Journal of Physical & Theoretical Chemistry
Islamic Azad University of Iran 2 (2)
Science and Research Campus
ISSN: 1735-2126

Solvent Effects on Complexation of Dioxovanadium (V) with Glycine in Methanol-Water Mixtures

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ABSTRACT

The formation constants of the species formed in the systems H^+ + glycine + dioxovanadium(V) + and H^+ + glycine have been determined in aqueous solutions of methanol at 25 °C and constant ionic strength, using spectrophotometric and potentiometric techniques. It was shown that dioxovanadium(V) forms two mononuclear 1:1and 1:2 complexes with glycine. The formation constants in various media were analyzed in terms of Kamlet and Taft's parameters. Single-parameter correlation of the formation constants, β_{111} and β_{122}, versus α (hydrogen-bond donor acidity) and β (hydrogen-bond accepter basicity) are poor in all solutions, except for π^* (dipolarity/polarizability), but multi-parameter correlation represents significant improvement with regard to the single-parameter models. Linear relationships are observed when $\log\beta_{111}$ and $\log\beta_{122}$ are plotted versus π^*. Finally, the results are discussed in terms of the effect of solvent on complexation.

INTRODUCTION

Stability constants of chelate compounds and protonation constants of chelating ligands have often been measured in mixed solvents because of the insolubility of one or more of the reactants in water. The application of all methods for determining the stability constant requires that the system to be homogeneous in a single phase, in order that concentrations at equilibrium are calculated from the initial composition. However, in organic solvents of low dielectric constant, the predictions of the interionic attraction theory will differ more from the observed behavior than in water by the reason of greater effect of the electrostatic interactions and the resulting ion association.[1] Besides the pure electrostatic interactions, there exist other specific and nonspecific interaction forces such as ion-dipole, hydrogen bonding, ion-pair formation, actual shape and size of the individual ions, solvation capability of ions, etc.[2]

The first attempt to introduce an empirical relationship between an equilibrium constant and solvent polarity goes back to the work of Meyer [2] who found proportionality between the equilibrium constants of various tautomeric compounds in different solvent solutions. Solvent effects on organic reactivity and on absorption spectra have been studied for more than a century. Great attempt have been performed to understand the solvent effects in terms of polarity of the solvent. Solvent polarity is a commonly used term related to the capacity of a solvent for solvating dissolved charged or dipolar species. The solvent dielectric constant is often predicted to serve as a quantitative measure of solvent polarity. However, this is often inadequate since this approach regard solvents as a non-structured continuum, not composed of individual solvent molecules with their own solvent-solvent interactions, and they do not take into account specific solute-solvent interactions such as hydrogen bonding which often play a dominating role in solute-solvent interactions.

At present, there are two more important approaches to quantitative description of this effect. The theoretical approach describes solvent as an isotropic environment of dissolved particles and characterizes it by its bulk properties. Unfortunately, this approach involves only the influence of the nonspecific interactions. Another approach is based on description of the solvent effect by suitably chosen empirical parameters measuring specific and nonspecific interactions. The drawback of this approach is that such parameters are not universal and depend on each other. The interactions between solvent and solute molecules are separated in literature into specific and nonspecific. As a result, linear functions with few parameters for description of the solvent effect are proposed.[3-7] The most interesting is that proposed by Kamlet and Taft.[8]

Recently, solvent effects on transition metal complexes is reviewed [9] and more attention has been paid to binary solvent mixtures in this field.[10-14] Solute-solvent interactions are much more complex in mixed solvent systems than in pure solvents due to the possibility of preferential solvation by any of the solvents present in the mixtures. Moreover, the solvent-solvent interactions produced in solvent mixtures can affect the solute-solvent interactions and therefore they can also affect preferential solvations.[15]

In present work we have chosen a well understood system, complexation of dioxovanadium (V) with glycine [16] in different solutions of methanol + water to show how the solvents and their mixtures with various dielectric constants affect the formation of such a complex.

EXPERIMENTAL SECTION

Reagents. Methanol was obtained from Merck as analytical reagent grade material and was used without further purification. Glycine (Merck, analytical reagent grade) was recrystallized from hot water, washed with ethanol, and dried over P_2O_5. Equivalent weights were checked by titration against a standard alkali. The NaOH solution was prepared from titrisol solution (Merck), and its concentration was determined by several titrations with standard HCl. Perchloric acid, sodium perchlorate, and sodium monovanadate were supplied from Merck (analytical reagent grade) and were used without further purification. Dilute perchloric acid solution was standardized against standard NaOH solution. All dilute solutions were prepared from double-distilled water with a specific conductance equal to $1.3 \pm 0.1\ \mu\Omega^{-1}cm^{-1}$.

A stock solution of dioxovanadium(V), VO_2^+, was prepared by dissolution of sodium monovanadate in perchloric acid solution, causing the destruction of decavanadate. To avoid isopolyvanadate formation and obtaining only the VO_2^+ ion, the solution was allowed to stand overnight before use. Under this condition both polymerization and hydrolysis of VO_2^+ were negligible.[17-18] The concentration of VO_2^+ ion in the stock solution was checked by potentiometric titration using saturated calomel and platinum wire electrodes. Titration was performed in aliquots after dilution in H_2SO_4 solution.[19]

Apparatus. An Eyela pH meter (PHM 2000) was used for pH measurements. The hydrogen ion concentration was measured with an Ingold UO 3234 glass electrode and an Ingold UO 3236 calomel electrode. Spectrophotometric measurements were performed using a UV-Vis Shimadzu 2100 spectrophotometer with a GDU-20 computer and thermostated matched 10 mm quartz cells.

Measurements. All measurements were carried out at 25 ± 0.1 °C. The ionic strength was maintained at 0.1 mol dm^{-3} with sodium perchlorate. The pH meter was calibrated for the relevant H^+ concentration with a solution of 0.01 mol dm^{-3} perchloric acid solution containing 0.09 mol dm^{-3} sodium perchlorate (for adjusting the ionic strength to 0.1 mol dm^{-3}). For this standard solution, we set $-\log[H^+] = 2.00$.[20] Junction potential corrections have been calculated from eq 1.

$$-\log[H^+]_{real} = -\log[H^+]_{measured} + a + b[H^+]_{measured} \quad (1)$$

a and b were determined by measuring the hydrogen ion concentration for two different solutions of $HClO_4$ with sufficient $NaClO_4$ to adjust the ionic media.

Procedure. A 50 cm^3 acidic solution of VO_2^+ (4.91×10^{-4} mol dm^{-3}) was titrated with an alkali solution (0.1 mol dm^{-3} NaOH) of the ligand containing a large excess (0.002 mol dm^{-3}) both of the same ionic strength and mole fraction of the solvents. The $-\log[H^+]$ and absorbance were measured after the addition of a few drops of titrant, and this procedure was continued up to the required $-\log[H^+]$. 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.

Calibration of the Glass Electrode. The term pH has significance only in aqueous media.[21] The glass electrode potential in an aqueous solution differs from that in solution of mixed solvents, and a liquid-junction potential of uncertain magnitude may affect the results. To overcome this difficulty, it was necessary to calibrate the glass electrode in different solvent mixtures. The experimental method outlined by Van Uitert and Hass [22] was employed for this purpose. The pH meter reading B in methanol + water media was converted into $[H^+]$ using the equation

$$-\log[H^+] = B + \log\mu_H \quad (2)$$

where the concentration factor, μ_H, was obtained for the ionic strength 0.1 mol dm^{-3} $NaClO_4$ from the expression $\log\mu_H = \log\mu°_H + \log\gamma_\pm$. The value of $\mu°_H$ is independent of ionic concentration but is dependent on solvent composition, and $\gamma_\pm$ is the mean activity coefficient of perchloric acid in the solvent mixtures. In this work, the values of B were recorded in various solvent mixtures containing known concentrations of perchloric acid and sufficient sodium perchlorate to give a constant ionic strength of 0.1 mol dm^{-3}. The difference between the logarithm of known hydrogen-ion concentrations and the corresponding values of B were used to calculate values of the correction term $\log\mu_H = \log(\mu°_H\gamma_\pm)$.[14]

Results and Discussion

The complex $M_xH_yL_z^{(x+y-z)}$ formed, is characterized by its stoichiometry (x:y:z), where M and L represent the metal ion and the ligand, respectively. To determine the stability constant of the complexation or the protonation, eq 3 is defined by β_{xyz},[20]

$$xM^+ + yH^+ + zL^- \leftrightarrows M_xH_yL_z^{(x+y-z)} \qquad (3)$$

$$\beta_{xyz} = [M_xH_yL_z^{(x+y-z)+}] / ([M^+]^x[H^+]^y[L^-]^z) \qquad (4)$$

The protonation constant of glycine has been used for computation of the stability constant, β_{xyz}, of the metal ion + ligand. The protonation constants of the ligand have been studied in different kind of background electrolytes, and the results were reported in the literature. The protonation constant of the ligand determined using potentiometric technique and calculated using a computer program which employs a nonlinear least-squares method.[23] These value are listed in Table 1 together with the earliest value reported in the literature, which are in good agreement with that reported before.[24]

Table 1. Protonation constants of the carboxylic, β_{021}, and the amino, β_{011}, groups of glycine in different solutions of methanol + water, 25 °C, and ionic strength of 0.1 mol dm^{-3} sodium perchlorate

methanol percent (w/w)	logβ_{021}	logβ_{011}	ref.
0.0	2.43 ± 0.05	9.80 ± 0.11	this work
8.0	2.44 ± 0.04	9.81 ± 0.09	″
16.0	2.45 ± 0.06	9.83 ± 0.08	″
25.0	2.47 ± 0.08	9.86 ± 0.10	″
35.0	2.50 ± 0.05	9.91 ± 0.08	″
44.0	2.54 ± 0.03	9.95 ± 0.07	″
54.0	2.59 ± 0.04	10.01 ± 0.10	″
0.0	-	9.82	24

The method of determination of the stability constant based on the relation A = f([H$^+$]).[17] Absorbance, A, and –log[H$^+$] were measured as described before.[25-26] Treatments of the spectrophotometric data (each 5 nm) obtained during the titrations, as a function of the H$^+$ concentration, were conducted to the computer program.[23] The program allows calculation of stability constant for models of different stoichiometries.

Considering the protonation constants of the ligand, in acidic solution the predominant species for complexation is HL. In this case the spectrophotometric titration data were analyzed by using the absorbance of VO_2^++ glycine at a wavelength in UV range that is given by

$$A = \varepsilon_M[VO_2^+] + \varepsilon_C[\text{complex}] \qquad (5)$$

where ε_M and ε_C are the molar absorptivities of VO_2^+ and the formed complex, respectively. For the mass balance

$$[VO_2^+] = C_M - [\text{complex}] \qquad (6)$$

$$[HL] = C_L - [\text{complex}] - [\text{free ligand}] \qquad (7)$$

Substituting eqs 4 and 6-7 into eq 5 gives the final equation for fitting, where C_M and C_L are the total concentration of VO_2^+ and the ligand, respectively.

The method of determining ε_M was previously described [27] and its values at different wavelengths are used in this work. Using a suitable computer program [23] the data were fitted to the final equation for estimating the formation constant of eq 3. We used the Gauss-Newton nonlinear least-squares method in computer program to refine the absorbance by minimizing the error squares sum from eq 8

$$S = \sum(a_i - b_i)^2 \quad (i = 1, 2, 3, \ldots) \qquad (8)$$

where a_i and b_i are the experimental and calculated absorbances, respectively. The computer program consisted of two different kinds of fitting, (a) graphical, (b) numerical. The final selection of the species was based on both graphical and numerical methods, considering in addition the various statistical criteria, i. e. sums of squared residuals, differences of C_M(exp) and C_L(exp) from those of calculated ones. Figure 1 is shown as a typical example of a graphical fitting for the observed and calculated absorbances (from the computer program) of VO_2^++ glycine against –log[H$^+$] at 265 nm.

Different models including MHL^+, $M(HL)_2^+$ and several polynuclear and protonated species were tested by the program. As expected, polynuclear complexes were systematically rejected by the computer program, as also were MH_3L^{3+}, MHL_2, and $MH_3L_3^+$. A value for the MH_2L^{2+} species was calculated by the program, but the species was not further considered because the estimated error in its formation constant is unacceptable, and its inclusion does not improve the goodness of the fit. The models finally chosen, formed by VO_2HL^+ and $VO_2(HL)_2^+$, for the system studied, resulted in a satisfactory numerical and graphical fitting. The average values for various wavelengths calculated for the stability constants are listed in Table 2.

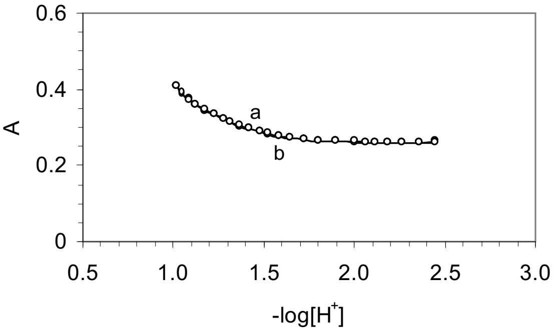

Figure 1. Typical graphical fitting for the VO_2^++glycine system at 25 °C, 265 nm, and ionic strength 0.1 mol dm^{-3} $NaClO_4$, (a) experimental absorbance and (b) calculated absorbance from the computer program.

Table 2. Formation constants of VO_2^+ + glycine in different solutions of methanol + water at 25 °C and Kamlet and Taft's solvatochromic parameters

methanol percent (w/w)	$\log\beta_{111}$	$\log\beta_{122}$	π^{*} [a]	α [a]	β [b]	dielectric constant [c]
0.0	3.48	7.26	1.14	1.26	0.19	78.74
8.0	3.49	7.27	1.12	1.19	0.22	74.09
16.0	3.52	7.31	1.11	1.13	0.26	68.92
25.0	3.55	7.35	1.09	1.08	0.32	63.80
35.0	3.59	7.39	1.05	1.04	0.38	58.91
44.0	3.65	7.43	1.01	1.01	0.44	54.10
54.0	3.71	7.51	0.95	1.01	0.50	49.36

[a] Obtained from ref. 14. [b] Obtained from ref. 28. [c] Obtained from ref. 29.

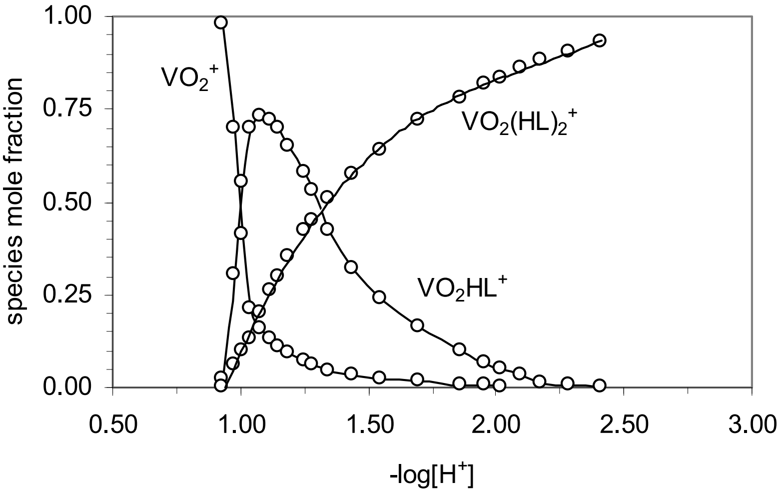

Figure 2. Equilibrium distribution of the species in the VO_2^+ + glycine system as a function of $-\log[H^+]$ at 25 °C, 265 nm, and ionic strength 0.1 mol dm^{-3} $NaClO_4$.

In Figure 2 the equilibrium distribution of various species in VO_2^++ glycine is shown as a function of $-\log[H^+]$. The calculation is based on the stability constant values given before.

SOLVENT EFFECT

Solvent effects on formation constants often define in terms of the polarity of the organic solvent. Solvent polarity is a commonly used term related to the capacity of the solvent for solvating dissolved charged or dipolar species. Attempts to express it quantitatively involved mainly physical solvent properties such as dielectric constant of the solvent. However, this approach is often inadequate since dielectric constant regards solvents as a non-structured system, which is not composed of individual molecules with their own solvent-solvent and solvent-solute interactions such as hydrogen-bonding interactions which often play a dominating role in any reaction. The problem is to identify and to assess the relative importance of these various factors on the solvent effects.

Recently, a quantitative measurement of the solvent polarity has been introduced by Kamlet and Taft.[2] Kamlet and Taft's solvatochromic parameters have been used in one, two, or three-parameter correlations involving different combination of these parameters which are called linear solvation energy relationships. In general, all these parameters constitute more comprehensive measures of solvent polarity than the dielectric constant or any other single physical characteristic, since they reflect more reliably the complete picture of all intermolecular forces acting between solute and solvent molecules. Using the solvatochromic solvent parameters, the multi-parameter equation 9 has been proposed

$$\log\beta = A_0 + p(\pi^* + d\delta) + a\alpha + b\beta \qquad (9)$$

where A_0 represents the regression value, π^* is the index of the solvent dipolarity/polarizability, which is a measure of the ability of a solvent to stabilize a charge or a dipole by its own dielectric effects. The π^* scale was selected to run from 0.0 for cyclohexanone to 1.0 for dimethylsulfoxide. The α coefficient represents the solvent hydrogen-bond donor (HBD) acidity, in other words it describes the ability of a solvent to donate a proton in a solvent to solute hydrogen-bond. The α scale extends from 0.0 for non-HBD solvents to about 1.0 for methanol. The β coefficient is a measure of a solvent hydrogen-bond acceptor (HBA) basicity, and describes the ability of a solvent to accept a proton in a solute to solvent hydrogen-bond. The β scale was selected to extend from 0.0 for non-(HBA) solvents to about 1.0 for hexamethylphosporic acid triamide. δ is a discontinuous polarizability correction term equal to 0.0 for non-chlorine substituted aliphatic solvents, 0.5 for poly-chlorine substituted aliphatics, and 1.0 for aromatic solvents,[2] The regression coefficients, p, d, a, and b in eq 9 measure the relative susceptibilities of the solvent-dependent of logβ to the indicated solvent parameters.

The solvent polarity parameter of media, π^*, increases with increasing the mole fraction of water in aqueous solutions of methanol. If the π^* of media was the only factor for the solvent effect on the complexation, it may be expected that the logβ in water should be greater than those of all the other aqueous solution of methanol. However, the formation constant increases with increasing the solvent hydrogen-bond acceptor basicity parameter, β, and decreases with increasing the solvent polarity π^*. Also, the hydrogen-bond donor acidity parameter of the solvents, α, first decrease and then increase with increasing the mole fraction of methanol in aqueous solutions of methanol.

In order to explain the obtained logβ values through Kamlet and Taft's solvent parameter, the formation constants were correlated with solvent properties by means of single and multiple linear regression analysis by a suitable computer program.[23] We used the Gauss-Newton linear least-squares method in the computer program to refine the logβ by minimizing the error squares sum from eq 8. Single-parameter correlations of logβ_{111} and logβ_{122} in terms of individually with α or β did not give a good results, eqs 10 and 11.

$$\log\beta_{111} = 9.39 - 3.15\alpha \quad (10a)$$
$$\log\beta_{122} = 12.91 - 3.95\alpha \quad (10b)$$

(n = 7, r = 0.89 and 0.91, respectively)

$$\log\beta_{111} = 4.98 + 2.61\beta \quad (11a)$$
$$\log\beta_{122} = 7.40 + 3.20\beta \quad (11b)$$

(n = 7, r = 0.98 and 0.98, respectively)

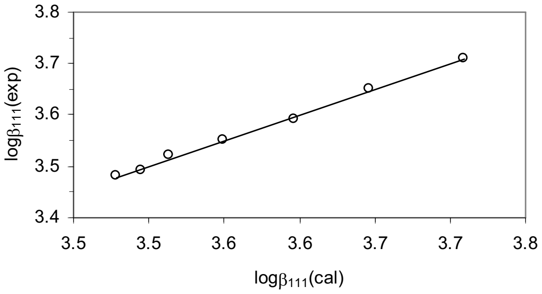

Figure 3. Plot of the experimental values of logβ_{111} versus the calculated values from eq 12a.

So, we thought it interesting to correlate logβ versus a multi-parametric equation involving both α, β, and π^*. However, the result presented in eq 12, multi-parametric equation, indicates significant improvement with regard to the single-parameter models.

$$\log\beta_{111} = 7.07 + 0.25\alpha + 1.25\beta - 1.82\pi^* \quad (12a)$$
$$\log\beta_{122} = 11.70 - 0.56\alpha + 0.65\beta - 2.69\pi^* \quad (12b)$$

(n = 7, r = 0.9984 and 0.9959, respectively)

The coefficients of π^*, α, and β in eq 12 are very different with each other, in both cases, and are in the order of $\pi^* > \beta > \alpha$. This indicates that the polarity parameter power of the solvent is the most important, the hydrogen-bond accepter basicity parameter plays a relatively small role, and finally the hydrogen-bond donor acidity parameter nearly has no significant in changing the formation constant of VO_2^+ + glycine system in the proposed various aqueous solutions of methanol.

In order to show the efficiency of suggested multi-parameter correlations, experimental values of logβ_{122} is plotted versus their calculated ones from eq 12a for different aqueous solutions of methanol. It can be seen, Fig. 3, the experimental and calculated values of logβ_{111} are in good agreement with each other, r = 0.9984.

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