Ionic Strength Dependence of Formation Constants, Protonation and Complexation of Proline with Dioxovanadium(V)

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The stability constants of dioxovanadium(V) complexes of L-proline at different ionic strengths ranging from 0.1 to 0.7 mol dm^{-3} at 25 ºC were determined using spectrophometric technique. The parameters based on the formation constants were calculated and the dependence of protonation and the stability constants on ionic strength were described by a Debye-Huckel type equation.

Key Words: Stability constant, Ionic strength, Dioxovanadium(V), L-Proline.

INTRODUCTION

The chemistry and biochemistry of vanadium has been the subject of many investigations in recent years. This is due to the fact that the free pervanadyl ion readily hydrolyzes[1] to HVO_3 and VO_3^-. In addition pervanadyl ion is often reduced by organic substances in acidic media[2,3].

Metal ion complexes with amino acids have been extensively studied because of their possible significance as models for biological process assisted by them.On the ionic strength dependence of formation constants we recently[4-7] reported some interesting features of the function log k = f(I). According to literature, no work has been reported on ionic strength dependence of dioxovanadium(V) with proline. The present paper deals with the study of complexes of dioxovanadium(V) with L-proline in an ionic strength range of 0.1, 0.7 mol dm^{-3} in presence of sodium chloride at 25 ºC. 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 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 of $0.1 \leq I \leq 0.7$ mol dm^{-3} and therefore may give a significant contribution to solving many analytical and speciation problems.

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EXPERIMENTAL

L-proline (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 titrations with standard HCl.

Sodium chloride and hydrochloric acid were supplied from E. Merck and vanadium(V) dioxide was from fluka. All these reagents were used without further purification. All dilute solutions were prepared from double-distilled water with specific conductance equal to 1.3 ± 0.1 $\mu\Omega^{-1}$ cm^{-1}. Vanadium solution was standardized against a standard iron(II) sulfate solution[8].

Measurements were preformed by using an apparatus consisting of an Eyela model pHM 2000, equipped with an Ingold 3236 calomel electrode and an Ingold 3234 glass electrode for measuring the hydrogen ion concentration. The pH meter was calibrated for the relevant H^+ concentration with a solution of 0.01 mol dm^{-3} hydrochloric acid solution containing 0.09 mol dm^{-3} sodium chloride (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[9], we set -log $[H^+]$ = 2.00. All titrations were carried out in a double-jacketed glass cell. The temperature was maintained (25 ºC) by circulating water from the thermostat through the outer jacket of the cell.

The thermostat was constant to ± 0.1 ºC. All titrations were performed by stirring magnetically and by bubbling purified nitrogen through the solution, in order to exclude O_2 and CO_2 inside.

For each experiment an acidic solution of VO_2^+ (2.5×10^{-4} mol dm^{-3}) was titrated with an alkali solution of proline (containing a large excess of proline, 8×10^{-2} 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.

RESULTS AND DISCUSSION

The proton-ligand and the metal ion-ligand stability constants were determined by carrying out proline and dioxovanadium(V), VO_2^+, titrations by keeping the temperature constant at 25 ± 0.1 ºC and varying the ionic strength ($0.1 \le I \le 0.7$ mol dm^{-3}).

The following equilibrium was studied.

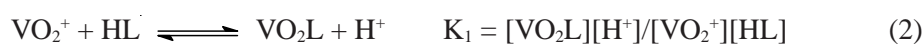$$H^+ + L^- \rightleftharpoons HL \qquad K_p = [HL]/[H^+][L^-] \qquad (1)$$
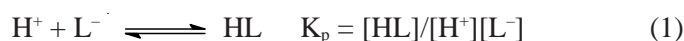
where L^- represents the fully dissociated amino acid anion. The protonation constant of the amino group, k_p, have been determined using a computer program that employs a non-linear least squares method[10,11].

To determine the formation constants of complexation[12], eqns. 2 and 3 is defined by k_1 and k_2,

TABLE-1
PROTONATION CONSTANT OF L-PROLINE, k_p, (AMINO GROUP) AT
DIFFERENT IONIC STRENGTHS (I) OF NaCl AT 25 ºC

Ionic strength (I) (mol dm^{-3})	log k_p
0.1	9.2564
0.3	9.1946
0.5	9.1745
0.7	9.1343

$$VO_2^+ + HL \rightleftharpoons VO_2L + H^+ \qquad K_1 = [VO_2L][H^+]/[VO_2^+][HL] \qquad (2)$$

$$[VO_2L] + [HL] \rightleftharpoons VO_2L_2^- + H^+ \quad K_2 = [VO_2L_2^-][H^+]/[VO_2L][HL] \qquad (3)$$

The method of determination of the determination of the stability constant based on the relationship A = f(pH) was employed[12], on account of the high stability of the complexes 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-2. To avoid isopolyvanadate formation, the pH of the solutions were lowered by adding appropriate HCl solution and were allowed to stand overnight before use. Under this condition both polymerization and hydrolysis of VO$_2^+$ were negligible[12,13].

It seems very likely that two complexes are formed for the ligand. Considering the protonation constants of the amino acid, in acidic pH the predominant species for complexation is HL.

In this case data were analyzed by using the absorbance of VO$_2^+$ + proline at wavelengths in the UV range is given by:

$$A = \epsilon_0 [VO_2^+] + \epsilon_1 [Complex]$$

where ϵ_0 and ϵ_1 are the molar absorptivities of VO$_2^+$ and the formed complex, respectively.

For the mass balance

$$[VO_2^+] = C_M - [Complex] \qquad (5)$$

$$[HL] = C_L - [Complex] \qquad (6)$$

where C_M and C_L are the total concentration of VO$_2^+$ and the ligand, respectively. Substituting eqns. 2 and 5-6 into eqn. 4 and canceling like terms and rearranging gives.

$$A = \epsilon_0 C_M + 0.5(\epsilon_1 - \epsilon_0)\left(C_M + C_L + [H^+]/\beta_1\right) +$$

$$0.5(\epsilon_1 - \epsilon_0) \times \left\{\left(C_M + C_L + [H^+]/\beta_1\right)^2 - 4C_M C_L\right\}^{0.5} \qquad (7)$$

The method of determining ϵ_0 was previously described[14] and its values at different wavelengths are used in the work. Using a suitable computer program[11],

the data were fitted to eqn. 7 for estimating the formation constant of eqn. 2. We used the Gauss-Newton non-linear least-squares method in the program to refine the absorbances by minimizing the error squares sum from eqn. 8.

$$U = \Sigma(A_i - A_j)^2 \tag{8}$$

where A_i is a quasi-experimental quantity and A_j 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 $\overline{\in}_1$ [15] as eqn. 9.

$$\overline{\in}_1 = \in_0 X_M + \in_1 X_{ML} \tag{9}$$

Through the rearrangement of eqn. 9, the average ligand number $\overline{n}_1$ can be calculated directly from.

$$n_1 = (\overline{\in}_1 - \in_0)/(\in_1 - \in_0) \tag{10}$$

where X_M and X_{ML} are the mole fractions of VO_2^+ and VO_2L, respectively. When $\overline{n}_1$ equals to 1.00 the complexation is completed and proline forms a mono-nuclear 1:1 complex with VO_2^+ and the averages of β_1 at different wavelengths are shown in Table-2. The second complex is apparently attributed to eqn. 3 and its stability constant, β_2 was determined in usual manner, using eqn. 11

$$A = \in_1 C_M + 0.5(\in_2 - \in_1)(C_L + [H^+]/\beta_2) \pm 0.5(\in_2 - \in_1) \times$$
$$\left\{ \left(C_L + [H^+]/\beta_2 \right)^2 - 4C_M C_L + 4C_M^2 \right\}^{0.5} \tag{11}$$

where $\in_2$ is the molar absorptivity of $VO_2L_2^-$. Through the rearrangement of eqn. 9 for the species $VO_2L_2^-$, the average ligand number, $\overline{n}_2$, can be calculated from eqn. 12:

$$\overline{n}_2 = (\overline{\in}_2 + \in_2 - 2\in_1)/(\in_2 - \in_1) \tag{12}$$

where $\overline{\in}_2$ is similar to $\overline{\in}_1$ but for the species $VO_2L_2^-$. When that $\overline{n}_2$ equals to 2.00 complexation is completed and proline forms a mononuclear 1:2 complex[16,17] with VO_2^+. The average of their stability constants, β_2, at different wavelengths are listed in Table-2.

TABLE-2
AVERAGE VALUES OF log β_1 AND log β_2 IN VARIOUS WAVELENGTHS
(195-205 nm) AT DIFFERENT IONIC STRENGTHS (I) OF NaCl AT 25 ºC

I (mol dm⁻³)	log β_1	log β_2
0.1	10.1692	20.0310
0.3	10.0571	19.8282
0.5	10.0740	19.7869
0.7	9.9907	19.6428

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

$$f(I) = Z^*AI^{1/2} / (I+BI^{1/2}) \tag{14}$$

and $\log k_j (I)$ and $\log k_j (I^*)$ are the protonation constants of the actual and the reference ionic strength at the minimum dilution, respectively. A is the parameter of the extended Debye-Huckel equation (A = 0.51115 at 25 ºC), $Z^* = 1 + Z_L^2 - jZ_j$ (Z_L and Z_j are the charges on the anion and the species H_jL, respectively); C is an empirical parameter that its value is considered and B is set equal to 1.5 (a small error in fixing B is absorbed in the linear term C)[4]. If an approximate value of C is known, the protonation constant can be determined for the variation of ionic strength from I* to I by the equation:

$$\log k_j(I) = \log k_j(I^*) - f(I,I^*) + C(I-I^*) \tag{15}$$

where

$$f(I,I^*) = Z^*A[I^{1/2} / (I + 1.5\ I^{1/2}) - I^{*1/2} / (1 + 1.5\ I^{*1/2}] \tag{16}$$

where I and I* are the ionic strength of the solution of NaCl.

The values of $\log k_j$ are reported in Table-1. The dependence of the protonation constant on ionic strength was then studied. A preliminary analysis of the data showed that if a fixed value is assigned to C, the fit with eqn. 13 is not always good over the whole range of ionic strength from 0.1 to 1.0 mol dm^{-3}. This equation may by useful for small changes of ionic strength, but a better fit is obtained by adding a further term of the form $DI^{3/2}$ (D is another adjustable parameter).

Therefore the data were fitted to the equation:

$$\log k_j(I) = \log k_j(I^*) - f(I,I^*) + D(I^{3/2} - I^{*3/2}) \tag{17}$$

As can be seen from Table-1, the parameters which characterize the dependence of protonation constants on ionic strength show a regular trend and seem to be a function of the approximated value of Z*.
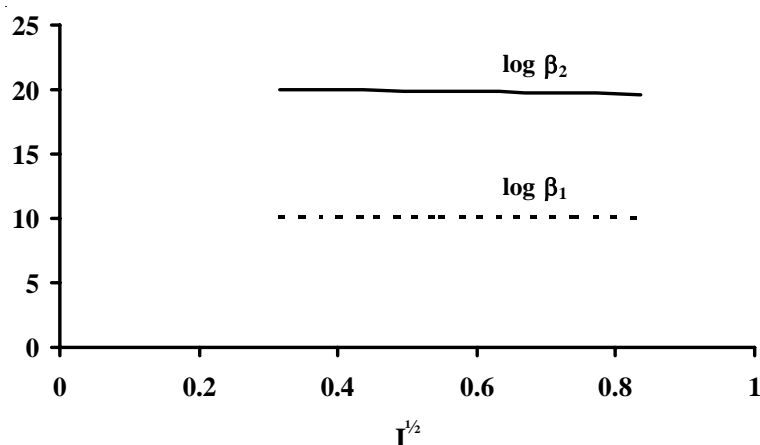

Fig. 1. Plots of $\log \beta_1$ and $\log \beta_2$ *vs.* the square root of the ionic strength (NaCl) at 25 ºC

The same procedure was applied for determining the dependence of the stability constants of VO_2^+ + proline complexes on ionic strength Fig. 1, 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[18].

REFERENCES

1. S. Yamada, S. Funahashi and M. Tanaka, *J. Inorg. Nucl. Chem.*, **37**, 835 (1975).
2. F.J.C. Rossotti and H. Rossotti, *Acta Chem. Scand.*, **10**, 957 (1956).
3. J.S. Littler and W.A. Waters, *J. Chem. Soc.*, 1299 (1959).
4. F. Gharib and N. Lahouti Fard, *J. Chem. Eng. Data*, **45**, 210 (2000).
5. F. Gharib, K. Zare and K. Majlesi, *J. Chem. Res.*, 186 (2000).
6. F. Gharib, K. Zare and K. Majlesi, *J. Chem. Eng. Data*, **45**, 833 (2000).
7. F. Gharib, K. Zare, A. Taghvamanesh and M. Monajjemi, *J. Chem. Eng. Data*, **46**, 1140 (2001).
8. G. Charlot, Les Methods de la chimie Analytique, Analyse Quantitative Minerale, 4th ed, Masson et cie, Paris (1961).
9. P. Lagrange, M. Schneider, K. Zare and J. Lagrange, *Polyhedron*, **13**, 861 (1994).
10. W.E. Van Der Linden and C. Beers, *Anal. Chim. Acta*, **68**, 143 (1973).
11. M. Maeder and A.D. Zuberbuhler, *Anal. Chem.*, **62**, 2220 (1990).
12. J. Itoh, T. Yotsuyanagi and K. Aomura, *Anal. Chim. Acta*, **76**, 471 (1975).
13. S. Yamada, J. Nagase, S. Funahashi and M. Tanaka, *J. Inog. Nucl. Chem.*, **38**, 617 (1976).
14. F. Gharib, K. Zare and S.A. Khorrami, *J. Chem. Eng. Data*, **38**, 602 (1993).
15. M. Beck and J. Nagypal, Chemistry of Complex Equilibria, Ellis Horwood, New York (1990).
16. F. Gharib and M. Vadi, *Russ. J. Inorg. Chem.*, **47**, 1926 (2002).
17. F. Gharib, H. Aghaei and A. Shamel, *Phys. Chem. Liq.*, **40**, 637 (2002).
18. F. Gharib, M. Vadi, S. Momeni and H. Jalali, *Int. J. Chem.*, **12**, 55 (2002).