Stability Constants of Vanadium(V) with Glycine and Alanine in Acid Solution

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Equilibria in aqueous solutions in the systems glycine + VO_2^+ and alanine + VO_2^+ have been studied by a combination of potentiometric and spectrophotometric methods, in the pH range 1.3–2.3 with high ligand-to-metal ratios. In this study an equilibrium model, MY, is assumed, where M and Y represent the metal ion and fully dissociated amino acid anion, respectively. The stability constants of these complexations and protonation constants of glycine and alanine are also given.

Introduction

The biochemistry of vanadium has attracted increasing interest (*1–6*), particularly in studies related to its accumulation in certain tunicates (*7–10*), and in the mushroom amanita (*10–17*).

Although knowledge of the system amino acid + dioxovanadium(V) are relevant to understanding its possible interaction with likely biological ligands, few reliable data exist. The equilibria in aqueous solution containing vanadium with amino acids have been reviewed recently (*18*). Several experimental methods have been used, and the isolation of solids has also been claimed (*19*).

The present paper describes the formation of the complexes dioxovanadium(V) with glycine and alanine by a spectrophotometric method. These metal–ligand equilibria have been studied with high acid concentration at 25 ± 0.1 °C with 1.0 mol·dm^{-3} sodium perchlorate as the ionic medium.

Experimental Section

Reagents. Sodium perchlorate, perchloric acid, and sodium hydroxide were obtained from E. Merck. DL-Glycine and DL-alanine were from E. Merck and sodium metavanadate was from Riedel-De Haenag Seelze-Hannover as analytical reagent grade materials. All three were used without further purification. Dilute perchloric 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 and stored in a polyethylene bottle; dilute solutions were prepared from double-distilled water with conductivity equal to 1.3 ± 0.1 $\mu\ \Omega^{-1}$, and this stock solution was standardized against $HClO_4$. Vanadium(V) solutions were standardized titrimetrically against a standard iron(II) sulfate solution (*20*).

Measurements. All measurements were carried out at 25 ± 0.1 °C. The ionic strength was maintained at 1.0 mol·dm^{-3} with sodium perchlorate. 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. A 1.00×10^{-2} mol·dm^{-3} perchloric acid solution containing 0.99 mol·dm^{-3} sodium perchlorate was employed as a standard solution of hydrogen ion concentration (*21*). Spectrophotometric measurements were performed on a UV–vis Shimadzu 2100 spectrophotometer with a GDU-20 C 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 solutions could be measured simultaneously.

For each experiment two solutions of VO_2^+ + amino acid have been prepared with the same concentration, but the ionic strength of the first is maintained with sodium perchlorate, and the second with perchloric acid. The first solution is then titrated with the second one. The pH and absorbance is measured after addition of a few drops, and this procedure extends up to the pH of interest.

Results and Discussion

(a) Protonation Equilibria of Aminocarboxylic Acids. Prior to studying the metal–aminocarboxylate complexes, we determined the stability constants of the protonation equilibria of glycine and alanine under the above conditions. The different species present in an acidic medium of pH 2.3 were considered.

The following equilibrium was studied:

$$H^+ + Y^- \rightleftharpoons HY \quad (1)$$

$$K_p = [HY]/[H^+][Y^-] \quad (2)$$

The protonation constants, K_p^G and K_p^A, have been determined using potentiometric techniques and calculated using a nonlinear least-squares method. The logarithms of the protonation constants are given by

$$\log K_p^G = 9.63 \pm 0.03$$

$$\log K_p^A = 9.71 \pm 0.05$$

where G and A denote glycine and alanine, respectively.

(b) Complexes of Vanadium(V) with the Amino Acids. In acidic solution (pH < 2.5), vanadium(V) exists as the VO_2^+ ion (*22, 23*). This ion hydrolyzes to $H_2VO_4^-$,

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Table 1. Values of Molar Absorptivities of the Vanadyl Ion

λ/nm	$10^{-2}\epsilon_0$	λ/nm	$10^{-2}\epsilon_0$
245	5.46	265	4.82
250	5.55	270	4.29
255	5.54	275	3.68
260	5.23	280	2.97

HVO_4^{2-}, VO_4^{3-}, and $HV_2O_7^{3-}$ in alkaline solutions (*24*), and polymerizes in moderately acidic solutions (*23*), giving an instability range. However, in the presence of a large excess of a ligand at pH < 7.5 both polymerization and hydrolysis of VO_2^+ were found to be negligible (*21*). In the pH range of interest (1.3–2.3), absorbance and pH were measured for solutions containing V(V)(10^{-4} mol·dm^{-3}) with a large excess of ligands ((1–4) × 10^{-2} mol·dm^{-3}).

The following equilibrium was considered in acidic solution:

$$VO_2^+ + H_{1-m}Y^{m-} \rightleftharpoons VO_2H_{1-m-n}Y^{(m+n-1)-} + nH^+ \quad (3)$$

The formation constant is defined as

$$K^{H}_{VO_2Y} = \frac{[VO_2H_{1-m-n}Y^{(m+n-1)-}][H^+]^n}{[VO_2^+][H_{1-m}Y^{m-}]} \quad (4)$$

Considering the protonation constants of the amino acids, HY is the predominant species in the pH range of interest for the complex formation. In this case, data were analyzed by using HY ($m = 0$ in eqs 3 and 4) as the reactant. It was assumed that only a single complex was formed in the above pH range (*21*). The absorbance at a wavelength of UV range is given by

$$A = \epsilon_0[VO_2^+] + \epsilon_1[VO_2Y] \quad (5)$$

where ϵ_0 and ϵ_1 are the molar absorptivities of the vanadyl ion and the complex VO_2Y, respectively. For the material balance,

$$[VO_2^+] = C_{VO_2} - [VO_2Y] \quad (6)$$

$$[HY] = C_{HY} - [VO_2Y] \quad (7)$$

where C_{VO_2} and C_{HY} are the total concentrations of VO_2^+ and each amino acid, respectively. Thus, the equilibrium constant for eq 3, $K^{H}_{VO_2Y}$, is given by (*24–28*)

$$\frac{C_{VO_2}}{A} = \frac{1}{\epsilon_1} + \frac{(\epsilon_1 - \epsilon_0)(A - \epsilon_0 C_{VO_2})[H^+]^n}{\epsilon_1 K^{H}_{VO_2Y}(\epsilon_1 C_{HY} - \epsilon_0 C_{HY} - A + \epsilon_0 C_{VO_2})A} \quad (8)$$

Considering that A is a function of pH (*29*), the values of ϵ_0 are shown in Table 1.

The number of protons, n, was examined by applying eq 8; 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 for both amino acids. The values of ϵ_1 were determined from the intercept of the plots, and are shown in Table 2 (from Figures 1 and 2).

If we define $\bar{\epsilon}$ as (*30*)

$$\bar{\epsilon} = \frac{\epsilon_0[VO_2^+]}{[VO_2^+] + [VO_2Y]} + \frac{\epsilon_1[VO_2Y]}{[VO_2^+] + [VO_2Y]} \quad (9)$$

Table 2. Values of Molar Absorptivities of VO_2Y

	$10^{-3}\epsilon_1$			$10^{-3}\epsilon_1$	
λ/nm	VO_2^+ + glycine	VO_2^+ + alanine	λ/nm	VO_2^+ + glycine	VO_2^+ + alanine
240	1.45	1.54	265	0.90	0.94
245	1.17	1.24	270	0.87	0.90
250	1.03	1.02	275	0.83	0.84
255	0.96	0.96	280	0.79	0.81
260	0.93	0.95			

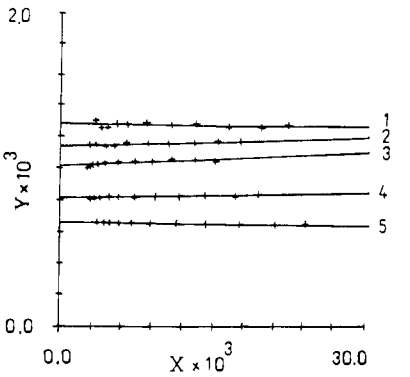

Figure 1. $X = C_{VO_2}/A$ versus $Y = (A - \epsilon_0 C_{VO_2})[H^+]/A$ for solutions of concentrations $C_{VO_2} = 10^{-4}$ M and $C_{glycine} = 2 \times 10^{-2}$ M at different wavelengths: (1) 280, (2) 270, (3) 260, (4) 250, (5) 240 nm.

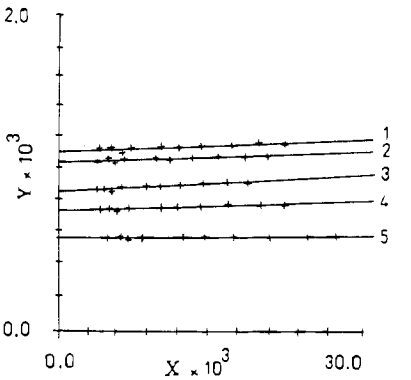

Figure 2. $X = C_{VO_2}/A$ versus $Y = (A - \epsilon_0 C_{VO_2})[H^+]/A$ for solutions of concentrations $C_{VO_2} = 10^{-4}$ M and $C_{alanine} = 4 \times 10^{-2}$ M at different wavelengths: (1) 275, (2) 265, (3) 255, (4) 245, (5) 235 nm.

through the rearrangement of eq 9, the average ligand number, $\bar{n}$, can be calculated directly (30):

$$\bar{n} = \frac{\bar{\epsilon} - \epsilon_0}{\epsilon_1 - \epsilon_0} \quad (10)$$

Calculation has shown that $\bar{n} = 1$ for both complexes; thus, the complexes are mononuclear 1:1, and $K^{H}_{VO_2Y}$ can be calculated from the slope of eq 8.

From Tables 3–7, the averages of log $K^{H}_{VO_2Y}$ for glycine and alanine are 1.61 ± 0.30 and 1.75 ± 0.20, respectively. Considering the following equation

$$VO_2^+ + Y^- \rightleftharpoons VO_2Y \quad (11)$$

the stability constants of the complexes, K_{VO_2Y}, can be calculated from

$$K_{VO_2Y} = K^{H}_{VO_2Y}K_p$$

$$\log K^{G}_{VO_2Y} = 11.24 \pm 0.33$$

$$\log K^{A}_{VO_2Y} = 11.46 \pm 0.25$$

Table 3. Absorbance, A, of Solutions of Concentrations $C_{VO_2} = 10^{-4}$ M and $C_{glycine} = 10^{-2}$ M at Different pH Values and Wavelengths, λ

	A							
pH	240 nm	245 nm	250 nm	255 nm	260 nm	265 nm	270 nm	275 nm
2.17	0.140	0.116	0.102	0.095	0.092	0.089	0.086	0.084
2.13	0.140	0.117	0.103	0.096	0.093	0.090	0.088	0.083
1.79	0.140	0.116	0.101	0.092	0.092	0.089	0.085	0.083
1.73	0.139	0.115	0.101	0.094	0.092	0.088	0.085	0.082
1.67	0.139	0.116	0.101	0.094	0.092	0.089	0.086	0.082
1.62	0.141	0.116	0.101	0.094	0.092	0.089	0.086	0.083
1.57	0.140	0.116	0.101	0.094	0.091	0.089	0.086	0.083
1.52	0.139	0.114	0.100	0.094	0.090	0.088	0.084	0.082

Table 4. Absorbance, A, of Solutions of Concentrations $C_{VO_2} = 10^{-4}$ M and $C_{glycine} = 2 \times 10^{-2}$ M at Different pH Values and Wavelengths, λ

	A							
pH	245 nm	250 nm	255 nm	260 nm	265 nm	270 nm	275 nm	280 nm
2.49	0.114	0.101	0.094	0.094	0.090	0.088	0.089	0.081
2.43	0.114	0.101	0.093	0.090	0.088	0.084	0.085	0.077
2.32	0.114	0.100	0.092	0.089	0.087	0.084	0.082	0.076
2.22	0.112	0.099	0.092	0.089	0.085	0.083	0.082	0.076
1.93	0.111	0.099	0.092	0.088	0.087	0.084	0.083	0.076
1.84	0.113	0.100	0.092	0.089	0.086	0.082	0.081	0.076
1.78	0.112	0.100	0.092	0.088	0.085	0.083	0.081	0.077
1.72	0.111	0.098	0.091	0.088	0.086	0.081	0.080	0.075
1.68	0.112	0.099	0.092	0.087	0.086	0.082	0.079	0.076
1.63	0.112	0.098	0.091	0.088	0.086	0.082	0.079	0.075
1.58	0.112	0.100	0.091	0.088	0.086	0.082	0.080	0.076
1.53	0.113	0.099	0.092	0.088	0.085	0.083	0.080	0.075

Table 5. Absorbance, A, of Solutions of Concentrations $C_{VO_2} = 10^{-4}$ M and $C_{glycine} = 4 \times 10^{-2}$ M at Different pH Values and Wavelengths, λ

	A							
pH	240 nm	245 nm	250 nm	255 nm	260 nm	265 nm	270 nm	275 nm
2.24	0.155	0.107	0.121	0.100	0.094	0.092	0.087	0.085
2.18	0.156	0.107	0.123	0.099	0.094	0.092	0.088	0.085
2.13	0.156	0.107	0.122	0.099	0.095	0.092	0.088	0.084
2.05	0.155	0.105	0.121	0.098	0.093	0.090	0.088	0.083
1.97	0.155	0.105	0.121	0.097	0.093	0.090	0.086	0.083
1.87	0.155	0.104	0.122	0.096	0.093	0.090	0.087	0.083
1.76	0.156	0.104	0.120	0.096	0.092	0.089	0.087	0.083
1.67	0.155	0.103	0.120	0.096	0.092	0.089	0.086	0.082
1.58	0.156	0.103	0.120	0.095	0.091	0.091	0.086	0.082
1.50	0.155	0.104	0.121	0.095	0.092	0.089	0.085	0.083
1.44	0.155	0.104	0.120	0.096	0.092	0.089	0.085	0.082

Table 6. Absorbance, A, of Solutions of Concentrations $C_{VO_2} = 10^{-4}$ M and $C_{alanine} = 10^{-2}$ M at Different pH Values and Wavelengths, λ

	A							
pH	245 nm	250 nm	255 nm	260 nm	265 nm	270 nm	275 nm	280 nm
2.09	0.119	0.102	0.095	0.091	0.089	0.088	0.081	0.079
2.02	0.117	0.101	0.095	0.090	0.088	0.086	0.081	0.077
1.94	0.118	0.101	0.094	0.091	0.088	0.086	0.081	0.079
1.86	0.118	0.100	0.095	0.091	0.088	0.085	0.080	0.077
1.78	0.119	0.102	0.094	0.091	0.089	0.088	0.082	0.080
1.71	0.118	0.100	0.094	0.089	0.088	0.086	0.080	0.079
1.56	0.119	0.100	0.094	0.090	0.087	0.087	0.082	0.078
1.44	0.116	0.098	0.092	0.088	0.085	0.085	0.079	0.077

Table 7. Absorbance, A, of Solutions of Concentrations $C_{VO_2} = 10^{-4}$ M and $C_{alanine} = 2 \times 10^{-2}$ M at Different pH Values and Wavelengths, λ

	A							
pH	240 nm	245 nm	250 nm	255 nm	260 nm	265 nm	270 nm	275 nm
2.14	0.163	0.128	0.109	0.101	0.097	0.093	0.092	0.085
2.04	0.162	0.128	0.108	0.101	0.096	0.093	0.091	0.085
1.99	0.167	0.131	0.110	0.104	0.100	0.098	0.093	0.090
1.90	0.163	0.127	0.106	0.098	0.095	0.092	0.090	0.085
1.74	0.162	0.126	0.106	0.098	0.097	0.094	0.090	0.084
1.68	0.163	0.126	0.106	0.098	0.094	0.092	0.091	0.085
1.60	0.162	0.125	0.105	0.097	0.094	0.092	0.090	0.084
1.52	0.163	0.123	0.104	0.097	0.093	0.090	0.089	0.084
1.45	0.164	0.125	0.104	0.097	0.093	0.091	0.089	0.083
1.40	0.163	0.125	0.104	0.097	0.093	0.090	0.089	0.084

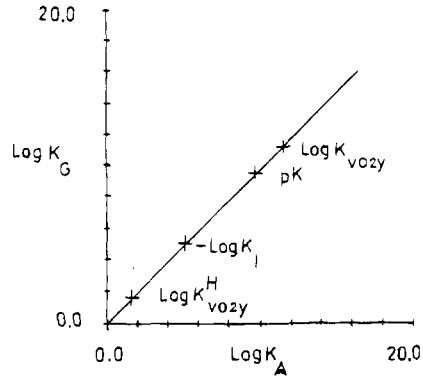

Figure 3. Linear plot of log K_G versus log K_A. The pK of protonation for glycine and alanine and isoelectric pH, $-\log K_1$, are also represented.

Figure 3 shows a representation of the log K obtained in this work for glycine + VO_2^+ and alanine + VO_2^+ systems. The linear plot can be used to estimate log $K^H_{VO_2Y}$ and log K_{VO_2Y} values for species with the same stoichiometry and type of coordination. This type of plot, Figure 3, also can be used to estimate protonation constants of amino acids.

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