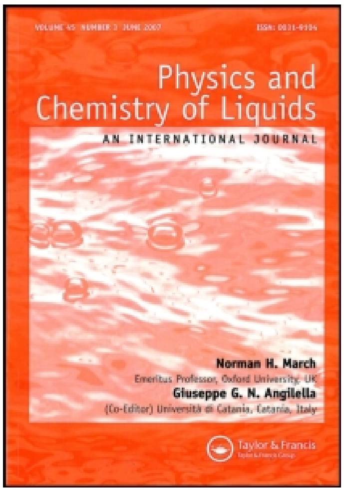

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Ionic Strength Dependence of Formation Constants, Complexation of Asparagine with Dioxovanadium(V)

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IONIC STRENGTH DEPENDENCE OF FORMATION CONSTANTS, COMPLEXATION OF ASPARAGINE WITH DIOXOVANADIUM(V)

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The stability constants of the complexes between dioxovanadium(V) ion and L-asparagine, at different ionic strengths ranging from 0.1 to 1.0 mol dm^{-3} and 25°C were determined using a combination of potentiometric and spectrophotometric techniques. Sodium perchlorate solution was used to maintain the ionic strength. The parameters based on the formation constants were calculated and the dependence of protonation and the stability constants on ionic strength are described by a semi-empirical Debye–Huckel type equation.

Keywords: Stability constant; Ionic strength; Asparagine; Dioxovanadium(V)

INTRODUCTION

The chemistry and biochemistry of vanadium has been the subject of many investigations over a period of more than fifty years. Most of this interest has concerned on complexation of oxovanadium, particularly of V(IV) and (V) oxidation states, with several amino acids [1–10] and a few with di- or tripeptides [11–14]. Some works have been published concerning the interaction of vanadium with proteins,

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particularly albumin, transferin and as activator in various enzymes [15,16]. Most of these studies included the stability constant determination of the formed complexes. However, one unsolved question still remaining about vanadium(V) complexes by peptides is whether the oxygen or the nitrogen in –CONH– group is a donor atom. The study of asparagine complexes may provide further evidence about the nature of the peptide complexes.

The present work deals with the study of dioxovanadium(V), VO_2^+ complexes by L-asparagine, asn, and the purpose of it is first to establish which functional groups of the ligand are necessary for complexation and second, calculating the stability constant of the formed complexes in various ionic strengths of sodium perchlorate as a background salt in the range 0.1–1.0 mol dm^{-3}, moreover, establishing a semi-empirical Debye–Huckel type equation for the protonation and the formation constants dependence on ionic strength, and finally a comparison will be done with the similar systems.

EXPERIMENTAL SECTION

Reagents

L-asparagine (E. Merck, analytical reagent grade) was recrystallized from hot water, washed with ethanol, and dried over P_2O_5. Equivalent weights were checked by titration against standard alkali. The NaOH solution was prepared from titrisol solution (E. Merck) and its concentration was determined by several titrations with standard HCl. Perchloric acid, sodium perchlorate and sodium monovanadate were supplied from E. Merck as analytical reagent grade materials and were used without further purification. Dilute perchloric acid solution was standardized against standard NaOH solution. Vanadium(V) solution was standardized titrimetrically against a standard iron(II) sulfate solution [17]. All dilute solutions were prepared from double-distilled water with specific conductance equal to $1.3 \pm 0.1\,\mu\Omega^{-1}\,cm^{-1}$.

Measurements

All measurements were carried out at $25 \pm 0.1°C$. The ionic strength was maintained from 0.1 to 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 Ingold UO 3236 calomel electrode. The pH-meter was calibrated for the relevant H^+ concentration with a solution of 1.00×10^{-2} mol dm^{-3} perchloric acid solution containing 0.09 mol dm^{-3} sodium perchlorate (for adjusting the ionic strength on 0.1 mol dm^{-3}). The same procedure was performed for the other ionic strengths. For these standard solutions, we set $-\log[H^+] = 2.00$. Spectrophotometric measurements were performed on a UV–Vis Shimadzu 2100 spectrophotometer with GDU-20 computer and using thermostated matched 10 mm quartz cells. The measurements 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 an acidic solution of VO_2^+ (10^{-4} mol dm^{-3}) was titrated with an alkali solution of asn (containing a large excess of asn, 0.02 mol dm^{-3}), both in the same ionic media. The $-\log[H^+]$ and the absorbance were measured after addition of a few drops of titrant, and this procedure extended up to the required $-\log[H^+]$. 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 complex $M_xH_yL_z{}^{(nx+y-z)+}$ formed, is characterized by its stoichiometry $(x:y:z)$, where M and L represent the metal ion and the ligand, respectively. To determine the stability constant of the complexation or the protonation, Eq. (1) is defined by β_{xyz} [1],

$$xM^{+n} + yH^+ + zL^- \rightleftarrows M_x H_y L_z^{(nx+y-z)+} \tag{1}$$

$$\beta_{xyz} = [M_x H_y L_z^{(nx+y-z)+}]/([M^{+n}]^x [H^+]^y [L^-]^z) \tag{2}$$

The protonation constant of asn has been used for computation of the stability constant, β_{xyz}, of the metal–ligand. The protonation constant of asn has been extensively studied in different kind of

TABLE I Protonation constant of L-asparagine, β_{011}, (amino group) at different ionic strengths, *I*, of $NaClO_4$ and 25°C

I/mol dm^{-3}	log β_{011}	*Experimental Condition*	*Ref.*
0.1	8.57 ± 0.10		this work
0.3	8.48 ± 0.08		this work
0.5	8.53 ± 0.09		this work
0.7	8.56 ± 0.10		this work
1.0	8.71 ± 0.11		this work
	8.88	1.0 M, KNO_3, 30°C	27
	8.72	0.1 M, KNO_3, 25°C	28
	8.74	0.2 M, KCl, 25°C	29

background electrolytes, and the results were reported in the literature. The protonation constant of asn has been determined using potentiometric techniques and calculated using a computer program which employs a least-squares method [18,19]. These values are listed in Table I together with the values reported in the literature, which are in good agreement with those reported before.

A comparison of the protonation constant of asn (obtained in this work) with the homologous value of L-glutamine, gln, [20] shows that the presence of the electrophilic amide group close to the α-carbon (in asn) and β-carbon (in gln) decreases the basicity for the amino and increases the acidity of the carboxyl groups, but in the case of gln this effect is softened by the length of the interposed carbon chain and causes a greater protonation constant for the amino group in gln, that agrees with the obtained result.

The method of determination of stability constant based on the relationship $A = f(\mathrm{pH})$ was employed [21], on account of the high stability of the complex studied. Absorbance, A, and $-\log[H^+]$ were measured for a solution containing dioxovanadium(V) with a large excess of the ligand at different ionic strengths, and the results are listed in Table II. To avoid isopolyvanadate formation, the pH of the solutions were lowered by adding appropriate $HClO_4$ solution and were allowed to stand overnight before use. Under this condition both polymerization and hydrolysis of VO_2^+ were negligible [21,22].

From Table II it seems very likely that two complexes are formed (pH 2.18 and 5.41). Considering the protonation constant of the amino acid, in acidic pH the predominant species for complexation is HL. In this case data were analysed by using the absorbance of

TABLE II Absorbances, A, of the system VO_2^+ + L-asparagine at different wavelengths, pH and ionic strength, I

PH	*A*				*PH*	*A*			
	260 nm	265 nm	270 nm	275 nm		260 nm	265 nm	270 nm	275 nm
$I = 0.1$ mol dm^{-3}									
0.99	0.432	0.422	0.410	0.392	2.44	0.272	0.263	0.254	0.240
1.11	0.378	0.368	0.358	0.342	2.59	0.279	0.268	0.258	0.243
1.24	0.346	0.338	0.328	0.314	2.91	0.314	0.298	0.283	0.264
1.37	0.322	0.314	0.305	0.292	3.43	0.531	0.497	0.456	0.410
1.51	0.301	0.293	0.285	0.272	3.91	0.621	0.578	0.528	0.470
1.80	0.279	0.271	0.264	0.252	4.10	0.632	0.589	0.537	0.477
2.03	0.269	0.261	0.254	0.242	4.56	0.646	0.602	0.547	0.486
2.18	0.265	0.259	0.253	0.241	5.51	0.655	0.610	0.555	0.492
$I = 0.3$ mol dm^{-3}									
0.98	0.434	0.424	0.413	0.397	3.09	0.508	0.476	0.438	0.398
1.14	0.365	0.357	0.347	0.334	3.56	0.619	0.578	0.528	0.473
1.30	0.326	0.318	0.310	0.298	3.67	0.630	0.588	0.537	0.480
1.51	0.294	0.288	0.281	0.270	3.82	0.638	0.594	0.542	0.485
1.82	0.271	0.265	0.258	0.247	4.10	0.646	0.603	0.550	0.491
2.10	0.262	0.255	0.247	0.237	5.32	0.658	0.613	0.558	0.498
2.50	0.273	0.262	0.252	0.238	5.62	0.660	0.614	0.560	0.499
2.86	0.390	0.367	0.342	0.282	5.92	0.662	0.615	0.561	0.500
$I = 0.5$ mol dm^{-3}									
0.97	0.403	0.394	0.386	0.374	2.92	0.510	0.483	0.453	0.416
1.11	0.360	0.352	0.345	0.333	3.21	0.632	0.597	0.554	0.502
1.30	0.332	0.326	0.318	0.308	3.45	0.674	0.637	0.590	0.534
1.49	0.309	0.302	0.295	0.285	3.75	0.700	0.659	0.610	0.550
1.77	0.296	0.290	0.283	0.274	4.32	0.718	0.675	0.625	0.563
2.03	0.291	0.283	0.276	0.266	4.96	0.722	0.680	0.630	0.566
2.29	0.296	0.287	0.279	0.267	5.41	0.728	0.684	0.632	0.570
2.52	0.321	0.309	0.298	0.282	5.93	0.734	0.688	0.635	0.573
$I = 0.7$ mol dm^{-3}									
0.96	0.385	0.377	0.369	0.357	2.91	0.572	0.540	0.501	0.454
1.13	0.334	0.327	0.320	0.309	3.01	0.643	0.606	0.559	0.505
1.32	0.306	0.301	0.294	0.284	3.48	0.679	0.639	0.590	0.530
1.53	0.290	0.283	0.278	0.268	4.03	0.689	0.648	0.598	0.538
1.72	0.277	0.271	0.264	0.255	4.15	0.698	0.654	0.603	0.542
1.97	0.280	0.271	0.262	0.251	4.69	0.700	0.658	0.606	0.546
2.29	0.296	0.286	0.274	0.260	5.00	0.702	0.660	0.607	0.547
2.50	0.412	0.392	0.369	0.341	5.52	0.712	0.666	0.612	0.550
$I = 1.0$ mol dm^{-3}									
0.93	0.390	0.382	0.373	0.360	2.60	0.354	0.338	0.320	0.301
1.16	0.336	0.330	0.322	0.311	2.87	0.531	0.502	0.468	0.427
1.31	0.312	0.305	0.298	0.287	3.03	0.607	0.573	0.531	0.482
1.50	0.293	0.286	0.278	0.269	3.32	0.680	0.640	0.590	0.533
1.70	0.284	0.277	0.269	0.260	3.92	0.709	0.666	0.614	0.553
1.97	0.283	0.276	0.267	0.258	4.26	0.714	0.671	0.618	0.557
2.16	0.290	0.281	0.272	0.261	4.56	0.718	0.674	0.621	0.558
2.37	0.207	0.395	0.284	0.270	5.88	0.733	0.683	0.626	0.564

VO_2^+ + asn at wavelengths in the UV range that is given by

$$A = \varepsilon_0[VO_2^+] + \varepsilon_1[\text{complex}] \tag{3}$$

where ε_0 and ε_1 are the molar absorptivities of VO_2^+ and the formed complex, respectively. For the mass balance

$$[VO_2^+] = C_M - [\text{complex}] \tag{4}$$

$$[HL] = C_L - [\text{complex}] \tag{5}$$

where C_M and C_L are the total concentration of VO_2^+ and the ligand, respectively. Substituting Eqs. (2) and (4)–(5) into Eq. (3) and canceling like terms and rearranging gives

$$\begin{aligned} A = {} & \varepsilon_0 C_M + 0.5(\varepsilon_1 - \varepsilon_0)(C_M + C_L + [H^+]/\beta_{xyz}) \pm 0.5(\varepsilon_1 - \varepsilon_0) \\ & \times \{(C_M + C_L + [H^+]/\beta_{xyx})^2 - 4C_M C_L\}^{0.5} \end{aligned} \tag{6}$$

The method of determining ε_0 was previously described [7], and its values at different wavelengths are used in this work. Using a suitable computer program [23] the data were fitted to Eq. (6) for estimating the formation constant of Eq. (1). We used the Gauss–Newton nonlinear least-squares method in the computer program to refine the absorbance by minimizing the error squares sum from Eq. (7),

$$U = \sum_i (a_i - b_i)^2 \quad (i = 1, 2, 3, \ldots) \tag{7}$$

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

In the fitting program, when the stoichiometry coefficient of hydrogen ion was one, U approaches to a minimum value, confirming the formation of a single complex with the formula VO_2L. If we define $\bar{\varepsilon}_1$ [24] as Eq. (8)

$$\bar{\varepsilon}_1 = \varepsilon_0 X_M + \varepsilon_1 X_{ML} \tag{8}$$

Through the rearrangement of Eq. (8), the average ligand number, $\bar{n}_1$, can be calculated directly from

$$\bar{n}_1 = (\bar{\varepsilon}_1 - \varepsilon_0)/(\varepsilon_1 - \varepsilon_0) \tag{9}$$

TABLE III Average values of log β_{101} and log β_{102} in various wavelengths at different ionic strength of $NaClO_4$ and 25°C

I/mol dm^{-3}	*log* β_{101}	*log* β_{102}
0.1	9.47 ± 0.12	16.11 ± 0.14
0.3	9.37 ± 0.10	16.07 ± 0.15
0.5	9.60 ± 0.11	16.31 ± 0.15
0.7	9.63 ± 0.12	16.63 ± 0.13
1.0	9.81 ± 0.11	16.79 ± 0.12

where X_{M} and X_{ML} are the mole fractions of VO_2^+ and VO_2L, respectively. Calculation has shown $\bar{n}_1$ equals to 1.01 at pH 2.18. Thus, at this pH the complexation is completed and asn has formed a mononuclear 1 : 1 complex with VO_2^+ and the averages of β_{101} at different wavelengths are shown in Table III.

The second complex is apparently attributed to

$$VO_2L + HL \rightleftharpoons VO_2L_2^- + H^+ \tag{10}$$

and its stability constant, β_{102}, was determined in usual manner, using Eq. (11)

$$\begin{aligned} A = {} & \varepsilon_1 C_M + 0.5(\varepsilon_2 - \varepsilon_1)(C_L + [\mathrm{H}^+]/\beta_{102}) \pm 0.5(\varepsilon_2 - \varepsilon_1) \\ & \times \{(C_L + [\mathrm{H}^+]/\beta_{102})^2 - 4C_M C_L + 4C_M^2\}^{0.5} \end{aligned} \tag{11}$$

where ε_2 is the molar absorptivity of $VO_2L_2^-$. Through the rearrangement of Eq. (8) for the species $VO_2L_2^-$, the average ligand number, $\bar{n}_2$, can be calculated from Eq. (12)

$$\bar{n}_2 = (\bar{\varepsilon}_2 + \varepsilon_2 - 2\varepsilon_1)/(\varepsilon_2 - \varepsilon_1) \tag{12}$$

where $\bar{\varepsilon}_2$ is similar to $\bar{\varepsilon}_1$ but for the species $VO_2L_2^-$. Calculation has shown that $\bar{n}_2$ equals to 1.995 at pH 5.41. So, at this pH complexation is completed and asn forms a mononuclear 1 : 2 complex with VO_2^+, and the average of their stability constants, β_{102}, at different wavelengths are listed in Table III.

It was checked for other proposed species existed in significant concentration over a reasonable range of data. As expected, polynuclear complexes were systematically rejected by the computer program, as also $VO_2H_2L_2^+$. A value for VO_2HL^+ formation constant was calculated by the program, but the species was not further considered because the estimated error in its formation constant is unacceptable, and its inclusion does not improve the goodness-of-fit. The model finally chosen, formed by VO_2L and $VO_2L_2^-$ resulted in a satisfactory numerical and graphical fitting.

The natural amino acid L-asparagine is potentially a tridentate ligand towards metal ions, with three donor sites on the terminal amino and carboxyl, as well as the amide groups in the side chain of the molecule. Martin and his co-workers [25] showed the formation of two types of copper complexes for L-asparagine and L-glutamine: at $pH < 11$, the amino acids act as bidentate ligands with amide group not involved in coordination; at $pH > 11$, however, deprotonation of the amide group occurs, and the ligands presumably become tridentate in the complex. This is supported by comparing the circular dichroism spectrum of the solution of copper asparaginate at appropriate pH with those of a number of related ligands. Unfortunately, at high pH, where deprotonation of the amide group takes place, considerable precipitation of copper hydroxide occurs, which renders the determination of the accurate stability constant impossible. The same situation is occurred for VO_2^+ and it is impossible to calculate the stability constant at such a high pH. Since two positions of the metal ion are blocked by oxygen atoms, and in view of the preference of VO_2^+ for octahedral configuration in its complexes [26], it is unlikely that asn is tridentate in its complex. Assuming that asn is bidentate in their vanadium complexes, where VO_2^+ assumes its usual octahedron configuration, one can envisage only one way in which the amino acid can bind to dioxovanadium. The ligand may coordinate through the terminal amino and carboxyl groups with the amide group in the side chain remaining free. The ligand would then behave like a simple amino acid, e.g. alanine. The fact that the β_{xyz} values obtained in this work and those for $VO_2^+ + \text{gln}$ [20] are so similar indicates that the ligands probably coordinate as simple amino acids without involvement of the side chain, since in this way both complexes have the same coordinating centers and both form five-membered chelate rings with the oxometal ion.

In Fig. 1 the equilibrium distribution of various species in the $VO_2^+ + \text{asn}$ system is shown as a function of pH. The calculations are based on the stability constants given before. This figure shows when $\bar{n}$ value approaches to one and two the mole fractions of the complexes

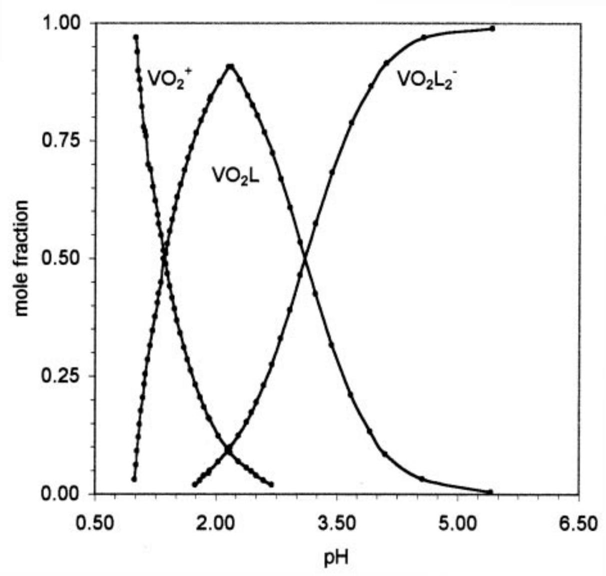

FIGURE 1 The equilibrium distribution of the species in asn + VO_2^+ system as a function of pH at $I = 0.1\,\text{mol}\,\text{dm}^{-3}$ and 25°C.

have the maximum values and very close to one. It is known that an approximate relationship exists between the protonation constants of a series of amino acids and the stability constants of their 1 : 1 and 1 : 2 complexes with a given metal ion. Such a relationship can be used to estimate the stability constants of the metal ion complexes of closely related substances, if their protonation constant values and one β_{101} value are known. Figure 2 demonstrates such a relationship for the stability constants of gln and asn complexes with VO_2^+.

The dependence of the protonation constant on ionic strength for the species H_jL can be described by a semi-empirical equation

$$\log K_j(I) = \log K_j(I^*) - f(I) + CI \tag{13}$$

where $F(I) = Z^* A I^{1/2}/(I + B I^{1/2})$, $K_j(I)$ and $K_j(I^*)$ are the protonation constants of the actual and the reference ionic media at the minimum dilution, respectively. A is the parameter of Debye–Hucke; equation ($A = 0.5115$ at 25°C); $Z^* = 1 + {Z_L}^2 - Z_j$ (Z_L and Z_j are the charges on the anion and the species H_jL, respectively), C is an empirical

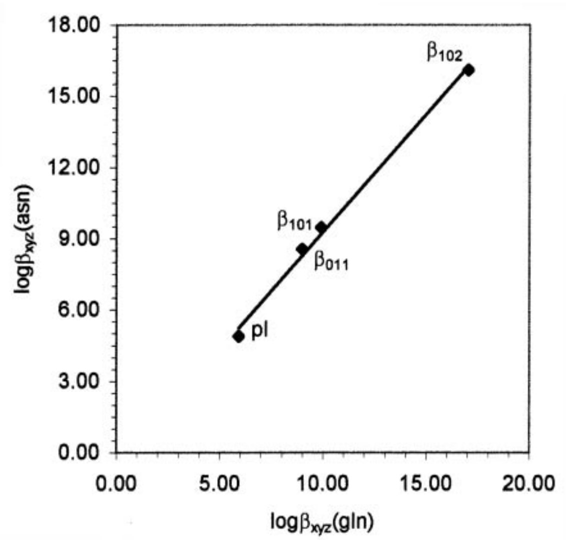

FIGURE 2 Linear plot of the protonation and the stability constants of asn *vs* the homologous values of gln at $I = 0.1\,\mathrm{mol\,dm^{-3}}$, the isoelectric pH of both amino acids are also represented.

parameter that its value is considered, and B is set equal to 1.5 [10] (a small error in fixing B is absorbed in the linear term C [10]). If an approximate value C is known, the protonation constant can be determined for the variation of ionic strength from I^* to I by the equation

$$\log K_j(I) = \log K_j(I^*) - f(I, I^*) + C(I - I^*) \tag{14}$$

where

$$f(I, I^*) = Z^* A[I^{1/2}/(I + 1.5\, I^{1/2}) - I^{*1/2}/(1 + 1.5\, I^{*1/2})] \tag{15}$$

where I and I^* are the ionic strength of the solution by $NaClO_4$. A preliminary analysis of the data showed that if a fixed value is assigned to C, the fit with Eq. (14) is not always good over the whole range of ionic strength from 0.1 to $1.0\,\mathrm{mol\,dm^{-3}}$. This equation may be useful for small changes of ionic strength, but a better fit is obtained by adding a further term of the $DI^{3/2}$ and EI^2 (D and E are another

TABLE IV Parameter for the dependence of ionic strength of protonation and complexation constant at 25°C

Species	*C*	*D*	*E*	*Z**
β_{011}	– 0.908	1.787	– 0.596	2
β_{101}	– 3.904	8.870	– 4.605	2
β_{102}	– 10.066	21.593	– 11.282	0.0

adjustable parameters). Therefore the data were fitted to the Eq. (16).

$$\log K_j(I) = \log K_j(I^*) - F(I, I^*) + C(I - I^*) + D(I^{3/2} - I^{*3/2}) + E(I^2 - I^{*2}) \tag{16}$$

The values obtained for C, D and E are collected in Table IV. It is noticeable that the introduction of the term $D(I^{3/2} - I^{*\,3/2})$ or $E(I^2 - I^{*2})$ very often improves the fit of the data. For example, for protonation constant of the amino group of L-asparagine, from Eq. (16) we obtained three sets of values depending on whether or not we take into account the term in D and E:

$$C = 0.303, \quad D = 0.0, \quad E = 0.0, \quad U = 0.009$$
$$C = -0.390, \quad D = 0.699, \quad E = 0.0, \quad U = 0.0008$$
$$C = -0.908, \quad D = 1.787, \quad E = -0.596, \quad U = 0.0006$$

The squares sum, U, shows that there is a significant improvement in the fit when D and E are introduced.

As can be seen from Table IV, the parameters which characterize the dependence of protonation constant on ionic strength show a regular trend and seem to be a function of Z^* value. The same procedure was applied for determining the dependence of the stability constants of asn + VO_2^+ complexes on ionic strength, where in this case $Z^* = Z_M^2 + jZ_j^2 - Z_C^2 - Z_C^2 - 1$ (for VO_2L) and $Z^* = jZ_j^2 + Z_C^2 - Z_{C*}^2 - 1$ (for $VO_2L_2^-$), where Z_M, Z_C and Z_{C*} are the charges on the metal ion, VO_2L, and $VO_2L_2^-$, respectively. The semi-empirical parameters were determined as before are shown in Table IV. Tables I and III show that the protonation constant , β_{101} have larger values at $I = 1.0$ and minima when the ionic strength approaches 0.3 mol dm^{-3}, which are in agreement with the results obtained for other species [4,10,18,24].

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