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Thermodynamic Studies on Complexation of Dioxyvanadium(V) with Serine

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The solution equilibria of the dioxyvanadium(V) complex formed by serine in acidic media (pH < 2.3) has been investigated potentiometrically and spectrophotometrically. Under these conditions the 1:1 complex has the formula VO_2Y, where Y^- represents the fully dissociated aminocarboxylate anion. The stability constant of VO_2Y was determined $\log K_{VO_2Y} = 10.098 \pm 0.146$ at 25 ± 0.1 °C and $I = 1$ mol·dm^{-3} sodium perchlorate. The protonation constant of serine was also determined potentiometrically under the above conditions.

Introduction

The chemistry of vanadium(V) has been the subject of many investigations, but a few quantitative studies on the stability of the oxygenated ion (VO_2^+) with poly(aminocarboxylate) ligands have been carried out (*1–18*).

The present paper describes the formation of the complex of V(V) with DL-serine by spectrophotometric methods. This metal–ligand equilibrium was studied at 25 ± 0.1 °C with 1 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-serine and sodium metavanadate were purchased from Aldrich Chemi and Riedel - De Haenag Seelze-Hannover, respectively, as analytical reagent grade materials and were used without further purification. Dilute perchloric acid solutions were standardized against $KHCO_3$. A 50 wt % 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 (*19*).

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 (*20*). Spectrophotometric measurements were performed on a UV–vis Shimadzu 2100 spectrophotometer with a GDU-20 C computer 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.

Results and Discussion

(a) Protonation Equilibrium of the Aminocarboxylic Acid. Prior to studying the metal–aminocarboxylate complex, we determined the stability constant of the protonation equilibrium of serine under the above conditions. The different species present in an acidic medium of pH < 2.3 were considered.

Table I. 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

Table II. Values of Molar Absorptivities of VO_2Y

λ/nm	ϵ_1	λ/nm	ϵ_1
240	1650.3	265	1166.5
245	1474.1	270	1111.3
250	1346.1	275	1044.8
255	1269.6	280	978.5
260	1229.2		

The following equilibrium was studied:

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

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

The protonation constant, K, has been determined using potentiometric techniques and calculated using the computer program Harward Graphic which employs a nonlinear least-squares method. The logarithm of the protonation constant is given by

$$\log K = 9.20 \pm 0.05$$

(b) Complex of Vanadium(V) with Serine. In acidic solution (pH < 2.5), vanadium(V) exists as the VO_2^+ ion (*21, 22*). This ion hydrolyzes to $H_2VO_4^-$, HVO_4^{2-}, VO_4^{3-}, and $HV_2O_7^{3-}$ in alkaline solutions (*23*), and polymerizes in moderately acidic solutions (*22*), 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 (*20*). 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 ligand (1×10^{-2}, 1.5×10^{-2}, and 2×10^{-2} mol·dm^{-3}).

The following equilibrium was considered in acidic solution:

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

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Table III. Absorbance, A, of Solutions of Concentrations $C_{VO_2} = 1 \times 10^{-4}$ M and $C_{HY} = 1 \times 10^{-2}$ M at Different pH and Wavelengths, λ

pH	A 245 nm	250 nm	255 nm	260 nm	265 nm	270 nm	275 nm	280 nm
1.46	0.126	0.113	0.106	0.104	0.102	0.097	0.092	0.088
1.57	0.128	0.115	0.108	0.106	0.103	0.099	0.096	0.089
1.62	0.131	0.118	0.112	0.109	0.106	0.101	0.096	0.091
1.68	0.132	0.118	0.111	0.110	0.107	0.102	0.096	0.091
2.03	0.144	0.131	0.122	0.119	0.116	0.110	0.104	0.098
2.20	0.150	0.138	0.130	0.126	0.122	0.116	0.110	0.102

Table IV. Absorbances, A, of Solutions of Concentrations $C_{VO_2} = 1 \times 10^{-4}$ M and $C_{HY} = 1.5 \times 10^{-2}$ M at Different pH and Wavelengths, λ

pH	A 245 nm	250 nm	255 nm	260 nm	265 nm	270 nm	275 nm	280 nm
1.50	0.124	0.108	0.099	0.099	0.098	0.093	0.089	0.086
1.89	0.126	0.112	0.105	0.104	0.101	0.095	0.092	0.088
2.15	0.133	0.119	0.112	0.108	0.105	0.099	0.095	0.090
2.24	0.134	0.121	0.113	0.109	0.106	0.100	0.095	0.091
2.30	0.136	0.123	0.115	0.112	0.109	0.101	0.097	0.091

Table V. Absorbance, A, of Solutions of Concentrations $C_{VO_2} = 1 \times 10^{-4}$ M and $C_{HY} = 2 \times 10^{-2}$ M at Different pH and Wavelengths, λ

pH	A 245 nm	250 nm	255 nm	260 nm	265 nm	270 nm	275 nm	280 nm
1.46	0.132	0.115	0.106	0.103	0.101	0.096	0.093	0.088
1.65	0.133	0.115	0.109	0.106	0.105	0.099	0.094	0.090
1.82	0.136	0.122	0.112	0.111	0.107	0.101	0.096	0.092
1.91	0.138	0.122	0.115	0.111	0.110	0.103	0.097	0.093
2.11	0.145	0.130	0.122	0.119	0.114	0.108	0.100	0.095
2.23	0.146	0.131	0.123	0.119	0.115	0.108	0.101	0.095
2.30	0.152	0.136	0.127	0.123	0.118	0.112	0.104	0.097

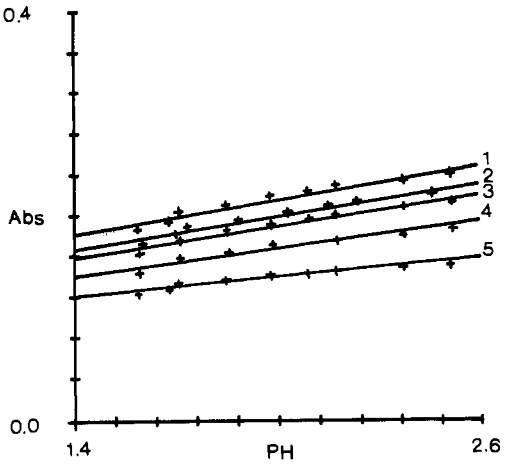

Figure 1. Absorbance–pH curves for V(V) at different wavelengths: (1) 245, (2) 250, (3) 260, (4) 270, (5) 280 nm.

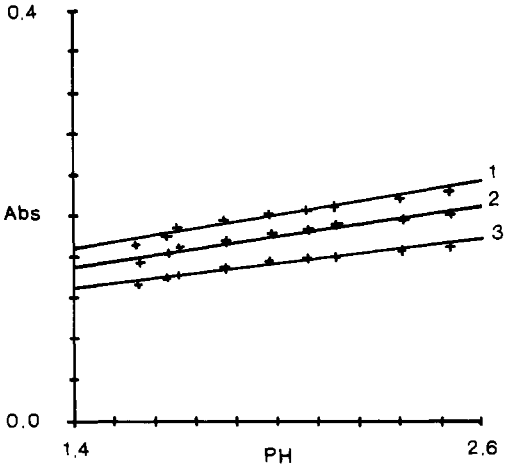

Figure 2. Absorbance–pH curves for V(V) at different wavelengths: (1) 255, (2) 265, (3) 275 nm.

The stability constant was defined as

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

Considering the protonation constant of serine, HY is the predominant species in the pH range 1.3–2.3 for the complex formation. In this case, the 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 (*20*). The absorbance at a wavelength in the UV range is given by

$$A = \epsilon_0[VO_2{}^+] + \epsilon_1[VO_2Y] \qquad (5)$$

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

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

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

where C_{VO_2} and C_{HY} are the total concentrations of $VO_2{}^+$ and serine, respectively. Thus, the equilibrium constant for eq 3, $K^{H}{}_{VO_2Y}$, is given by

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

Considering that A is a function of pH (*8, 23*), the values of ϵ_0 are shown in Table I (from Figures 1 and 2).

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. The values of ϵ_1 were determined from the intercept of the plot, and are shown in Table II.

If we define $\bar{\epsilon}$ as (*24*)

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

through the rearrangement of eq 9, the average ligand numbers, $\bar{n}$, can be calculated directly (*24*):

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

Calculation has shown that $\bar{n} = 1$; thus, the complex V(V)–serine is a mononuclear 1:1 complex, and $K^H{}_{VO_2Y}$ can be calculated from the slope of eq 8.

From Tables III–V log $K^H{}_{VO_2Y}$ is 0.916, 0.977, and 0.802, respectively. Thus, the average of them is 0.898 ± 0.096.

Results

log $K^H{}_{VO_2Y}$ and log K were determined to be 0.898 ± 0.096 and 9.20 ± 0.05, respectively. Thus, by combining these values, the stability constant of the VO_2Y complex can be calculated from eq 11.

$$K_{VO_2Y} = [VO_2Y]/[VO_2^+][Y^-] = K^H{}_{VO_2Y}K \quad (11)$$

$$\log k_{VO_2Y} = 10.098 \pm 0.146$$

The values of $K^H{}_{VO_2Y}$ are fairly close to each other for different concentrations of ligands and wavelengths, which verifies the assumption of the formation of the species VO_2Y in the pH range studied (1.3–2.3). The logarithms of the stability constants of mononuclear 1:1 complexes of dioxyvanadium(V) with EDDA (*7*), CDTA (*9*), NTA (*7*), and EDTA (*20*) were investigated spectrophotometrically at 25 °C; they were found to be 14.5 ± 0.3, 16.61, 13.8 ± 0.4, and 15.54 ± 0.3, respectively. Serine is a bidentate ligand; thus, it is possible to speculate that the stability constant of this amino acid would be lower than EDDA (quadridentate), CDTA (sexadentate), NTA (quadridentate), and EDTA (sexadentate). This speculation agrees with the present results.

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