarboxylic Acid

Prior to studying the metal – aminocarboxylate complexes, we determined the stability constants of the protonation equilibria of leucine under the above conditions.

$$H^+ + Y^- \leftrightarrow HY \qquad (1)$$

$$K_P = [HY]/[H^+][Y^-] \qquad (2)$$

The protonation constants, K_P has been determined using potentiometric techniques and calculated using a nonlinear least-square method.

3.2. Complexes of Vanadium (V) with the Amino Acid

The following equilibrium was considered in acidic solutions:

$$VO_2^+ + H_{\ell-m}Y^{m-} \leftrightarrow VO_2H_{\ell-m-n}Y^{(m+n-\ell)-} + nH^+ \qquad (3)$$

The formation constant is defined as

$$K^H_{VO_2Y} = \left[VO_2H_{\ell-m-n}Y^{(m-n-\ell)-}\right][H^+]^n/\left[VO_2^+\right]\left[H_{\ell-m}Y^{m-}\right] \qquad (4)$$

In this case, data were analyzed by using HY ($m = 0$ and $l = 1$) as the reactant. The absorbance at a wave length of UV range is given by

$$A = \varepsilon_0[VO_2^+] + \varepsilon_1[VO_2H_{1-n}Y^{(n-1)-}] \tag{5}$$

Where ε_0 and ε_1 are the molar absorptivities of the vanadyl ion, VO_2^+ and the complex VO_2Y, respectively. For the material balance,

$$C_{VO_2^+} = [VO_2^+] + [VO_2H_{1-n}Y^{(n-1)-}] \tag{6}$$

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

Where $C_{VO_2^+}$ and C_{HY} are the total concentrations of VO_2^+ and amino acid, respectively. Thus, the equilibrium constant $K^H_{VO_2Y}$, is given by Eqs. (4–7).

$$\frac{C_{VO_2^+}}{A} = \frac{1}{\varepsilon_1} + \frac{(\varepsilon_1 - \varepsilon_0)(A - \varepsilon_0 C_{VO_2^+})[H^+]^n}{\varepsilon_1 K^H_{VO_2Y}(\varepsilon_1 C_{HY} - \varepsilon_0 C_{HY} - A + \varepsilon_0 C_{VO_2^+})A} \tag{8}$$

Considering that A is a function of pH [20], the values of ε_0 in mixed solvent at different dielectric constants are shown in Table I.

The number of protons, n, was examined by applying Eq. (8), the straight line plots of $x = (A - \varepsilon_0 C_{VO_2^+})[H^+]^n/A$ *vs.* $y = C_{VO_2^+}/A$ with $n = 1$ confirmed the formation of a single complex with the formula VO_2Y. The values of ε_1 in mixed solvent at different dielectric constants were determined from the intercept of the plots. Table I also gives ε_1 values obtained from Figure 1.

If we define $\bar{\varepsilon}$ as [21]:

$$\bar{\varepsilon} = \frac{\varepsilon_0[VO_2^+]}{[VO_2^+] + [VO_2Y]} + \frac{\varepsilon_1[VO_2Y]}{[VO_2^+] + [VO_2Y]} \tag{9}$$

TABLE I Values of molar absorptivities, ε_0 and ε_1 of VO_2^+ and VO_2Y, respectively, in mixed solvents of methanol + water at different dielectric constants

$\lambda/(nm)$	280		275		270	
$1/D$	$10^{-2}\varepsilon_0$	$10^{-3}\varepsilon_1$	$10^{-2}\varepsilon_0$	$10^{-3}\varepsilon_1$	$10^{-2}\varepsilon_0$	$10^{-3}\varepsilon_1$
0.0127	2.88	1.84	3.52	2.17	3.99	2.55
0.0137	3.04	1.81	3.48	2.15	4.26	2.61
0.0149	3.10	1.87	3.92	2.27	3.95	2.28
0.0164	3.81	1.84	4.41	2.03	5.33	2.21

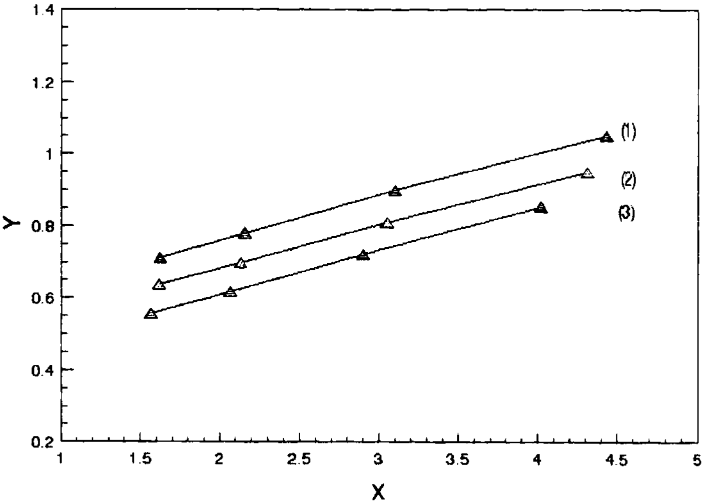

FIGURE 1 $x = (A - \varepsilon_0 C_{VO_2^+})[H^+]^n/A$ *vs.* $y = C_{VO_2^+}/A$ for solutions of concentrations $C_{VO_2^+} = 10^{-4}$ M and $C_{\text{leucine}} = 10^{-2}$ M in mixed solvents of methanol + water at different wave lengths: (1) 280, (2) 275, (3) 270 nm.

TABLE II Values of the logarithms of equilibrium constants, $K^H_{VO_2Y}$ and stability constants, K_{VO_2Y} in mixed solvents of methanol + water at different dielectric constants

$\lambda/(nm)$	280		275		270	
$1/D$	$-\log K^H_{VO_2Y}$	$\log K_{VO_2Y}$	$-\log K^H_{VO_2Y}$	$\log K_{VO_2Y}$	$-\log K^H_{VO_2Y}$	$\log K_{VO_2Y}$
0.0127	1.53	7.66	1.52	7.42	1.57	7.34
0.0137	1.31	8.07	1.39	7.97	1.51	7.85
0.0149	1.28	8.20	1.32	8.16	1.34	8.14
0.0164	1.19	8.46	1.24	8.41	1.28	8.37

through the rearrangement of Eq. (9), the average ligand number, $\bar{n}$, can be calculated directly [21]:

$$\bar{n} = \frac{\bar{\varepsilon} - \varepsilon_0}{\varepsilon_1 - \varepsilon_0} \tag{10}$$

Calculation has shown that $n = 1$; thus, the complexes are mononuclear 1 : 1, and $K^H_{VO_2Y}$ can be calculated in mixed solvent at different dielectric constants from the slope of Eq. (8), and are shown in Table II.

Considering the following equation

$$VO_2^+ + Y^- \leftrightarrow VO_2Y \tag{11}$$

the stability constant, K_{VO_2Y} of the complexes in mixed solvent at different dielectric constants can be calculated from

$$K_{VO_2Y} = [VO_2Y]/[VO_2^+][Y^-] \tag{12}$$

$$K_{VO_2Y} = K^H_{VO_2Y} \cdot K_P \tag{13}$$

Table II also gives K_{VO_2Y} values obtained from Eq. (13).

The values of $\log K_P$ in mixed solvent of methanol + water at different dielectric constants are reported in Table III and graphically shown in Figure 2.

TABLE III Values of the logarithms of $\log K_P$ in mixed solvents of methanol + water at different dielectric constants

$1/D$	$\log K_P$
0.0127	9.19
0.0137	9.33
0.0149	9.48
0.0164	9.65

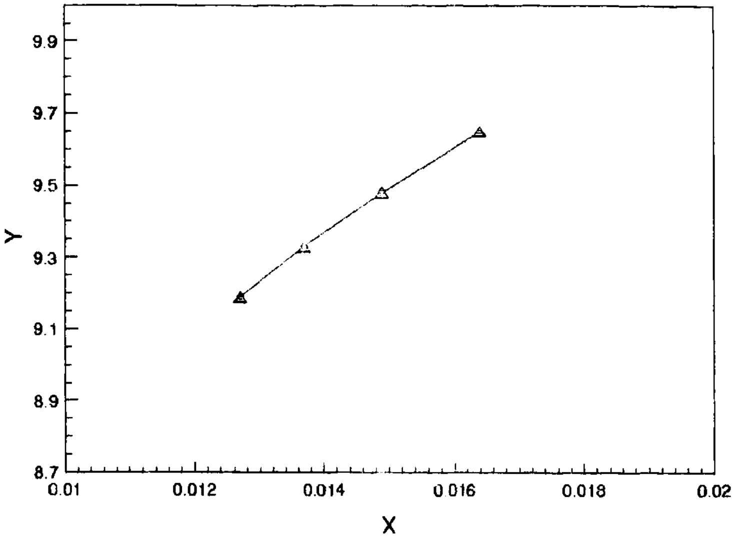

FIGURE 2 $x = 1/D$ vs. $y = \log K_P$ in mixed solvents of methanol + water at different dielectric constants.

Acknowledgements

The authors thank to the university authorities for providing the necessary facilities to carry out the work.

References

[1] Iloukhani, H. (1997). *J. Chem. Eng. Data*, **42**(4), 802.
[2] Iloukhani, H. and Ghorbani, R. (1998). *J. Solution Chem.*, **27**(2), 141.
[3] Iloukhani, H. and Parsa, J. B. (1998). *J Phys. Chem. Liq.*, **36**, 141.
[4] Schwarz, K. and Milne, D. B. (1971). *Science*, **174**, 426.
[5] Chasteen, N. D. (1983). *Struct. Bonding* (*Berlin*), **53**, 105.
[6] Kustin, K., McLeod, G. C., Gilbert, T. R. and Briggs, R. (1983). *Struct. Bonding* (*Berlin*), **53**, 139.
[7] Boyd, D. W. and Kustin, K. (1984). *Inorg. Bio Chem.*, **6**, 311.
[8] Bruening, E. M., Furukawa, J., Nakanishi, K. and Kustin, K. (1985). *J. Am. Chem. Soc.*, **107**, 5298.
[9] Seltzer, R. J. (1985). *J. Chem. Eng. News*, **53**, 67.
[10] Frank, P., Carlson, R. M. K. and Hodgson, K. O. (1986). *Inorg. Chem.*, **25**, 470.
[11] Brand, S. G., Hawkins, C. J. and Parry, D. L. (1987). *Inorg. Chem.*, **26**, 627.
[12] Gillard, R. D. and Lancashire, R. (1984). *J. Phyto Chemistry*, **23**, 179.
[13] Felcman, J., Vaz, M. C. T. A. and Frausto, J. J. R. (1984). *Inorg. Chem. Acta*, **93**, 101.
[14] Nawi, M. A. and Riechei, T. L. (1984). *Inorg. Chem. Acta*, **93**, 131.
[15] Bemski, G., Felcman, J., Frausto, J. J. R. and Moura, I., *Bioinorganic Chemistry*; (*VCH Verlagsgese llxchalt*: *Weinheim*, *1986*).
[16] Kneifel, H. and Bayer, E. (1986). *J. Am. Chem. Soc.*, **108**, 3075.
[17] Vilas-Boas, L. F. and Costa Pessoa, J. (1987). *Comprehensive Coordination Chemistry* (Pergamon Press, Oxford).
[18] Malik, W. U., Bembi, R. B. and Ashral, Y. (1976). *Indian J. Chem.* (**14A**), 542.
[19] Charlot, G. (1961). *Les Methods de la Chimie Analytique, Analyse Quantitative Minerale*, 4th, edn. (Masson et Cie., Paris).
[20] Itob, J. I., Yotsuyanagi, T. and Aomura, K. (1975). *Anal. Chim. Acta*, **77**, 229.
[21] Beck, M. T. and Nagypal, I. (1990). *Chemistry of Complex Equilibria* (Ellis Horwood Limited, New York).