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Calculation of the stability constants for complex formation of dioxovanadium(V) with methyliminodiacetic acid in various H₂O + CH₃OH solutions using the Kamlet–Abboud–Taft equation

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Abstract: The stability constants for the complex formation of VO₂⁺ with methyliminodiacetic acid (MIDA) were determined in this study for various volume fractions of methanol (0–45 %, v/v) at *T* = 298 K, *I* = 0.1 mol dm⁻³ (sodium perchlorate). Potentiometric and UV spectrophotometric methods were utilized for the collection of experimental data. Different species were investigated but the best model contained VO₂HL and VO₂L⁻ for the employed data treatment. One-, two- and three-parameter Kamlet–Abboud–Taft (KAT) equations were applied for the determination and calculation of the solvatochromic regression coefficients for the KAT models.

Keywords: vanadium(V); linear solvation energy relationships; solvent effects; methanol; methyliminodiacetic acid.

INTRODUCTION

Yamada and coworkers reported a value of the stability constant for the formation of only one species, VO₂L⁻ (L = MIDA) in the complexation of dioxovanadium(V) with MIDA at *I* = 1.0 mol dm⁻³ sodium perchlorate.¹ The present study was performed in H₂O + CH₃OH medium with the aim of comparing the results with those of a previously published paper obtained at different ionic strengths.² Vanadium(V) oxometalates have found application as analytical reagents for the determination of various pharmacologically active substances and biochemical parameters. The antitumoral effects of vanadium can be evaluated by the determination of different parameters, such as cell proliferation, morphology and disruption of cellular architecture. The biological effects of vanadium(V) vary greatly in different biological systems.³ Vanadium plays a catalytic role in metalloenzyme systems, such as nitrogenase and haloperoxi-

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dases.⁴ Aminopolycarboxylic acids complexes with metals are usually very stable and have been used in different fields, such as selective NMR line broadening, magnetic resonance imaging (MRI), chelation therapy and several other industrial applications.⁵ In the present study, the aim was to clarify the role of various specific and nonspecific interactions in solution by application of the KAT equation, similarly to previous reports concerning the complexation of dioxovanadium(V) and molybdenum(VI) with ethylene glycol bis(2-aminoethyl ether)-*N,N,N',N'*-tetraacetic acid (EGTA) and ethylenediamine-*N,N'*-diacetic acid (EDDA).⁶⁻⁸

EXPERIMENTAL

MIDA, 99 % (Fig. 1) was obtained from Aldrich. Sodium perchlorate, 99%; sodium hydroxide titrisol solution (1 mol dm⁻³); anhydrous sodium monovanadate, minimum 99%; sodium carbonate anhydrous, 99.5%; perchloric acid, 60%; potassium hydrogen carbonate \geq 99.5%; hydrochloric acid, 37% and methanol, 99.8% were purchased from Merck as analytical reagent grade materials. The chemicals were used as were received.

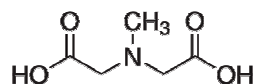


Fig. 1. The chemical structure of MIDA.

Anhydrous sodium monovanadate was dissolved in perchloric acid solution for the preparation of the vanadium(V) stock solution and prevention of decavanadate formation.⁹ Isopolyvanadates should not be present, therefore the solution was left overnight before use in order to obtain only the VO₂⁺.^{9,10} Titrisol solutions were used for the preparation of the NaOH solutions. Several titrations with standard HCl were performed to obtain their concentration. KHCO₃ and sodium carbonate solutions were used for the standardization of dilute perchloric and hydrochloric acids solutions, respectively. The specific conductance of the double-distilled water used for the preparation of the stock solutions was (1.3±0.1) μS cm⁻¹.

The medium for all measurements at $T = 298$ K had an ionic strength of 0.10 mol dm⁻³ of sodium perchlorate. The pH values were measured with a Metrohm pH-meter, 827. A Metrohm combination electrode, model 6.0228.010 was used for the hydrogen ion concentration measurements. A standard solution of hydrogen ion concentration was employed which consists of a 0.01 mol dm⁻³ perchloric acid solution, and 0.09 mol dm⁻³ sodium perchlorate for the ionic strength adjustment to 0.10 mol dm⁻³. The liquid junction potential was calculated using Eq. (1):⁶

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

Adjustment of the ionic medium was realized by hydrogen ion concentration measurement of two different solutions of HClO₄ with sufficient NaClO₄ and in this way, the values of a and b were obtained.⁶ Literature survey shows the glass electrode calibration for various methanol mixtures.^{6,11} For an aqueous methanol solution, the value of pH is denoted by B (which was measured using the pH meter) and the following equation shows its relation to the hydrogen ion concentration:⁶

$$-\log [\text{H}^+] = B + \log \mu_{\text{H}} \quad (2)$$

Different aqueous methanol solutions containing a known concentrations of sodium perchlorate and perchloric acid were used to maintain a constant ionic strength of 0.10 mol dm^{-3} and for the calculation of the B values.⁶ The values of the correction term $\log \mu_{\text{H}} = \log(\mu_{\text{H}}^0 \gamma_{+})$ were obtained based on the difference between the logarithm of known hydrogen ion concentrations and the corresponding values of B .⁶ The value of μ_{H}^0 is only dependent on the solvent composition.⁶ The mean activity coefficient of perchloric acid in the solvent mixtures is denoted by γ_{+} .⁶ Three titrations have been performed for each volume fraction of methanol and approximately 200 points were used in the calculations at each volume fraction of methanol.^{2,12}

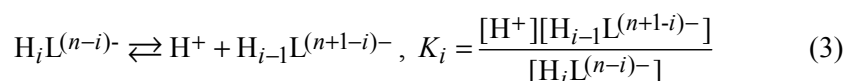
A flow type cell has been used for the spectrophotometric measurements, which were performed using a Varian Cary 300 UV-Vis spectrophotometer. The absorbance values were collected in the wavelength range 245–280 nm in a thermoregulated matched 10-mm quartz cells. The acquisition of the couple of data A versus λ (nm) was performed by means of the built in computer program of the UV-Vis spectrophotometer. Simultaneous measurement of pH and absorbance was enabled by using a Masterflux pump that circulated the solution between the potentiometric and spectrophotometric cells.

Different metal and ligand concentrations and ligand–metal mole ratios were tested and finally $c_{\text{L}} = 2.0 \times 10^{-2}$ and $c_{\text{VO}_2} = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ gave good fits and speciation patterns with minimum error functions. Thus, 50 ml acidic solutions of dioxovanadium(V) ($5.0 \times 10^{-4} \text{ mol dm}^{-3}$) were titrated with basic solutions of MIDA ($2.0 \times 10^{-2} \text{ mol dm}^{-3}$) at different volume fractions of methanol. The absorbance and pH of the solutions were measured simultaneously after each addition. VO_2^{+} is dominant when a large excess of ligand was present in the acidic solution ($\text{pH} < 3.0$).^{6,10} All experiments were repeated three times, and the average values of experimental dissociation and stability constants along with their deviations from the average are given.

RESULTS AND DISCUSSION

Dissociation constants

The two dissociation constants for MIDA are given by the following equilibria:



L^{2-} represents the fully deprotonated ligand. The values of the dissociation constants were obtained using the potentiometric technique and Microsoft Excel 2003 software.^{2,12} The experimental, calculated and literature data are gathered in Tables I–IV.^{2,5} The experimental data for 0 % methanol in the first lines of Tables I–IV were from the literature² but all the calculated values were obtained in this work based on the KAT equation, which will be discussed later.

Data treatment

Various stoichiometric models were investigated in order to find the best one. Finally, two species were identified that allowed the attainment of suitable fitting and distribution diagrams, similar to a previous work pertaining to complex formation of VO_2^{+} with MIDA at different ionic strengths.² The values of

stability constants can be calculated from the summation of dissociation and formation constants. The two equations for complex formation of dioxovanadium(V) with MIDA are represented below:

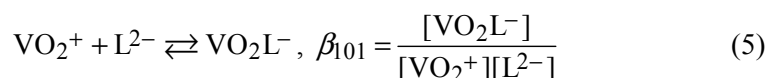
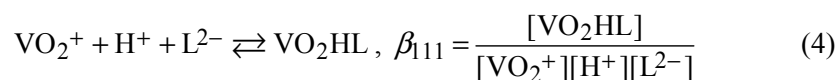


TABLE I. Average experimental and calculated values of $\log K_1$ at $I = 0.1 \text{ mol dm}^{-3}$ of NaClO_4 and different aqueous solutions of CH_3OH for MIDA, based on one and three solvatochromic parameters: α , hydrogen bond donor acidity; β , hydrogen bond acceptor basicity; π^* , dipolarity/polarizability. $T = 298 \text{ K}$

Methanol content % (v/v)	Experimental	Calculated			
		α	β	π^*	α, β, π^*
0	2.54±0.04	2.54±0.02	2.53±0.03	2.53±0.02	2.54±0.01
5	2.58±0.02	2.58±0.02	2.57±0.03	2.60±0.02	2.58±0.01
10	2.64±0.03	2.61±0.02	2.61±0.03	2.61±0.02	2.62±0.01
15	2.65±0.01	2.65±0.02	2.65±0.03	2.64±0.02	2.65±0.01
20	2.67±0.02	2.69±0.02	2.70±0.03	2.69±0.02	2.69±0.01
25	2.72±0.02	2.73±0.02	2.74±0.03	2.72±0.02	2.72±0.01
30	2.76±0.01	2.77±0.02	2.78±0.03	2.77±0.02	2.76±0.01
35	2.79±0.02	2.81±0.02	2.82±0.03	2.81±0.02	2.80±0.01
40	2.85±0.01	2.85±0.02	2.86±0.03	2.86±0.02	2.84±0.01
45	2.95±0.01	2.92±0.02	2.90±0.03	2.92±0.02	2.95±0.01
0	2.12±0.09 ^a	—	—	—	—
0	2.28±0.02 ^b	—	—	—	—
0	2.32±0.03 ^c	—	—	—	—
0	2.40±0.10 ^d	—	—	—	—

^a $I = 0.1 \text{ mol dm}^{-3}$ KCl, $T = 298 \text{ K}$; ^b $I = 0.5 \text{ mol dm}^{-3}$ NaClO_4 , $T = 298 \text{ K}$; ^c $I = 0.5 \text{ mol dm}^{-3}$ KNO_3 , $T = 298 \text{ K}$; ^d $I = 1.0 \text{ mol dm}^{-3}$ NaClO_4 , $T = 298 \text{ K}$ (a, b, c and d data were taken from the literature⁵)

The absorbance data in the UV range 255 to 280 nm were collected for minimizing the error function base on the Gauss–Newton nonlinear least squares method in the Microsoft Excel 2003 software based on the function $A = f(\text{pH})$. Error function calculation could be realized according to the following equation:²

$$U = \sum (A_{\text{exp}} - A_{\text{cal}})^2 \quad (6)$$

A_{exp} values were obtained from the UV spectrophotometric measurements at different pH values, wavelengths and volume fractions of methanol. A_{cal} values were determined for the model consisting of VO_2HL and VO_2L^- species. A_{exp} and A_{cal} values at $T = 298 \text{ K}$, $I = 0.10 \text{ mol dm}^{-3}$, 5 % volume fraction of methanol and 270 nm are shown in Fig. 2. After optimization of error function, the values of $U = 0.00243$ and standard error of y , $SE(y) = 0.00834$ were obtained for

Fig. 2, which shows a good fit. The other volume fractions of methanol showed similar fits.

TABLE II. Average experimental and calculated values of $\log K_1$ at $I = 0.1 \text{ mol dm}^{-3}$ of NaClO_4 and different aqueous solutions of CH_3OH for MIDA, based on two solvatochromic parameters: α , hydrogen bond donor acidity; β , hydrogen bond acceptor basicity; π^* , dipolarity/polarizability. $T = 298 \text{ K}$

Methanol content, % (v/v)	Experimental	Calculated		
		α, β	α, π^*	β, π^*
0	2.54±0.04	2.54±0.01	2.54±0.02	2.53±0.02
5	2.58±0.02	2.58±0.01	2.57±0.02	2.60±0.02
10	2.64±0.03	2.62±0.01	2.61±0.02	2.61±0.02
15	2.65±0.01	2.65±0.01	2.65±0.02	2.64±0.02
20	2.67±0.02	2.69±0.01	2.69±0.02	2.69±0.02
25	2.72±0.02	2.72±0.01	2.73±0.02	2.72±0.02
30	2.76±0.01	2.76±0.01	2.77±0.02	2.77±0.02
35	2.79±0.02	2.80±0.01	2.81±0.02	2.80±0.02
40	2.85±0.01	2.83±0.01	2.85±0.02	2.85±0.02
45	2.95±0.01	2.95±0.01	2.92±0.02	2.93±0.02

TABLE III. Average experimental and calculated values of $\log K_2$ at $I = 0.1 \text{ mol dm}^{-3}$ of NaClO_4 and different aqueous solutions of CH_3OH for MIDA, based on one and three solvatochromic parameters: α , hydrogen bond donor acidity; β , hydrogen bond acceptor basicity; π^* , dipolarity/polarizability. $T = 298 \text{ K}$

Methanol content % (v/v)	Experimental	Calculated			
		α	β	π^*	α, β, π^*
0	9.67±0.10	9.63±0.02	9.62±0.03	9.62±0.02	9.63±0.03
5	9.68±0.06	9.68±0.02	9.68±0.03	9.71±0.02	9.69±0.03
10	9.70±0.06	9.73±0.02	9.73±0.03	9.73±0.02	9.73±0.03
15	9.76±0.01	9.78±0.02	9.78±0.03	9.77±0.02	9.78±0.03
20	9.83±0.08	9.83±0.02	9.84±0.03	9.83±0.02	9.83±0.03
25	9.87±0.07	9.88±0.02	9.89±0.03	9.87±0.02	9.88±0.03
30	9.95±0.12	9.93±0.02	9.94±0.03	9.94±0.02	9.94±0.03
35	9.97±0.10	9.98±0.02	9.99±0.03	9.98±0.02	9.98±0.03
40	10.06±0.07	10.03±0.02	10.05±0.03	10.04±0.02	10.04±0.03
45	10.13±0.09	10.13±0.02	10.10±0.03	10.13±0.02	10.13±0.03
0	9.65±0.07 ^a	—	—	—	—
0	9.59±0.02 ^b	—	—	—	—
0	9.43±0.03 ^c	—	—	—	—
0	9.46±0.03 ^d	—	—	—	—
0	9.48±0.06 ^e	—	—	—	—

^a $I = 0.1 \text{ mol dm}^{-3} \text{ KCl}$, $T = 293 \text{ K}$; ^b $I = 0.1 \text{ mol dm}^{-3} \text{ KCl/KNO}_3$, $T = 298 \text{ K}$; ^c $I = 0.5 \text{ mol dm}^{-3} \text{ NaClO}_4$, $T = 298 \text{ K}$; ^d $I = 0.5 \text{ mol dm}^{-3} \text{ KNO}_3$, $T = 298 \text{ K}$; ^e $I = 1.0 \text{ mol dm}^{-3} \text{ NaClO}_4$, $T = 298 \text{ K}$ (a, b, c, d and e data were taken from the literature⁵)

The distribution diagrams are gathered in Fig. 3 for different volume fractions of methanol. The combination of the formation constants, mass-balance and

the Lambert–Beer law enabled the determination of the A_{cal} values for the model including VO_2HL and VO_2L^- ($\text{L} = \text{MIDA}$):²

$$A = \varepsilon_0[\text{VO}_2^+] + \varepsilon_{\text{VO}_2\text{HL}}[\text{VO}_2\text{HL}] + \varepsilon_{\text{VO}_2\text{L}^-}[\text{VO}_2\text{L}^-] \quad (7)$$

$$c_{\text{VO}_2^+} = [\text{VO}_2^+] + [\text{VO}_2\text{HL}] + [\text{VO}_2\text{L}^-] \quad (8)$$

$$c_{\text{L}} = [\text{VO}_2\text{HL}] + [\text{VO}_2\text{L}^-] + [\text{H}_2\text{L}] + [\text{HL}^-] \quad (9)$$

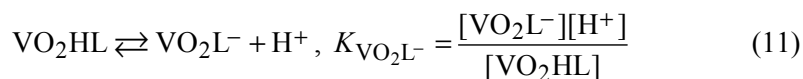
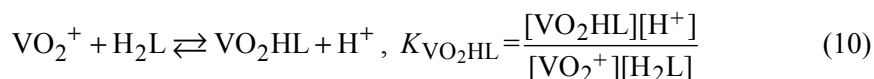


TABLE IV. Average experimental and calculated values of $\log K_2$ at $I = 0.1 \text{ mol dm}^{-3}$ of NaClO_4 and different aqueous solutions of CH_3OH for MIDA, based on two solvatochromic parameters: α , hydrogen bond donor acidity; β , hydrogen bond acceptor basicity; π^* , dipolarity/polarizability. $T = 298 \text{ K}$

Methanol content, % (v/v)	Experimental	Calculated		
		α, β	α, π^*	β, π^*
0	9.67±0.10	9.63±0.02	9.63±0.02	9.62±0.02
5	9.68±0.06	9.68±0.02	9.69±0.02	9.70±0.02
10	9.70±0.06	9.73±0.02	9.73±0.02	9.73±0.02
15	9.76±0.01	9.78±0.02	9.78±0.02	9.77±0.02
20	9.83±0.08	9.83±0.02	9.83±0.02	9.83±0.02
25	9.87±0.07	9.88±0.02	9.88±0.02	9.88±0.02
30	9.95±0.12	9.93±0.02	9.94±0.02	9.94±0.02
35	9.97±0.10	9.98±0.02	9.98±0.02	9.98±0.02
40	10.06±0.07	10.03±0.02	10.04±0.02	10.04±0.02
45	10.13±0.09	10.13±0.02	10.13±0.02	10.12±0.02

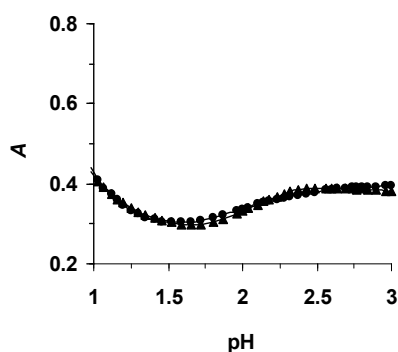


Fig. 2. A_{exp} and A_{cal} values at $T = 298 \text{ K}$, $I = 0.10 \text{ mol dm}^{-3}$, 5 % (v/v) and 270 nm. ●, A_{cal} ; ▲, A_{exp} for the model including VO_2HL , and VO_2L^- . $SE(y) = 0.00834$.

Comparison with literature data

Yamada and coworkers published the value of $\log \beta_{101} = 10.16 \pm 0.12$ at $I = 1.0 \text{ mol dm}^{-3}$ (NaClO_4) for the formation of only one species VO_2L^- .¹ On the

other hand, stability constants for the formation of two species, VO_2HL and VO_2L^- , at different ionic strengths of sodium perchlorate in the range of $0.1 < I < 1.0 \text{ mol dm}^{-3}$ was previously reported.² A difference exists between the stability constants data (Tables V and VII) at 0 % methanol reported in this work and those presented in the previously published paper ($1.00 < \text{pH} < 2.50$, $c_{\text{L}} = 5.18 \times 10^{-2}$ and $c_{\text{VO}_2^+} = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$), especially for the values of $\log \beta_{101}$ (Tables V and VII).² It seems that the main reason is due to the selection of different concentrations and pH range for the calculations, which was up to pH 3.00 in the current work. Values of $\log \beta_{111}$ and $\log \beta_{101}$ from the literature together with the results of the present work are gathered in Tables V and VII.

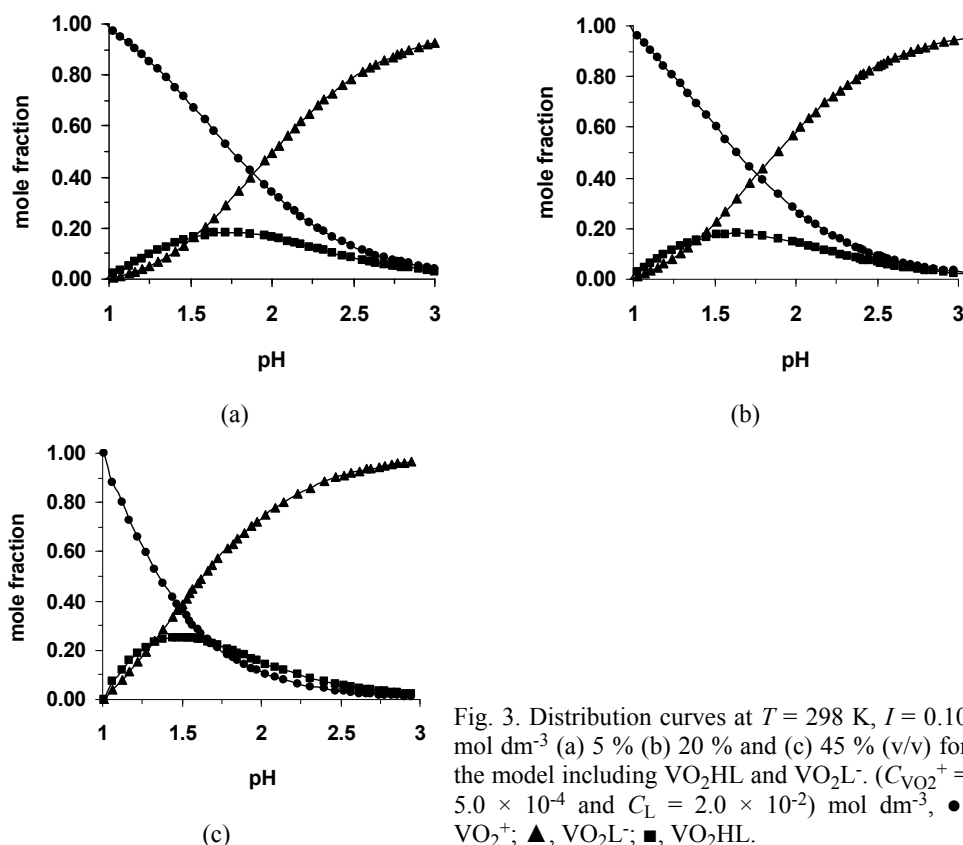


Fig. 3. Distribution curves at $T = 298 \text{ K}$, $I = 0.10 \text{ mol dm}^{-3}$ (a) 5 % (b) 20 % and (c) 45 % (v/v) for the model including VO_2HL and VO_2L^- . ($C_{\text{VO}_2^+} = 5.0 \times 10^{-4}$ and $C_{\text{L}} = 2.0 \times 10^{-2}$) mol dm^{-3} , ●, VO_2^+ ; ▲, VO_2L^- ; ■, VO_2HL .

Solvent effect investigation in the complex formation reaction using the KAT equation

The Kamlet–Abboud–Taft equation is a subset of linear solvation energy relationships (LSER), which has been used for the interpretation of different interactions in solution:^{13–37}

$$\log K = A_0 + p(\pi^* + d\delta) + a\alpha + b\beta \quad (12)$$

where A_0 is the value for $\log K$ in the setup when α , β , and π^* are all zero. α is the solvent hydrogen-bond donor (HBD) acidity. A solvent can give a proton to a solute and form a hydrogen bond. The α values are between zero for non-HBD solvents up to 1.0 for methanol.¹³ β is the solvent hydrogen-bond acceptor (HBA) basicity. A solvent can accept a proton from a solute during hydrogen bond formation. The β values vary from zero for non-HBA solvents up to 1 for hexamethylphosphoric acid triamide (HMPT).¹³ π^* is an index of the solvent dipolarity/polarizability. In other words, it is the capability of a solvent regarding charge, dipole and dielectric contributions. The π^* value is 0.00 and 1.00 for cyclohexane and dimethyl sulfoxide respectively.¹³ δ is discontinuous polarizability correlation term. The value of δ is 0.0 for non-chloro-substituted aliphatic solvents, 0.5 for poly-chloro-substituted aliphatics, and 1.0 for aromatic solvents.¹³ In the current work, δ is equal to zero.

TABLE V. Average experimental and calculated values of $\log \beta_{111}$ at $I = 0.1 \text{ mol dm}^{-3}$ of NaClO_4 and different aqueous solutions of CH_3OH for MIDA, based on one and three solvatochromic parameters: α , hydrogen bond donor acidity; β , hydrogen bond acceptor basicity; π^* , dipolarity/polarizability. $T = 298 \text{ K}$

Methanol content % (v/v)	Experimental	Calculated			
		α	β	π^*	α, β, π^*
0	12.50±0.04	12.43±0.07	12.41±0.06	12.40±0.07	12.41±0.07
5	12.60±0.10	12.60±0.07	12.58±0.06	12.68±0.07	12.61±0.07
10	12.75±0.06	12.77±0.07	12.76±0.06	12.75±0.07	12.76±0.07
15	12.87±0.04	12.94±0.07	12.94±0.06	12.90±0.07	12.93±0.07
20	13.01±0.20	13.10±0.07	13.12±0.06	13.11±0.07	13.11±0.07
25	13.25±0.02	13.27±0.07	13.29±0.06	13.25±0.07	13.28±0.07
30	13.51±0.10	13.44±0.07	13.47±0.06	13.46±0.07	13.46±0.07
35	13.69±0.10	13.61±0.07	13.65±0.06	13.60±0.07	13.63±0.07
40	13.82±0.15	13.77±0.07	13.82±0.06	13.81±0.07	13.81±0.07
45	14.04±0.10	14.11±0.07	14.00±0.06	14.09±0.07	14.04±0.07
0	12.79±0.15 ²	–	–	–	–

TABLE VI. Average experimental and calculated values of $\log \beta_{111}$ at $I = 0.1 \text{ mol dm}^{-3}$ of NaClO_4 and different aqueous solutions of CH_3OH for MIDA, based on two solvatochromic parameters: α , hydrogen bond donor acidity; β , hydrogen bond acceptor basicity; π^* , dipolarity/polarizability. $T = 298 \text{ K}$

Methanol content, % (v/v)	Experimental	Calculated		
		α, β	α, π^*	β, π^*
0	12.50±0.04	12.41±0.06	12.42±0.07	12.40±0.06
5	12.60±0.10	12.59±0.06	12.63±0.07	12.62±0.06
10	12.75±0.06	12.76±0.06	12.76±0.07	12.76±0.06
15	12.87±0.04	12.94±0.06	12.92±0.07	12.92±0.06
20	13.01±0.20	13.11±0.06	13.10±0.07	13.11±0.06

TABLE VI. Continued

Methanol content, % (v/v)	Experimental	Calculated		
		α, β	α, π^*	β, π^*
25	13.25±0.02	13.29±0.06	13.26±0.07	13.28±0.06
30	13.51±0.10	13.46±0.06	13.45±0.07	13.47±0.06
35	13.69±0.10	13.63±0.06	13.60±0.07	13.63±0.06
40	13.82±0.15	13.81±0.06	13.79±0.07	13.82±0.06
45	14.04±0.10	14.04±0.06	14.10±0.07	14.03±0.06

TABLE VII. Average experimental and calculated values of $\log \beta_{101}$ at $I = 0.1 \text{ mol dm}^{-3}$ of NaClO_4 and different aqueous solutions of CH_3OH for MIDA, based on one and three solvatochromic parameters: α , hydrogen bond donor acidity; β , hydrogen bond acceptor basicity; π^* , dipolarity/polarizability. $T = 298 \text{ K}$

Methanol content % (v/v)	Experimental	Calculated			
		α	β	π^*	α, β, π^*
0	10.96±0.10	10.90±0.09	10.86±0.07	10.86±0.09	10.86±0.08
5	11.08±0.20	11.09±0.09	11.07±0.07	11.18±0.09	11.10±0.08
10	11.27±0.10	11.28±0.09	11.27±0.07	11.26±0.09	11.27±0.08
15	11.45±0.05	11.47±0.09	11.47±0.07	11.42±0.09	11.46±0.08
20	11.57±0.20	11.66±0.09	11.68±0.07	11.66±0.09	11.67±0.08
25	11.77±0.20	11.85±0.09	11.88±0.07	11.83±0.09	11.87±0.08
30	12.06±0.30	12.04±0.09	12.08±0.07	12.07±0.09	12.08±0.08
35	12.33±0.20	12.24±0.09	12.28±0.07	12.23±0.09	12.28±0.08
40	12.58±0.10	12.43±0.09	12.49±0.07	12.47±0.09	12.49±0.08
45	12.70±0.10	12.81±0.09	12.69±0.07	12.79±0.09	12.70±0.08
0	11.74±0.25 ²	—	—	—	—
0	10.16±0.12 ^a	—	—	—	—

^a $I = 1.0 \text{ mol dm}^{-3} \text{ NaClO}_4$, $T = 298 \text{ K}$ (data were taken from the literature¹)

Different trends exist for the variation of solvatochromic parameters with the change in the concentration of various alcohols. Values of α , β and π^* for various aqueous solutions of methanol are listed in Table IX.⁶ The α and π^* values decrease but the β values increase with increasing methanol (Table IX). Several interactions exist in solution that are mainly classified as specific and non-specific interactions. All of these interactions can be defined as solvent polarity or solvation power. The famous specific interactions include different kinds of hydrogen bonding. All the other interactions except hydrogen bonding have been classified as non-specific interactions. The main intention of this work was to determine the contributions of different interactions by calculation of the regression coefficients a , b and p . Different one and two parameters KAT equations for the dissociation and stability constants are gathered in Table X.

TABLE VIII. Average experimental and calculated values of $\log \beta_{101}$ at $I = 0.1 \text{ mol dm}^{-3}$ of NaClO_4 and different aqueous solutions of CH_3OH for MIDA, based on two solvatochromic parameters: α , hydrogen bond donor acidity; β , hydrogen bond acceptor basicity; π^* , dipolarity/polarizability. $T = 298 \text{ K}$

Methanol content, % (v/v)	Experimental	Calculated		
		α, β	α, π^*	β, π^*
0	10.96±0.10	10.87±0.08	10.88±0.09	10.86±0.08
5	11.08±0.20	11.07±0.08	11.14±0.09	11.09±0.08
10	11.27±0.10	11.27±0.08	11.27±0.09	11.27±0.08
15	11.45±0.05	11.47±0.08	11.45±0.09	11.46±0.08
20	11.57±0.20	11.67±0.08	11.66±0.09	11.67±0.08
25	11.77±0.20	11.88±0.08	11.84±0.09	11.87±0.08
30	12.06±0.30	12.08±0.08	12.06±0.09	12.08±0.08
35	12.33±0.20	12.28±0.08	12.23±0.09	12.27±0.08
40	12.58±0.10	12.48±0.08	12.45±0.09	12.48±0.08
45	12.70±0.10	12.70±0.08	12.80±0.09	12.71±0.08

TABLE IX. Solvatochromic parameters for different aqueous solutions of methanol from the literature⁶

Methanol content, % (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

TABLE X. Different KAT equations with one and two solvatochromic parameters together with their standard errors and square values of the correlation coefficients (r^2) for the dissociation and stability constants at $T = 298 \text{ K}$, $I = 0.1 \text{ mol dm}^{-3}$ of NaClO_4 and different aqueous solutions of methanol: α , hydrogen bond donor acidity; β , hydrogen bond acceptor basicity; π^* , dipolarity/polarizability; $n = 10$

KAT Equation	r^2
$\log K_1 = (7.08 \pm 0.20) - (3.88 \pm 0.18)\alpha$	0.98
$\log K_1 = (0.62 \pm 0.15) + (4.07 \pm 0.29)\beta$	0.96
$\log K_1 = (4.30 \pm 0.08) - (1.63 \pm 0.09)\pi^*$	0.98
$\log K_1 = (13.86 \pm 2.79) - (7.94 \pm 1.67)\alpha - (4.31 \pm 1.77)\beta$	0.99
$\log K_1 = (7.22 \pm 1.99) - (4.08 \pm 2.77)\alpha + (0.08 \pm 1.16)\pi^*$	0.98
$\log K_1 = (5.68 \pm 2.07) - (1.53 \pm 2.30)\beta - (2.23 \pm 0.91)\pi^*$	0.98
$\log K_2 = (15.52 \pm 0.27) - (5.03 \pm 0.24)\alpha$	0.98
$\log K_2 = (7.13 \pm 0.15) + (5.31 \pm 0.29)\beta$	0.98
$\log K_2 = (11.92 \pm 0.10) - (2.11 \pm 0.10)\pi^*$	0.98
$\log K_2 = (14.54 \pm 5.13) - (4.44 \pm 3.07)\alpha + (0.62 \pm 3.25)\beta$	0.98

TABLE X. Continued

KAT Equation	r^2
$\log K_2 = (13.78 \pm 2.61) - (2.60 \pm 3.65)\alpha - (1.02 \pm 1.53)\pi^*$	0.98
$\log K_2 = (10.84 \pm 2.51) + (1.20 \pm 2.78)\beta - (1.64 \pm 1.10)\pi^*$	0.98
$\log \beta_{111} = (32.02 \pm 0.80) - (16.74 \pm 0.71)\alpha$	0.99
$\log \beta_{111} = (4.07 \pm 0.36) + (17.73 \pm 0.69)\beta$	0.99
$\log \beta_{111} = (20.06 \pm 0.30) - (7.02 \pm 0.31)\pi^*$	0.98
$\log \beta_{111} = (13.75 \pm 13.37) - (5.81 \pm 8.02)\alpha + (11.61 \pm 8.48)\beta$	0.99
$\log \beta_{111} = (27.45 \pm 7.69) - (10.34 \pm 10.75)\alpha - (2.69 \pm 4.51)\pi^*$	0.99
$\log \beta_{111} = (9.31 \pm 6.52) + (11.93 \pm 7.24)\beta - (2.31 \pm 2.87)\pi^*$	0.99
$\log \beta_{101} = (33.27 \pm 1.05) - (19.12 \pm 0.93)\alpha$	0.98
$\log \beta_{101} = (1.32 \pm 0.42) + (20.30 \pm 0.82)\beta$	0.99
$\log \beta_{101} = (19.61 \pm 0.38) - (8.03 \pm 0.39)\pi^*$	0.98
$\log \beta_{101} = (3.78 \pm 16.33) - (1.47 \pm 9.79)\alpha + (18.74 \pm 10.36)\beta$	0.99
$\log \beta_{101} = (26.35 \pm 10.02) - (9.42 \pm 14.00)\alpha - (4.08 \pm 5.88)\pi^*$	0.98
$\log \beta_{101} = (4.82 \pm 7.94) + (16.43 \pm 8.81)\beta - (1.54 \pm 3.49)\pi^*$	0.99

CONCLUSIONS

In general, it could be stated that increasing the methanol concentration (lower solvation and decrease in the polarity of the mixture) in the concentration range studied in this research cause an increase in the values of the dissociation and stability constants for the complexation of dioxovanadium(V) with aminopolycarboxylic acids. The standard errors for three parameters KAT equations were too high due to the strong intercorrelation of the methanol parameters. The standard errors for the two-parameter KAT equation in Table X are relatively high in comparison to those of the one parameter KAT equation. Therefore only one and two parameters KAT equations are presented in Table X. Although relatively good results were obtained with the one-parameter KAT equation, it could be concluded that KAT equation may not be applicable in the current research because the solvatochromic substances may be preferentially solvated to a greater or lesser degree than the substances involved in the studied chemical reaction. For the methanol + water system in the current work, it is very difficult to determine exactly the role of the KAT parameters because the variations in the stability and dissociation constants with the methanol concentration are linear and strong correlation exist for the KAT parameters.

ИЗВОД

ИЗРАЧУНАВАЊЕ КОНСТАНТИ СТАБИЛНОСТИ ЗА ФОРМИРАЊЕ КОМПЛЕКСА
ДИОКСОВАНАДИЈУМА(V) СА МЕТИЛИМИНОДИСИРЋЕТНОМ КИСЕЛИНОМ У
РАЗЛИЧИТИМ H₂O + CH₃OH РАСТВОРИМА КОРИШЋЕЊЕМ
КАМЛЕТ–АВБОУД–ТАФТ-ОВЕ ЈЕДНАЧИНЕ

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Константе стабилности за формирање комплекса VO₂⁺ са метилиминодисирћетном киселином (MIDA) су одређене у овом раду за различите запреминске уделе метанола (0–45 %, v/v) на T = 298 K, I = 0,1 mol dm⁻³ натријум-перхлората. Потенциометријска и УЉ спектрофотометријска метода су примењене за прикупљање података. Различите врсте су испитиване, а најбољи модел садржи VO₂HL и VO₂L⁻ (L = MIDA) за наш третман података. Једно-, дво- и тропараметарске Kamlet–Abboud–Taft-ове (КАТ) једначине су примењене за одређивање и израчунавање КАТ модела солватохромних регресионих коефицијената.

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