Interaction of Dioxovanadium(V) Ion with Methionine at Different Ionic Strengths

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ABSTRACT

The dependence on ionic strength of protonation of methionine and its complexation with dioxovanadium(V) is reported in sodium perchlorate solution as supporting electrolyte. The measurements have been performed at 25 °C using a combination of potentiometric and spectrophotometric techniques. The overall analysis of the present and the previous data dealing with determination of stability constants at different ionic strengths allowed us to obtain a general equation, by which a formation constant determined at a fixed ionic strength can be recalculated, with a good approximation for another ionic strength in the range of $0.1 - 0.7$ mol dm^{-3}.

Keywords: Ionic strength; Formation constant; Methionine; Dioxovanadium(V)

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INTRODUCTION

It is a long time that coordination chemists have been studying the complex formation species between metal ions and amino acids as models for metal-protein interaction. Sulfur-containing amino acids offer a wide scope, as these ligands can chelate via $-NH_2$ and COO-, -S and COO- or -S and $-NH_2$, or via all three chelating sites. Spaulding and Brittain[1] studied formation constants of complexes between cystine, cysteine, and methionine by terbium(III)-ethylendiaminetetraacetate using circularly polarized luminescence spectroscopy and showed that methionine could bond via the carboxyl and amino groups like alanine, a simple amino acid, and the sulfur functionality was not participated in coordination. The same results was obtained by (1) Farooq and Ahmad[2] in a potentiometric titration method of methionine with rhodium(III)chloride. They concluded that methionine acts as a bidentated amino acid; (2) Maslowska and Chruscinski[3] in a potentiometric titration method of methionine with Cr(III) perchlorate; (3) Nourmand and Meissami[4] and others.[5-9] However, according to literature, no work has been reported on ionic strength dependence of complexation of methionine with dioxovanadium(V).

In a series of papers [10-12] on the ionic strength dependence of formation constants we reported some interesting features of the function log β= f (I), where β and I refer to stability constant and ionic media, respectively. In particular, all the formation constants seem to follow the same trend as a function of ionic strength, if allowance is made for the different types of reaction stoichiometry and for the different charges of reactants and products. In determining a formation constant at a fixed ionic strength, in all cases, some uncertainties are always present. This fact is mainly due to the uncertainties in numerical values of stability constant. For example, when maintaining two different ionic media of 0.1 and 0.5 mol dm-3 of sodium perchlorate, we observed a difference of about 0.2 log units in the stability constant of VO_2^+ chelate by methionine.

The present work deals with the study of VO_2^+ + methionine system in an ionic strength range of 0.1-0.7 mol dm^{-3} sodium perchlorate. The parameters which define this dependency

were analyzed with the aim of obtaining further information with regard to their variation as a function of charges involved in the complex reaction. Moreover, a general equation was established for the dependence of formation constant 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} of sodium perchlorate and therefore may give a significant contribution of solving many analytical and speciation problems.

EXPERIMENTAL

Chemicals. L-methionine, CH_2-S-$(CH_2)_2$ $CH(NH_2)$-COOH, (Merck, analytical reagent grade) was recrystallized from hot water, washed with ethanol, and dried over P2O5. Its purity was then checked by titration against standard alkali solution that gave 99.9 % by weight. The NaOH solution was prepared from titrisol solution (Merck) and its concentration was determined by several titrations with standard HCl. Perchloric acid, sodium perchlorate and sodium monovanadate were supplied from Merck as analytical reagent grade materials and were used without further purification. Dilute perchloric solution was standardized against standard NaOH solution. All dilute solutions were prepared using double-distilled water with conductivity equal to $1.3 \pm 0.1 \mu$ S.

A stock solution of vanadium(V) was prepared by dissolution of sodium monovanadate in perchloric acid solution affecting destruction of decavanadate. To avoid isopolyvanadate formation, the solution was allowed to stand overnight before use to obtain only the VO_2^+ ion. Under such conditions both polymerization and hydrolysis of VO_2^+ were negligible.[13-15]The concentration of VO_2^+ ion in the stock solution was determined using potentiometric titration method of a solution of Fe^{+2} which is diluted in H_2SO_4, using saturated calomel and platinum wire electrodes.[16]

Apparatus. An Eyela pH-meter, PHM 2000, was used for $-\log[H^+]$ measurements. The hydrogen ion concentration was measured with an Ingold UO 3234 glass electrode and an Ingold UO 3236 calomel electrode. Spectrophotometric measurements were

performed on a UV-vis Shimadzu 2100 spectrophotometer with GDU-20 computer and 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 $-\log[H^+]$ of the solution could be measured simultaneously. To exclude carbon dioxide and oxygen from the system, a stream of purified nitrogen was passed through a sodium chloride and then bubbled slowly through the reaction solution.

Measurements. All measurements were carried out at $25 \pm 0.1\ ^{\circ}C$. The ionic strength was maintained to 0.1-0.7 mol dm^{-3} with sodium perchlorate. The pH-meter was calibrated for the relevant H^+ concentration with a solution of 0.01 mol dm^{-3} perchloric acid solution containing 0.09 mol dm^{-3} sodium perchlorate (for adjusting the ionic strength to 0.1 mol dm^{-3}). The same procedure was performed for the other ionic strengths. For these standard solutions, we set $-\log[H^+] = 2.00$.[15] Junction potential corrections have been calculated from eq 1

$-\log[H^+]_{real} = -\log[H^+]_{measured} + a + b[H^+]_{measured}$ (1)

Here a and b were determined by measuring of hydrogen ion concentration for two different solutions of HClO4 with sufficient NaClO4 to adjust the ionic media.

Procedure. 50 cm^3 acidic solution of VO_2^+ (2.21×10^{-4} mol dm^{-3}) was titrated with an alkali solution (0.1 mol dm^{-3} NaOH) of the ligand (1.91×10^{-3} - 2.19×10^{-3}) mol dm^{-3}, both of the same ionic strength. The $-\log[H^+]$ and absorbance were measured after addition of a few drops of titrant, and this procedure was 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 deviations from the average are shown in the text and Tables.

RESULTS AND DISCUSSION

The complex $M_xH_yL_z^{(x+y-z)}$ 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 2 is defined by β_{xyz},[15]

$xM^+ + yH^+ + zL^- \leftrightarrows M_xH_yL_z^{(x+y-z)}$ (2)

$\beta_{xyz} = [M_xH_yL_z^{(x+y-z)}] / ([M^+]^x[H^+]^y[L^-]^z)$ (3)

The protonation constant of methionine has been used for computation of the stability constant, β_{xyz}, of the metal-ligand. The protonation constants of the ligand have been extensively studied in different kind of background electrolytes, and the results were reported in the literature. The protonation constants of the ligand was determined in different ionic strengths of sodium perchlorate using potentiometric technique and calculated using a computer program which employs a nonlinear least-squares method.[13] These values are listed in Table 1 together with the values reported in literature, which are in good agreement with those reported earlier.[3-4] Determination of the stability constant was based on the relation $A = f[H^+]$.[13] Absorbance, A, and $-\log[H^+]$ were measured as described before. Treatments of the spectra photo metric data (each 5 nm) obtained during the titration as a function of the hydrogen ion concentration was conducted to the computer program. The program allows calculation of the stability constant for different stoichiometry models.

Table1. Protonation constant values of the carboxylic, β_{021}, and the amino, β_{011}, groups of L-methionine at 25 $^{\circ}C$ and different ionic strengths of NaClO$_4$, the reported values in literature are also listed for comparison

ionic strength (mol dm^{-3})	$\log\beta_{021}$	$\log\beta_{011}$	ref.
0.1	2.18 $\pm$ 0.04	9.11 $\pm$ 0.08	this work
0.3	2.11 $\pm$ 0.06	9.05 $\pm$ 0.08	″
0.5	1.95 $\pm$ 0.05	9.01 $\pm$ 0.07	″
0.7	1.96 $\pm$ 0.04	9.03 $\pm$ 0.03	″
0.1 (NaClO$_4$)	-	9.15	3
0.1 (KNO$_3$)	-	8.92	4

In aqueous solution, methionine exists in its anionic forms (L⁻), zwit terionic species (HL), and cationic form (H_2L^+).[17-18] Considering the protonation constants of the ligand, in acidic solution the predominant species for complexation is HL. In this case the spectrophotometric titration data were analyzed by using the absorbance of VO_2^++ methionine at a wavelength in UV range that is given by

$$A = \varepsilon_M[VO_2^+] + \varepsilon_C[\text{complex}]+ A_{\text{free ligand}} \quad (4)$$

where ε_M and ε_C are the molar absorbance coefficients of VO_2^+ and the complex species, respectively. For the mass balance:

$$[VO_2^+] = C_M - [\text{complex}] \quad (5)$$
$$[HL] = C_L - [\text{complex}] - [\text{free ligand}] \quad (6)$$

Substituting eqs 3, 5-6 into eq 4 gives the final equation for fitting, where C_M and C_L are the total concentration of VO_2^+ and the ligand, respectively.

The method of determining ε_M was previously described[19] and its values at different wavelengths are used in this work. Using a suitable computer program[20] the data were fitted to the final equation for estimating the formation constant of eq 2. We used the Gauss-Newton nonlinear least-squares method in computer program to refine the absorbance by minimizing the error squares sum from eq 7

$$S = \sum(A_{obs} - A_{cal})^2 \quad (7)$$

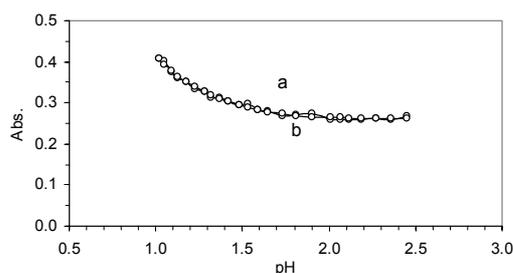**Figure 1**. A typical graphical fitting for the system VO_2^++L-methionine at 25 °C, 265 nm, and an ionic strength of 0.1 mol dm⁻³ NaClO₄, (a) experimental absorbance, and (b) calculated absorbance.

Where Aobs is the observed absorbance and Acal is a calculated one. The computer program permits two different kinds of fitting, (a) graphical, (b) numerical. The final selection of the species was based on both graphical and numerical methods, considering in addition the various statistical criteria, i. e. sum of squared residuals, differences of C_M(exp) and C_L(exp) from those of calculated ones. Figure 1 is shown as a typical example of a graphical fitting for the observed and calculated absorbances (from the computer program) of VO_2^++ methionine system against $-\log[H]^+$.

Different models of complexation including MHL^+, $M(HL)_2^+$ and several polynuclear and protonated species were tested by the program. As expected, polynuclear complexes were systematically rejected by the computer program, as also were $MH_2L_2^+$, MHL_2, and $MH_2L_2^+$. A value for the $MH_2L_2^+$ species 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 the fit. The models finally chosen, formed by VO_2HL^+ and $VO_2(HL)_2^+$, for the system studied, resulted in a satisfactory numerical and graphical fitting. The average values for various wavelengths calculated for the stability constants are listed in Table 2.

Table 2. Average values of $\log\beta_{111}$ and $\log\beta_{122}$ for the system of VO_2^++ L-methionine at 25 °C and different ionic strength of sodium perchlorate

ionic strength (mol dm⁻³)	$\log\beta_{111}$	$\log\beta_{122}$
0.1	4.02 ± 0.06	2.34 ± 0.04
0.3	3.92 ± 0.05	2.25 ± 0.05
0.5	3.89 ± 0.07	2.21 ± 0.04
0.7	3.98 ± 0.03	2.29 ± 0.06

In Figure 2 the equilibrium distribution of various species in VO_2^+ + methionine system is shown as a function of $-\log[H^+]$. The calculation is based on the stability constant values given before.
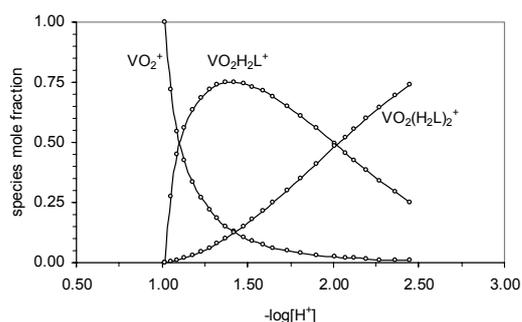
Figure 2. The equilibrium distribution of the species in the VO_2^+ + L-methionine system as a function of $-\log[H^+]$ at 25 °C and ionic strength of 0.1 mol dm^{-3} sodium perchlorate.

Ionic strength dependence. The dependence of the stability constants on ionic strength for the complex species can be described by a semi-empirical equation.[10-12, 21-22]

$$\log\beta(I) = \log \beta(I^*) - f(I) + CI \qquad (8)$$

where $f(I) = Z^*AI^{1/2}/(1 + BI^{1/2})$, $\beta(I)$ and $\beta(I^*)$ are the stability constants of the actual and the reference ionic media, respectively. A is the parameter of Debye-Hückel equation, ($A = 0.51$ mol$^{-1/2}$ dm$^{3/2}$ at 25 °C), $Z^* = \Sigma(charges)^2_{reactants} - \Sigma(charges)^2_{products}$, C is an empirical parameter that its value is considered, and B is set equal to1.5 mol$^{-1/2}$ dm$^{3/2}$ (a small error in fixing B is absorbed in the linear term C [23]). Results of a series of investigations done by Daniele et al.,[21-22] De Stefano et al.,[24-25] and Gharib et al.[10-12] showed that, when all the interactions occurring in the solution are considered, in the range $0 \leq I \leq 1$ mol dm^{-3}, the empirical parameters are dependent on the stoichiometry of the formation reaction. If an approximate value of C is known, the stability constant can be determined for the variation of ionic strength from I^* to I by the equation

$$\log\beta(I) = \log\beta(I^*) - f(I, I^*) + C(I - I^*) \qquad (9)$$

where

$$f(I, I^*) = Z^*A[I^{1/2}/(1 + 1.5I^{1/2}) - I^{*\ 1/2}/(1 + 1.5I^{*\ 1/2})] \qquad (10)$$

I and I* are the ionic strength of the solution by appropriate electrolyte. A preliminary analysis of the data showed that if a fixed value is assigned to C, the fit with eq 9 is not

always good over the whole range of ionic strength from 0.1 to 0.7 mol dm^{-3}. This equation may be useful for small changes of ionic strength, but a better fit is obtained by adding a further terms of the form DI$^{3/2}$ (D is another adjustable parameters). Therefore the data were fitted to the eq 11.

$$\log\beta(I) = \log\beta(I^*) - f(I,I^*) + C(I - I^*) + D(I^{3/2} - I^{*\ 3/2})$$

$$(11)$$

It is noticeable that the introduction of the term $D(I^{3/2} - I^{*\ 3/2})$ very often improves the goodness of the fit. For example, for the $\log\beta_{111}$ in sodium perchlorate media, from eq 11, we obtained three sets of values depending on whether or not we take into account the term in D:

$C = 0.12$, $S = 5.85 \times 10^{-3}$

$C = -0.97$, $D = 1.25$, $S = 4.89 \times 10^{-4}$

The squares sum, S, shows that there is a significant improvement in the fit when D term is introduced. The parameters for the dependence on ionic strength (C, and D) were calculated by the fitting method and reported in Table 3.
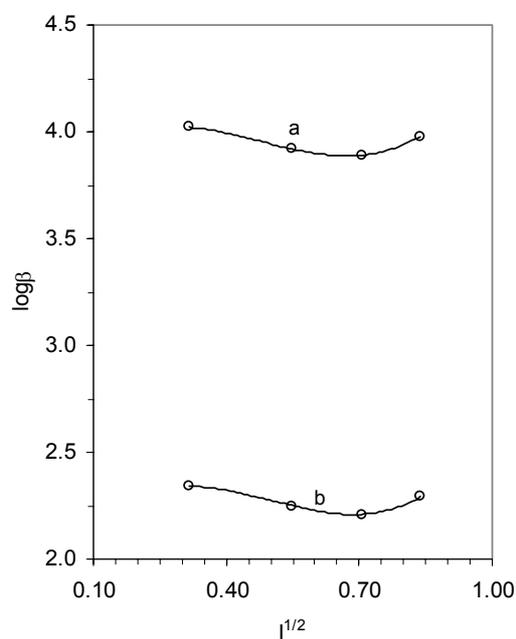

Figure 3. Plots of $\log\beta_{111}$ and $\log\beta_{122}$ versus the square root of ionic strength at 25 °C and 265 nm.

The dependence of $\log\beta$ on ionic strength determined in NaClO$_4$ as background

electrolyte, Fig. 3, show a regular trend and is in good agreement with other complex species.[10-12, 21-25] Our previous results on ionic strength dependence of complex formation constants [10-12] and this work reveal the $\log\beta$ values are nearly always at their minimum at an ionic strength range 0.3 - 0.7 mol dm^{-3}, that is a characteristic of the curve $\log\beta = f(I)$. According to the theory of electrolytic solutions [26] the $AI^{1/2}$ term in equation11 accounts for Coulomb interactions between ions screened by the ion atmosphere,

while the BI term accounts for disturbances in ion-solvent interaction. At low ionic strength (less than about 0.1 mol dm^{-3}) these interactions are of primary importance. However, as the ionic strength increases, the ionic atmosphere becomes more compressed and screens the ionic charges more effectively, so that intermolecular interactions (dipole-dipole or multipole-multipole) become more important. These forces at higher ionic strength possibly have primary role between the ions and contribute to the C and D terms in eq 11.

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