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Solvent Effects on Complexation of Dioxovanadium(V) with Penicillamine in Methanol−Water Mixtures

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The formation constants of the species formed in the systems H^+ + dioxovanadium(V) + penicillamine and H^+ + penicillamine 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 1:1 and 1:2 complexes with penicillamine. The formation constants in various media were analyzed in terms of Kamlet and Taft's parameters. Single-parameter correlation of the formation constants, β_{121} and β_{142}, versus α (hydrogen-bond donor acidity) and β (hydrogen-bond acceptor basicity) is poor in all solutions, except for π^* (dipolarity/polarizability), but multiparameter correlation represents significant improvement with regard to the single-parameter models. Linear relationships are observed when log β_{121} and log β_{142} are plotted versus π^*. Finally, the results are discussed in terms of the effect of the 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 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 because of a 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, the actual shape and size of the individual ions, solvation capability of ions, and so forth.[2]

The first attempt to introduce an empirical relationship between an equilibrium constant and solvent polarity goes back to 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 the polarity of the solvent. Solvent polarity is a commonly used term related to the ability of a solvent to solvate 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 because this approach regards solvents as a nonstructured continuum, not composed of individual solvent molecules with their own solvent−solvent interactions, and it does not take into account specific solute−solvent interactions such as hydrogen bonding that often play a dominating role in solute−solvent interactions.

At present, there are two more important approaches to a quantitative description of this effect. The theoretical approach describes the 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 a 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 the literature into specific and nonspecific. As a result, linear functions with few parameters that describe 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 have been 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 because of 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; therefore, they can also affect preferential solvations.[15]

In the present work, we have chosen a well-understood system, the complexation of dioxovanadium(V) with penicillamine[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 an analytical reagent grade material and was used without further purification. L-Penicillamine (Fluka, 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 (analyti-

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Table 1. Protonation Constants of the Carboxylic, β_{031}, Sulfydryl, β_{021}, and Amino, β_{011}, Groups of L-Penicillamine in Different Solutions of Methanol + Water, 25 °C, and an Ionic Strength of 0.1 mol dm^{-3} Sodium Perchlorate

X_{methanol}	log β_{031}	log β_{021}	log β_{011}	experimental conditions	ref
0.000	3.05 ± 0.05	7.99 ± 0.08	10.69 ± 0.10		this work
0.047	3.11 ± 0.06	8.01 ± 0.05	10.71 ± 0.09		this work
0.100	3.13 ± 0.04	8.06 ± 0.08	10.75 ± 0.08		this work
0.161	3.16 ± 0.02	8.09 ± 0.04	10.79 ± 0.11		this work
0.229	3.21 ± 0.08	8.12 ± 0.07	10.84 ± 0.09		this work
0.308	3.23 ± 0.04	8.15 ± 0.06	10.89 ± 0.10		this work
0.401	3.30 ± 0.07	8.22 ± 0.05	10.95 ± 0.06		this work
0.509	3.37 ± 0.06	8.28 ± 0.04	10.99 ± 0.08		this work
0.000		7.95	10.45	$I = 0.1$ M $NaClO_4$, $t = 23$ °C	24

cal 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 ± 0.1) $\mu\Omega^{-1}$cm^{-1}.

A stock solution of dioxovanadium(V), VO_2^+, was prepared by dissolving sodium monovanadate in perchloric acid solution, causing the destruction of decavanadate. To avoid isopolyvanadate formation and obtain only the VO_2^+ ion, the solution was allowed to stand overnight before use. Under this condition, both the polymerization and hydrolysis of VO_2^+ were negligible.[17,18] The concentration of the 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 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.

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

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^+ (5.1×10^{-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 at 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 a 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. pH meter reading B in dioxane or methanol + water media was converted in $[H^+]$ using the equation

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

where the concentration factor, μ_H, was obtained for an ionic strength of 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 was used to calculate values of the correction term $\log \mu_H = \log(\mu°_H \gamma_\pm)$.[14]

Results and Discussion

The complex $M_xH_yL_z^{(nx+y-z)+}$ that is 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]

$$xM^{+n} + yH^+ + zL^- \, \Delta M_xH_yL_z^{(nx+y-z)+} \quad (3)$$

$$\beta_{xyz} = \frac{[M_xH_yL_z^{(nx+y-z)+}]}{[M^{+n}]^x[H^+]^y[L^-]^z} \quad (4)$$

The protonation constant of penicillamine has been used to compute 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 was determined using the potentiometric technique and was calculated using a computer program that employs a nonlinear least-squares method.[23] These value are listed in Table 1 together with the values reported in the literature, which are in good agreement with those reported before.[24]

The method of determining the stability constant is 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 the calculation of stability constants for models of different stoichiometries.

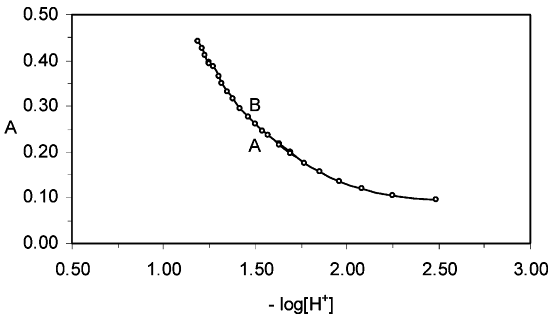

Figure 1. Typical graphical fitting for the VO_2^+ + penicillamine system at 25 °C, 265 nm, and ionic strength 0.1 mol dm^{-3} $NaClO_4$. (A) Experimental absorbance and (B) calculated absorbance from the computer program.

Considering the protonation constants of the ligand, we find that in acidic solution the predominant species for complexation is H_2L. In this case, the spectrophotometric titration data were analyzed by using the absorbance of VO_2^+ + penicillamine at a wavelength in the UV range that is given by

$$A = \epsilon_M[VO_2^+] + \epsilon_C[\text{complex}] + A_{\text{ligand}} \tag{5}$$

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

$$[VO_2^+] = C_M - [\text{complex}] \tag{6}$$

and

$$[H_2L] = C_L - [\text{complex}] - [\text{free ligand}] \tag{7}$$

Substituting eqs 4, 6, and 7 into eq 5 gives the final equation for fitting, where C_M and C_L are the total concentrations 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] we fit the data to the final equation for estimating the formation constant of eq 3. We used the Gauss−Newton nonlinear least-squares method in the computer program to refine the absorbance by minimizing the sum of the squares of the errors from eq 8

$$U = \sum(a_i - b_i)^2 \qquad (i = 1, 2, 3, ...) \tag{8}$$

where a_i and b_i are the experimental and calculated ones, respectively. The computer program consisted of two different kinds of fitting: (a) graphical and (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 and 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^++ penicillamine against $-\log[H^+]$ at 265 nm.

Different models including MH_2L^+, $M(H_2L)_2^+$, and several polynuclear and protonated species were tested by the program. As expected, polynuclear complexes were systematically rejected by the computer program, as were MH_3L^{+2}, MHL_2^{-2}, and $MH_3L_3^{-2}$. A value for the MHL 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 $VO_2H_2L^+$ and $VO_2(H_2L)_2^+$, 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.

Table 2. Formation Constants of VO_2^+ + Penicillamine in Different Solutions of Methanol + Water at 25 °C and Kamlet and Taft's Solvatochromic Parameters

mole fraction of methanol	log β_{121}	log β_{142}	π^{*a}	α^a	β^b	dielectric constant^c
0.000	5.56 ± 0.08	8.06 ± 0.10	1.14	1.26	0.19	78.74
0.047	5.58 ± 0.07	8.15 ± 0.09	1.12	1.19	0.22	74.09
0.100	5.68 ± 0.11	8.26 ± 0.08	1.11	1.13	0.26	68.92
0.161	5.75 ± 0.05	8.39 ± 0.10	1.09	1.08	0.32	63.80
0.229	5.89 ± 0.09	8.51 ± 0.09	1.05	1.04	0.38	58.91
0.308	6.05 ± 0.11	8.72 ± 0.08	1.01	1.01	0.44	54.10
0.401	6.21 ± 0.07	8.91 ± 0.08	0.95	1.01	0.50	49.36
0.509	6.39 ± 0.05	9.09 ± 0.09	0.88	1.03	0.53	44.80
0.640	6.57 ± 0.08	9.35 ± 0.08	0.79	1.04	0.54	40.28

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

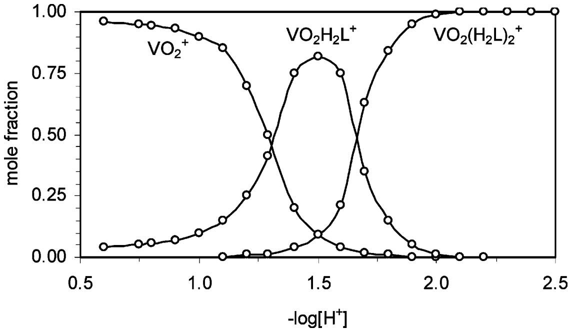

Figure 2. Equilibrium distribution of the species in the VO_2^+ + penicillamine system as a function of $-\log[H^+]$ at 25 °C, 270 nm, and ionic strength 0.1 mol dm^{-3} $NaClO_4$.

In Figure 2, the equilibrium distribution of various species in VO_2^++ penicillamine 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 are often defined in terms of the polarity of the organic solvent. Solvent polarity is a commonly used term related to the ability of the solvent to solvate dissolved charged or dipolar species. Attempts to express it quantitatively involved mainly physical solvent properties such as the dielectric constant of the solvent. However, this approach is often inadequate because the dielectric constant applies to solvents as a nonstructured system, which is not composed of individual molecules with their own solvent−solvent and solvent−solute interactions such as hydrogen-bonding interactions that often play a dominating role in any reaction. The problem is to identify and to assess the relative importance of these various factors in the solvent effects.

Recently, a quantitative measurement of solvent polarity has been introduced by Kamlet and Taft.[2] Kamlet and Taft's solvatochromic parameters have been used in one, two, or three-parameters correlations involving different combination of these parameters that are called linear solvation energy relationships. In general, all of these parameters constitute more comprehensive measures of solvent polarity than the dielectric constant or any other single physical characteristic because they reflect more reliably the complete picture of all intermolecular forces acting between solute and solvent molecules. Using the solvatochromic solvent parameters, a multiparameter equation (eq 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 and 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 dimethyl sulfoxide. 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 a 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 the solvent hydrogen-bond acceptor (HBD) basicity and describes the ability of a solvent to accept a proton in a solute to the solvent hydrogen bond. The β scale was selected to extend from 0.0 for non-(HBD) 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] Regression coefficients p, d, a, and b in eq 9 measure the relative susceptibilities of the solvent dependence of log β to the indicated solvent parameters.

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

To explain the obtained log β 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 log β by minimizing the sum of the squares of the errors from eq 8. Single-parameter correlations of log β_{121} and log β_{142} in terms of α or β individually did not give a good results (eqs 10 and 11).

$$\log \beta_{121} = 9.39 - 3.15\alpha \qquad (10a)$$

$$\log \beta_{142} = 12.91 - 3.95\alpha \qquad (10b)$$

($n = 9$, $r = 0.76$ and 0.78, respectively)

$$\log \beta_{121} = 4.98 + 2.61\beta \qquad (11a)$$

$$\log \beta_{142} = 7.40 + 3.20\beta \qquad (11b)$$

($n = 9$, $r = 0.96$ and 0.97, respectively) Therefore, we thought it would be interesting to correlate log β versus a multiparametric equation involving α, β, and π^*. However, the result presented in eq 12, a multiparametric equation, indicate significant improvement with regard to the single-parameter models.

$$\log \beta_{121} = 7.07 - 0.25\alpha + 1.25\beta - 1.82\pi^* \qquad (12a)$$

$$\log \beta_{142} = 11.70 - 0.56\alpha + 0.65\beta - 2.69\pi^* \qquad (12b)$$

($n = 9$, $r = 0.9992$ and 0.9993, respectively)

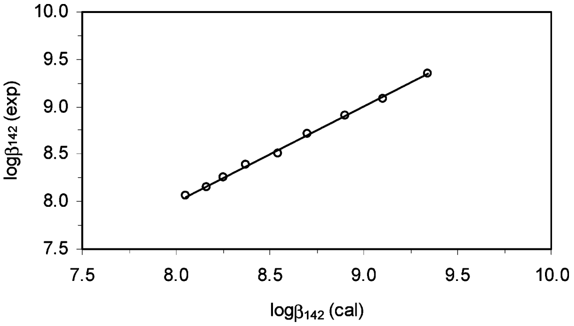

Figure 3. Plot of the experimental values of log β_{142} versus the calculated values from eq 12b.

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

To show the efficiency of suggested multiparameter correlations, experimental values of log β_{142} are plotted versus their calculated values from eq 12b for different aqueous solutions of methanol. It can be seen (Figure 3) that the experimental and calculated values of log β_{142} are in good agreement with each other ($r = 0.9993$).

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