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# Solvatochromic Effect Studies on the Stability of Dioxovanadium(V) Complexes with Ethylene Glycol-bis(2-aminoethylether)-*N*,*N*,*N*′,*N*′-tetraacetic Acid in Different Water + Methanol Mixtures[†]

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The stability constants for the reaction of dioxovanadium(V) with ethylene glycol-bis(2-aminoethylether)-*N*,*N*,*N*′,*N*′-tetraacetic acid (EGTA) and the dissociation constants of EGTA were determined at 25 °C and a constant ionic strength of 0.05 $\text{mol}\cdot\text{dm}^{-3}$ sodium perchlorate in ten different compositions of water + methanol by a combination of potentiometric and UV spectrophotometric methods. The Solver, Microsoft Excel 2000 optimization package, has been used to perform nonlinear least-squares curve fitting on the basis of the Gauss−Newton method for calculation of the solvatochromic regression coefficients. Nonspecific and specific solute−solvent interactions were interpreted by correlating the equilibrium data with solvent parameters using the Kamlet−Abboud−Taft (KAT) solvatochromic equation. Finally, the influence of the solvent on the stability of the complex was discussed on the basis of the correlation results and the contribution of $\alpha$ (hydrogen-bond donor acidity), $\beta$ (hydrogen-bond acceptor basicity), and $\pi^*$ (dipolarity/polarizability) parameters.

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## Introduction

Vanadium is widely distributed in biological systems, and many applications for its pharmaceutical effect have been reported.[1] Ethylene glycol-bis(2-aminoethylether)-*N*,*N*,*N*′,*N*′-tetraacetic acid (EGTA) can be used as an anticoagulant when dissolved at 1 g per 100 mL of blood and chelates the calcium ion from blood.[2] EGTA serves as an effective inhibitor of metalloproteinases.[2,3]

Organic chemists have usually attempted to understand solvent effects in terms of the solvent polarity.[4] The concept of solvent polarity is easily understood qualitatively, but it is difficult to define exactly and even more difficult to express quantitatively. According to idealized theories, the solvent dielectric constant (i.e., the relative permittivity, $\varepsilon_r$) is often used as a quantitative measure of solvent polarity. Also, very often it has been found that there is no correlation between the relative permittivity (or its different functions such as $1/\varepsilon_r$, $(\varepsilon_r - 1)/(2\varepsilon_r + 1)$, etc.) and the logarithms of rate or equilibrium constants of solvent-dependent chemical reactions. On the other hand, solvent dipole moments are not sufficient for measuring the solvent polarity because the charge distribution of a solvent molecule may be given not only by its dipole moment but also by its quadrupole or higher multipole moments.[4] Therefore, it is stated that the polarity of a solvent is determined by its solvation capability (or solvation power) for reactants and activated complexes as well as for molecules in their ground and excited states.[5,6] Thus, solvation power depends on all specific and nonspecific intermolecular forces between solvent and solute molecules which include Coulomb interactions between ions, directional interactions between dipoles, inductive, dispersion, hydrogen bonding, and charge-transfer forces, as well as solvophobic interactions. Until now, the complexity of solute−solvent interactions prevented the derivation of generally applicable mathematical equations that make it feasible to calculate the reaction rates or equilibrium constants of reactions carried out in solvents at different polarity, but one of the well-known equations which works very well in this field is the Kamlet−Abboud−Taft equation (KAT). Although several multiparameter equations have been proposed, the KAT equation seems to be the most widely applied multiparameter approach. A literature survey reveals that in spite of several papers about application of the KAT equation[7−21] there are no reports on the complexation of dioxovanadium(V) with ethylene glycol-bis(2-aminoethylether)-*N*,*N*,*N*′,*N*′-tetraacetic acid (EGTA) in different aqueous solutions of methanol by using the KAT equation. The present study deals with the aforementioned system to investigate the contribution of the KAT parameters. The results have been also compared with similar aminopolycarboxylic acid complexes reported and interpreted.

## Experimental Section

***Reagents.*** All chemicals were analytical reagent grade. Perchloric acid, sodium hydroxide, potassium hydrogen carbonate, sodium perchlorate, hydrochloric acid, sodium carbonate, sodium monovanadate, and methanol were purchased from Merck, and EGTA was purchased from Fluka. All were used without further purification. The NaOH solutions were prepared from titrisol solutions, and their concentration was determined by several titrations with standard HCl. The HCl solution was standardized with sodium carbonate solution ($Na_2CO_3$). Dilute perchloric acid solution was standardized against $KHCO_3$. A stock solution of vanadium(V) was prepared by dissolution of anhydrous sodium monovanadate in perchloric acid solution affecting the destruction of the decavanadate.[22] The solution stood overnight before use to obtain only the $VO_2^+$ ion. Isopolyvanadates will not be formed, or if small amounts still exist they will be decomposed.[22] In all experiments, double-distilled water with a specific conductance equal to $(1.3 \pm 0.1)\ \mu\text{S}\cdot\text{cm}^{-1}$ was used.

***Measurements.*** All measurements were carried out at $T = 298$ K and an ionic strength of 0.05 $\text{mol}\cdot\text{dm}^{-3}$ sodium perchlorate. A Metrohm pH-meter, 827, was used for pH measurements. The hydrogen ion concentration was measured with a Metrohm

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combination electrode, model 6.0228.010. A 0.01 $mol \cdot dm^{-3}$ perchloric acid solution containing 0.04 $mol \cdot dm^{-3}$ sodium perchlorate (for adjusting the ionic strength to 0.05 $mol \cdot dm^{-3}$) was employed as a standard solution of hydrogen ion concentration. The calibration was done for the whole pH ($pH = -\log[H^+]$) range used. The change in liquid junction potential[22] was calculated from eq 1

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

$a$ 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.[22] Spectrophotometric measurements were performed with a Varian Cary 300 UV−vis spectrophotometer with a Pentium 4 computer between (245 and 280) nm in thermoregulated matched 10-mm quartz cells.[22] The measurement cell was of the flow type.[22] 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.[22] Calibration of the glass electrode for different methanol mixtures has been done according to the literature.[23,24] $B$ is the value from the pH meter for a methanol mixture and is related to $[H^+]$ by using the following equation

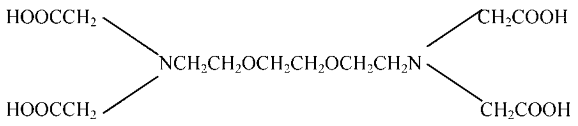
$$-\log[H^+] = B + \log \mu_H \tag{2}$$

In this research, the values of $B$ were obtained in different methanol mixtures containing known concentrations of HCl and $NaClO_4$ to give a constant ionic strength of 0.05 $mol \cdot dm^{-3}$.[23] The difference between the logarithm of known hydrogen ion concentrations and the corresponding values of $B$ was used to calculate values of the correction term $\log \mu_H = \log(\mu_H{}^0 \gamma_+)$.[23] The value of $\mu_H{}^0$ is independent of ionic concentration but is dependent on solvent composition. $\gamma_+$ is the mean activity coefficient of perchloric acid in the solvent mixtures.[23]

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 $C_L = 8.1 \cdot 10^{-4}$ and $C_{VO2} = 6.0 \cdot 10^{-4}$ $mol \cdot dm^{-3}$. Therefore, 50 $cm^3$ acidic solutions of dioxovanadium(V) ($6.0 \cdot 10^{-4}$ $mol \cdot dm^{-3}$) were titrated with basic solutions of EGTA ($8.1 \cdot 10^{-4}$ $mol \cdot dm^{-3}$) at different volume fractions of methanol. The absorbance of the solution was measured after each addition and adjusting the pH. According to the literature,[22,25] in acidic solution (pH < 2.5) and in the presence of a large excess of ligand, vanadium(V) exists as the $VO_2^+$ ion. Therefore, the pH range was 1.00 to 2.50. In all cases, the procedure was repeated at least three times, and the resulting average values and corresponding standard deviations are shown in the text and tables.

## Results and Discussion

***Complexation of Dioxovanadium(V) with EGTA. Theory and Calculation.*** The chemical structure of EGTA is shown below:



Four values of dissociation constants of EGTA have been used in this research according to the following equilibria

$$H_4L \rightleftharpoons H^+ + H_3L^- \qquad K_1 = \frac{[H^+][H_3L^-]}{[H_4L]} \tag{3}$$

$$H_3L^- \rightleftharpoons H^+ + H_2L^{2-} \qquad K_2 = \frac{[H^+][H_2L^{2-}]}{[H_3L^-]} \tag{4}$$

$$H_2L^{2-} \rightleftharpoons H^+ + HL^{3-} \qquad K_3 = \frac{[H^+][HL^{3-}]}{[H_2L^{2-}]} \tag{5}$$

$$HL^{3-} \rightleftharpoons H^+ + L^{4-} \qquad K_4 = \frac{[H^+][L^{4-}]}{[HL^{3-}]} \tag{6}$$

The values of the dissociation constants which were obtained by using the potentiometric technique and the Microsoft Excel 2000 program[23] are gathered in Table 1 together with literature values. Three titrations have been done for different volume fractions of methanol, and approximately 200 points have been used in the calculations at each volume fraction.[23]

***Speciation Studies.*** Different stoichiometric models were studied as follows:

(a) Although a good fit and speciation diagram were obtained by assuming only one deprotonated species, $VO_2L^{3-}$, and even the error function was lower than the main model, it was not preferred (which will be discussed later in the Conclusion section)

$$\begin{array}{l} VO_2^+ + H_4L \rightleftharpoons VO_2L^{3-} + 4H^+ \\ H^+ + H_3L^- \rightleftharpoons H_4L \\ H^+ + H_2L^{2-} \rightleftharpoons H_3L^- \\ H^+ + HL^{3-} \rightleftharpoons H_2L^{2-} \\ H^+ + L^{4-} \rightleftharpoons HL^{3-} \\ \hline VO_2^+ + L^{4-} \rightleftharpoons VO_2L^{3-} \end{array} \tag{7}$$

$$\beta'_{101} = \frac{[VO_2L^{3-}]}{[VO_2{}^+][L^{4-}]} \tag{8}$$

(b) We have assumed the $VO_2H_4L^+$ and $VO_2H_3L$ species on the basis of the following reactions and the ligand as $H_4L$

$$\begin{array}{l} VO_2^+ + H_4L \rightleftharpoons VO_2H_4L^+ \\ H^+ + H_3L^- \rightleftharpoons H_4L \\ H^+ + H_2L^{2-} \rightleftharpoons H_3L^- \\ H^+ + HL^{3-} \rightleftharpoons H_2L^{2-} \\ H^+ + L^{4-} \rightleftharpoons HL^{3-} \\ \hline VO_2^+ + 4H^+ + L^{4-} \rightleftharpoons VO_2H_4L^+ \end{array} \tag{9}$$

$$\beta_{141} = \frac{[\mathrm{VO_2H_4L^+}]}{[\mathrm{VO_2}^+][\mathrm{H}^+]^4[\mathrm{L}^{4-}]} \tag{10}$$

$$\begin{array}{l}
\mathrm{VO_2^+ + H_4L \rightleftharpoons VO_2H_4L^+} \\
\mathrm{VO_2H_4L^+ \rightleftharpoons VO_2H_3L + H^+} \\
\mathrm{H^+ + H_3L^- \rightleftharpoons H_4L} \\
\mathrm{H^+ + H_2L^{2-} \rightleftharpoons H_3L^-} \\
\mathrm{H^+ + HL^{3-} \rightleftharpoons H_2L^{2-}} \\
\mathrm{H^+ + L^{4-} \rightleftharpoons HL^{3-}} \\
\hline
\mathrm{VO_2^+ + 3H^+ + L^{4-} \rightleftharpoons VO_2H_3L}
\end{array} \tag{11}$$

$$\beta'_{131} = \frac{[\mathrm{VO_2H_3L}]}{[\mathrm{VO_2}^+][\mathrm{H}^+]^3[\mathrm{L}^{4-}]} \tag{12}$$

This model was not acceptable due to unsuitable fitting and speciation.

(c)

$$\begin{array}{l}
\mathrm{VO_2^+ + H_4L \rightleftharpoons VO_2H_3L + H^+} \\
\mathrm{VO_2H_3L \rightleftharpoons VO_2H_2L^- + H^+} \\
\mathrm{VO_2H_2L^- \rightleftharpoons VO_2HL^{2-} + H^+} \\
\mathrm{VO_2HL^{2-} \rightleftharpoons VO_2L^{3-} + H^+}
\end{array}$$

A good fit and speciation diagram were not obtained for the simultaneous presence of four species according to this model.

(d) Assuming three species, $VO_2H_3L$, $VO_2H_2L^-$, and $VO_2HL^{2-}$, was also rejected on the basis of speciation and fitting diagrams.

***Calculations.*** Stability constants were derived from the summation of dissociation and formation constant values. Our accepted model is based on the following reactions

$$\begin{array}{l}
\mathrm{VO_2^+ + H_4L \rightleftharpoons VO_2H_3L + H^+} \\
\mathrm{H^+ + H_3L^- \rightleftharpoons H_4L} \\
\mathrm{H^+ + H_2L^{2-} \rightleftharpoons H_3L^-} \\
\mathrm{H^+ + HL^{3-} \rightleftharpoons H_2L^{2-}} \\
\mathrm{H^+ + L^{4-} \rightleftharpoons HL^{3-}} \\
\hline
\mathrm{VO_2^+ + 3H^+ + L^{4-} \rightleftharpoons VO_2H_3L}
\end{array} \tag{13}$$

$$\beta_{131} = \frac{[\mathrm{VO_2H_3L}]}{[\mathrm{VO_2}^+][\mathrm{H}^+]^3[\mathrm{L}^{4-}]} \tag{14}$$

$$\begin{array}{l}
\mathrm{VO_2^+ + H_4L \rightleftharpoons VO_2H_3L + H^+} \\
\mathrm{VO_2H_3L \rightleftharpoons VO_2H_2L^- + H^+} \\
\mathrm{H^+ + H_3L^- \rightleftharpoons H_4L} \\
\mathrm{H^+ + H_2L^{2-} \rightleftharpoons H_3L^-} \\
\mathrm{H^+ + HL^{3-} \rightleftharpoons H_2L^{2-}} \\
\mathrm{H^+ + L^{4-} \rightleftharpoons HL^{3-}} \\
\hline
\mathrm{VO_2^+ + 2H^+ + L^{4-} \rightleftharpoons VO_2H_2L^-}
\end{array} \tag{15}$$

$$\beta_{121} = \frac{[\mathrm{VO_2H_2L^-}]}{[\mathrm{VO_2}^+][\mathrm{H}^+]^2[\mathrm{L}^{4-}]} \tag{16}$$

The absorbance data in the UV range (255 to 280) nm were used for minimizing the error function on the basis of a Gauss−Newton nonlinear least-squares method in the Microsoft Excel 2000 program according to the function $A = f(\mathrm{pH})$. The error function is defined as[1,22]

$$U = \sum (A_{\mathrm{exp}} - A_{\mathrm{cal}})^2 \tag{17}$$

$A_{\mathrm{exp}}$ values have been gathered from the UV spectrophotometric measurements and are reported at different pH and wavelengths in Tables A1 to A10 as Supporting Information. $A_{\mathrm{cal}}$ values have been obtained for the accepted model which was discussed above. Species having no significant effect on the statistical fit were neglected. The concentration of the complexes contributing to the general species distribution in our experimental conditions was calculated by the Microsoft Excel 2000 program. Complexes with negligible concentrations over the entire range of experimental conditions are not taken into account in our proposed results. Finally, the best fit and minimum error function were obtained

**Table 1. Dissociation Constants $K_4$, $K_3$, $K_2$, and $K_1$ of EGTA in Different Aqueous Solutions of Methanol at $I = 0.05\ \mathrm{mol \cdot dm^{-3}}$ of $NaClO_4$ and $T = 298$ K**

| methanol % (v/v) | log $K_4$ | log $K_3$ | log $K_2$ | log $K_1$ | ref |
|---|---|---|---|---|---|
| 0 | 9.41 ± 0.20 | 8.53 ± 0.11 | 2.68 ± 0.15 | 2.09 ± 0.10 | this work |
| 5 | 9.48 ± 0.13 | 8.61 ± 0.20 | 2.71 ± 0.10 | 2.13 ± 0.25 | this work |
| 10 | 9.57 ± 0.19 | 8.66 ± 0.14 | 2.75 ± 0.13 | 2.19 ± 0.14 | this work |
| 15 | 9.65 ± 0.10 | 8.75 ± 0.25 | 2.81 ± 0.26 | 2.23 ± 0.12 | this work |
| 20 | 9.71 ± 0.25 | 8.83 ± 0.10 | 2.85 ± 0.15 | 2.30 ± 0.20 | this work |
| 25 | 9.79 ± 0.18 | 8.90 ± 0.19 | 2.88 ± 0.12 | 2.34 ± 0.10 | this work |
| 30 | 9.86 ± 0.23 | 8.99 ± 0.12 | 2.92 ± 0.20 | 2.39 ± 0.15 | this work |
| 35 | 9.97 ± 0.10 | 9.09 ± 0.20 | 2.94 ± 0.10 | 2.47 ± 0.20 | this work |
| 40 | 10.09 ± 0.27 | 9.22 ± 0.09 | 2.99 ± 0.10 | 2.58 ± 0.10 | this work |
| 45 | 10.22 ± 0.25 | 9.33 ± 0.10 | 3.05 ± 0.20 | 2.68 ± 0.17 | this work |
| 0 | 9.51 | 8.92 | 2.82 | 2.46 | 34[a] |
| 0 | 9.54 | 8.93 | 2.73 | 2.08 | 35[b] |
| 0 | 9.53 | 8.88 | – | – | 36[c] |
| 0 | 9.46 | 8.85 | 2.65 | 2.0 | 37[d] |
| 0 | 9.60 | 8.79 | 2.67 | 2.04 | 38[e] |
| 0 | 9.22 | 8.39 | 2.49 | 2.01 | 38[f] |
| 0 | 8.89 | 8.40 | 2.50 | 0.93 | 38[g] |

[a] 0.1 $KNO_3$. [b] 0.1 $KNO_3$. [c] 0.1 KCl. [d] 0.1 $KNO_3$, $T = 293$ K. [e] 0.1 NaCl. [f] 0.5 NaCl. [g] 0.5 $NaClO_4$.

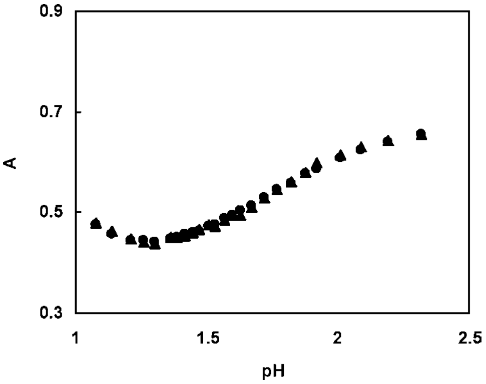
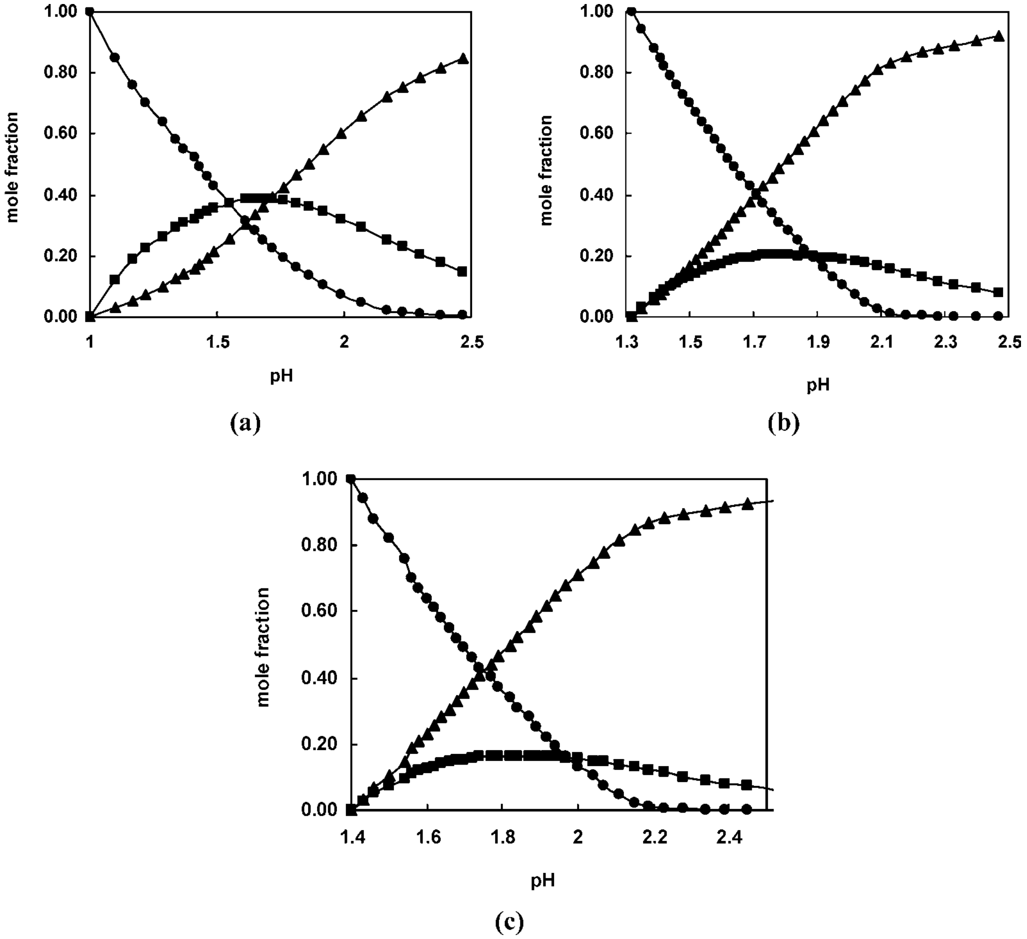


**Figure 1.** $A_{\mathrm{exp}}$ and $A_{\mathrm{cal}}$ values at $T = 298$ K, $I = 0.05\ \mathrm{mol \cdot dm^{-3}}$, 5 % (v/v), and 270 nm. ●, $A_{\mathrm{cal}}$; ▲, $A_{\mathrm{exp}}$ for the model including $VO_2H_3L$ and $VO_2H_2L^-$.



(a) (b)

(c)

**Figure 2.** Speciation diagrams at $T = 298$ K, $I = 0.05$ mol·dm$^{-3}$, and (a) 0 %, (b) 20 %, and (c) 40 % (v/v) for the model including $VO_2H_3L$ and $VO_2H_2L^-$. $C_{VO_2^+} = 6.0 \cdot 10^{-4}$ mol·dm$^{-3}$ and $C_L = 8.1 \cdot 10^{-4}$ mol·dm$^{-3}$. ●, $VO_2^+$; ▲, $VO_2H_2L^-$; ■, $VO_2H_3L$.

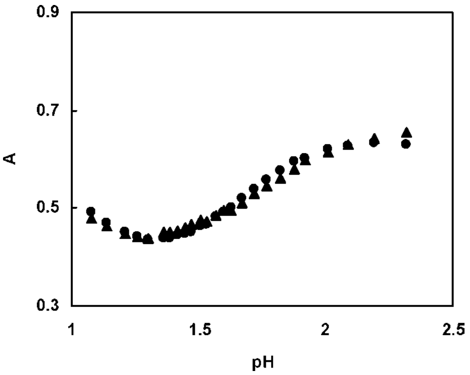


**Figure 3.** $A_{exp}$ and $A_{cal}$ values at $T = 298$ K, $I = 0.05$ mol·dm$^{-3}$, 5 % (v/v), and 270 nm. ●, $A_{cal}$; ▲, $A_{exp}$ for the model including only $VO_2L^{3-}$.

with the $VO_2H_3L$ and $VO_2H_2L^-$ species. $A_{exp}$ and $A_{cal}$ values at $T = 298$ K, $I = 0.05$ mol·dm$^{-3}$, 5 % volume faction of methanol, and 270 nm are shown in Figures 1 and 3 for protonated and deprotonated species which shows a very good graphical fit. Similar fits have been obtained for the other volume fractions. The chosen model is also in close agreement with experimental data. The speciation diagrams are shown in Figures 2 and 4 for protonated and deprotonated species and 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 = EGTA)

$$A = \varepsilon_0[VO_2^+] + \varepsilon_{VO_2H_3L}[VO_2H_3L] + \varepsilon_{VO_2H_2L^-}[VO_2H_2L^-] \tag{18}$$

$$C_{VO_2^+} = [VO_2^+] + [VO_2H_3L] + [VO_2H_2L^-] \tag{19}$$

$$C_L = [VO_2H_3L] + [VO_2H_2L^-] + [H_4L] + [H_3L^-] + [H_2L^{2-}] + [HL^{3-}] \tag{20}$$

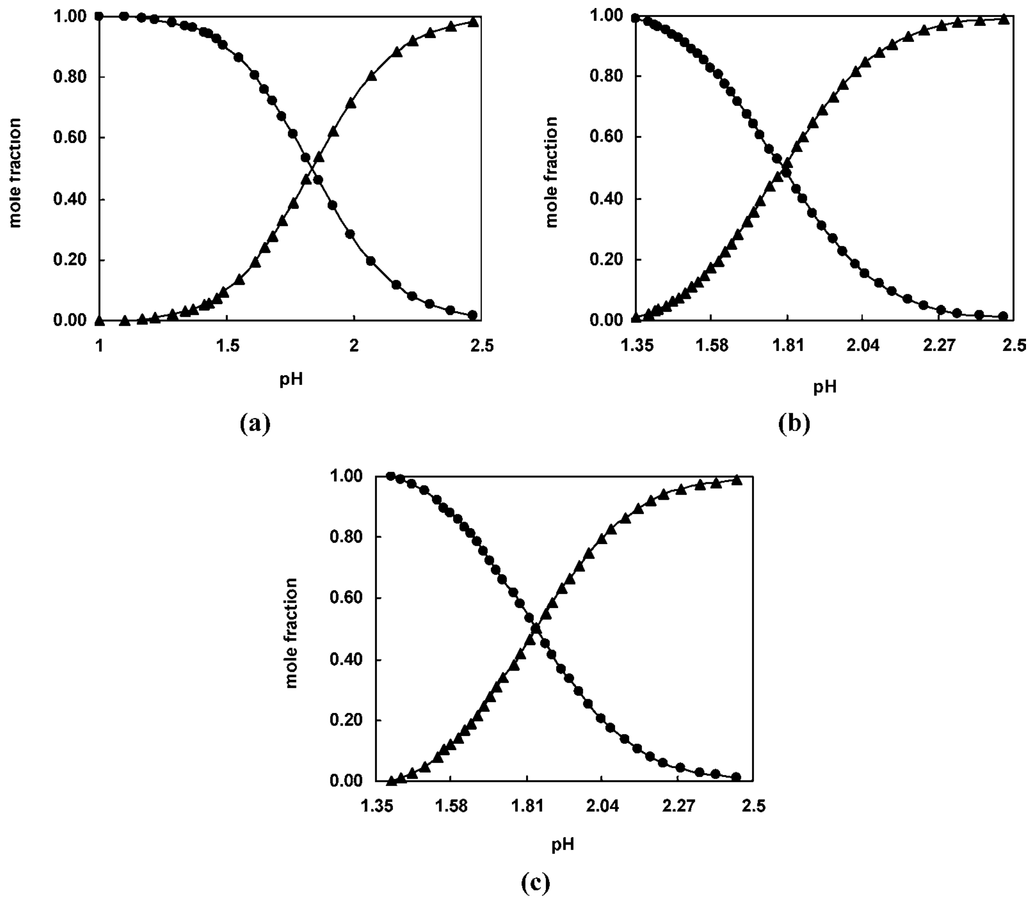
and the formation constants

$$VO_2^+ + H_4L \rightleftharpoons VO_2H_3L + H^+$$

$$K_{VO_2H_3L} = \frac{[VO_2H_3L][H^+]}{[VO_2^+][H_4L]} \tag{21}$$

$$VO_2H_3L \rightleftharpoons VO_2H_2L^- + H^+$$

$$K_{VO_2H_3L^-} = \frac{[VO_2H_2L^-][H^+]}{[VO_2][H_3L]} \tag{22}$$



(a)

(b)

(c)

**Figure 4.** Speciation diagrams at $T = 298$ K, $I = 0.05$ mol·dm$^{-3}$, and (a) 0 %, (b) 20 %, and (c) 40 % (v/v) for the model including only $VO_2L^{3-}$. $C_{VO_2^+} = 6.0 \cdot 10^{-4}$ mol·dm$^{-3}$ and $C_L = 8.1 \cdot 10^{-4}$ mol·dm$^{-3}$. ●, $VO_2^+$; ▲, $VO_2L^{3-}$.

**Table 2. Average Experimental and Calculated Values of log $\beta_{131}$ at pH = 1.00 to 2.50, $I = 0.05$ mol·dm$^{-3}$, and Different Aqueous Solutions of Methanol for the Complexation of Dioxovanadium(V) with EGTA, on the Basis of Different Solvatochromic Parameters, $t$ = 25 °C**

| methanol % (v/v) | log $\beta_{131}$ | | | | ref |
|---|---|---|---|---|---|
| | exptl | calcd (α, β) | calcd (α, π*) | calcd (β, π*) | |
| 0 | 27.48 ± 0.20 | 27.35 ± 1.86 | 27.81 ± 4.00 | 27.32 ± 1.07 | this work |
| 5 | 27.70 ± 0.11 | 27.63 ± 1.87 | 27.85 ± 3.91 | 27.70 ± 1.06 | this work |
| 10 | 27.96 ± 0.10 | 27.91 ± 1.88 | 27.87 ± 3.88 | 27.89 ± 1.07 | this work |
| 15 | 28.18 ± 0.15 | 28.19 ± 1.89 | 28.07 ± 3.82 | 28.15 ± 1.07 | this work |
| 20 | 28.48 ± 0.07 | 28.47 ± 1.90 | 28.46 ± 3.75 | 28.46 ± 1.06 | this work |
| 25 | 28.60 ± 0.05 | 28.75 ± 1.91 | 28.66 ± 3.69 | 28.72 ± 1.06 | this work |
| 30 | 28.92 ± 0.10 | 29.03 ± 1.92 | 29.04 ± 3.62 | 29.04 ± 1.05 | this work |
| 35 | 29.29 ± 0.09 | 29.31 ± 1.93 | 29.24 ± 3.57 | 29.29 ± 1.05 | this work |
| 40 | 29.72 ± 0.12 | 29.59 ± 1.94 | 29.63 ± 3.49 | 29.60 ± 1.05 | this work |
| 45 | 29.99 ± 0.10 | 29.95 ± 1.94 | 30.03 ± 3.38 | 29.98 ± 1.04 | this work |

**Table 3. Average Experimental and Calculated Values of log $\beta_{121}$ at pH = 1.00 to 2.50, $I = 0.05$ mol·dm$^{-3}$, and Different Aqueous Solutions of Methanol for the Complexation of Dioxovanadium(V) with EGTA, on the Basis of Different Solvatochromic Parameters, $t$ = 25 °C**

| methanol % (v/v) | log $\beta_{121}$ | | | | ref |
|---|---|---|---|---|---|
| | exptl | calcd (α, β) | calcd (α, π*) | calcd (β, π*) | |
| 0 | 25.75 ± 0.12 | 26.04 ± 2.21 | 25.98 ± 6.58 | 26.01 ± 1.61 | this work |
| 5 | 26.25 ± 0.08 | 26.32 ± 2.22 | 26.55 ± 6.43 | 26.39 ± 1.59 | this work |
| 10 | 26.81 ± 0.05 | 26.60 ± 2.23 | 26.57 ± 6.37 | 26.59 ± 1.60 | this work |
| 15 | 26.87 ± 0.04 | 26.88 ± 2.24 | 26.76 ± 6.28 | 26.84 ± 1.60 | this work |
| 20 | 27.07 ± 0.06 | 27.16 ± 2.26 | 27.15 ± 6.16 | 27.16 ± 1.59 | this work |
| 25 | 27.38 ± 0.22 | 27.44 ± 2.27 | 27.35 ± 6.07 | 27.42 ± 1.59 | this work |
| 30 | 27.63 ± 0.07 | 27.73 ± 2.28 | 27.74 ± 5.95 | 27.73 ± 1.58 | this work |
| 35 | 28.03 ± 0.06 | 28.01 ± 2.29 | 27.93 ± 5.86 | 27.99 ± 1.58 | this work |
| 40 | 28.41 ± 0.20 | 28.29 ± 2.30 | 28.32 ± 5.74 | 28.30 ± 1.57 | this work |
| 45 | 28.64 ± 0.08 | 28.65 ± 2.30 | 28.72 ± 5.56 | 28.68 ± 1.55 | this work |

where $C_{VO_2^+}$ and $C_L$ are the total concentration of $VO_2^+$ and the ligand, respectively.

The combination of the reactions shown in eqs 13 and 15 have been used for the calculation of stability constants given in eqs 14 and 16. The average values of the experimental and calculated stability constants at various wavelengths are gathered in Tables 2 to 4.

***Solvent Effect on the Complexation of Dioxovanadium(V) with EGTA by Using the Kamlet−Abboud−Taft Equation.*** A solvent should not be considered a macroscopic continuum characterized only by physical constants such as density, dielectric constant, and index of refraction, but as a discontinuum which consists of individual, mutually interacting solvent molecules.[4] According to the extent of these interactions, there are solvents with a pronounced internal structure (e.g., water) and others in which the interaction between the solvent molecules is small.[4] The solvent neither is an indifferent medium in which the dissolved material diffuses to distribute itself evenly and randomly nor possesses an ordered structure resembling a crystal lattice.[4] Due to the complexity of the interactions, the structure of liquids is the least known. Thus, the experimental and theoretical examination of the structure of liquids is among the most difficult tasks of physical chemistry.[4]

Solvent polarity can be estimated empirically by using actual chemical or physical reference processes. In 1937, Hammett introduced an equation for the calculation of substituent effects on reaction rates and chemical equilibria.[26,27] Linear Gibbs energy relationships, frequently referred to as linear free energy (LFE) relationships, are the functional relationships between substituent or solvent parameters and various substituent or

**Table 4. Average Experimental and Calculated Values of log $\beta'_{101}$ at pH = 1.00 to 2.50, $I$ = 0.05 mol·dm$^{-3}$, and Different Aqueous Solutions of Methanol for the Complexation of Dioxovanadium(V) with EGTA, on the Basis of Different Solvatochromic Parameters, $t$ = 25 °C**

| methanol % (v/v) | log $\beta'_{101}$ | | | | ref |
|---|---|---|---|---|---|
| | exptl | calcd ($\alpha$, $\beta$) | calcd ($\alpha$, $\pi^*$) | calcd ($\beta$, $\pi^*$) | |
| 0 | 20.70 ± 0.30 | 21.26 ± 4.96 | 21.22 ± 10.75 | 21.24 ± 3.38 | this work |
| 5 | 21.39 ± 0.17 | 21.48 ± 4.99 | 21.67 ± 10.50 | 21.54 ± 3.34 | this work |
| 10 | 21.98 ± 0.20 | 21.71 ± 5.02 | 21.68 ± 10.41 | 21.69 ± 3.36 | this work |
| 15 | 21.62 ± 0.26 | 21.92 ± 5.04 | 21.83 ± 10.26 | 21.89 ± 3.35 | this work |
| 20 | 21.91 ± 0.19 | 22.15 ± 5.07 | 22.14 ± 10.06 | 22.14 ± 3.34 | this work |
| 25 | 22.81 ± 0.14 | 22.37 ± 5.10 | 22.29 ± 9.92 | 22.34 ± 3.34 | this work |
| 30 | 22.63 ± 0.28 | 22.59 ± 5.12 | 22.60 ± 9.72 | 22.59 ± 3.32 | this work |
| 35 | 22.77 ± 0.12 | 22.81 ± 5.15 | 22.75 ± 9.57 | 22.80 ± 3.31 | this work |
| 40 | 22.98 ± 0.38 | 23.04 ± 5.18 | 23.06 ± 9.38 | 23.04 ± 3.29 | this work |
| 45 | 23.29 ± 0.42 | 23.32 ± 5.18 | 23.37 ± 9.08 | 23.34 ± 3.26 | this work |

**Table 5. Solvatochromic Parameters for Different Aqueous Solutions of Methanol**

| methanol % (v/v) | $\alpha$ | $\beta$ | $\pi^*$ |
|---|---|---|---|
| 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 6. Different Equations with Two Solvatochromic Parameters Together with Their Error Functions (erf) and Values of Coefficients of Determination ($r^2$) for Dissociation and Stability Constants at 25 °C, $I$ = 0.05 mol·dm$^{-3}$ (NaClO$_4$), and Different Aqueous Solutions of Methanol, $n$ = 10**

| equation | erf | $r^2$ |
|---|---|---|
| $\log K_1 = (2.04 \pm 0.56) - (1.85 \pm 0.26)\alpha + (4.61 \pm 0.56)\beta$ | 0.006 | 0.98 |
| $\log K_1 = (2.02 \pm 0.98) + (4.04 \pm 0.40)\alpha - (4.33 \pm 0.47)\pi^*$ | 0.005 | 0.99 |
| $\log K_1 = (2.04 \pm 0.32) + (3.17 \pm 0.31)\beta - (1.37 \pm 0.16)\pi^*$ | 0.004 | 0.99 |
| $\log K_2 = (2.68 \pm 0.21) - (1.13 \pm 0.10)\alpha + (2.81 \pm 0.21)\beta$ | 0.001 | 0.99 |
| $\log K_2 = (2.67 \pm 0.82) + (2.43 \pm 0.34)\alpha - (2.61 \pm 0.39)\pi^*$ | 0.003 | 0.98 |
| $\log K_2 = (2.68 \pm 0.17) + (1.93 \pm 0.16)\beta - (0.83 \pm 0.09)\pi^*$ | 0.001 | 0.99 |
| $\log K_3 = (8.49 \pm 0.49) - (2.53 \pm 0.22)\alpha + (6.31 \pm 0.49)\beta$ | 0.004 | 0.99 |
| $\log K_3 = (8.46 \pm 0.92) + (5.52 \pm 0.38)\alpha - (5.92 \pm 0.43)\pi^*$ | 0.004 | 0.99 |
| $\log K_3 = (8.48 \pm 0.24) + (4.34 \pm 0.23)\beta - (1.87 \pm 0.12)\pi^*$ | 0.002 | 1.00 |
| $\log K_4 = (9.38 \pm 0.52) - (2.49 \pm 0.24)\alpha + (6.21 \pm 0.52)\beta$ | 0.005 | 0.99 |
| $\log K_4 = (9.36 \pm 1.35) + (5.40 \pm 0.56)\alpha - (5.80 \pm 0.64)\pi^*$ | 0.009 | 0.99 |
| $\log K_4 = (9.37 \pm 0.32) + (4.26 \pm 0.31)\beta - (1.84 \pm 0.16)\pi^*$ | 0.004 | 0.99 |
| $\log \beta_{131} = (27.35 \pm 1.86) - (8.02 \pm 0.85)\alpha + (19.96 \pm 1.85)\beta$ | 0.06 | 0.99 |
| $\log \beta_{131} = (27.81 \pm 4.00) + (17.42 \pm 1.65)\alpha - (18.70 \pm 1.90)\pi^*$ | 0.08 | 0.99 |
| $\log \beta_{131} = (27.32 \pm 1.07) + (13.73 \pm 1.03)\beta - (5.92 \pm 0.54)\pi^*$ | 0.05 | 0.99 |
| $\log \beta_{121} = (26.04 \pm 2.21) - (8.08 \pm 1.01)\alpha + (20.11 \pm 2.19)\beta$ | 0.09 | 0.99 |
| $\log \beta_{121} = (25.98 \pm 6.58) + (17.36 \pm 2.72)\alpha - (18.64 \pm 3.12)\pi^*$ | 0.20 | 0.97 |
| $\log \beta_{121} = (26.01 \pm 1.61) + (13.78 \pm 1.54)\beta - (5.94 \pm 0.81)\pi^*$ | 0.10 | 0.98 |
| $\log \beta'_{101} = (21.26 \pm 4.96) - (6.38 \pm 2.26)\alpha + (15.88 \pm 0.93)\beta$ | 0.44 | 0.91 |
| $\log \beta'_{101} = (21.22 \pm 10.75) + (13.63 \pm 4.44)\alpha - (14.63 \pm 5.10)\pi^*$ | 0.55 | 0.88 |
| $\log \beta'_{101} = (21.24 \pm 3.38) + (10.86 \pm 3.23)\beta - (4.68 \pm 1.70)\pi^*$ | 0.46 | 0.90 |

solvent-dependent processes.[4] Although single parameters can be used as good approximations of solvent polarity, there are many solvent-dependent processes in which one empirical solvent parameter correlation is not sufficient. Now it is well-known that the simple concept of "polarity" as a general determinable and applicable solvent characteristic is an over-simplification. Many different kinds of interaction mechanisms between the solute molecules and solvent can result in nonspecific and specific solute−solvent interaction. Solvent effects are more complicated and often more specific than substituent effects. In the latter case, linear Gibbs energy relationships such as the Hammett equation are known to work very well. In order to take into account two or more aspects of solvation, a multiparameter equation has been proposed by Kamlet, Abboud, and Taft (KAT).[4] In the KAT approach, nonspecific and specific solute−solvent interactions have been considered separately, and the solute−solvent interactions are subdivided into solvent Lewis-acidity interactions (hydrogen bond acceptor (HBA) solute/hydrogen bond donor (HBD) solvent) and solvent Lewis-basicity interactions (hydrogen bond donor (HBD) solute/hydrogen bond acceptor (HBA) solvent). The following multiparameter equation has been suggested for use in linear solvation energy relationships (LSER) by using the solvatochromic solvent parameters, $\alpha$, $\beta$, and $\pi^*$

$$\log K = A_0 + p(\pi^* + d\delta) + a\alpha + b\beta \tag{23}$$

$A_0$ is the regression value. This property can represent for example the logarithm of a stability constant or dissociation constant in this work. $\delta$ is a discontinuous polarizability correlation term equal to 0.0 for nonchlorosubstituted aliphatic solvents, 0.5 for polychloro-substituted aliphatics, and 1.0 for aromatic solvents. In our research, $\delta$ is equal to zero. $\alpha$ is a measure of the solvent hydrogen-bond donor (HBD) acidity and shows the ability of a solvent to release a proton in a solvent-to-solute hydrogen bond. The $\alpha$ values are from zero for non-HBD solvents to about 1.0 for methanol. $\pi^*$ is an index of solvent dipolarity/polarizability, which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect. The $\pi^*$ values are from 0.00 for cyclohexane to 1.00 for dimethylsulfoxide. $\beta$ is a measure of the solvent hydrogen-bond acceptor (HBA) basicity and shows the solvent's ability to accept a proton in a solute-to-solvent hydrogen bond. The $\beta$-scale values are from zero for non-HBD solvents to about 1 for hexamethylphosphoric acid triamide (HMPT). The regression coefficients $p$, $d$, $a$, and $b$ in eq 23 measure the relative susceptibilities of the solvent-dependent dissociation and stability constants to the indicated solvent parameters.[4] It was found, for example, by analysis of the variation of $\beta$ values for mixtures of methanol and other organic solvents that an important factor influencing the basicity of solvent mixtures is due to order/disorder processes, particularly in binary mixtures of protic with non-hydrogen bond donor (non-HBD) solvents.[28] In aqueous solutions of methanol, the nonspecific solute/solvent contributions are nearly constant.[28] For this solvent group, a clear mutual Lewis acidity/basicity dependence was found, suggesting that these solvents behave similar to the Brönsted type properties for aqueous solutions.[28] In alcohol−water mixtures, rearrangement of the hydrogen bonds caused by the alcohol enhances the water structure.[29] The enhancement of the water structure by different alcohols can affect the values of KAT solvatochromic parameters, but the variation of the mentioned parameters is very small for methanol−water mixtures.[29] The values of $\alpha$, $\beta$, and $\pi^*$ are gathered from the literature[30] in Table 5. On the basis of values of coefficients of determination and standard errors, it was found that the best results are obtained when we use two parameters. Therefore, different equations with two solvatochromic parameters are gathered in Table 6 for dissociation and stability constants of EGTA and V(V) + EGTA systems, respectively.

***Comparison with Literature Data.*** A literature survey shows that there is no report for this complexation reaction in different aqueous solutions of methanol, and further, we did not find any report regarding the complexation of dioxovanadium(V) with EGTA in other alcohol−water mixtures. Therefore, comparison of this work with the literature is not easy. Regarding aminopolycarboxylic acids, we only found complexation of molybdenum(VI) with some aminopolycarboxylic acids in different alcohol−water mixtures by using the KAT equation.[20,31]

We have recently found the order of $\beta > \pi^* > \alpha$ for the complexation of Mo(VI) with ethylenediamine *N*,*N′*-diacetic acid (EDDA)[23] which is similar to the order obtained by Gharib[31] for the complexation of molybdenum(VI) with nitrilotriacetic acid (NTA) in different aqueous solutions of methanol. Another report in the literature[20] is about the solvent effects on the complexation of tungsten(VI) with EDDA in different aqueous solutions of propanol in which stability constants increase with increasing mole fractions of propanol, and the solvatochromic parameters are in the order of $\pi^* > \alpha > \beta$. As was mentioned above, in this research with three parameters large uncertainties were obtained, and therefore only two parameters in the KAT equation are found to be useful and reported in Table 6.

## Conclusions

Three species, $VO_2H_2L^-$, $VO_2HL^{2-}$, and $VO_2L^{3-}$, have been assumed in the literature[32] for the complexation of dioxovanadium(V) with ethylenediaminetetraacetic acid (EDTA), and three stability constants, $\log \beta_{121} = 22.94 \pm 0.40$, $\log \beta_{111} = 19.64 \pm 0.40$, and $\log \beta_{101} = 15.54 \pm 0.30$, were calculated solely on the basis of experimental UV absorbance data as a function of pH (pH < 2) at an ionic strength of $3.0\ \mathrm{mol \cdot dm^{-3}}$ sodium perchlorate aqueous solution and using the LETAGROP-SPEFO program. EGTA is very similar to EDTA and, in addition to the carboxylate donor groups, contains an etheric oxygen which can interact as well with the $VO_2^+$ ion. Sammartano[33] showed the contribution to the stabilization of metal−ligand species by the presence of etheric oxygens in the ligand structure, and it seems that the mentioned contribution is also important in this research. It seems that the etheric groups in the long alkyl chain have the main contribution to the stability constants of the dioxovanadium(V) complex with EGTA, and therefore we have larger stability constants in comparison to the dioxovanadium(V) complex with EDTA. Of course, with regard to the difference in experimental conditions (ionic strength, investigated pH range, kinds of species in different media, and methods of calculation), we can not exactly compare this work with the literature.

Uncertainties can be considered as a measurement of the capability of the models for predicting the stability of the complex or the ligand. According to Tables 2, 3, 4, and 6, minimum uncertainties and error functions exist when we have only two $\beta$ and $\pi^*$ parameters in the KAT equation. Therefore we confine our discussions only to the KAT equation with two $\beta$ and $\pi^*$ parameters. Of course, uncertainties and error functions for all of the calculated stability constants and KAT parameters of the $VO_2L^{3-}$ species are larger in comparison to the protonated species (Tables 2 to 4 and 6), and there is no trend for the experimental values of stability constants for $VO_2L^{3-}$ (Table 4). Therefore, $VO_2L^{3-}$ was not the preferred species. For $\log \beta_{131}$, $\log \beta_{121}$, and $\log \beta'_{101}$, negative $\pi^*$ coefficients have been obtained (Table 6) which shows that with increasing methanol fraction (polarity decrease) we have an increase in the values of the stability constants because the values of $\pi^*$ decrease with increasing percentage of methanol according to Table 5. Positive large $\beta$ coefficients for $\log \beta_{131}$, $\log \beta_{121}$, and $\log \beta'_{101}$ in Table 6 (when we have two parameters $\beta$ and $\pi^*$) which is very different from $\pi^*$ indicates that the basicity of the solvent mixtures is very important. When polarity decreases, $\beta$ values increase (Table 5), and therefore stability constants will increase. A similar trend exists for the dissociation constants, but the $\beta$ coefficients are not as large as the coefficients for stability constants. Finally, we can conclude that the hydrogen-bond acceptor basicity parameter, $\beta$, is the most important parameter for both dissociation and complex formation reactions, and the $\pi^*$ parameter is much less important.

### Supporting Information Available:

Experimental values of absorbance at different pH and wavelengths at $T = 298$ K, $I = 0.05\ \mathrm{mol \cdot dm^{-3}}$, and different volume fractions of methanol have been gathered from the UV spectrophotometric measurements and are included in Tables A1 to A10. This material is available free of charge via the Internet at http://pubs.acs.org.

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