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

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The stability constant for complexation of VO_2^+ with isoleucine has been determined at different ionic strengths ranging from 0.2 to 0.8 mol dm^{-3} of sodium perchlorate as a background salt, in the pH range 1.3−10 with high ligand to metal ratios, by a combination of potentiometric and spectrophotometric methods at (25 ± 0.1) °C. Our studies have shown that isoleucine forms mononuclear 1:1 and 1:2 complexes with VO_2^+ ion. The protonation constants of isoleucine were also determined potentiometrically at different ionic strengths.

Introduction

In recent years considerable studies have been performed on the ionic strength dependence of the formation constants of some weak complexes of alkali and alkaline earth metals with some organic and inorganic ligands (Daniele et al., 1983, 1985; Robertis et al., 1987, 1995; Stefano et al., 1994, 1996), but on the ionic strength dependence of the stability constants of some strong complexes of aminocarboxylic acids with transition metal ions little work has been reported. A related investigation has been reported by Khorrami et al. (1996 and 1997), who studied complexes of glycine and leucine with VO_2^+ ions at low pH values, suggesting relatively strong bond formation between the ions and oxygen and the nitrogen donors.

On determining the stability constants of weak or strong complexes there are always some uncertainties present. This fact is mainly due to the uncertainties in the numerical values of the stability constant. For example, when maintaining two different ionic media of 0.2 and 0.8 mol dm^{-3} of sodium perchlorate, we observed a difference about 2 log units in the stability constants of isoleucine and dioxovanadium(V).

The present paper describes the complexation of dioxovanadium(V) with L-isoleucine in the ionic strength range 0.2 to 0.8 mol dm^{-3} sodium perchlorate. The parameters which define the dependence on ionic strength were analyzed with the aim of obtaining further information with regard to their variation as a function of the charges involved in the complex reaction. Moreover, a general equation was established for the dependence of the formation constants on ionic strength. This equation gives the possibility of estimating a stability constant at a fixed ionic strength when its value is known at another ionic strength in the range $0.2 \le I \le 0.8$ mol dm^{-3} and therefore may give a significant contribution to solving many analytical and speciation problems.

Experimental Section

Reagents. Sodium perchlorate, perchloric acid, sodium hydroxide, sodium metavanadate, and L-isoleucine were obtained from E. Merck, as analytical reagent grade materials, and 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 a specific conductance equal to (1.3 ± 0.1) $\mu\Omega^{-1}$ cm^{-1}, and this stock solution was standardized against $HClO_4$. The vanadium(V) solution was standardized titrimetrically against a standard iron(II) sulfate solution (Charlot, 1961).

Measurements. All measurements were carried out at (25 ± 0.1) °C. The ionic strength was maintained from 0.2 to 0.8 mol dm^{-3} with sodium perchlorate. An Eyela pH meter, PHM 2000, was used for pH measurements. The pH meter had a sensitivity of 0.01 units. 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 0.19 mol dm^{-3} sodium perchlorate (for adjusting the ionic strength to 0.2 mol dm^{-3}) was employed as a standard solution of hydrogen ion concentration. The same procedure was performed for the other ionic strengths. Spectrophotometric 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 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. For each experiment two solutions of VO_2^+ + isoleucine were prepared with the same concentration, but the ionic strength of the first was maintained with sodium perchlorate and that of the second with sodium hydroxide or perchloric acid. The first solution was then

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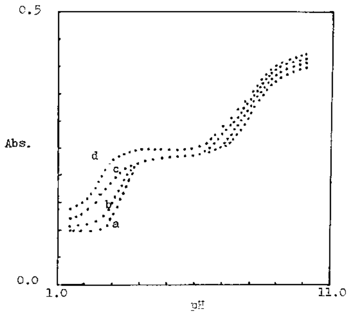

Figure 1. Absorbance−pH curves for VO_2^+ + isoleucine at 265 nm and diifferent ionic strengths: (a) 0.2, (b) 0.4, (c) 0.6, and (d) 0.8 mol dm^{-3}.

Table 1. Values of Protonation Constants of Isoleucine *K* at Different Ionic Strengths *I* of Sodium Perchlorate and 25 °C

I/mol dm^{-3}	0.2	0.4	0.6	0.8
log K	9.34 ± 0.05	9.18 ± 0.05	9.06 ± 0.05	8.89 ± 0.04

titrated with the second one. The pH and absorbance were measured after addition of a few drops of titrant, and this procedure extended up to the required pH.

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 protonation equilibria of isoleucine have been extensively studied in different kinds of background electrolyte, and the results were reported in the literature. However, no studies have been performed on the ionic strength dependence of the protonation constants of isoleucine. The following equilibrium was studied

$$H^+ + L^- \rightleftharpoons HL \tag{1}$$

$$K = [HL]/[H^+][L^-] \tag{2}$$

where L^- represents the fully dissociated amino acid anion. The protonation constant of the amino group of the amino acid K has been determined using potentiometric techniques and calculated using a computer program which employs a nonlinear least-squares method; the results are shown in Table 1. These values are in agreement with those reported before (Nourmand and Meissami, 1983).

Complexation of Vanadium(V) with Isoleucine. The method based on the relationship $A = f(pH)$ was employed (Gharib et al., 1993), on account of the high stability of the complex studied. Absorbance A and pH were measured for a solution containing dioxovanadium (10^{-4} mol dm^{-3}) with a large excess of ligand (10^{-2} mol dm^{-3}) of pH ranging from 1.3 to 10 in various ionic strengths, and the results are shown in Figure 1 and are listed in Table 2. Under this condition both polymerization and hydrolysis of dioxovanadium were negligible (Gharib et al., 1995).

From Figure 1, it seems very likely that a complex is formed in acidic solution (pH 2.5 to 4.0), and the general equation for complexation is given by

$$VO_2^{\ +} + H_{l-m}L^{m-} \rightleftharpoons VO_2H_{l-m}L^{(m+n-1)-} + nH^+ \tag{3}$$

with the formation constant $K^{H}{}_{VO_2L}$ expressed as

$$K^{H}{}_{VO_2L} = \frac{[VO_2H_{l-m}L^{(m+n-1)-}][H^+]^n}{[VO_2^{\ +}][H_{l-m}L^{m-}]} \tag{4}$$

Considering the protonation constant of isoleucine, the predominent species in the pH range 2.5 to 4.0 for complexation is HL. In this case, data were analyzed by using HL ($m = 0$ in eqs 3 and 4) as the reactant. It was assumed that only a single complex, VO_2L, was formed (Khorrami and Gharib, 1995). To determine the molar absorptivity of VO_2L ϵ_1 and the formation constant of complexation, we derived eq 5 (Gharib and Zare, 1992).

$$\frac{C_{VO_2}}{A} = \frac{1}{\epsilon_1} + \frac{(\epsilon_1 - \epsilon_0)(A - \epsilon_0 C_{VO_2})[H^+]^n}{\epsilon_1 K^{H}{}_{VO_2L}(\epsilon_1 C_{HL} - \epsilon_0 C_{HL} - A + \epsilon_0 C_{VO_2})A} \tag{5}$$

The method of determining ϵ_0 was previously describod (Gharib and Zare, 1992), and its values at different wavelengths and various ionic strengths are used in this work (Table 3). The number of protons n was examined by applying eq 5; 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_2L. The values of ϵ_1 were determined from the intercept of the plots and are listed in Table 3.

If we define $\bar{\epsilon}_1$ as (Beck and Nagypal, 1990)

$$\bar{\epsilon}_1 = \epsilon_0\left(\frac{\epsilon_1 C_{VO_2} - A}{C_{VO_2}(\epsilon_1 - \epsilon_0)}\right) + \epsilon_1\left(\frac{A - \epsilon_0 C_{VO_2}}{C_{VO_2}(\epsilon_1 - \epsilon_0)}\right) \tag{6}$$

through the rearrangement of eq 6, the average ligand number $\bar{n}_1$ can be calculated directly

$$\bar{n}_1 = \frac{\bar{\epsilon}_1 - \epsilon_0}{\epsilon_1 - \epsilon_0} \tag{7}$$

Calculation has shown that $\bar{n}_1$ equals 0.96 in various ionic strengths. Thus, at this range of pH, isoleucine forms a mononuclear 1:1 complex with VO_2^+ and $K^{H}{}_{VO_2L}$ can be calculated from the slope of eq 5. The stability constant of the complex can be calculated considering eq 8

$$VO_2^{\ +} + L^- \rightleftharpoons VO_2L \tag{8}$$

and the averages of them at different wavelengths and various ionic strengths are shown in Table 4.

From Figure 1, above pH 6 a second increase in absorbance was observed that is attributed to formation of another species that is given by

$$VO_2L + HL \rightleftharpoons VO_2L_2^{\ -} + H^+ \tag{9}$$

The formation constant of eq 9 was determined in the usual manner

$$\frac{C_{VO_2}}{A} = \frac{1}{\epsilon_2} + \frac{(\epsilon_2 - \epsilon_1)(A - \epsilon_1 C_{VO_2})[H^+]}{\epsilon_2 K^{H}{}_{VO_2L_2}(\epsilon_2 C_{HL} - \epsilon_1 C_{HL} - \epsilon_2 C_{VO_2} + 2\epsilon_1 C_{VO_2} - A)A} \tag{10}$$

where $K^{H}{}_{VO_2L_2}$ is the formation constant of eq 9 and ϵ_2 is the molar absorptivity of $VO_2L_2^-$ that was calculated from the intercept of the plot C_{VO_2}/A versus $(A - \epsilon_1 C_{VO_2})[H^+]/A$ at different wavelengths and various ionic strengths (Table

Table 2. Absorbance *A* of a Solution at Different pH Values, Wavelengths, and Ionic Strengths

	A					*A*			
pH	250 nm	260 nm	270 nm	280 nm	pH	250 nm	260 nm	270 nm	280 nm
					$I = 0.2$				
1.50	0 .117	0.106	0.102	0.096	5.41	0.266	0.251	0.219	0.174
1.64	0.118	0.106	0.102	0.095	5.87	0.270	0.253	0.221	0.174
1.72	0.118	0.106	0.102	0.096	6.82	0.270	0.259	0.225	0.179
1.92	0.117	0.105	0.100	0.094	7.12	0.284	0.269	0.235	0.185
2.20	0.115	0.103	0.098	0.090	7.47	0.297	0. 285	0.253	0.199
2.49	0.113	0.103	0.098	0.089	7.99	0.320	0.318	0.291	0.226
2.69	0.123	0.111	0.106	0.096	8.31	0. 338	0.344	0.320	0.245
3.06	0.144	0.131	0.120	0.105	8.73	0.350	0.362	0.343	0.259
3.47	0.223	0.206	0.181	0.148	8.97	0.353	0.372	0.356	0.269
3.76	0.245	0.229	0.201	0.162	9.22	0.363	0.379	0.365	0.275
4.10	0.258	0.242	0.211	0.169	9.48	0.364	0.387	0.372	0.278
4.59	0.264	0.248	0.215	0.172	10.0	0.369	0.394	0.376	0.281
5.09	0.267	0.249	0.217	0.171					
					$I = 0.4$				
1.50	0.118	0.104	0.096	0.090	5.95	0.273	0.289	0.219	0.175
1.69	0.122	0.109	0.102	0.092	6.48	0.279	0.260	0.222	0.196
1.90	0.128	0.113	0.105	0.093	7.14	0.298	0.282	0.250	0.221
2.16	0.136	0.121	0.110	0.098	7.65	0.317	0.313	0.285	0.239
2.85	0.198	0.135	0.122	0.108	7.90	0.335	0.335	0.312	0.252
3.12	0.204	0.184	0.160	0.133	8.14	0.344	0.351	0.330	0.263
3.33	0.245	0.227	0.195	0.158	8.34	0.352	0.363	0.345	0.275
3.78	0.257	0.240	0.210	0.166	8.63	0.363	0.377	0.362	0.286
4.13	0.262	0.245	0.214	0.169	9.30	0.372	0.392	0.380	0.291
4.59	0.266	0.249	0.215	0.170	9.85	0.375	0.396	0.385	0.290
4.94	0.268	0.252	0.215	0.170	10.12	0.376	0.398	0.387	0.291
5.22	0.269	0.253	0.215	0.172					
					$I = 0.6$				
1.02	0.123	0.113	0.105	0.097	6.15	0.267	0.249	0.214	0.172
1.40	0.162	0.149	0.135	0.118	6.43	0.272	0.252	0.219	0.175
1.82	0.190	0.174	0.157	0.142	6.86	0.279	0.264	0.232	0.184
2.26	0.204	0.180	0.168	0.146	7.11	0.285	0.276	0.245	0.192
2.60	0.217	0.199	0.174	0.159	7.50	0.300	0.297	0.269	0.210
2.91	0.202	0.185	0.161	0.135	7.90	0.323	0.324	0.304	0.233
3.38	0.243	0.225	0.196	0.154	8.20	0.331	0.339	0.319	0.244
3.79	0.256	0.239	0.206	0.166	8.52	0.342	0.354	0.336	0.253
4.16	0.258	0.241	0.209	0.166	8.93	0.345	0.361	0.345	0.260
4.81	0.260	0.243	0.209	0.167	9.36	0.346	0.363	0.348	0.262
5.60	0.264	0.245	0.212	0.169	10.08	0.350	0.368	0.354	0.266
					$I = 0.8$				
1.03	0.116	0.107	0.099	0.092	5.89	0.290	0.268	0.226	0.182
1.24	0.131	0.121	0.110	0.101	6.09	0.292	0.268	0.228	0.183
1.46	0.140	0.128	0.116	0.106	6.41	0.294	0.274	0.233	0.187
1.96	0.165	0.152	0.134	0.117	6.85	0.304	0.285	0.249	0.195
2.10	0.167	0.155	0.138	0.119	7.26	0.317	0.304	0.268	0.210
2.59	0.180	0.165	0.147	0.126	7.59	0.332	0.326	0.292	0.227
2.89	0.242	0.225	0.194	0.161	8.01	0.344	0.344	0.315	0.244
3.22	0.267	0.249	0.214	0.172	8.39	0.350	0.355	0.331	0.253
3.61	0.275	0.258	0.221	0.177	8.69	0.353	0.362	0.336	0.257
3.91	0.278	0.259	0.222	0.177	8.94	0.356	0.368	0.345	0.261
4.24	0.279	0.262	0.223	0.180	9.19	0.359	0.371	0.350	0.265
4.46	0.280	0.263	0.225	0.180	9.59	0.359	0.378	0.352	0.268
5.10	0.283	0.263	0.226	0.181	10.04	0.360	0.394	0.352	0.268

3). Through the rearrangement of eq 6 for the species $VO_2L_2^-$, the average ligand number $\bar{n}_2$ (in the pH range 6 to 9) can be calculated directly from eq 11

$$\bar{n}_2 = \frac{\bar{\epsilon}_2 + \epsilon_2 - 2\epsilon_1}{\epsilon_2 - \epsilon_1} \qquad (11)$$

where $\bar{\epsilon}_2$ is similar to $\bar{\epsilon}_1$ but for the species $VO_2L_2^-$. Calculation has shown that $\bar{n}_2$ equals 1.95. Thus, at this range of pH isoleucine forms a mononuclear 1:2 complex with VO_2^+, and $K^{H}_{VO_2L_2}$ can be calculated from the slope of eq 10. The stability constant of this species

$$VO_2^+ + 2L^- \rightleftharpoons VO_2L_2^- \qquad (12)$$

can be calculated considering eq 12, and the averages of stability constant values at different wavelengths and various ionic strengths are shown in Table 4.

Isoleucine is potentially a bidentate ligand toward metal ions, with two donor sites on the terminal amino and carboxyl groups. Dioxovanadium(V) ion has an octahydral configuration with four positions to form its complexes (Cotton and Wilkinson, 1972). Thus, at higher pH, it is likely that two isoleucine molecules, each as a bidentate ligand, coordinate to each metal ion to form a mononuclear 1:2 complex, while at acidic pH a mononuclear 1:1 species will be formed.

The dependence of the stability constants on ionic strengths can be described by a general equation (Daniele et al., 1985)

Table 3. Values of ϵ_0, ϵ_1, and ϵ_2 at Different Ionic Strengths and Wavelengths

	ϵ_0			
I/mol dm^{-3}	250 nm	260 nm	270 nm	280 nm
0.2	587	566	463	339
0.4	327	301	242	172
0.6	427	405	385	220
0.8	608	560	446	316

	ϵ_1			
I/mol dm^{-3}	250 nm	260 nm	270 nm	280 nm
0.2	2602	2477	2000	1541
0.4	2111	1940	1683	1390
0.6	2717	2544	2182	1723
0.8	2841	2666	2271	1815

	ϵ_2			
I/mol dm^{-3}	250 nm	260 nm	270 nm	280 nm
0.2	3444	3652	3331	2516
0.4	3295	3310	3114	2405
0.6	3432	3617	3645	2728
0.8	3486	3531	3631	2694

Table 4. Average Values of log K_{VO_2L} and log $K_{VO_2L_2}$ at Different Ionic Strengths

I/mol dm^{-3}	log K_{VO_2L}	log $K_{VO_2L_2}$
0.2	8.61 ± 0.10	13.88 ± 0.13
0.4	8.41 ± 0.09	12.85 ± 0.15
0.6	7.86 ± 0.09	11.66 ± 0.10
0.8	8.05 ± 0.10	11.94 ± 0.10

$$\log K_s(\mathrm{I}) = \log K_s(I_1) - AZ^*\left(\frac{I^{0.5}}{1 + BI^{0.5}} - \frac{I_1^{\ 0.5}}{1 + BI_1^{\ 0.5}}\right) + C(I - I_1) \quad (13)$$

where I and I_1 are the actual and reference ionic strengths, respectively, and according to eq 14

$$p\mathrm{M}^{m+} + q\mathrm{L}^{n-} + r\mathrm{H}^+ \rightleftharpoons (\mathrm{M}_p\mathrm{L}_q\mathrm{H}_r)^{pm+qn+r} \quad (14)$$

$Z^* = pm^2 + qn^2 + r - (pm + qn + r)^2$, where m and n are the charges on the metal ion and the ligand, respectively. Considering

$$A = 0.5115 + 8.885 \times 10^{-4}(t - 25) + 2.953 \times 10^{-6}(t - 25)^2 \quad (15)$$

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

where t is the temperature in degrees Celesius, eq 13 can be simplified at $t = 25$ °C as

$$\log K_s(I) = \log K_s(I_1) - Z^*\left(\frac{I^{0.5}}{2 + 3I^{0.5}} - \frac{I_1^{\ 0.5}}{2 + 3I_1^{\ 0.5}}\right) + C(I - I_1) \quad (16)$$

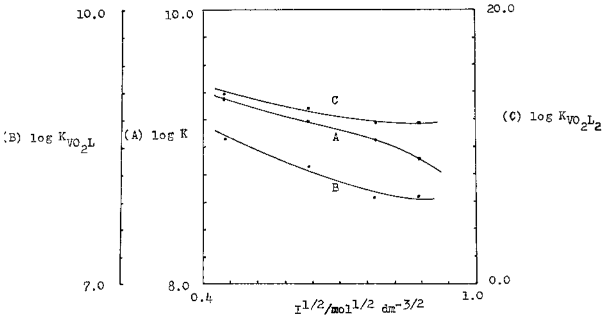

Figure 2. Plots of (A) log K, (B) log K_{VO_2L} , and (C) log $K_{VO_2L_2}$ versus the square root of the ionic strength.

Table 5. Parameters for the Dependence on Ionic Strength of Protonation, VO_2L, and $VO_2L_2^-$ (C) at 25 °C

	C
protonation constant	−0.532
VO_2L	−0.999
$VO_2L_2^-$	−3.825

where C is an empirical coefficient and its value was obtained by a regression method by a suitable computer program and is shown in Table 5. We used the Gauss−Newton nonlinear least-squares method, in a computer program, to refine the parameter of eq 16 by minimizing the error squares sum from eq 17,

$$U = \sum_i (a_i - b_i)^2 \quad (i = 1, 2, 3, ...) \quad (17)$$

where b_i is a quasi-experimental quantity and a_i is a calculated one.

The dependences on ionic strength of log K, log K_{VO_2L}, and log $K_{VO_2L_2}$ are shown in Figure 2. Figure 2 shows that Δ log K_{VO_2L} = log $K_{VO_2L}(I = 0.2)$ − log K_{VO_2L} $(I = 0.6)$ is 0.74; for the second species at the same ionic strengths, Δ log $K_{VO_2L_2}$ = 2.33 and Δ log K = log $K(I = 0.2)$ − log $K(I = 0.8)$ = 0.45. In Figure 2 log K_{VO_2L}, log $K_{VO_2L_2}$, and log K have larger values at $I = 0.2$ and a minimum when the ionic strength approaches 0.6, which are in good agreement with the results obtained for other complexes (Beck and Nagypal, 1990).

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