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Stability Constant of Vanadium(V) with Glycine at Different Ionic Strengths

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The stability constant on complexation of VO_2^+ with glycine has been determined by a combination of spectrophotometric and potentiometric methods at (25 ± 0.1) °C and ionic strengths ranging from 0.2 to 0.8 mol dm^{-3} (sodium chloride) in the pH range 1.3−2.5, with high ligand-to-metal ratios. Also, the results are discussed in terms of the effect of ionic strengths on protonation and complexation.

Introduction

In a series of papers (Khorrami et al., 1992; Khorrami and Gharib, 1995; Gharib et al., 1993, 1995) on the stability constants we reported some features of the absorbance of VO_2^+ + amino acid complexes as a function of pH (Beck and Nagypal, 1990). But, there are very few quantitative studies on protonation constants of mineral acids in different ionic strengths (Stefano et al., 1994).

The present paper describes the formation of the complex of oxovanadium(V) with glycine by a combination of spectrophotometric and potentiometric methods in different ionic strengths ranging from 0.2 to 0.8 mol dm^{-3} (sodium chloride) in acidic solution, to show how it affects formation of such a complex.

Experimental Section

Reagents. Sodium chloride, hydrochloric acid, glycine, and sodium hydroxide were obtained from E. Merck. Sodium metavanadate was from Riedel-De Haenag Seelze, Hannover, as analytical reagent grade materials. All materials were used without further purification. Dilute hydrochloric acid solution was standardized against $KHCO_3$. A 50 mass % sodium hydroxide solution free from carbonate was prepared from analytical grade material filtered through a G4 Jena Glass filter. Vanadium(V) solutions were standardized titrimetrically against a standard iron(II) sulfate solution (Zare et al., 1979). The glass electrode was calibrated (in $-\log [H^+]$ units) in the acid and alkaline regions by titrating nitric acid (3−8 mM) with standard 1.0 M carbonate-free potassium hydroxide, at ionic strengths ranging from 0.1 to 0.8 mol dm^{-3} (sodium chloride). This ionic medium was employed since interaction between sodium ions and the ligands concerned can be considered negligible (Daniele et al., 1985a). For determining the protonation constants of glycine, the results in Table 1 are the average of five potentiometric titrations.

Measurements. All measurements were carried out at (25 ± 0.1) °C. A Horiba pH meter F-12 was used for pH measurements. The hydrogen ion concentration was measured with an Ingold UO3234 glass electrode and an Ingold UO3236 calomel electrode. Spectrophotometric measurements were performed on a UV−vis Shimadzu 2101PC spectrophotometer with an "AcerMate 486 SX/250" computer and using thermostated matched 10 mm quartz cells. The measurement cell was a flow type. A masterflex pump allowed circulation of the solution under study from the potentiometric cell to the spectrophotometric cell so the absorbance and pH of the solution could be measured simultaneously. Absorbance, *A*, and pH were measured for solutions containing a large excess of a ligand (pH < 3.00) at (25 ± 0.1) °C. Under these experimental conditions, hydrolysis of the vanadium(V) ion, VO_2^+, was negligible.

Table 1. Protonation Constants of Glycine, log K_p, at Different Ionic Strengths (NaCl)

	I/mol dm^{-3}			
	0.2	0.4	0.6	0.8
log K_p	9.88	9.86	9.82	9.80

Results and Discussion

(a) Protonation Equilibria of the Amino Carboxylic Acid. Equilibrium 1 was studied, where Y^- represents the fully dissociated ligand anion (Itoh et al., 1975):

$$H_3O^+ + Y^- \rightleftharpoons HY + H_2O \tag{1}$$

$$K_p = [HY]/[H_3O^+][Y^-] \tag{2}$$

The protonation constants, K_p, have been determined using potentiometric techniques at various ionic strengths and calculated using a nonlinear least-squares method. The protonation constants of the ligand are collected in Table 1.

The dependence of these values on ionic strength can be described by the general eq 3 (Daniele et al., 1983, 1985b):

$$\log K_p(I) = \log K_p(I') - AZ^*\left(\frac{I^{1/2}}{1 + BI^{1/2}} - \frac{I'^{\,1/2}}{1 + BI'^{\,1/2}}\right) + C(I - I') + D(I^{3/2} - I'^{\,3/2}) \tag{3}$$

where

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Table 2. Values of Molar Absorptivities of the Vanadyl Ion at Various Ionic Strengths (NaCl)

	λ/nm								
I/mol dm^{-3}	240	245	250	255	260	265	270	275	280
0.2	945.45	878.69	830.30	799.52	773.03	739.25	692.21	637.44	571.39
0.4	1119.94	1064.60	1021.83	989.28	955.85	908.93	845.22	770.59	683.25
0.6	1255.63	1206.21	1164.75	1130.59	1091.57	1035.96	960.93	871.09	787.81
0.8	1436.16	1394.09	1354.24	1314.55	1268.33	1201.87	1115.07	1014.86	896.43

Table 3. Values of Molar Absorptivities of VO_2Y at Various Ionic Strengths (NaCl)

	λ/nm								
I/mol dm^{-3}	240	245	250	255	260	265	270	275	280
0.2	1701.98	1442.18	1352.08	1279.27	1224.25	1183.21	1106.65	1103.62	935.65
0.4	1992.03	1700.10	1981.84	2336.45	2052.28	1801.80	1574.40	1399.31	1140.32
0.6	2105.26	1904.76	2004.01	2288.33	2180.13	1988.07	1669.45	1404.49	1243.35
0.8	2103.00	1981.70	1936.28	1739.76	1667.20	1503.76	1372.16	1248.02	1229.10

Table 4. Values of log $K^{H}_{VO_2Y}$ at Different Wavelengths and Ionic Strengths (NaCl)

	λ/nm								
I/mol dm^{-3}	240	245	250	255	260	265	270	275	280
0.2	0.1216	0.2315	0.5750	0.6919	0.6817	0.6840	0.5234	0.5828	
0.4	0.1656	0.4332	1.0866	1.4027	1.3301	1.1932	1.0170	0.8649	0.5284
0.6	0.2103	0.5540	0.9464	1.2221	1.2280	1.1599	0.9663	0.7502	0.6086
0.8	0.2349	0.6130	0.8534	0.8097	0.8055	0.6527	0.5176	0.3692	0.5560

$$A = 0.5115 + 8.885 \times 10^{-4}(t - 25) + 2.953 \times 10^{-6}(t - 25)^2$$

$$B = 1.489 + 8.772 \times 10^{-4}(t - 25) + 4.693 \times 10^{-6}(t - 25)^2$$

I and I' represent the actual and reference ionic strengths, respectively. t is temperature in centrigrade. Z^* is the charge on Y. C and D are parameters experimentally determined. Considering that $A \simeq 0.5$ M$^{-1/2}$ and $B \simeq 1.5$ cm^{-1} at 25 °C, eq 3 can be simplified, since small errors in A and B are absorbed in the linear term,

$$\log K_p(I) = \log K_p(I') - Z^*\left(\frac{I^{1/2}}{2 + 3I^{1/2}} - \frac{I'^{\,1/2}}{2 + 3I'^{\,1/2}}\right) + C(I - I') + D(I^{3/2} - I'^{\,3/2}) \quad (4)$$

C and D are empirical coefficients that were determined to be −0.28 and +0.67 from eq 4, respectively.

(b) Complex of Vanadium(V) with Glycine at Various Ionic Strengths. In acidic solution (pH < 3.00), vanadium(V) exists as the VO_2^+ ion. In the pH range of interest (1.50−3.00), absorbance and pH were measured for solutions containing V(V) (10^{-4} mol dm^{-3}) with a large excess of ligands (2×10^{-2} mol dm^{-3}). The following equilibrium was considered in acidic solution:

$$VO_2^{+} + H_{1-m}Y^{m-} \rightleftharpoons VO_2H_{1-m-n}\,Y^{(m+n-1)-} + nH^{+} \quad (5)$$

The formation constant was defined as $K^{H}_{VO_2Y}$ (Khorrami et al., 1992, 1995). HY is the predominant species in the pH range of interest. In this case, data were analyzed by using HY ($m = 0$ in eq 5) as the reactant. It was assumed that only a single complex was formed in the pH range (Itoh et al., 1975). The absorbance at a wavelength of UV range is given by

$$A = \epsilon_0[VO_2^{+}] + \epsilon_1[VO_2Y] \quad (6)$$

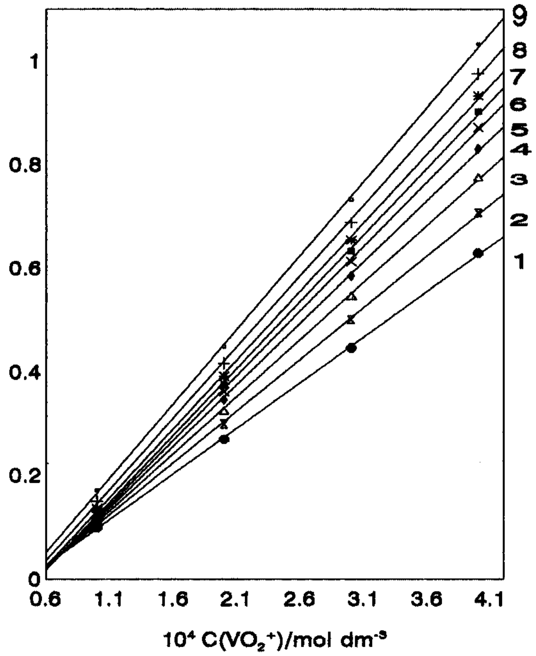

Figure 1. Plot of absorbance against concentration of VO_2^+ at different wavelengths and ionic strength 0.4 mol dm^{-3} (NaCl): (1) 240, (2) 245, (3) 250, (4) 255, (5) 260, (6) 265, (7) 270, (8) 275, (9) 280 nm.

Table 5. Values of log K_{VO_2Y} at Different Ionic Strengths (NaCl)

	I/mol dm^{-3}			
	0.2	0.4	0.6	0.8
log K_{VO_2Y}	10.48 ± 0.08	11.06 ± 0.19	10.90 ± 0.14	10.48 ± 0.17

where ϵ_0 and ϵ_1 are the molar absorptivities of the vanadyl ion and the complex VO_2Y, respectively. Thus $K^{H}_{VO_2Y}$ is given by (Khorrami et al., 1992; Khorrami and Gharib, 1995; Gharib et al., 1993, 1995)

$$\frac{C_{VO_2}}{A} = \frac{1}{\epsilon_1} + \frac{(\epsilon_1 - \epsilon_0)(A - \epsilon_0 C_{VO_2})[H^+]^n}{\epsilon_1 K^{H}{}_{VO_2Y}(\epsilon_1 C_{HY} - \epsilon_0 C_{HY} - A + \epsilon_0 C_{VO_2})A} \quad (7)$$

where C_{VO_2} and C_{HY} are the total concentrations of VO_2^+ and glycine, respectively. Considering that A is a function

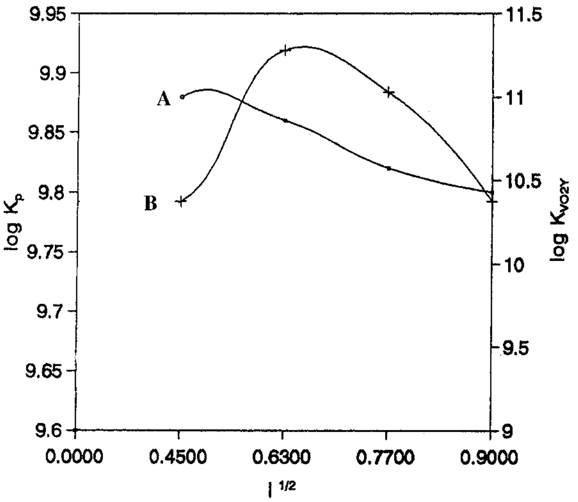

Figure 2. Plot of log K_p (A) and log K_{VO_2Y} (B) against the square root of the ionic strength.

of pH (Itoh et al., 1975), the values of ϵ_0 at (25 ± 0.1) °C are shown in Table 2 (from Figure 1).

The number of protons, *n*, was examined by applying eq 7; the straight line plots of C_{VO_2}/A against $(A - \epsilon_0 C_{VO_2})[H^+]^n/A$ with $n = 1$ confirmed the formation of a single complex with the formula VO_2Y. The values of ϵ_1 were determined from the intercept of the plot and are shown in Table 3.

In our previous work (Khorrami et al., 1992; Khorrami and Gharib, 1995; Gharib et al., 1993, 1995), we reported $\bar{\epsilon}$, $\bar{n}$. Calculation has shown that $n = 1$; thus, the complex V(V) + glycine is a mononuclear 1:1 complex and $K^H{}_{VO_2Y}$ values can be calculated from the slope of eq 7 at different ionic strengths and are shown in Table 4.

Thus, a general equation, log $K = f(I)$, can be used for all the stability constants. Values of log $K^H{}_{VO_2Y}$ were determined at wavelengths ranging from (250 to 270) nm. Thus, by combining these values, the stability constant of the VO_2Y complex can be calculated from eq 8. Figure 2

$$K_{VO_2Y} = K^H{}_{VO_2Y} K_p \qquad (8)$$

shows the dependence of log K_p and log K_{VO_2Y} on ionic strength. The protonation constant of glycine and the stability constant of the system under study have varied with ionic strength. In this figure log K_p has a larger value at $I = 0.2$ and a minimum at $I = 0.8$. Also log K_{VO_2Y} has a larger value at $I = 0.4$ and a minimum when the ionic strength approaches 0.2; that is in good agreement with the results obtained for other complexes (Beck and Nagypal, 1990).

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