J. Chem. Eng. Data **2004,** *49,* 271−275

Ionic Strength Dependence of Formation Constants: Complexation of Dioxovanadium(V) with Tyrosine

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The dependence on ionic strength of protonation of L-tyrosine and its complexation with dioxovanadium(V) is reported in sodium perchlorate solution as a background salt. The measurements have been performed at (25 ± 0.1) °C and various ionic strengths in the range (0.1 to 1.0) mol dm^{-3}, using a combination of potentiometric and spectrophotometric techniques. The overall analysis of the present and the previous data dealing with the determination of stability constants at different ionic strengths allowed us to obtain a general equation, by which a formation constant determined at a fixed ionic strength can be calculated, with a good approximation, at another ionic strength, in the range (0.1 ≤ ionic strength ≤ 1.0) mol dm^{-3} sodium perchlorate.

Introduction

Amino acids occupy a special place in the coordination chemistry of transition metal ions. Since amino acids are the constituents from which proteins are built, the complexes formed by metal ions and amino acids have served as model systems for metalloprotein studies. Knowledge of the interaction between metal ions and amino acids is of possible significance for understanding the biological action of these metals. Although much knowledge is available about the complex formation between almost all metal ions and amino acids, to our knowledge, no work has been reported on the complexation of dioxovanadium(V) by tyrosine. The only interesting information found in the literature is the complexation of vanadate ion by a dipeptide, glycyl-tyrosine, system.[1] It has been suggested that vanadium(V) will spontaneously vanadylate a tyrosine residue in the insulin receptor, leading to a vanadylated tyrosine protein or protein receptor which will then mediate a response.[2,3] Protein kinases and phosphatases are activated or inhibited in the presence of vanadium, and it has been proposed that these phenomena may be related to whether the enzymes contain tyrosine or serine/threonine residues that are phosphorylated.[2]

Although the number of works on the determination of thermodynamic parameters for metal ion complex formation is very large, some uncertainties are still present. This fact is mainly due to the uncertainties in numerical values of the stability constants. For example, when using two different ionic media, 0.5 and 1.0 mol dm^{-3} sodium perchlorate, we observed a difference of about 1 log unit in the stability constant of tyrosine chelate by dioxovanadium(V).

This work deals with the study of complexes of dioxovanadium(V) with tyrosine in the ionic strength range (0.1−1.0) mol dm^{-3} sodium perchlorate. The wide range of ionic media allows calculated stability constants to be applied to the solution of many analytical and speciation problems. The parameters which define the dependence on ionic strength were analyzed, as in previous papers,[4−12] with the aim of obtaining further information with regard to their variation as a function of the charges involved in the reaction of complex formation. Finally, a general equation was established for the dependence of formation constants on ionic strength. The general significance of this equation is strictly connected to the great number of experimental data available in the different concentrations of ions in the complexation reactions. This equation gives the possibility of estimating a stability constant at a fixed ionic strength when its value is known in another ionic medium in the range of (0.1 ≤ ionic strength ≤1.0) mol dm^{-3} $NaClO_4$ and therefore may give a significant contribution to solving many analytical and speciation problems.

Experimental Section

Chemicals. L-Tyrosine (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 standard alkali. The NaOH solution was prepared from titrisol solution (E. Merck), and its concentration was determined by several titrations with standard HCl. Perchloric acid, sodium perchlorate, and sodium monovanadate were supplied from E. Merck as analytical reagent grade materials 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 vanadium(V) was prepared by dissolution of sodium monovanadate in perchloric acid solution affecting destruction of decavanadate. To avoid isopolyvanadate formation, the solution was allowed to stand overnight before use to obtain only the VO_2^+ ion. Under this condition, both polymerization and hydrolysis of VO_2^+ were negligible.[13−15] The concentration of VO_2^+ ion in the stock solution was checked by potentiometric titration using saturated calomel and platinum wire electrodes. Titrations were performed on aliquots after dilution in H_2SO_4 solution.[16]

Apparatus. An Eyela pH-meter, PHM 2000, was used for $-\log [H^+]$ measurements. The hydrogen ion concentration was measured with an Ingold UO 3234 glass electrode and an Ingold UO 3236 calomel electrode. Spectropho-

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10.1021/je0301996 CCC: $27.50

Table 1. Protonation Constant Values of Carboxylic, K_1, and Amino, K_2, Groups of L-Tyrosine at (25 ± 0.1) °C and Different Ionic Strengths, I, $NaClO_4$

I/mol dm^{-3}	log K_1	log K_2	experimental conditions	reference
0.1	2.10 ± 0.09	9.05 ± 0.12		this work
0.3	1.95 ± 0.10	8.91 ± 0.13		this work
0.5	1.97 ± 0.12	9.04 ± 0.15		this work
0.7	2.11 ± 0.11	9.25 ± 0.12		this work
1.0	2.54 ± 0.10	9.55 ± 0.15		this work
		9.21	0.16 M, $NaNO_3$, $t = 25$ °C	18
	2.34	9.11	0.1 M, $NaNO_3$, $t = 25$ °C	19
		9.18	0.1 M, KNO_3, $t = 25$ °C	20

metric measurements were performed on a UV−vis Shimadzu 2100 spectrophotometer with a GDU-20 computer, using thermostated matched 10 mm quartz cells. The measurement cell was of the flow type. A Masterflex pump allowed circulation of the solution under study from the potentiometric cell to the spectrophotometric cell, so the absorbance and −log [H^+] of the solution could be measured simultaneously. A purified nitrogen atmosphere was maintained in the vessel during the titrations.

Measurements. All measurements were carried out at (25 ± 0.1) °C. The ionic strength was maintained at (0.1−1.0) 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}). The same procedure was performed for the other ionic strengths. For these standard solutions, we set −log [H^+] = 2.00.[15] Junction potential corrections have been calculated from eq 1:

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

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. An acidic solution (50 cm^3) of VO_2^+ (2.11 × 10^{-4} mol dm^{-3}) was titrated with an alkali solution (0.1 mol dm^{-3} NaOH) of the ligand (0.002 mol dm^{-3}), both in the same ionic strength. The −log [H^+] and absorbance were measured after addition of a few drops of titrant, and this procedure was extended 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.

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, eq 2 is defined by β_{xyz},[15]

$$x\text{M}^{n+} + y\text{H}^+ + z\text{L}^- \leftrightarrows \text{M}_x\text{H}_y\text{L}_z^{(nx+y-z)+} \qquad (2)$$

$$\beta_{xyz} = [\text{M}_x\text{H}_y\text{L}_z^{(nx+y-z)+}]/([\text{M}^{n+}]^x[\text{H}^+]^y[\text{L}^-]^z) \qquad (3)$$

The protonation constant of tyrosine 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 kinds of background electrolytes, and the results were reported in the literature. The protonation constant of the ligand was determined using the potentiometric technique and calculated using a computer program which employs a nonlinear least-squares method.[5,17] These values are listed in Table 1 together with the values reported in the literature, which are in good agreement with those reported before.[18−20] The protonation equilibrium of the phenolic group of tyrosine was not measured in this work, since in the pH range of study the phenolic group is protonated and possibly not coordinated.

The method of determination of the stability constant was based on the relation $A = f([H^+])$.[13] Absorbance, A, and −log [H^+] were measured as described before,[9,10] and the results are listed in Table 2. 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.[17] The program allows calculation of stability constants for different stoichiometric models.

Considering the protonation constants of the ligand, in acidic solution the predominant species for complexation is HL (without considering the phenolic proton of tyrosine). In this case, the spectrophotometric titration data were analyzed by using the absorbance of VO_2^+ + tyrosine at a wavelength in the UV range that is given by

$$A = \epsilon_{\text{M}}[\text{VO}_2^{\ +}] + \epsilon_{\text{C}}[\text{complex}] + A_{\text{ligand}} \qquad (4)$$

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

$$[\text{VO}_2^{\ +}] = C_{\text{M}} - [\text{complex}] \qquad (5)$$

$$[\text{HL}] = C_{\text{L}} - [\text{complex}] - [\text{free ligand}] \qquad (6)$$

Substituting eqs 3, 5, and 6 into eq 4 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,[21] and its values at different wavelengths are used in this work. Using a suitable computer program,[17] the data were fitted to the final equation for estimating the formation constant of eq 2. We used the Gauss−Newton nonlinear least-squares method in the computer program to refine the absorbance by minimizing the error squares sum from eq 7:

$$U = \sum (a_i - b_i)^2 \qquad (i = 1, 2, 3, ...) \qquad (7)$$

where a_i is a quasi-experimental value 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, that is, sums of squared residuals, differences of C_M(exp) and C_L(exp) from those of calculated

Table 2. Absorbance, *A*, of the System VO_2^+ + Tyrosine at 25 °C and Different −log [H^+], Wavelengths, and Ionic Strengths, *I*, of $NaClO_4$[a]

	A					*A*			
−log [H^+]/mol dm^{-3}	260 nm	265 nm	270 nm	275 nm	−log [H^+]/mol dm^{-3}	260 nm	265 nm	270 nm	275 nm
				$I = 0.1$ mol dm^{-3}					
0.93	0.181	0.177	0.173	0.166	1.70	0.428	0.568	0.704	0.771
0.98	0.213	0.229	0.244	0.247	1.86	0.430	0.572	0.710	0.787
1.12	0.314	0.389	0.462	0.497	1.96	0.435	0.574	0.712	0.808
1.19	0.330	0.425	0.518	0.564	2.02	0.430	0.575	0.702	0.812
1.28	0.392	0.500	0.606	0.657	2.10	0.407	0.567	0.692	0.778
1.35	0.408	0.526	0.637	0.696	2.18	0.398	0.563	0.697	0.772
1.44	0.414	0.537	0.659	0.720	2.29	0.398	0.560	0.701	0.776
1.55	0.427	0.559	0.687	0.752	2.41	0.400	0.555	0.702	0.781
				$I = 0.3$ mol dm^{-3}					
1.19	0.200	0.198	0.196	0.192	1.62	0.350	0.468	0.586	0.646
1.21	0.223	0.238	0.252	0.255	1.72	0.356	0.485	0.609	0.674
1.24	0.251	0.282	0.314	0.327	1.85	0.363	0.500	0.630	0.701
1.31	0.278	0.343	0.401	0.424	1.90	0.366	0.504	0.637	0.709
1.35	0.289	0.364	0.438	0.474	2.06	0.372	0.514	0.653	0.728
1.40	0.304	0.390	0.477	0.520	2.15	0.375	0.518	0.661	0.737
1.46	0.325	0.421	0.519	0.567	2.28	0.389	0.534	0.677	0.756
1.54	0.339	0.448	0.557	0.612	2.46	0.396	0.543	0.689	0.769
				$I = 0.5$ mol dm^{-3}					
1.13	0.181	0.176	0.173	0.168	1.66	0.380	0.521	0.659	0.735
1.21	0.243	0.280	0.317	0.334	1.79	0.393	0.543	0.688	0.772
1.25	0.273	0.332	0.390	0.419	1.91	0.411	0.563	0.716	0.800
1.28	0.296	0.371	0.445	0.483	1.98	0.407	0.566	0.719	0.807
1.37	0.326	0.428	0.530	0.582	2.07	0.409	0.568	0.726	0.816
1.42	0.341	0.455	0.567	0.623	2.20	0.414	0.576	0.736	0.828
1.48	0.354	0.477	0.569	0.663	2.35	0.418	0.581	0.744	0.837
1.57	0.369	0.500	0.630	0.701	2.44	0.421	0.587	0.753	0.848
				$I = 0.7$ mol dm^{-3}					
0.94	0.183	0.179	0.173	0.166	1.59	0.354	0.490	0.623	0.687
1.01	0.232	0.271	0.306	0.320	1.76	0.359	0.503	0.640	0.710
1.07	0.280	0.349	0.416	0.446	1.84	0.364	0.510	0.649	0.722
1.16	0.293	0.373	0.450	0.485	1.92	0.370	0.518	0.660	0.734
1.22	0.307	0.397	0.487	0.527	2.04	0.369	0.519	0.663	0.740
1.29	0.314	0.414	0.513	0.559	2.19	0.367	0.521	0.667	0.746
1.37	0.327	0.438	0.547	0.597	2.31	0.367	0.521	0.671	0.750
1.47	0.342	0.462	0.576	0.632	2.40	0.373	0.526	0.676	0.757
				$I = 1.0$ mol dm^{-3}					
1.19	0.160	0.157	0.154	0.152	1.63	0.400	0.435	0.463	0.495
1.24	0.230	0.265	0.293	0.325	1.73	0.427	0.464	0.495	0.525
1.27	0.252	0.286	0.317	0.342	1.84	0.464	0.500	0.530	0.550
1.31	0.300	0.336	0.363	0.387	1.95	0.485	0.521	0.551	0.578
1.35	0.310	0.346	0.374	0.410	2.05	0.491	0.526	0.557	0.587
1.40	0.321	0.356	0.384	0.419	2.18	0.502	0.539	0.564	0.596
1.46	0.347	0.382	0.413	0.440	2.28	0.520	0.556	0.585	0.614
1.54	0.380	0.416	0.445	0.475	2.46	0.543	0.578	0.602	0.630

[a] The uncertainty values for −log [H^+] and *A* are ±0.01 and ±0.001 units, respectively.

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^+ + tyrosine 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 ML 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 3.

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

Dependence on Ionic Strength. The general Debye−Huckel type equation, eq 8, can be used to take into account the dependence on ionic strength of formation constants:

$$\log \beta(I) = \log \beta(I_1) - AZ[I^{0.5}/(1 + BI^{0.5}) - I_1^{\,0.5}/(1 + BI_1^{\,0.5})] + C(I - I_1) + D(I^{1/2} - I_1^{\,1/2}) + E(I^2 - I_1^{\,2}) \quad (8)$$

where I and I_1 are the actual and reference ionic strengths, $Z = \sum(\text{charges}^2_{\text{reactants}}) - \sum(\text{charges}^2_{\text{products}})$, A and B are the parameters of the Debye−Huckel equation (0.511 and 0.489, respectively, at 25 °C[5]), and C, D, and E are empirical parameters which can be obtained by fitting the experimental data. Results of our previous studies[4−12] and a series of investigations by Daniele et al.[22,23] and De Stefano et al.[24,25] showed that when all the interactions occurring in the solution are considered, in the range $0.1 \le I \le 1.0$ mol dm^{-3}, the empirical parameters C, D, and E at constant temperature are dependent only on the stoichiometry of the formation reactions. The parameter E

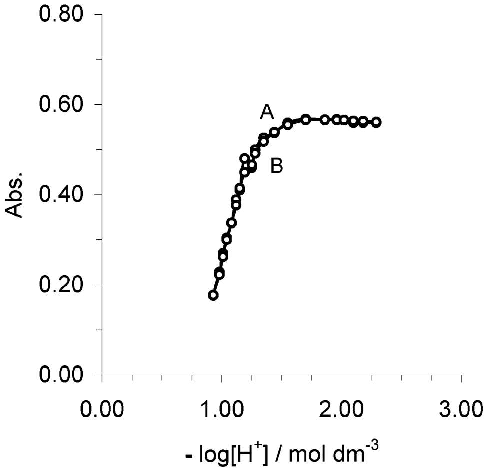

Figure 1. A typical graphical fitting for the VO_2^+ + tyrosine system at 25 °C, 265 nm, and an ionic strength of 0.1 mol dm^{-3} ($NaClO_4$): (A) experimental absorbance; (B) calculated absorbance from the computer program by the fitting method.

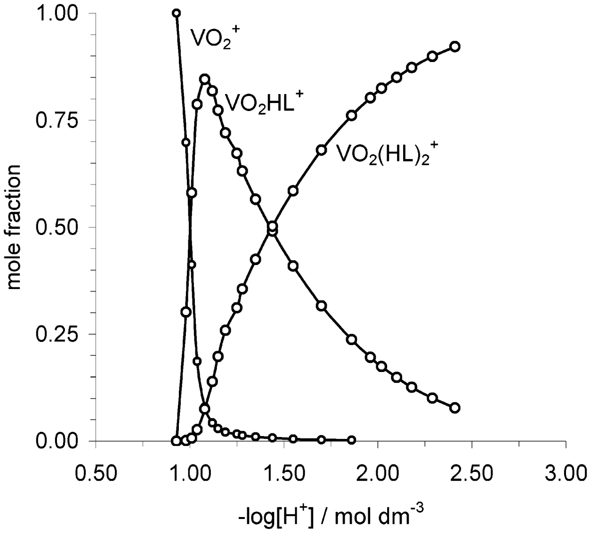

Figure 2. The equilibrium distribution of the species in mole fraction for the VO_2^+ + tyrosine system as a function of $-\log [H^+]$ at 25 °C, 265 nm, and an ionic strength of 0.1 mol dm^{-3} sodium perchlorate.

Table 3. Average Values of log β_{111} and log β_{122} at 25 °C and Different Ionic Strengths of Sodium Perchlorate

I/mol dm^{-3}	log β_{111}	log β_{122}
0.1	7.45 ± 0.14	5.57 ± 0.16
0.3	6.91 ± 0.10	5.32 ± 0.12
0.5	6.80 ± 0.11	5.43 ± 0.11
0.7	7.05 ± 0.10	5.82 ± 0.12
1.0	7.82 ± 0.15	6.85 ± 0.15

usually becomes relevant for $I > 1.0$ mol dm^{-3}. The values of empirical parameters were determined by a regression method with a suitable computer program[17] and reported in Table 4.

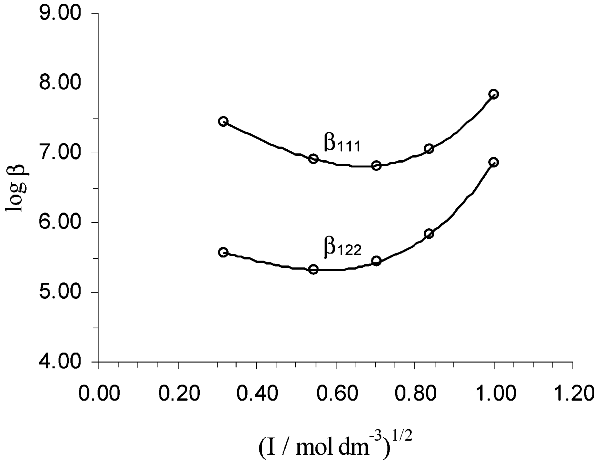

Figure 3. Plots of log β_{111} and log β_{122} versus the square root of ionic strength.

Table 4. Parameters for the Dependence on Ionic Strength of Protonation and Complexation Constant Values at 25 °C

species	C	D	species	C	D
K_1	−2.79	3.05	β_{111}	−7.52	7.38
K_2	−1.86	2.27	β_{122}	−5.61	6.53

The dependence of log β on ionic strength determined in $NaClO_4$ as the background electrolyte is shown in Figure 3 and listed in Tables 1 and 3. The dependencies show a regular trend and are in good agreement with data for other complex species.[4−12,22−25] Our previous results on the ionic strength dependence of complex formation constants[4−12] and this work reveal that the log β values are nearly always at their minimum in the ionic strength range (0.3−0.5) mol dm^{-3} $NaClO_4$, that is a characteristic of the curve $\log \beta = f(I)$, Figure 3. According to the theory of electrolytic solutions,[26] the $AI^{1/2}$ term in eq 8 accounts for ion−ion interaction, while the BI term accounts for disturbances in ion−solvent interaction. Consideration of A and B should therefore yield information about these interactions in the system studied. At low ionic strength, as the ions become separated, the solvent shell of each ion is freed of disturbances and the term BI becomes negligible, making log β a linear function of $AI^{1/2}$. At higher ionic strength, on the other hand, the term due to the solvent interaction dominates the $AI^{1/2}$ term and log β is a linear function of ionic strength (Figure 3).

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Received for review July 2, 2003. Accepted September 25, 2003.

JE0301996