Scientific paper

Solvent Effect Investigation for the Dioxovanadium (V) Complexation with Iminodiacetic Acid on the Basis of the Kamlet-Abboud-Taft Equation

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Abstract

Fits for the calculation of solvatochromic regression coefficients were done using the regression tool for the complexation of dioxovanadium(V) with iminodiacetic acid (IDA) and dissociation constants at $T = 298$ K and constant ionic strength of 0.1 mol dm^{-3} sodium perchlorate in different volume fractions of methanol (0 to 45 percent). A combination of potentiometric and UV spectrophotometric methods have been used for experimental measurements. Kamlet-Abboud-Taft (KAT) solvatochromic equation enables us to find out the contribution of various non specific and specific solute-solvent interactions. The results have been interpreted on the basis of the hydrogen-bond donor and acceptor ability and solvent polarity.

Keywords: Solvent effect, dioxovanadium (V), Kamlet-Abboud-Taft equation, iminodiacetic acid

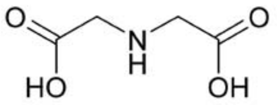
1. Introduction

Vanadium is a transition element which occurs in nature as a trace element and has a wide range of oxidation states together with beautiful colors of its complexes. It is essential for several organisms and in particular is implicated in the synthesis of chlorophyll in green plants and in the normal growth of some animals.[1] Vanadium compounds have attracted scientific attention due to their potential therapeutic applications which may lead to the induction of apoptosis and finally to cell death. Dioxovanadium (V) and molybdenum (VI) complexes with various ligands in different solutions consisting of water + methanol as a solvent and at different ionic strengths have been investigated by our group.[2–10] In our recent paper the V (V) + IDA system has been studied at different ionic strengths of sodium perchlorate using Bronsted-Guggenheim-Scatchard specific ion interaction theory (SIT), extended Debye-Hückel type equation (EDH) and parabolic model.[2] Aminopolycarboxylic acids have a long history in chemistry and there is a vast range of publications due to the new applications in medicine, biology and industry in recent years.[11–14] These ligands chelate and stabilize VO_2^+ ion and other metals by forming stable complexes. Therefore in view of the relevance of vanadium compounds for both their biological and industrial applications, the present work investigates the variation of stability constant values in different aqueous solutions of methanol for the complexation of dioxovanadium (V) with iminodiacetic acid by using Kamlet-Abboud-Taft model. The stability of the complexes is the interesting parameter in this research. Solvating power is important for the estimation of the stability of the complexes. Existence of methanol can change the solvating power of the solvent. The correlation between solvating power of the solvent and the stability of the complexes in aqueous solutions of methanol will also be discussed.

2. Experimental and Methods

2. 1. Reagents

Double-distilled water with a specific conductance equal to (1.3 ± 0.1) μS.cm^{-1} was used to prepare the stock solutions.[15] A stock solution of vanadium(V) was prepared by dissolution of anhydrous sodium monovanadate in hydrochloric acid solution in order to prevent the formation of the decavanadate.[15] The solution stood overnight before use to obtain only the VO_2^+ ion and isopolyvanadates will not be formed or if small amounts still exist they will be decomposed.[15] All chemicals used were of analytical reagent grade. Iminodiacetic acid, ≥ 98% (Scheme I); sodium perclorate, ≥ 99.5%; hydrochloric acid, 37%; sodium hydroxide titrisol solution (1 mol dm^{-3}); sodium monovanadate anhydrous, minimum 99%; sodium carbonate anhydrous, 99.5%; potassium hydrogen carbonate, ≥ 99.5 % and perchloric acid, 60% were purchased from Merck and were used without further purification. Dilute perchloric acid solution was standardized against $KHCO_3$.[10] The NaOH solutions were prepared from titrisol solutions and their concentration was determined by several titrations with standard HCl.[15] The HCl solution was standardized with sodium carbonate solution.[15]



Scheme I The chemical structure of IDA

2. 2. Measurements

All measurements were carried out at $T = 298$ K and an ionic strength of 0.10 mol dm^{-3} sodium perchlorate.[10] A Metrohm pH-meter, 827, was used for pH measurements.[10] The hydrogen ion concentration was measured with a Metrohm combination electrode, model 6.0228.010.[10] A 0.01 mol dm^{-3} perchloric acid solution containing 0.09 mol dm^{-3} sodium perchlorate (for adjusting the ionic strength to 0.10 mol dm^{-3}) was employed as a standard solution of hydrogen ion concentration.[10] The change in liquid junction potential was calculated from Eq. 1:[10]

$$\text{pH(real)} = \text{pH (measured)} + a + b[H^+]\text{(measured)} \qquad (1)$$

a and *b* were determined by measurement of the hydrogen ion concentration for two different solutions of $HClO_4$ with sufficient $NaClO_4$ to adjust the ionic media.[10] Calibration of the glass electrode for different methanol mixtures has been done according to the literature.[10,16] Many glass electrodes show the theoretical response to hydrogen ion, at least up to alcohol concentrations near 90 weight percent.[16] There are several possible units for expressing acidity in alcohol-water solvents in terms of the experimental quantity (pH).[16] The $pa_H{}^*$ is related most directly to the experimental quantity by using the following equation:[16]

$$pa_H{}^* = pH - \delta \qquad (2)$$

$a_H{}^*$ is the hydrogen ion activity referred to the standard state in the mixed solvent.[16] The value of the quantity δ is substantially small (up to about 80 weight percent methanol) and constant for a solvent medium of given composition.[16] In this research the values of the experimental quantity (pH) were obtained in different methanol mixtures containing known concentrations of $HClO_4$ and $NaClO_4$ to give a constant ionic strength of 0.1 mol dm^{-3}.[10] The standard solutions of known $pa_H{}^*$ having the same solvent composition as the unknowns have been used to calculate values of the correction term δ.[10,16] Approximate $pa_H{}^*$ values can also be determined experimentally by using tabulated δ corrections in the literature.[16] There is good agreement between correction terms from our previous paper[10] with the literature values.[16] Spectrophotometric measurements were performed with a Varian Cary 300 UV-Vis spectrophotometer with a Pentium 4 computer between 245 nm and 280 nm in thermoregulated matched 10-mm quartz cells.[10] The measurement cell was of the flow type.[10] A Masterflux pump allowed circulation of the solution under study from the potentiometric cell to the spectrophotometric cell so the pH and absorbance of the solution could be measured simultaneously.[10]

Measurements have been done for different metal and ligand concentrations and ligand/metal molar ratios but a good fit and the speciation pattern and minimum error function have been obtained with $C_L = 1 \times 10^{-2}$ and $C_{VO2} = 1.0 \times 10^{-3}$ mol dm^{-3}. Therefore 50 cm^3 acidic solutions of dioxovanadium(V) (1.0×10^{-3} mol dm^{-3}) were titrated with basic solutions of iminodiacetic acid (1.0×10^{-2} mol dm^{-3}) at different volume fractions of methanol. The absorbance of the solution was measured after each addition and adjusting the pH.[10] According to the literature in acidic solution (pH < 3.00) and in the presence of a large excess of ligand, vanadium(V) exists as the $VO_2{}^+$ ion.[17] In all cases, the procedure was repeated at least three times and the resulting average values and corresponding deviations from the average are shown in the text and Tables.

3. Results and Discussion

3. 1. Complexation of Dioxovanadium (V) with IDA

Theory and calculation. The following equilibria were studied for L = IDA:

$$H_iL^{(n-i)-} \rightarrow H^+ + H_{i-1}L^{(n+1-i)-}$$
$$K_i = \frac{[H^+][H_{i-1}L^{(n+1-i)-}]}{[H_iL^{(n-i)-}]} \qquad (3)$$

Where L^{n-} represents the fully dissociated ligand anion. The values of the experimental, calculated and literature data for dissociation constants of IDA, were obtained at different volume fractions of methanol by using the potentiometric technique and the Microsoft Excel 2003 program[10,18] and the values are gathered in Tables 1 and

1S-5S. The experimental values of dissociation constants at 0% methanol have been taken from our previous published paper in Tables 1 and 1S-5S.[2]

Table 1. Average experimental and calculated values of log K_1 at $I = 0.10$ mol dm^{-3} of $NaClO_4$ and different aqueous solutions of CH_3OH for IDA, on the basis of one and three solvatochromic parameters, $T = 298$ K.

Methanol % (v/v)	**Exptl.**	**Calcd. (α)**	**log K_1** **Calcd. (β)**	**Calcd. (π*)**	**Calcd. (α, β, π*)**
0	2.47 ± 0.05[a]	2.53 ± 0.03	2.52 ± 0.03	2.52 ± 0.02	2.51 ± 0.02
5	2.61 ± 0.02	2.58 ± 0.03	2.57 ± 0.03	2.60 ± 0.02	2.60 ± 0.02
10	2.64 ± 0.03	2.62 ± 0.03	2.62 ± 0.03	2.62 ± 0.02	2.62 ± 0.02
15	2.67 ± 0.03	2.67 ± 0.03	2.67 ± 0.03	2.66 ± 0.02	2.66 ± 0.02
20	2.72 ± 0.04	2.72 ± 0.03	2.72 ± 0.03	2.72 ± 0.02	2.72 ± 0.02
25	2.78 ± 0.10	2.76 ± 0.03	2.77 ± 0.03	2.76 ± 0.02	2.76 ± 0.02
30	2.83 ± 0.04	2.81 ± 0.03	2.82 ± 0.03	2.82 ± 0.02	2.82 ± 0.02
35	2.86 ± 0.02	2.86 ± 0.03	2.87 ± 0.03	2.86 ± 0.02	2.86 ± 0.02
40	2.90 ± 0.01	2.91 ± 0.03	2.92 ± 0.03	2.92 ± 0.02	2.93 ± 0.02
45	2.98 ± 0.03	3.00 ± 0.03	2.97 ± 0.03	3.00 ± 0.02	2.98 ± 0.02
0	1.92 ± 0.04[b]				

[a] Literature data were taken from reference 2.
[b] Literature data were taken from reference 29. $I = 3.0$ mol dm^{-3} $NaClO_4$, $T = 298$ K

The general equation for the complex formation of dioxovanadium(V) with IDA is represented below:

$$pVO_2^{+} + qH^{+} + rL^{3-} \rightarrow (VO_2)_pH_qL_r^{(p+q-3r)}$$

$$\beta_{pqr} = \frac{[(VO_2)_pH_qL_r^{(p+q-3r)}]}{[VO_2^{+}]^p[H^{+}]^q[L^{3-}]^r} \qquad (4)$$

The absorbance data in the UV range (255 to 280) nm were collected for minimizing the error function on the basis of a Gauss-Newton nonlinear least squares method in the Microsoft Excel 2003 program based on the function $A = f(pH)$. The error function is defined as:[10]

$$U = \sum (A_{exp} - A_{cal})^2 \qquad (5)$$

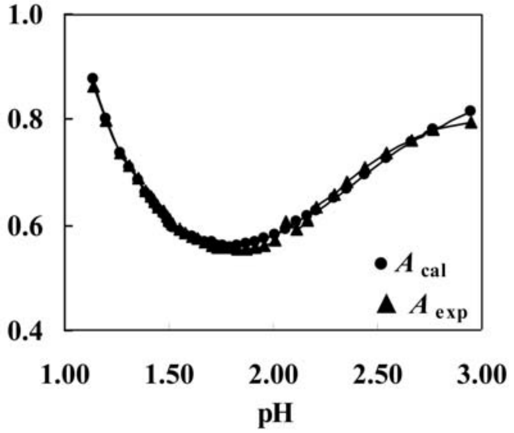


Figure 1. A_{exp} and A_{cal} values at $T = 298$ K, $I = 0.10$ mol dm^{-3}, 5% (v/v) and 270 nm for the model including VO_2H_2L and VO_2HL^{-}.

A_{exp} values have been gathered from the UV spectrophotometric measurements. In this research the best fit and minimum error function were obtained with the VO_2H_2L and VO_2HL^{-} species. A_{exp} and A_{cal} values at $T = 298$ K, $I = 0.1$ mol dm^{-3}, 5% (V/V) and 270 nm are shown in Fig. 1 which shows a very good graphical fit. Similar fits have been obtained for the other volume fractions of methanol. The speciation diagrams are shown in Fig. 2 for different volume fractions of methanol.

A_{cal} values have been determined from the combination of the following mass-balance and Beer-Lambert laws for our accepted model (L = IDA):

$$A = \varepsilon_0[VO_2^{+}] + \varepsilon_{VO_2H_2L}[VO_2H_2L] + \varepsilon_{VO_2HL^-}[VO_2HL^{-}] \qquad (6)$$

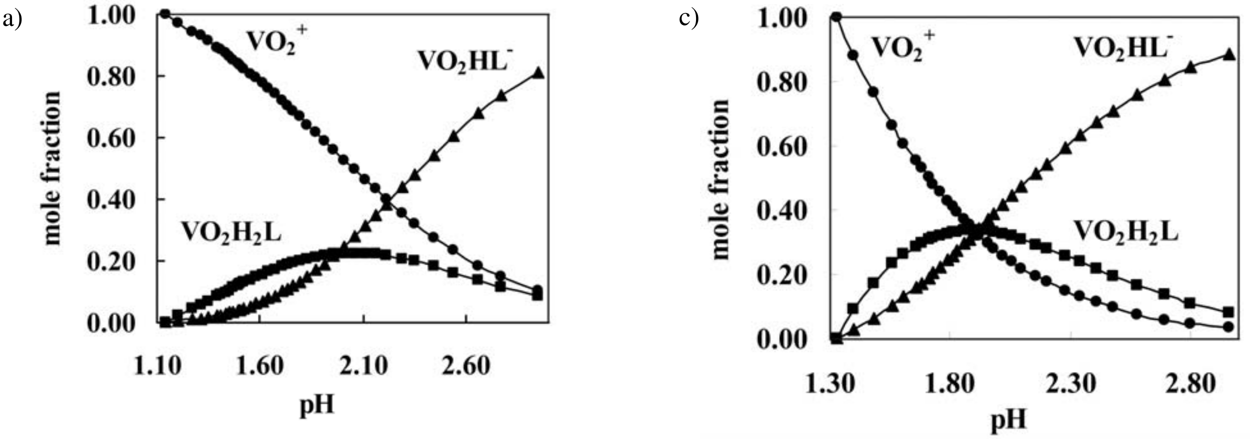
$$C_{VO_2^+} = [VO_2^{+}] + [VO_2H_2L] + [VO_2HL^{-}] \qquad (7)$$

$$\begin{gathered} C_L = [VO_2H_2L] + [VO_2HL^{-}] + [H_3L] + [H_2L^{-}] + [HL^{2-}] \\ VO_2^{+} + H_3L \rightarrow VO_2H_2L + H^{+} \end{gathered} \qquad (8)$$

$$\begin{gathered} K_{VO_2H_2L} = \frac{[VO_2H_2L][H^{+}]}{[VO_2^{+}][H_3L]} \\ VO_2H_2L \rightarrow VO_2HL^{-} + H^{+} \end{gathered} \qquad (9)$$

$$K_{VO_2HL^-} = \frac{[VO_2HL^{-}][H^{+}]}{[VO_2H_2L]} \qquad (10)$$

$C_{VO2}{}^{+}$ and C_L are the total concentration of VO_2^{+} and the ligand respectively. The average values of the experimental and calculated stability constants at various wavelengths are gathered in Table 2 and 6S-8S.



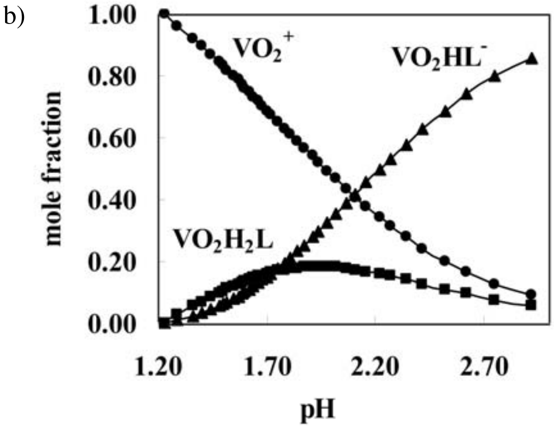


Figure 2. Distribution curves at T = 298 K, I = 0.10 mol dm^{-3} (a) 5% (b) 20 % and (c) 45 % (v/v) for the model including VO_2H_2L and VO_2HL^-. ($C_{VO2}{}^+ = 1.0 \times 10^{-3}$ and $C_L = 1 \times 10^{-2}$) mol dm^{-3}.

3. 2. Solvent Effect Study by Using Kamlet-Abboud-Taft Equation

The following multiparameter equation has been suggested for use in linear solvation energy relationships (LSER) by using the solvatochromic solvent parameters, α, β and π^*: [19–28]

$$\log K = A_0 + p(\pi^* + d\delta) + a\alpha + b\beta \tag{11}$$

A_0 is value for log K in setup when α, β, and π^* are equal to zero. In this work it is the logarithm of stability constant or dissociation constant. Dissociation constants from the literature are gathered in Tables 1, 2S and 4S.[29–32] Solvent effect, solvation and measurement of solvent physical properties has been the subject of several investigations. There are several interactions in the solution. All of the specific and non specific interactions can be defined as solvent polarity or solvation power. The famous specific interactions include different kinds of hydrogen bonding. All of the other interactions except hydrogen bonding have been classified as non specific interactions. π^* describes the solvent dipolarity/polarizability effects. The π^* values are from 0.00 for cyclohexane to 1.00 for dimethylsulfoxide.[19] The solvation parameters α and β describe the hydrogen bond interactions and represent the hydrogen-bond donor (HBD) and hydrogen-bond acceptor (HBA) properties of the solvents, respectively. The α values are from zero for non-HBD solvents to about 1.0 for methanol and the β-scale values are from zero for non-HBD solvents to about 1 for hexamethylphosphoric

Table 2. Average experimental and calculated values of log β_{121} at I = 0.10 mol dm^{-3} of $NaClO_4$ and different aqueous solutions of CH_3OH on the basis of one and three solvatochromic parameters, T = 298 K.

Methanol % (v/v)	**Exptl.**	**Calcd. (α)**	**log β_{121} Calcd. (β)**	**Calcd. (π^*)**	**Calcd. (α, β, π^*)**
0	15.10 ± 0.06	15.38 ± 0.14	15.33 ± 0.12	15.33 ± 0.13	15.29 ± 0.12
5	15.70 ± 0.04	15.61 ± 0.14	15.58 ± 0.12	15.72 ± 0.13	15.66 ± 0.12
10	15.96 ± 0.05	15.84 ± 0.14	15.82 ± 0.12	15.82 ± 0.13	15.81 ± 0.12
15	16.16 ± 0.04	16.07 ± 0.14	16.07 ± 0.12	16.01 ± 0.13	16.03 ± 0.12
20	16.30 ± 0.03	16.30 ± 0.14	16.31 ± 0.12	16.30 ± 0.13	16.32 ± 0.12
25	16.50 ± 0.09	16.53 ± 0.14	16.56 ± 0.12	16.49 ± 0.13	16.54 ± 0.12
30	16.75 ± 0.15	16.76 ± 0.14	16.80 ± 0.12	16.78 ± 0.13	16.83 ± 0.12
35	17.08 ± 0.07	16.99 ± 0.14	17.05 ± 0.12	16.98 ± 0.13	17.05 ± 0.12
40	17.32 ± 0.09	17.22 ± 0.14	17.29 ± 0.12	17.27 ± 0.13	17.34 ± 0.12
45	17.49 ± 0.06	17.68 ± 0.14	17.54 ± 0.12	17.66 ± 0.13	17.49 ± 0.12
0	15.00 ± 0.02[a]				

[a] Literature data were taken from reference 2

Table 3. Solvatochromic parameters for different aqueous solutions of methanol from the literature.[10]

Methanol % (v/v)	α	β	π^*
0	1.17	0.47	1.09
5	1.16	0.48	1.05
10	1.15	0.49	1.04
15	1.14	0.50	1.02
20	1.13	0.51	0.99
25	1.12	0.52	0.97
30	1.11	0.53	0.94
35	1.10	0.54	0.92
40	1.09	0.55	0.89
45	1.07	0.56	0.85

acid triamide (HMPT).[19] δ is a discontinuous polarizability correlation term equal to 0.0 for non-chloro substituted aliphatic solvents, 0.5 for poly-chloro-substituted aliphatics, and 1.0 for aromatic solvents.[19] In our research δ is equal to zero. The regression coefficients *p*, *d*, *a*, and *b* in Eq. 11 show the contribution of the abovementioned parameters to the values of dissociation and stability constants. The values of α, β and π^* for water + methanol solutions are gathered from literature in Table 3.[10] The intermolecular interaction types in the V(V) + iminodiacetic acid solutions have been established on the basis of one, two and three parameter linear regression analysis and the results are gathered in Table 4. The fitting coefficients obtained from this analysis allowed us to estimate the total stability constants in the studied solutions.

4. Conclusion

Comparison with literature data had been carried out with complete details in our previous published paper (on-

Table 4. Different KAT equations with one, two and three solvatochromic parameters together with their standard errors and square values of correlation coefficients (r^2) for dissociation and stability constants at $T = 298$ K, $I = 0.1$ mol dm^{-3} of $NaClO_4$ and different aqueous solutions of methanol, n = 10.

KAT equation	r^2
$\log K_1 = (8.06 \pm 0.32) - (4.72 \pm 0.28)\alpha$	0.97
$\log K_1 = (0.17 \pm 0.15) + (5.01 \pm 0.28)\beta$	0.98
$\log K_1 = (4.69 \pm 0.10) - (2.00 \pm 0.10)\pi^*$	0.98
$\log K_1 = (2.39 \pm 5.60) - (1.33 \pm 3.36)\alpha + (3.60 \pm 3.56)\beta$	0.98
$\log K_1 = (3.68 \pm 2.67) + (1.42 \pm 3.72)\alpha - (2.58 \pm 1.56)\pi^*$	0.98
$\log K_1 = (3.49 \pm 2.49) + (1.33 \pm 2.76)\beta - (1.46 \pm 1.10)\pi^*$	0.98
$\log K_1 = -(0.10 \pm 5.52) + (3.33 \pm 4.54)\alpha + (2.67 \pm 3.38)\beta - (2.33 \pm 1.64)\pi^*$	0.98
$\log K_2 = (10.06 \pm 0.48) - (6.10 \pm 0.42)\alpha$	0.96
$\log K_2 = -(0.13 \pm 0.23) + (6.46 \pm 0.45)\beta$	0.96
$\log K_2 = (5.72 \pm 0.14) - (2.58 \pm 0.14)\pi^*$	0.98
$\log K_2 = (4.78 \pm 8.77) - (2.94 \pm 5.26)\alpha + (3.36 \pm 5.57)\beta$	0.96
$\log K_2 = (0.82 \pm 3.15) + (6.84 \pm 4.40)\alpha - (5.45 \pm 1.84)\pi^*$	0.98
$\log K_2 = (7.40 \pm 3.37) - (1.87 \pm 3.74)\beta - (3.32 \pm 1.48)\pi^*$	0.98
$\log K_2 = -(0.90 \pm 6.79) + (7.72 \pm 5.58)\alpha + (1.22 \pm 4.16)\beta - (5.33 \pm 2.02)\pi^*$	0.98
$\log K_3 = (16.73 \pm 0.96) - (6.03 \pm 0.86)\alpha$	0.86
$\log K_3 = (6.61 \pm 0.42) + (6.47 \pm 0.82)\beta$	0.88
$\log K_3 = (12.42 \pm 0.35) - (2.53 \pm 0.36)\pi^*$	0.86
$\log K_3 = -(7.97 \pm 15.54) + (8.75 \pm 9.32)\alpha + (15.70 \pm 9.86)\beta$	0.90
$\log K_3 = (14.10 \pm 9.45) - (2.34 \pm 13.20)\alpha - (1.55 \pm 5.54)\pi^*$	0.86
$\log K_3 = (1.53 \pm 7.88) + (12.10 \pm 8.75)\beta + (2.24 \pm 3.47)\pi^*$	0.89
$\log K_3 = -(8.06 \pm 17.70) + (8.92 \pm 14.55)\alpha + (15.67 \pm 10.86)\beta - (0.08 \pm 5.26)\pi^*$	0.90
$\log \beta_{121} = (42.30 \pm 1.68) - (23.01 \pm 1.49)\alpha$	0.97
$\log \beta_{121} = (3.82 \pm 0.66) + (24.50 \pm 1.27)\beta$	0.98
$\log \beta_{121} = (25.89 \pm 0.56) - (9.68 \pm 0.58)\pi^*$	0.97
$\log \beta_{121} = -(8.50 \pm 25.03) + (7.39 \pm 15.01)\alpha + (32.29 \pm 15.88)\beta$	0.98
$\log \beta_{121} = (25.34 \pm 15.23) + (0.77 \pm 21.27)\alpha - (10.00 \pm 8.93)\pi^*$	0.97
$\log \beta_{121} = (7.31 \pm 12.46) + (20.63 \pm 13.82)\beta - (1.54 \pm 5.48)\pi^*$	0.98
$\log \beta_{121} = -(16.23 \pm 26.71) + (21.89 \pm 21.96)\alpha + (29.39 \pm 16.39)\beta - (7.25 \pm 7.93)\pi^*$	0.98
$\log \beta_{111} = (41.74 \pm 2.28) - (24.18 \pm 2.03)\alpha$	0.95
$\log \beta_{111} = (1.24 \pm 0.88) + (25.86 \pm 1.70)\beta$	0.97
$\log \beta_{111} = (24.47 \pm 0.82) - (10.16 \pm 0.84)\pi^*$	0.95
$\log \beta_{111} = -(37.66 \pm 30.78) + (23.33 \pm 18.46)\alpha + (50.47 \pm 19.53)\beta$	0.97
$\log \beta_{111} = (30.46 \pm 22.13) - (8.36 \pm 30.91)\alpha - (6.66 \pm 12.98)\pi^*$	0.95
$\log \beta_{111} = -(10.40 \pm 16.20) + (38.73 \pm 17.97)\beta + (5.13 \pm 7.13)\pi^*$	0.97
$\log \beta_{111} = -(39.79 \pm 34.94) + (27.33 \pm 28.74)\alpha + (49.67 \pm 21.44)\beta - (2.00 \pm 10.38)\pi^*$	0.97

ly one species, $VO_2H_2L^+$, was assumed based on two stoichiometric models)[2] which will not be repeated here again. It is important to note that the last data about the complex formation of VO_2^+ cation with IDA has been reported in the literature with the value of log $\beta_{101} = 11.70 \pm 0.20$ and log $\beta_{102} = 22.20 \pm 0.30$ at $I = 3.0$ mol dm^{-3} of sodium perchlorate and $T = 298$ K for 1:1 and 1:2 stoichiometries respectively without considering protonated species.[17] Once again it should be emphasized that the difference for the data at 0% methanol reported in this work with the literature[2,17] is due to the different method of calculation and concentration of metal, two species: VO_2H_2L, VO_2HL^- and range of pH in the present work. Therefore it is not possible to compare the results of this research with previous published data in the literature.[2,17] Comparison of the coefficients (Table 4) suggests that all of the stability constants values increase as the solvent becomes a better hydrogen-bond donor or acceptor and decrease as it becomes more polarizable. Increase in the hydrogen-bond acceptor basicity of the solvent, β, favors a higher thermodynamic stability of the products in comparison to the reactants and therefore we have an increase in the values of stability constants for the complex formation reaction between dioxovanadium(V) and IDA in various mixtures of water + methanol in this research. The large uncertainty in the coefficients (Table 4) are due to the fact that the solvatochromic KAT parameters (Table 3) are all relatively linear with the methanol composition. Although the solvatochromic KAT parameters are generally not correlated, the results of this research show that in the case of the methanol + water system, due to the correlation between parameters it was very difficult to determine the contribution of different KAT parameters for this complex formation reaction exactly. It can be concluded that there is an inverse relation between the solvating power of the solvent and the stability of the complexes in this research. Therefore the values of stability constants in the current work are higher than the values in pure aqueous solution.

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Povzetek

S pomočjo potenciometričnih meritev in UV spektroskopije smo raziskovali kompleksacijo dioksovanadija (V) z iminodiocetno kislino (IDA) ter konstante disociacije pri $T = 298$ K v raztopinah s konstantno ionsko močjo (0.1 mol dm^{-3} natrijevega perklorata) v mešanicah z metanolom (0 do 45 %). Z uporabo Kamlet-Abboud-Taft (KAT) solvatokromatske enačbe smo določili prispevke različnih interakcij med topljencem in topilom. Rezultate smo interpretirali na osnovi zmožnosti tvorbe vodikove vezi (donor-akceptor) in polarnosti topila.

Supporting information

Solvent Effect Investigation for the Dioxovanadium (V) Complexation with Iminodiacetic Acid on the Basis of the Kamlet-Abboud-Taft Equation

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Table 1S. Average experimental and calculated values of log K_1 at $I = 0.10$ mol dm $^{-3}$ of $NaClO_4$ and different aqueous solutions of CH_3OH for IDA, on the basis of two solvatochromic parameters, $T = 298$ K.

Methanol		**log K_1**		
% (v/v)	**Exptl.**	**Calcd. (α, β)**	**Calcd. (α, π^*)**	**Calcd. (β, π^*)**
0	2.47 ± 0.05	2.52 ± 0.03	2.52 ± 0.02	2.52 ± 0.02
5	2.61 ± 0.02	2.57 ± 0.03	2.61 ± 0.02	2.59 ± 0.02
10	2.64 ± 0.03	2.62 ± 0.03	2.62 ± 0.02	2.62 ± 0.02
15	2.67 ± 0.03	2.67 ± 0.03	2.66 ± 0.02	2.66 ± 0.02
20	2.72 ± 0.04	2.72 ± 0.03	2.72 ± 0.02	2.72 ± 0.02
25	2.78 ± 0.10	2.77 ± 0.03	2.76 ± 0.02	2.76 ± 0.02
30	2.83 ± 0.04	2.82 ± 0.02	2.82 ± 0.02	2.82 ± 0.02
35	2.86 ± 0.02	2.87 ± 0.03	2.86 ± 0.02	2.86 ± 0.02
40	2.90 ± 0.01	2.92 ± 0.03	2.92 ± 0.02	2.92 ± 0.02
45	2.98 ± 0.03	2.98 ± 0.03	3.00 ± 0.02	2.99 ± 0.02

Table 2S. Average experimental and calculated values of log K_2 at $I = 0.10$ mol dm^{-3} of $NaClO_4$ and different aqueous solutions of CH_3OH for IDA, on the basis of one and three solvatochromic parameters, $T = 298$ K.

Methanol			**log K_2**		
% (v/v)	**Exptl.**	**Calcd. (α)**	**Calcd. (β)**	**Calcd. (π^*)**	**Calcd. (α, β, π^*)**
0	2.86 ± 0.04^a	2.92 ± 0.04	2.91 ± 0.04	2.91 ± 0.03	2.89 ± 0.03
5	3.04 ± 0.01	2.98 ± 0.04	2.97 ± 0.04	3.01 ± 0.03	3.04 ± 0.03
10	3.05 ± 0.09	3.04 ± 0.04	3.04 ± 0.04	3.03 ± 0.03	3.03 ± 0.03
15	3.12 ± 0.02	3.10 ± 0.04	3.10 ± 0.04	3.09 ± 0.03	3.07 ± 0.03
20	3.16 ± 0.01	3.16 ± 0.04	3.17 ± 0.04	3.16 ± 0.03	3.17 ± 0.03
25	3.19 ± 0.03	3.22 ± 0.04	3.23 ± 0.04	3.22 ± 0.03	3.21 ± 0.03
30	3.30 ± 0.05	3.29 ± 0.04	3.30 ± 0.04	3.29 ± 0.03	3.30 ± 0.03
35	3.31 ± 0.04	3.35 ± 0.04	3.36 ± 0.04	3.34 ± 0.03	3.34 ± 0.03
40	3.46 ± 0.10	3.41 ± 0.04	3.43 ± 0.04	3.42 ± 0.03	3.44 ± 0.03
45	3.51 ± 0.09	3.53 ± 0.04	3.49 ± 0.04	3.53 ± 0.03	3.51 ± 0.03
0	2.77 ± 0.03^b 2.57^c 2.2.58^d				

[a] Literature data were taken from reference 2

[b] Literature data were taken from reference 29. $I = 3.0$ mol dm^{-3} $NaClO_4$, $T = 298$ K

[c] Literature data were taken from reference 30. $I = 0.5$ mol dm^{-3} $NaClO_4$

[d] Literature data were taken from reference 31. $I = 1$ mol dm^{-3} $NaClO_4$

Table 3S. Average experimental and calculated values of log K_2 at I = 0.10 mol dm $^{-3}$ of $NaClO_4$ and different aqueous solutions of CH_3OH for IDA, on the basis of two solvatochromic parameters, T = 298 K.

Methanol	log K_2			
% (v/v)	Exptl.	Calcd. (α, β)	Calcd. (α, π*)	Calcd. (β, π*)
0	2.86 ± 0.04	2.91 ± 0.04	2.89 ± 0.03	2.91 ± 0.03
5	3.04 ± 0.01	2.98 ± 0.04	3.04 ± 0.03	3.02 ± 0.03
10	3.05 ± 0.09	3.04 ± 0.04	3.03 ± 0.03	3.03 ± 0.03
15	3.12 ± 0.02	3.10 ± 0.04	3.07 ± 0.03	3.08 ± 0.03
20	3.16 ± 0.01	3.17 ± 0.04	3.16 ± 0.03	3.16 ± 0.03
25	3.19 ± 0.03	3.23 ± 0.04	3.21 ± 0.03	3.21 ± 0.03
30	3.30 ± 0.05	3.29 ± 0.04	3.30 ± 0.03	3.29 ± 0.03
35	3.31 ± 0.04	3.35 ± 0.04	3.34 ± 0.03	3.34 ± 0.03
40	3.46 ± 0.10	3.42 ± 0.04	3.44 ± 0.03	3.42 ± 0.03
45	3.51 ± 0.09	3.51 ± 0.04	3.52 ± 0.03	3.53 ± 0.03

Table 4S. Average experimental and calculated values of log K_3 at I = 0.10 mol dm^{-3} of $NaClO_4$ and different aqueous solutions of CH_3OH for IDA, on the basis of one and three solvatochromic parameters, T = 298 K.

Methanol	log K_3				
% (v/v)	Exptl.	Calcd. (α)	Calcd. (β)	Calcd. (π*)	Calcd. (α, β, π*)
0	9.50 ± 0.01[a]	9.67 ± 0.08	9.65 ± 0.08	9.66 ± 0.08	9.64 ± 0.08
5	9.73 ± 0.01	9.73 ± 0.08	9.72 ± 0.08	9.76 ± 0.08	9.71 ± 0.08
10	9.88 ± 0.01	9.79 ± 0.08	9.78 ± 0.08	9.78 ± 0.08	9.78 ± 0.08
15	9.93 ± 0.08	9.85 ± 0.08	9.85 ± 0.08	9.83 ± 0.08	9.85 ± 0.08
20	9.95 ± 0.02	9.91 ± 0.08	9.91 ± 0.08	9.91 ± 0.08	9.92 ± 0.08
25	9.97 ± 0.07	9.97 ± 0.08	9.98 ± 0.08	9.96 ± 0.08	9.99 ± 0.08
30	10.04 ± 0.03	10.03 ± 0.08	10.04 ± 0.08	10.04 ± 0.08	10.06 ± 0.08
35	10.12 ± 0.02	10.09 ± 0.08	10.11 ± 0.08	10.09 ± 0.08	10.13 ± 0.08
40	10.16 ± 0.10	10.15 ± 0.08	10.17 ± 0.08	10.16 ± 0.08	10.20 ± 0.08
45	10.18 ± 0.10	10.27 ± 0.08	10.24 ± 0.08	10.27 ± 0.08	10.18 ± 0.08
0	9.68 ± 0.05[b]				
	9.52 ± 0.02[c]				
	9.12[d]				
	9.29[e]				

[a] Literature data were taken from reference 2

[b] Literature data were taken from reference 29. I = 3.0 mol dm^{-3} $NaClO_4$, T = 298 K

[c] Literature data were taken from reference 32. I = 0.15 mol dm^{-3}, T = 298 K

[d] Literature data were taken from reference 30. I = 0.5 mol dm^{-3} $NaClO_4$

[e] Literature data were taken from reference 31. I = 1 mol dm^{-3} $NaClO_4$

Table 5S. Average experimental and calculated values of log K_3 at I = 0.10 mol dm $^{-3}$ of $NaClO_4$ and different aqueous solutions of CH_3OH for IDA, on the basis of two solvatochromic parameters, T = 298 K.

Methanol	**log K_3**			
% (v/v)	**Exptl.**	**Calcd. (α, β)**	**Calcd. (α, π*)**	**Calcd. (β, π*)**
0	9.50 ± 0.01	9.64 ± 0.08	9.66 ± 0.09	9.66 ± 0.08
5	9.73 ± 0.01	9.71 ± 0.08	9.75 ± 0.09	9.69 ± 0.08
10	9.88 ± 0.01	9.78 ± 0.08	9.79 ± 0.09	9.79 ± 0.08
15	9.93 ± 0.08	9.85 ± 0.08	9.84 ± 0.09	9.86 ± 0.08
20	9.95 ± 0.02	9.92 ± 0.08	9.91 ± 0.09	9.92 ± 0.08
25	9.97 ± 0.07	9.99 ± 0.08	9.96 ± 0.09	9.99 ± 0.08
30	10.04 ± 0.03	10.06 ± 0.08	10.03 ± 0.09	10.05 ± 0.08
35	10.12 ± 0.02	10.13 ± 0.08	10.09 ± 0.09	10.12 ± 0.08
40	10.16 ± 0.10	10.20 ± 0.08	10.16 ± 0.09	10.18 ± 0.08
45	10.18 ± 0.10	10.18 ± 0.08	10.27 ± 0.09	10.21 ± 0.08

Table 6S. Average experimental and calculated values of log β_{121} at I = 0.10 mol dm $^{-3}$ of $NaClO_4$ and different aqueous solutions of CH_3OH on the basis of two solvatochromic parameters, T = 298 K.

Methanol	**log β_{121}**			
% (v/v)	**Exptl.**	**Calcd. (α, β)**	**Calcd. (α, π*)**	**Calcd. (β, π*)**
0	15.10 ± 0.06	15.32 ± 0.12	15.33 ± 0.14	15.33 ± 0.12
5	15.70 ± 0.04	15.57 ± 0.12	15.72 ± 0.14	15.60 ± 0.12
10	15.96 ± 0.05	15.82 ± 0.12	15.82 ± 0.14	15.82 ± 0.12
15	16.16 ± 0.04	16.07 ± 0.12	16.01 ± 0.14	16.06 ± 0.12
20	16.30 ± 0.03	16.32 ± 0.12	16.30 ± 0.14	16.31 ± 0.12
25	16.50 ± 0.09	16.57 ± 0.12	16.49 ± 0.14	16.55 ± 0.12
30	16.75 ± 0.15	16.82 ± 0.12	16.79 ± 0.14	16.80 ± 0.12
35	17.08 ± 0.07	17.07 ± 0.12	16.98 ± 0.14	17.04 ± 0.12
40	17.32 ± 0.09	17.31 ± 0.12	17.27 ± 0.14	17.29 ± 0.12
45	17.49 ± 0.06	17.49 ± 0.12	17.66 ± 0.14	17.56 ± 0.12

Table 7S. Average experimental and calculated values of log β_{111} at I = 0.10 mol dm^{-3} of $NaClO_4$ and different aqueous solutions of CH_3OH on the basis of one and three solvatochromic parameters, T = 298 K.

Methanol	**log β_{111}**				
% (v/v)	**Exptl.**	**Calcd. (α)**	**Calcd. (β)**	**Calcd. (π*)**	**Calcd. (α, β, π*)**
0	13.07 ± 0.05	13.45 ± 0.20	13.40 ± 0.16	13.40 ± 0.19	13.35 ± 0.16
5	13.72 ± 0.02	13.69 ± 0.20	13.65 ± 0.16	13.81 ± 0.19	13.66 ± 0.16
10	14.06 ± 0.01	13.93 ± 0.20	13.91 ± 0.16	13.91 ± 0.19	13.90 ± 0.16
15	14.31 ± 0.03	14.17 ± 0.20	14.17 ± 0.16	14.11 ± 0.19	14.16 ± 0.16
20	14.51 ± 0.06	14.41 ± 0.20	14.43 ± 0.16	14.42 ± 0.19	14.45 ± 0.16
25	14.73 ± 0.08	14.66 ± 0.20	14.69 ± 0.16	14.62 ± 0.19	14.71 ± 0.16
30	14.89 ± 0.10	14.90 ± 0.20	14.95 ± 0.16	14.92 ± 0.19	14.99 ± 0.16
35	15.28 ± 0.15	15.14 ± 0.20	15.21 ± 0.16	15.13 ± 0.19	15.26 ± 0.16
40	15.45 ± 0.10	15.38 ± 0.20	15.46 ± 0.16	15.43 ± 0.19	15.54 ± 0.16
45	15.57 ± 0.05	15.86 ± 0.20	15.72 ± 0.16	15.84 ± 0.19	15.57 ± 0.16

Table 8S. Average experimental and calculated values of log β_{111} at $I = 0.10$ mol dm $^{-3}$ of $NaClO_4$ and different aqueous solutions of CH_3OH on the basis of two solvatochromic parameters, $T = 298$ K.

Methanol	**log β_{111}**			
% (v/v)	**Exptl.**	**Calcd. (α, β)**	**Calcd. (α, π^*)**	**Calcd. (β, π^*)**
0	13.07 ± 0.05	13.36 ± 0.15	13.42 ± 0.20	13.40 ± 0.16
5	13.72 ± 0.02	13.63 ± 0.15	13.77 ± 0.20	13.58 ± 0.16
10	14.06 ± 0.01	13.90 ± 0.15	13.92 ± 0.20	13.92 ± 0.16
15	14.31 ± 0.03	14.18 ± 0.15	14.13 ± 0.20	14.20 ± 0.16
20	14.51 ± 0.06	14.45 ± 0.15	14.42 ± 0.20	14.44 ± 0.16
25	14.73 ± 0.08	14.72 ± 0.15	14.63 ± 0.20	14.72 ± 0.16
30	14.89 ± 0.10	14.99 ± 0.15	14.92 ± 0.20	14.96 ± 0.16
35	15.28 ± 0.15	15.26 ± 0.15	15.13 ± 0.20	15.24 ± 0.16
40	15.45 ± 0.10	15.53 ± 0.15	15.42 ± 0.20	15.47 ± 0.16
45	15.57 ± 0.05	15.57 ± 0.15	15.85 ± 0.20	15.66 ± 0.16