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Stability Constants of Dioxy Vanadium(V)-Glycylglycine System and a Related Calculating Model

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ABSTRACT

In this research some mathematical calculations has been explained on the "VO_2^+ + glycylglycine" system and some equations has been deduced to determine the stability constants of the equilibrium models including MLH^+, ML and ML_2H species (while $M^+ \equiv VO_2^+$, $H_2L^+ \equiv$ protonated glycylglycine and MLH^+, ML and ML_2H represent the considered complexes). The calculations are based on some relations between variation of absorbance (in the UV-vis region) and hydrogen ion concentration. The absorptivities and stability constants of complexes could be obtained from the intercept and slope of resulting linear equations. According to this approach the complexes refer to "VO_2^+ + glycylglycine" system has been investigated in aqueous solutions at ionic strength 0.5mol dm^{-3} sodium perchlorate at 25^0C (± 0.1); and a combination of potentiometric and spectrophotometric (UV-vis) method was used.

***Keywords*:** Stability constant;Glycylglycine;DioxyVanadium(V).

INTRODUCTION

Vanadium (V) ion reacts with many peptides to form various complexes (1-5). This reaction is influenced through variation of the pH and different complexes of "VO_2^+ + glycylglycine" are formed by varying the pH(6-10). So the formation of the complexes MLH^+, ML and ML_2H are assumed. The ligand in MLH^+ has lost a proton and coordinated through the carboxylate group and the terminal amino group remains protonated. In the complex ML, a chelation occurs and the protonated amino group loses a hydrogen ion and binds to metal ion. In the complex ML_2H two ligands have attached to VO_2^+ ion, first from carboxylate group and the second from terminal amino nitrogen.

In the pH range corresponding to formation of these complexes the absorbance varies as a function of pH in the UV-vis region and we can conclude some linear equations for calculating the stability constants of these complexes.

MATERIALS AND METHODS

Sodium perchlorate, acid perchloric, sodium hydroxide, sodium metavanadate and glycylglycine with a high purity were supplied from E.Merck chemical.

Spectrophotometric measurements were performed on a UV-vis Shimadzu 2101PC equipped with an AcerMate 486 SX /250 computer and a bath from mLW8UH ($\pm 0.1^0$C) and a Horiba pH meter (D-14 model) with S8720 composite glass electrode.

All experiments have been done with high ligand to metal ratio. Therefore in the presence of a large excess of ligand in the pH<7.5 ,polymerization and hydrolysis of VO_2^+ both could be negligible (11-15). The ionic strength was maintained at 0.5 mol dm^{-3} with sodium perchlorate. Aqueous solutions of dioxy vanadium (V) and glycylglycine were prepared 10^{-4} mol dm^{-3} and 0.01 mol dm^{-3} respectively. All measurements have been done at 25^0C ($\pm$ 0.1). The formation and stability constants of the complexes have been determined by using resulting linear equations in the wavelengths 260 to 280 nm.

Furthermore the protonation constants of glycylglycine have been determined using potentiometric techniques and employing a non

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linear least squares method.

RESULTS AND DISCUSSION

In acidic solutions at pH<2.5, vanadium (V) ions exists as VO_2^+ ion (11,12), therefore the reaction of VO_2^+ ion with glycylglycine can be assumed as follows:

$$M^+ + H_{1-m}L^{m-} \rightleftarrows MH_{1-m-n}L^{(-m-n+1)+} + nH^+$$

(1)

(M$^+$ ≡ VO_2^+ and $H_{1-m}L^{m-}$ ≡ protonated glycylglycine)

In the pH range 2-2.8 glycylglycine is predominated in the form of H_2L^+ consequently m becomes -1. Accordingly, the equation 1 becomes

$$M^+ + H_2L^+ \rightleftarrows MLH^+ + H^+ \qquad (2)$$

and its formation constant could be shown as:

$$K^H_{MLH^+} = \frac{[MLH^+][H^+]}{[M^+][H_2L^+]} \qquad (3)$$

On the other hand the stability constant for the reaction

$$M^+ + HL \rightleftarrows MLH^+ \qquad (4)$$

is

$$K_{MLH^+} = \frac{[MLH^+]}{[M^+][HL]} \qquad (5)$$

In addition, the following equation, based on a mathematical treatment is available (16)

$$\frac{C_M}{A} = \frac{1}{\varepsilon_2} + \frac{(\varepsilon_2 - \varepsilon_1)(A - \varepsilon_1 C_M)[H^+]^n}{\varepsilon_2 K^H_{MLH^+}(\varepsilon_2 C_{H_2L} - \varepsilon_1 C_{H_2L} + \varepsilon_1 C_M - A)A} \qquad (6)$$

where ε_1 and ε_2 represent the molar absorptivities of VO_2^+ and the complex VO_2LH^+ respectively ; C_M and C_{H_2L} are the total concentrations of VO_2^+ ion and glycylglycine and $K^H_{MLH^+}$ is the formation constant of VO_2LH^+. Accordingly, if n=1, the plot of C_M / A against $(A - \varepsilon_1 C_M)[H^+]^n / A$ would be linear. Our experimental results show a linear plot of C_M / A against $(A - \varepsilon_1 C_M)[H^+]/A$. Therefore we conclude that $n = 1$ and one complex, MLH^+ ,is formed in the above pH range.

In addition we have confirmed the above result by using equation 7

$$\bar{n} = \frac{\bar{\varepsilon} - \varepsilon_1}{\varepsilon_2 - \varepsilon_1} \qquad (7)$$

where $\bar{n}$ represent the average ligand number (17).

In the system of "VO_2^+ + glycylglycine" the extend of complex formation depends on the hydrogen concentration. So the protonation constants of the ligand must be known if we want to determine the stability constant of the reaction 4 ,through the equation 8.

$$K_{MLH^+} = K^H_{MLH^+} . K^H_2 \qquad (8)$$

The protonation constants of the ligand K^H_1 and K^H_2 can be determined from equations 9 and 10

$$H^+ + L^- \rightleftarrows HL \qquad K^H_1 = \frac{[H\ L]}{[H^+][L^-]} \qquad (9)$$

$$H^+ + HL \rightleftarrows H_2L^+ \qquad K^H_2 = \frac{[H_2L^+]}{[H^+][HL]} \qquad (10)$$

where K^H_1 and K^H_2 refer to the protonation constants of the terminal amino group and the carboxylate group of glycylglycine respectively. In the pH range 3-3.8 ,we assume two new complexes, ML and ML_2H may be formed ; one through a chelation,

$$MLH^+ \rightleftarrows ML + H^+ \qquad K^H_{ML} = \frac{[ML][H^+]}{[MLH^+]} \qquad (11)$$

$$M^+ + L^- \rightleftarrows ML \qquad K_{ML} = \frac{[ML]}{[M^+][L^-]}$$

(12)

and the other through the following reaction

$$MLH^+ + HL \rightleftarrows ML_2H + H^+ \qquad (13)$$

In order to obtain the ultimate equation for calculating the formation constant of ML we define the following equations

$$A = \varepsilon_2[MLH^+] + \varepsilon_3[ML] \qquad (14)$$

$$C_M = [MLH^+] + [ML] \qquad (15)$$

$$[MLH^+] = \frac{A - \varepsilon_3 C_M}{\varepsilon_2 - \varepsilon_3} \qquad (16)$$

$$[ML] = \frac{A - \varepsilon_2 C_M}{\varepsilon_3 - \varepsilon_2} \qquad (17)$$

where A , C_M and ε_3 represent the total absorbance,the total concentration of VO_2^+ and molar absorptivitie of ML respectively. If we now introduce 16 and 17 into 11and arrange it,then we get the ultimate equation

$$\frac{C_M}{A} = \frac{1}{\varepsilon_3} + \frac{(A - \varepsilon_2 C_M)[H^+]}{K^H_{ML}\varepsilon_3 A} \qquad (18)$$

According to this work,in the pH range 3-3.8 the plot of C_M / A against $(A - \varepsilon_1 C_M)[H^+]/A$ gives two straight lines with different slopes,that we can conclude one of them corresponds to ML formation and the other to ML_2H . On the other hand when we use the equations 7 and 19 to estimate $\bar{n}$ (18-20),we get $\bar{n} \cong 0$ for ML formation and

$\bar{n} \cong 1$ for ML_2H ,which is in agreement with our above conclusion .

$$\bar{n} = \frac{\varepsilon_3 + \bar{\varepsilon} - 2\varepsilon_2}{\varepsilon_3 - \varepsilon_2} \qquad (19)$$

Consequently, the formation constant of ML , K_{ML}^{H} and ε_3 can be calculated from the slope and intercept of equation 18. In addition, the stability constant of ML can be resulted from equation 20

$$K_{ML} = K_{ML}^{H} . K_{MLH^+} . K_1^H \qquad (20)$$

The formation of ML_2H is assumed to occur in the pH range 3.3-3.8 and its constants are given as follows:

$$MLH^+ + HL \rightleftarrows ML_2H + H^+$$

$$K_{ML_2H}^{H} = \frac{[ML_2H][H^+]}{[MLH^+][HL]} \qquad (21)$$

$$M^+ + HL + L^- \rightleftarrows ML_2H$$

$$K_{ML_2H} = \frac{[ML_2H]}{[HL][L^-][M^+]} \qquad (22)$$

For calculating the formation constant of ML_2H ,we define the following equations,

$$A = \varepsilon_2[MLH^+] + \varepsilon_3[ML] + \varepsilon_4[ML_2H] \qquad (23)$$

$$C_M = [MLH^+] + [ML] + [ML_2H] \qquad (24)$$

$$C_{HL} = [HL] + 2[ML_2H] + [MLH] \qquad (25)$$

$$x = [ML] \qquad (26)$$

$$A' = \varepsilon_3[ML] \qquad (27)$$

$$C_M - x = [MLH^+] + [ML_2H] \qquad (28)$$

$$A'' = A - A' \qquad (29)$$

$$[MLH^+] = \frac{\varepsilon_4(C_M - x) - A''}{\varepsilon_4 - \varepsilon_2} \qquad (30)$$

$$[ML_2H] = \frac{A'' - \varepsilon_2(C_M - x)}{\varepsilon_4 - \varepsilon_2} \qquad (31)$$

where A , A' , C_M ,C_{HL} , ε_2, ε_3 and ε_4 represent the total absorbance ,the absorbance of ML ,the concentration of VO_2^+ ,the total concentration of ligand and the molar absorptivities of MLH^+ , ML and ML_2H respectively. Now ,by combining equations 30,31,25 and 21 ,the ultimate linear equation can be deduced

$$\frac{C_M - x}{A''} = \frac{1}{\varepsilon_4} + \frac{[A'' - \varepsilon_2(C_M - x)](\varepsilon_4 - \varepsilon_2)[H^+]}{K_{ML_2H}^{H}\varepsilon_4[C_{HL}(\varepsilon_4 - \varepsilon_2) - \varepsilon_4(C_M - x) + 2\varepsilon_2(C_M - x) - A'']A''} \qquad (32)$$

In order to calculate the formation constant of ML_2H , we assume x=0 at first approximation. Following this assumption the formation constant of ML_2H can be estimated with some order of uncertainty by plotting equation 32. But to improve our calculations ,we have estimated the concentration of ML_2H upon equation 21,and then introduced it into equation 11 to obtain an approximate value of x.Then by introducing these values of x and A' into equation 32 and replotting it ,the more accurate value of $K_{ML_2H}^{H}$ can be obtained. By repeating this procedure it may be obtained the more accurate value of $K_{ML_2H}^{H}$ .So ,this procedure was repeated until the difference between two successive formation constants became less than 0.001 ,and then we stopped the calculations. When ε_3 ,is replaced by ε_4,into equation 19 (which obtains from the intercept of equation 32) we get $\bar{n} \cong 2$,that is in agreement with ML_2H formation. Finally the stability constant of ML_2H ,can be deduced from the following equation,

$$K_{ML_2H} = K_{ML_2H}^{H} . K_{ML\,H^+} . K_1^H \qquad (33)$$

The tables I and II show the average values of protonation constants of glycylglycine and the average stability constants of VO_2LH^+, VO_2L and VO_2L_2H which have been obtained from this work. In addition, the table III summarizes the average absorptivities of VO_2^+, VO_2LH^+, VO_2L and VO_2L_2H .

Table 1. Values of protonation constants of glycylglycine at 25^{0}C (± 0.1) and ionic strength $I = 0.5 moldm^{-3} (NaClO_4)$

Species	**log K^H**
HL $(-NH_3^+)$	8.17
H_2L (-COOH)	3.20

Table 2. Values of stability constants of VO_2LH^+, VO_2L, VO_2L_2H at 25^{0}C (± 0.1) and ionic strength $I = 0.5 moldm^{-.3} (NaClO_4)$

Species	**logK**
MLH^+	3.61
ML	8.05
ML_2H	10.92

Table 3. Values of molar absorptivities of VO_2^+, VO_2LH^+, VO_2L, VO_2L_2H ($Lcm^{-1}mol^{-1}$) at the wavelengths 260 to 280 (nm).

$\lambda(nm)$	$\varepsilon_{VO_2^+}$	$\varepsilon_{VO_2LH^+}$	ε_{VO_2L}	$\varepsilon_{VO_2L_2H}$
260	652	1073.43	5488.11	2011.33
265	602	1005.44	4586.27	1975.23
270	543	975.08	4217.64	1780.88
275	474	918.17	4013.54	1614.29
280	402	871.61	3454.67	1448.06

CONCLUSION

There are different factors that influence the stability constant such as basicities, ionic radius, electronegativity, chelate effect, steric hindrance. In addition the stability constants of complexes of chelate forming ligands obviously depend on the distance between the doner groups, the number of groups in the chelate ring and also on the size of the metal ion and the geometry of the complex formed .

Our results show that the stability constant of VO_2L and VO_2L_2H are greater than VO_2LH^+ and the stability constant of VO_2L is less than VO_2L_2H and the equilibrium of VO_2L is influenced through the equilibrium of VO_2L_2H .So the tendency of VO_2^+ for amino group is greater than carboxilate group, and the factors such as closure and steric hindrance of the chelation ring is accompanied by a loss in the possibility of the ligand to rotate by an entropy decrease, and hence the stability constant of VO_2L is less than the complex VO_2L_2H .

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