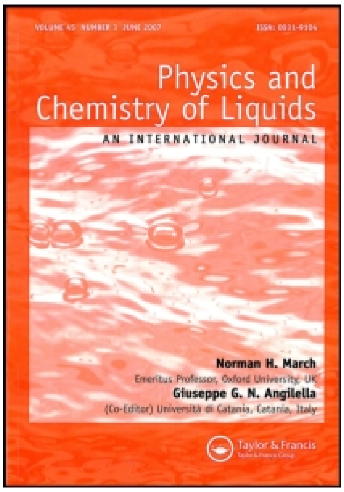

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Dielectric constant dependence of formation constants: complexation of dioxovanadium(V) with cysteine

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Dielectric constant dependence of formation constants: complexation of dioxovanadium(V) with cysteine

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The complexation of dioxovanadium(V) with L-cysteine was investigated in mixed solvent systems of methanol + water and dioxane + water at 25°C and 0.1 $\mathrm{mol\,dm^{-3}}$ ionic media, using a combination of potentiometric and spectrophotometric techniques. Sodium perchlorate solution was used to maintain the ionic strength. The compositions of the formed complexes were determined, and it was shown that dioxovanadium(V), VO_2^+, forms two mononuclear species with the ligand. The stability constants of the complexes formed are given in the above mixed solvent media and interpreted. Linear relationships are observed when plotted $\log\beta$ *versus* $1/D$, where β and D represent formation and dielectric constants, respectively. The results are discussed in terms of the effect on mole fraction of the solvent both for protonation and complexation of cysteine. An attempt has been made to ascertain the nature of the correction factor in determining the pH in the mixed solvent solutions and the effect of increasing organic solvent on $\log\beta$ is also considered.

Keywords: Dielectric constant; Spectrophotometry; Dioxovanadium

1. Introduction

The first report of a definite determination of vanadium content in plants came in 1931, when a low molecular weight vanadium complex was isolated from the toadstool Amanita muscaria [1] and subsequently a series of investigations has been carried out in complexation of this oxo-metal ion. It is now believed that vanadium is an essential nutrient for higher animals [2,3], although this has not yet been clearly established in humans [4]. Nevertheless, vanadium *in vivo* generates significant physiological responses [5–7], for example, vanadate inhibits ion transport ATPases [8], etc. Indisputably, the most important physiological effect of vanadium is the stimulation of glucose uptake and glucose metabolism, that is, its insulin-like properties [9]. Diabetes is one of many diseases that have been reported to have an oxidative pathology [10].

Although several investigations of complex formation reactions between oxo-vanadium and biological ligands have so far been made, little work has been done on complexation of this oxo-ion with amino acids in nonaqueous solution [11,12].

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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. However, the comparison and correlation of these constants is difficult owing to the wide range of experimental conditions. In addition, the thermodynamic quantities for these reactions calculated from these data are liited to specific solvent systems. The present work describes the complexation of dioxovanadium(V) with L-cysteine determined by a combination of potentiometric and spectrophotometric methods in nonaqueous solvents with high ligand-to-metal ratios, to show how solvents and solvent mixtures with dielectric constants affect the formation of such a complex.

2. Experimental

2.1. *Reagents*

Methanol and dioxane were obtained from Merck as analytical reagent grade materials and were used without further purifications. L-cysteine (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 Merch (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 $1.3 \pm 0.1\,\mu\Omega^{-1}\,\mathrm{cm}^{-1}$.

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 [13,14]. 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 [15].

2.2. *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.

2.3. *Measurements*

All measurements were carried out at 25 ± 0.1°C. The ionic strength was maintained at $0.1\,\mathrm{mol\,dm^{-3}}$ 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, we set $-\log[H^+]=2.00$ [16]. Junction potential corrections have been calculated from equation (1)

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

'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.

2.4. *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 in 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 3 times and the resulting average values and corresponding standard deviations are shown in the text and tables.

2.5. *Calibration of the glass electrode*

The term pH has significance only in aqueous media [17]. 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 of 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 [18] was employed for this purpose. The pH meter reading B in dioxane or methanol + water media was converted into $[H^+]$ using the equation

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

where the concentration factor $\log\mu_H$ was obtained for the ionic strength 0.1 mol dm^{-3} $NaClO_4$ from the expression $\log\mu_H = \log\mu_H^\circ + \log\gamma_\pm$. The value of μ_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 [19]. 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 concentration and the corresponding values of B was used to calculate values of the correction term $\log\mu_H = \log(\mu_H^\circ\ \gamma_\pm)$ [11].

In this work, we have used the results reported by Gentile *et al.* [20] for determining the dielectric constants of the systems methanol + water and dioxane + water.

3. Results and discussion

The complex $M_xH_yL_z^{(nx+y-z)+}$ 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, equation (3) is defined by β_{xyz} [16],

$$xM^{+n} + yH^{+} + zL^{-} \rightleftarrows M_xH_yL_z^{(nx+y-z)+} \tag{3}$$

$$\beta_{xyz} - [M_xH_yL_z^{(nx+y-z)+}]/\left([M^{+n}]^x[H^{+}]^y[L^{-}]^z\right) \tag{4}$$

The protonation constant of cysteine has been used for computation of the stability constant, β_{xyz}, of the metal + ligand. The protonation constants of the ligand have been extensively 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 [21,22]. These values are listed in table 1 together with the values reported in the literature, which are in good agreement with those reported before [23–25].

The method of determination of the stability constant based on the relation $A = f([H^{+}])$ [13]. Absorbance, A, and $-\log[H^{+}]$ were measured as described before [26,27]. 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 [22]. The program allows calculation of stability constant for different stoichiometries models.

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

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

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

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

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

Table 1. Protonation constants of L-cysteine, β_{011}, β_{021}, and β_{031} (carboxylic, sulphydryl, and amino groups, respectively) at 25°C, ionic strength, I, 0.1 mol dm^{-3} $NaClO_4$, and different mole fraction of methanol and dioxane in water.

Mole fraction of the solvent	$\log\beta_{011}$	$\log\beta_{021}$	$\log\beta_{031}$	Experimental condition	Ref.
0.000	1.79 ± 0.05	8.33 ± 0.10	10.47 ± 0.12	Water	This work
0.059	1.85 ± 0.03	8.38 ± 0.09	10.51 ± 0.10	Methanol + water	”
0.123	1.90 ± 0.06	8.45 ± 0.08	10.57 ± 0.11	”	”
0.194	1.97 ± 0.04	8.51 ± 0.09	10.64 ± 0.011	”	”
0.053	1.86 ± 0.02	9.00 ± 0.08	10.54 ± 0.10	Dioxane + water	”
0.128	1.95 ± 0.05	9.11 ± 0.07	10.63 ± 0.11	”	”
0.180	2.06 ± 0.04	9.21 ± 0.05	10.74 ± 0.10	”	”
0.0	–	7.91	10.36	0.1 M $NaClO_4$, 50°C	[23]
0.0	–	8.27	10.46	0.15 M $NaClO_4$, 37°C	[24]
0.0	–	8.24	10.55	0.1 M KNO_3, 25°C	[25]

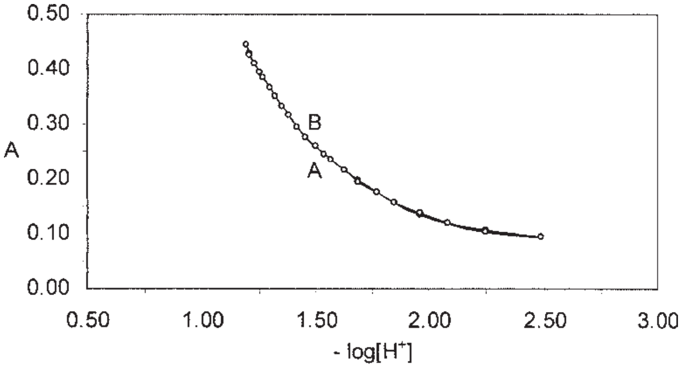

Figure 1. A typical graphical fitting for VO_2^+ + L-cysteine system at 25°C, 265 nm, and ionic strength 0.1 mol dm^{-3} $NaClO_4$, (A) experimental absorbance, and (B) calculated absorbance from the computer program.

Substituting equations (4), (6), and (7) into equation (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 [28] and its values at different wavelengths are used in this work. Using a suitable computer program [22] the data were fitted to the final equation for estimating the formation constant of equation (3). We used the Gauss–Newton nonlinear least-squares method in computer program to refine the absorbance by minimizing the error squares sum from equation (8)

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

where a_i is a quasi-experimental and b_i is a calculated one. 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, 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^+ + cysteine 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 also were MH_3L^{+3}, MHL_2, and $MH_3L_3^+$. A value for the MHL_2^{-2} species were 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.

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

Water has a high dielectric constant (about 80 D), so the electrostatic force of attraction between two ions of opposite charge is considerably reduced. Adding an

Table 2. Average values of $\log \beta_{121}$ and $\log \beta_{142}$ for VO_2^+ + L-cysteine system at 25°C, ionic strength $0.1\,mol\,dm^{-3}$ $NaClO_4$, and various mixtures of methanol and dioxane in water.

Mole fraction of solvent	Dielectric constant[a]	$\log \beta_{121}$	$\log \beta_{142}$
0.000	78.74	4.82	6.26
		Methanol + water	
0.059	72.99	4.99 ± 0.05	6.46 ± 0.04
0.123	67.11	5.13 ± 0.04	6.60 ± 0.06
0.194	60.98	5.35 ± 0.08	6.85 ± 0.03
		Dioxane + water	
0.053	59.88	5.16 ± 0.06	6.58 ± 0.05
0.128	42.02	5.70 ± 0.07	7.05 ± 0.04
0.180	33.11	6.15 ± 0.07	7.45 ± 0.08

[a] Obtained from reference [20].

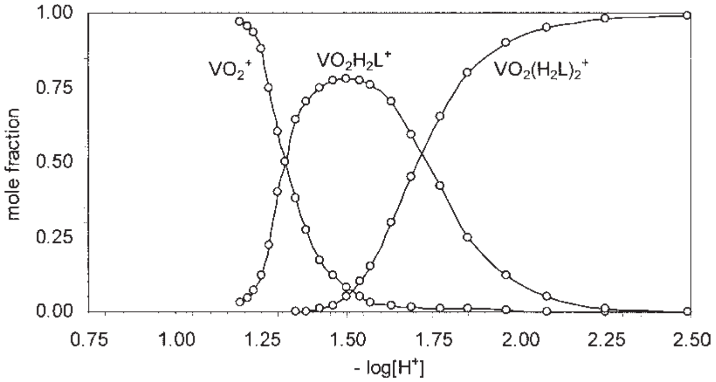

Figure 2. The equilibrium distribution of the species in VO_2^+ + L-cysteine system as a function of $-\log\,[H^+]$ at 25°C, 270 nm, and ionic strength $0.1\,mol\,dm^{-3}$ $NaClO_4$.

organic solvent decreases the dielectric constant of the solution and results in a greater attractive force and hence larger formation and protonation constants. The linear relationship between $\log \beta$ and $1/D$ of the solvent in methanol + water and dioxane + water systems is observed in figure 3. Below a dielectric range of 30, $\log \beta$ as a function of $1/D$ deviates from linearity as expected. It is believed that the deviation is attributed to the fact that organic solvent + water mixtures are generally treated as homogeneous media of the uniform dielectric constant. However, it is possible that in such solutions, there will be preferential orientation of the water molecule around the ions, thus placing them in an environment of a higher dielectric constant. Since the measured dielectric constant is that of the bulk of the medium, a lower $\log \beta$ is expected and observed. Note that such a plot yields lines of different slope for each solvent system and can be used to predict the protonation and stability constants of cysteine for any dielectric constant ranging from 60 to 80 in methanol + water and from 30 to 80 in dioxane + water systems under the same temperature and ionic strength conditions. A plot of $\log \beta$ *versus* $1/D$, likewise gives rise to a linear relationship. The equations for these curves in the linear region, as determined by the least squares are

$$\log \beta_{121}\ (\text{in methanol}) = 140.42(1/D) + 3.05 \tag{9}$$

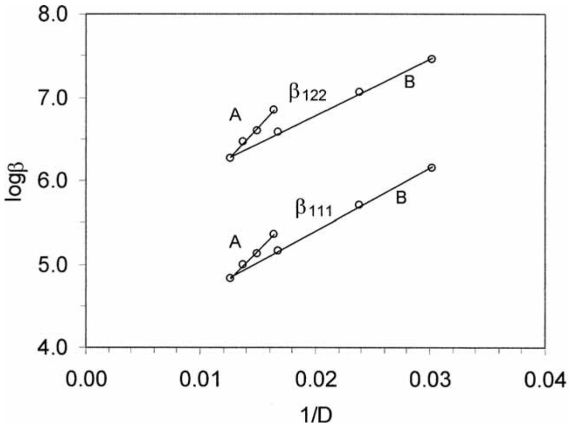

Figure 3. The plots of log β_{121} and log β_{142} *vs.* $1/D$ for VO_2^+ + cysteine system at 25°C, and ionic strength 0.1 mol dm^{-3} $NaClO_4$, (A) methanol + water, (B) dioxane + water.

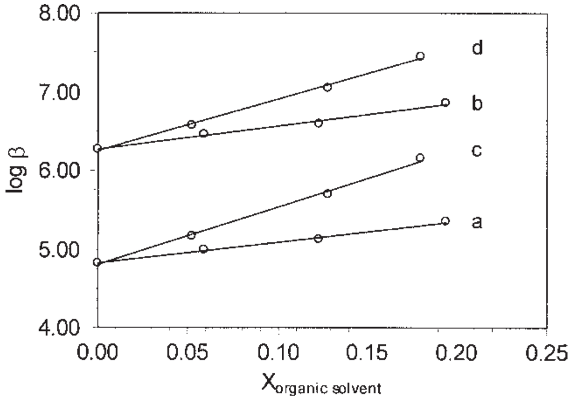

Figure 4. The log β values of VO_2^+ + cysteine system as a function of the mole fraction of the organic solvent, (a) log β_{121} in methanol, (b) log β_{142} in methanol, (c) log β_{121} in dioxane, and (d) log β_{142} in dioxane.

$$\log \beta_{142}\ (\text{in methanol}) = 154.98(1/D) + 4.31 \tag{10}$$

$$\log \beta_{121}\ (\text{in dioxane}) = 75.76(1/D) + 3.88 \tag{11}$$

$$\log \beta_{142}\ (\text{in dioxane}) = 67.46(1/D) + 5.43 \tag{12}$$

On the other hand, the expected linear relationship between log β and the mole fraction of the organic solvent studied is observed for each of the two-component solvent systems as shown in figure 4. It seems reasonable to presume that the log β values may be predicted from knowledge of the dielectric constant or the mole fraction of the solutions studied.

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