SHORT PAPER

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Ionic strength dependence of formation constants, protonation and complexation of phenylalanine with dioxovanadium(V) at different temperatures[†]

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The protonation constants of phenylalanine and the stability constants of the complexes between dioxovanadium(V) ion and phenylalanine have been determined spectrophotometrically, in the temperature range 15–35°C and ionic strength ranging from 0.1 to 1.5 mol dm^{-3} sodium perchlorate as a background salt, in the pH range 1.5–10.5, with high ligand to metal ratios. The values of enthalpy and entropy changes based on these formation constants were calculated. The dependence of protonation and the stability constants on ionic strength are described by a Debye-Huckel type equation.

Introduction

In recent years considerable studies have been performed on the ionic strength dependence of formation constants of some weak complexes of alkali and alkaline-earth metals with some organic and inorganic ligands,[1–3] but little work has been reported on the ionic strength dependence of stability constants of some strong complexes of aminocar- boxylic acids by transition metal ions. A related investigation has been made by Khorrami *et al*[4–5], who studied complexes of glycine and leucine with VO_2^+ ions at low pH values, which suggesting relatively strong bond formation between the ions and oxygen and nitrogen donors. On determining the stability constants of weak or strong complexes, there are always present some uncertainties. This fact is mainly due to the uncertainties in numerical values of stability constants. For example, when maintaining two different ionic media of 0.1 and 1.5 mol dm^{-3} of sodium perchlorate, we observed a difference of about one log unit in the stability constant of phenylalanine and dioxovanadium(V).

The present work deals with the study of complexes of VO_2^+ with phenylalanine in an ionic strength range of 0.1 to 1.5 mol dm^{-3} sodium perchlorate and various temperatures within a range of 15–35 ºC. Estimates were deduced for $\Delta H°$ and $\Delta S°$ values from the temperature dependence of stability constants. The parameters which define the dependence on ionic strength were analysed 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 formation constants on ionic strength. This equation gives the possibility of estimating a stability constant of a fixed ionic strength when its value is known at another ionic media in the range $0.1 \le I \le 1.5$ mol dm^{-3} and therefore may give a significant contribution to solving many analytical and speciation problems.

Results and Discussions

The proton–ligand and VO_2^+- ligand stability constants were determined by carrying out phenylalanine, ligand, and dioxovanadium(V), VO_2^+, titrations initially by keeping the temperature constant to 25ºC and varying the ionic strengths ($0.1 \le I \le 1.5$ mol dm^{-3}) and later by maintaining the ionic strength at 0.1 mol dm^{-3} and changing the temperature range from 15 to 35ºC.

The protonation equilibria of phenylalanine have been extensively studied in different kinds of background electrolytes and the results have been reported in the literature. However, no studies have been performed on the ionic strength dependence of protonation constants of phenylalanine. The protonation constant of the amino group of the amino acid, *K*, has been determined using a potentiometric technique and calculated using a computer program which employs a nonlinear least-squares method; the results are shown in Table 1, which are in agreement with those reported before.[6] We studied the following equilibria

$$VO_2^+ + L^- \rightleftharpoons VO_2L$$
$$VO_2L + L^- \rightleftharpoons VO_2L_2^-$$

Table 1 Average values of log$K$, logK_{VO2L}, and logK_{VO2L2} at different ionic strengths and temperatures, λ = 270 nm

	I (mol dm^{-3})	log$K$	logK_{VO2L}	logK_{VO2L2}
t=15°C				
	0.1	9.29	8.35±0.06	12.00±0.04
t=25°C				
	0.1	9.25	8.06±0.11	11.82±0.05
	0.3	9.15	8.19±0.06	11.87±0.03
	0.5	9.06	8.28±0.04	11.71±0.06
	0.7	8.82	8.28±0.03	11.28±0.03
	1.0	8.83	8.57±0.08	11.72±0.19
	1.5	8.98	8.94±0.10	12.09±0.11
t=35°C				
	0.1	9.03	8.14±0.03	11.58±0.03

The determination of the stability constant of VO_2^+ with an amino acid has been described before[7]. The method based on the relationship $A = f$(pH) was employed on account of the high stability of the complex studied. Absorbance, *A*, and pH were measured for solutions containing dioxovanadium(V) (10^{-4} mol dm^{-3}) with a large excess of the ligand (10^{-2} mol dm^{-3}) of pH ranging from 1.5 to 10.5 in various ionic strengths, and the results are shown in Table 1. Under these conditions both polymerization and hydrolysis of VO_2^+ were negligible[8].

Table 1 shows that the metal-ligand stability constants decrease on increasing the temperature and suggest a negative $\Delta H°$ and a positive $\Delta S°$. The $\Delta G°$ values evaluated using the relationship $\Delta G° = -2.303\ RT \log K$, are negative, hence the complexation is spontaneous, Table 2. The $\Delta H°$ values determined from the slope of the graph of log K versus T^{-1} are negative, exhibiting the exothermic nature of the reactions. The $\Delta S°$ values calculated using Gibbs equation are positive, confirming that the chelation effect is essentially an entropy effect[9].

The dependence of the stability constant on ionic strength

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can be described by a general equation (1):

$$\log K_S(I)=\log K_S(I_1)-Z^*\left(\frac{I^{0.5}}{2+3I^{0.5}}-\frac{I_1^{0.5}}{2+3I_1^{0.5}}\right)+C(I-I_1)+\mathrm{D}(I^{1.5}-I_1^{1.5}) \tag{1}$$

Table 2 VO_2^+–phenylalanine thermodynamic parameters at 25°C and I=0.1 mol dm^{-3}

Species	$-\Delta G°$ (kJ mol^{-1})	$-\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})
VO_2L	45.99±0.10	18.30±0.10	89.56±0.10
$VO_2L_2^-$	67.43±0.15	36.60±0.20	103.46±0.20

Table 3 Parameters, *C* and *D*, for the dependence on ionic strength of protonation constant, VO_2L, and $VO_2L_2^-$ at 25°C

Species	*C*	*D*
Protonation constant	–2.50	1.45
VO_2L	–0.47	0.74
$VO_2L_2^-$	–3.13	2.28

Where I and I_1 are the actual and reference ionic strength, respectively, and according to equation (2)

$$pM^{m+}+qL^{n-}+\mathrm{r}H^+ \rightleftharpoons (M_pL_qH_r)^{pm+qn+r} \tag{2}$$

$Z^* = pm^2 + qn^2 + r - (pm + qn + r)^2$, where m and n are charges on the metal ion and the ligand, respectively, and C and D are empirical coefficients whose values were obtained by a regression method by a suitable computer program and are shown in Table 3. We used the Gauss–Newton nonlinear least-squares method, in a computer program, to refine the parameter of equation (1) by minimizing the error squares sum from equation (3),

$$U=\Sigma(a_i-b_i)^2 \qquad (I=1, 2, 3, \ldots) \tag{3}$$

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

The dependence on ionic strength of log$K$, logK_{VO2L}, and logK_{VO2L2} are shown in Table 1 which shows, $\Delta\log K_{VO2L}=\log K_{VO2L}(\mathrm{I}=1.5)-\log K_{VO2L}(I=0.1)=0.87$, for the second species at the same ionic strengths $\Delta\log K_{VO2L2} = 0.27$, and $\Delta\log K = \log K(I=0.1)-\log K(I=0.7)=0.43$, also log$K$ has a larger value at I=0.1 and decreases as the ionic strength increases, logK_{VO2L} has a minimum value at I=0.1 and a maximum at I=1.5, and logK_{VO2L2} has a larger value at I=1.5 and a minimum when the ionic strength approaches 0.7, which are in agreement with the results obtained for other complexes.[10]

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