

## Complexation of dioxovanadium(V) with glycylglycine in sodium perchlorate aqueous solution

Kavosh Majlesi<sup>a,\*</sup>, Karim Zare<sup>a,b</sup>

<sup>a</sup> Chemistry Department, Islamic Azad University, Science and Research Campus, Tehran, Hesarak, Iran

<sup>b</sup> Chemistry Department, Shahid Beheshti University, Tehran, Evvin, Iran

Available online 4 January 2006

### Abstract

The present study deals with the complexation of dioxovanadium(V) with glycylglycine by a combination of potentiometric and spectrophotometric techniques in aqueous solution at 25 °C and 0.1 mol dm<sup>-3</sup> ionic strength (NaClO<sub>4</sub>). The stability constants of the complexes formed and their stoichiometries are given and interpreted.

The logarithms of the cumulative stability constant  $\beta_{cum}$  of the complex: [(oxometal)<sub>2</sub>(H)<sub>2</sub>(glycylglycine)<sub>2</sub>] are respectively, log  $\beta_{111}$  = 4.01 ± 0.1, log  $\beta_{112}$  = 7.03 ± 0.10 and log  $\beta_{112(OH)}$  = 5.85 ± 0.11.

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Stability constant; Dioxovanadium(V); Complexation; Glycylglycine

### 1. Introduction

Over the past decade an extraordinary expansion of interest has been in the aqueous chemistry and biochemistry of vanadium oxoanions, particularly of the V(IV) and (V) oxidation states. Much of this interest has been concentrated on the complexation of these ions with a number of proteins, particularly albumins, transferrins and as activator in various enzymes of plants and organisms [1,2]. Some work has been published concerning the interaction of vanadium with several amino acids [3–10] and a few with small peptides [11–13]. Most of the studies were concerned with the stability constants of the complexes, and the major complexes formed from amino acids and di- or tripeptides have the amino, amide nitrogen, and carboxylate groups chelated. A few related vanadium compounds were characterized in the solid state by X-ray crystallography. These included the vanadium(V) complexes with ethylenediaminetetraacetate (EDTA) [14], *N*-[1-(2-pyridyl)ethyl] iminodiacetate [15], triethanolamine (TEA) [16], and tri-2-propanolamine (TPA) [17]. In the first two complexes the vanadium atom was found to have an octahedral geometry and the ligands chelating in a tetradentate manner, with no

difference between the structure in solid state and in solution [18]. But in the case of V-TEA and V-TPA complexes, some differences have been observed in the solid state and in the aqueous solution [19], suggesting that the solid-state characterization of these complexes may not be sufficient.

A study of the available information on vanadate–peptide interactions revealed a surprising lack in fundamental studies concerning the solution structure of these complexes. However, Jaswal and Tracey [12] determined the formation constants of vanadate complexes with some peptides and characterized their structures using <sup>51</sup>V NMR and suggested that monovanadate–monoligand complexes require the terminal amino, the carboxylate groups and unsubstituted nitrogen in the peptide linkage in order for product formation to occur. Jaswal showed that when complexes considered to be formed from VO<sub>4</sub>H<sub>2</sub><sup>-</sup> and neutral peptide, giving off protons is not required, but when the carboxylate was replaced by the alcohol functionality a proton was released. Crans and Shin [13] characterized the preferred coordination geometry of vanadium(V) in aqueous solution with nitrogen and oxygen containing of some multidentate ligands including glycylglycine, using <sup>1</sup>H, <sup>13</sup>C, <sup>51</sup>V and <sup>17</sup>O NMR spectroscopy and IR and UV–Vis spectrophotometric techniques. They showed in several cases that the structures of the complexes in the solid state deviate from that observed in aqueous solution. On the

\* Corresponding author. Tel.: +98 21 66927264; fax: +98 21 66937074.  
E-mail address: kavoshmajlesi@hotmail.com (K. Majlesi).

Table 1

Dissociation constants of the carboxylic,  $K_1$ , and the amino,  $K_2$ , groups of GlyGly at 25 °C and ionic strength,  $I$ , 0.1 mol dm<sup>-3</sup> NaClO<sub>4</sub>

log $K_1$	log $K_2$	Experimental conditions	Reference
3.12±0.05	8.17±0.05		This work
3.18	8.04	$I=0.1$ M KNO <sub>3</sub> , $t=25.6$ °C	[30]
3.21	8.15	$I=1.0$ M KCl, $t=24.9$ °C	[30]
3.11	8.15	$I=0.1$ M NaClO <sub>4</sub> , $t=25$ °C	[31]

basis of their studies, at high pH, four functionalities that chelate vanadium exist when at least one of them is a carboxylate, and at low pH only three functionalities in these ligands are tightly bound to the vanadium, while the last functionality is either loosely bound or pendent.

Costa Pessoa et al. [11] studied the system VO<sup>2+</sup> with several dipeptides in the pH range 1.5–13 by a combination of spectroscopic methods (ESR, CD and visible absorption). They characterized the structures of the complexes and concluded that there is no evidence of the amide group to take part in complexation. Pessoa et al. [20] also studied the complexes of dioxovanadium(V) with *N*-salicyl-glycylglycine. Tan et al. [21] determined the crystal structures of glycylglycine complexes of *cis*-, *cis*-1,3,5-triaminocyclohexane-copper(II). Holtz et al. [22] studied *cis* to trans isomerization of glycylglycine derivatives by UV resonance Raman technique. Rios et al. [23] studied the formal stability of glycylglycine enolates in aqueous solution.

This work reports the complexation of dioxovanadium(V) by glycylglycine and the purpose of this study was to characterize the stoichiometry of the formed complexes and determine its stability constants in a constant ionic strength and temperature.

## 2. Experimental

### 2.1. Materials

Sodium monovanadate, sodium perchlorate, and perchloric acid were supplied from E. Merck and glygly was purchased from Sigma as analytical reagent grade material and were used without further purification. The NaOH solutions were prepared from titrisol solutions and their concentration was determined by several titrations with standard HCl. Dilute perchloric acid solution was standardized against standard solution of NaOH. All dilute solutions were prepared from double-distilled water with specific conductance equal to  $1.3 \pm 0.1 \mu\Omega^{-1} \text{cm}^{-1}$ .

### 2.2. Methods

All measurements were carried out at  $25 \pm 0.1$  °C. The ionic strength was maintained at 0.1 mol dm<sup>-3</sup> with sodium perchlorate. A Horiba pH meter, D14 was used for pH measurements. The pH meter has a sensitivity of 0.01 units. The hydrogen ion concentration was measured with a Horiba combination electrode, model S8720. A 0.01 mol dm<sup>-3</sup> perchloric acid solution containing 0.09 mol dm<sup>-3</sup> sodium

perchlorate (for adjusting the ionic strength to 0.1 mol dm<sup>-3</sup>) was employed as a standard solution of hydrogen ion concentration.

Spectrophotometric measurements were performed on a UV–Vis Shimadzu 2101 spectrophotometer with an Acer Mate 486 SX/250 computer using thermostated matched 10 mm quartz cells. For each experiment two solutions of VO<sub>2</sub><sup>+</sup> + glygly were prepared with the same concentration, but the ionic strength of the first was maintained with sodium perchlorate and that of the second with sodium hydroxide or perchloric acid. The first solution was then titrated with the second one. The pH and absorbance were measured after addition of a few drops of titrant, and this procedure extended up to the required pH.

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.

## 3. 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. (1) is defined by  $\beta_{xyz}$  [6],

$$xM^{n+} + yH^+ + zL^- \rightleftharpoons M_xH_yL_z^{(x+y-z)+} \quad (1)$$

$$\beta_{xyz} = \frac{[M_xH_yL_z^{(x+y-z)+}]}{[M^{n+}]^x [H^+]^y [L^-]^z} \quad (2)$$

The dissociation constants of glygly have been used for computation of the stability constants,  $\beta_{xyz}$ , of the metal–glygly. The dissociation constants of glygly have been extensively studied in different kinds of background electrolytes, and the results were reported in the literature. The dissociation constants of the carboxylate and the amino groups have been determined using potentiometric techniques and calculated using the Solver, Microsoft Excel 2000 powerful optimization package, to perform non-linear least-squares curve fitting [24–26]. These values are listed in Table 1

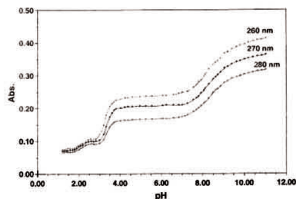


Fig. 1. Absorbance–pH curves for VO<sub>2</sub><sup>+</sup> + GlyGly at 25 ± 0.1 °C and ionic strength 0.1 mol dm<sup>-3</sup> NaClO<sub>4</sub> at (A) 260 nm, (B) 270 nm, (C) 280 nm.

Table 2

Average values of  $\log \beta_{ov}$  at pH 6.0 and different ionic strengths for the complexation of dioxovanadium (V) with glycylglycine,  $t = 25^\circ\text{C}$

Species	$\log \beta_{ov}$	Experimental conditions	Reference
$\text{VO}_2\text{HL}^+$	$4.01 \pm 0.10$	This work	
$\text{VO}_2\text{HL}_2$	$7.03 \pm 0.10$	This work	
$\text{VO}_2\text{HL}_2(\text{OH})$	$5.85 \pm 0.11$	This work	
Vanadate complex	$0.34 \pm 0.11$	[12]	

together with the values reported in the literature, which are in good agreement with those reported before.

The method of determination of the stability constant based on the relationship  $A=f(\text{pH})$  was employed [27], on account of the high stability of the complexes studied. Absorbance,  $A$ , and pH were measured for a solution containing dioxovanadium ( $10^{-4} \text{ mol dm}^{-3}$ ) with a large excess of the ligand ( $1 \times 10^{-2} \text{ mol dm}^{-3}$ ) at  $25 \pm 0.1^\circ\text{C}$  and constant ionic strength of  $0.1 \text{ mol dm}^{-3}$  sodium perchlorate, and the results are shown in Fig. 1. Under this condition both polymerization and hydrolysis of dioxovanadium were negligible [27,28].

From Fig. 1, it seems very likely that a complex is formed in acidic solution (pH 2.0 to 2.6). To determine the stability constant of the formed complex, we derived Eq. (7) [9] from the combination of the following mass-balance and Beer-Lambert laws:



$$[\text{VO}_2^+] = C_M - [\text{VO}_2\text{HL}^+] \quad (4)$$

$$[\text{HL}] = C_L - [\text{VO}_2\text{HL}^+] \quad (5)$$

$$A = \varepsilon_0[\text{VO}_2^+] + \varepsilon_1[\text{VO}_2\text{HL}^+] \quad (6)$$

$$\frac{C_M}{A} = \frac{1}{\varepsilon_1} + \frac{K_1(\varepsilon_1 - \varepsilon_0)(A - \varepsilon_0 C_M)[\text{H}^+]^n}{\varepsilon_1 \beta_{ov}(\varepsilon_1 C_L - \varepsilon_0 C_L - A + \varepsilon_0 C_M)A} \quad (7)$$

where  $C_M$ ,  $C_L$ ,  $A$ ,  $K_1$ ,  $\varepsilon_0$ , and  $\varepsilon_1$  are total concentration of the metal ion, total concentration of the ligand, absorbance, dissociation constant of the carboxylic group of the ligand, molar absorptivities of the metal ion and the formed complex, respectively. GlyGly and sodium perchlorate do not have absorbance in the wavelengths and pH region studied (Table 2).

The method of determining  $\varepsilon_0$  was previously described [29], and its values at different wavelengths are used in this work (Table 3). The number of protons,  $n$ , was examined by applying Eq. (7); the straight line plots of  $C_M/A$  against  $[\text{H}^+]^n$  with  $n=1$  confirmed the formation of a single complex with the formula  $\text{VO}_2\text{HL}^+$  and  $\beta_{111}$  can be calculated from the slope of Eq. (7). The average value of  $\log \beta_{111}$  at different wavelengths is  $4.01 \pm 0.10$ .

From Fig. 1, it seems very likely that another complex is formed in the pH range 3.00 to 3.81, that is attributed to the formation of  $\text{VO}_2\text{HL}_2$  according to the following reaction:



Table 3

Values of molar absorptivities of the metal ion,  $\varepsilon_0$ , at different wavelengths and  $25 \pm 0.1^\circ\text{C}$  [29]

	260 nm	270 nm	280 nm
	473	375	237

To determine  $\beta_{112}$ , we derived Eq. (13) [7], from the combination of mass-balance and Beer-Lambert laws:

$$[\text{VO}_2^+] = 0 \quad (9)$$

$$C_{\text{VO}_2} = [\text{VO}_2\text{HL}^+] + [\text{VO}_2\text{HL}_2] \quad (10)$$

$$C_{\text{HL}} = [\text{HL}] + [\text{VO}_2\text{HL}^+] + 2[\text{VO}_2\text{HL}_2] \quad (11)$$

$$A = \varepsilon_1[\text{VO}_2\text{HL}^+] + \varepsilon_2[\text{VO}_2\text{HL}_2] \quad (12)$$

$$\frac{C_M}{A} = \frac{1}{\varepsilon_2} + \frac{K_2(\varepsilon_2 - \varepsilon_1)(A - \varepsilon_1 C_M)[\text{H}^+]}{\varepsilon_2 \beta_{112}(\varepsilon_2 C_L - \varepsilon_1 C_L - \varepsilon_2 C_M + 2\varepsilon_1 C_M - A)A} \quad (13)$$

where  $\varepsilon_2$  and  $K_2$  are the molar absorptivity of the second formed complex and the dissociation constant of the amino group of glygly, respectively. By applying Eq. (13), we determined  $\beta_{112}$  from the slope of the straight line plots of  $C_M/A$  versus  $[\text{H}^+]$ . The average of  $\log \beta_{112}$  at different wavelengths is  $7.03 \pm 0.10$ .

Above pH 7 an increase in absorbance was observed (Fig. 1), that is attributed to the hydrolysis of  $\text{VO}_2\text{HL}_2$  [28],



and similarly we derived Eq. (15) for calculating the hydrolysis constant of reaction (14):

$$\frac{C_M}{A} = \frac{1}{\varepsilon_3} + \frac{K_W(A - \varepsilon_2 C_M)[\text{H}^+]}{\beta_{112(\text{OH})}\varepsilon_3 A} \quad (15)$$

where  $\varepsilon_2$  and  $K_W$  are the molar absorptivity of  $\text{VO}_2\text{HL}_2(\text{OH})^-$  and the ion-product constant of water, respectively. According to Eq. (15) the hydrolysis constant of Eq. (14),  $\beta_{112(\text{OH})}$ , can be calculated directly from the slope of the straight line plots of

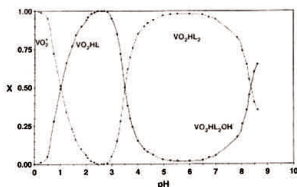


Fig. 2. Distribution of  $\text{VO}_2$  species present in aqueous solution as a function of pH.

$C_M/A$  against  $[H^+]$ . The average of  $\log \beta_{112(OH)}$  at different wavelengths is  $5.85 \pm 0.11$ .

The distribution of the various species present in solution as a function of  $H^+$  concentration for the metal ion and the complexes of  $VO_2^+$ –glygly are shown in Fig. 2.

#### 4. Conclusions

We did not find any reference that uses UV spectrophotometric technique at a fixed ionic strength. The values of the NMR method are not at a fixed ionic strength and the concentrations are usually high (minimum of 0.1 M in metal and ligand) and this was mentioned in a paper by Kula [34]. It has been clearly mentioned in Ref. [12] that the reactions are between vanadate and peptides. So it seems that we cannot compare our results with them, because our reactions are based on the formation of  $VO_2^+$  in the acidic medium according to the literature [6,32,33]. Then we have assumed that all of the  $VO_2^+$  has been changed to  $VO_2HL^+$  and finally to  $VO_2HL_2$  at higher pH values. We have confirmed our assumptions by curve fitting methods using Mathematica and Excel.

Study on the complexation of dioxovanadium(V) with glycylglycine in aqueous solution at 25 °C and 0.1 mol  $dm^{-3}$  ionic strength ( $NaClO_4$ ) in the pH range 1.50 to 10.0 revealed that three species exist in the solution:  $VO_2HL^+$ ,  $VO_2HL_2$  and  $VO_2HL_2(OH)^-$ .

In the pH range 2.0 to 2.6 one proton is released from the COOH group and the  $VO_2HL^+$  species is formed. Then at pH above 3.0 another proton is released and the  $VO_2HL_2$  species will be formed. Finally in the alkaline medium at pH=9.0 we have the hydrolysis reaction and  $VO_2HL_2(OH)^-$  will be formed. Curve fitting method confirms the assumption for the existence of the aforementioned species.

#### References

- [1] A. Butler, C.J. Carrano, Chem. Rev. 109 (1991) 61.
- [2] M.J. Kendrick, M.T. May, M.J. Plishka, K.D. Robinson, Metals in Biological Systems, Ellis Horwood, New York, 1992.
- [3] J. Costa Pessoa, L.F. Vilas Boas, R.D. Gillard, J. Lancashire, Polyhedron 7 (1988) 1245.
- [4] J. Costa Pessoa, R.L. Marques, L.F. Vilas Boas, R.D. Gillard, Polyhedron 9 (1990) 81.
- [5] J. Costa Pessoa, L.F. Vilas Boas, R.D. Gillard, Polyhedron 8 (1989) 1173.
- [6] P. Lagrange, M. Schneider, K. Zare, J. Lagrange, Polyhedron 13 (1994) 861.
- [7] F. Gharib, K. Zare, K. Majlesi, J. Chem. Res. (2000) 186.
- [8] F. Gharib, N. Lahoutifard, J. Chem. Eng. Data 45 (2000) 210.
- [9] F. Gharib, M. Molaei, J. Chem. Eng. Data 44 (1999) 77.
- [10] F. Gharib, K. Zare, J. Chem. Eng. Data 40 (1995) 186.
- [11] J. Costa Pessoa, S.M. Luz, R.D. Gillard, J. Chem. Soc. Dalton Trans. (1997) 569.
- [12] J.S. Jaswal, A.S. Tracey, Can. J. Chem. 69 (1991) 1600.
- [13] D.C. Crans, P.K. Shin, J. Am. Chem. Soc. 116 (1994) 1305.
- [14] W.R. Scheidt, R. Countryman, J.L. Hoard, J. Am. Chem. Soc. 93 (1971) 3878.
- [15] W.R. Scheidt, D.M. Collins, J.L. Hoard, J. Am. Chem. Soc. 93 (1971) 3873.
- [16] A. Kojima, K. Okazaki, S. Ooi, K. Saito, Inorg. Chem. 22 (1983) 1168.
- [17] D.C. Crans, H. Chen, O.P. Anderson, M.M. Miller, J. Am. Chem. Soc. 115 (1993) 6769.
- [18] L.W. Amos, D.T. Sawyer, Inorg. Chem. 11 (1972) 2692.
- [19] D.C. Crans, P.K. Shin, Inorg. Chem. 27 (1988) 1797.
- [20] J.C. Pessoa, I. Correia, T. Kiss, T. Jukusch, M.M.C.A. Castro, C.F.G.C. Geraldies, J. Chem. Soc. Dalton Trans. 23 (2002) 4440.
- [21] X.S. Tan, Y. Fujii, T. Sato, Y. Nakano, M. Yashiro, Chem. Commun. 10 (1999) 881.
- [22] J.S.W. Holtz, P. Li, S.A. Asher, J. Am. Chem. Soc. 121 (1999) 3762.
- [23] A. Rios, J.P. Richard, T.L. Amyes, J. Am. Chem. Soc. 124 (2002) 8251.
- [24] F. Gharib, K. Zare, K. Majlesi, J. Chem. Eng. Data 45 (2000) 833.
- [25] K. Majlesi, K. Zare, F. Teimouri, J. Chem. Eng. Data 49 (2004) 439.
- [26] E. Joseph Billo, Excel for Chemists, 2nd edn., John Wiley & Sons, New York, 2001.
- [27] J. Itoh, T. Yotsuyanagi, K. Aomura, Anal. Chim. Acta 76 (1975) 471.
- [28] S. Yamada, J. Nagase, S. Funahashi, M. Tanaka, J. Inorg. Nucl. Chem. 38 (1976) 617.
- [29] F. Gharib, K. Zare, J. Sci. Islam. Azad Univ. 2 (1992) 397.
- [30] M.K. Kim, A.E. Martell, J. Am. Chem. Soc. 85 (1963) 3080.
- [31] H. Sigel, Inorg. Chem. 14 (1975) 1535.
- [32] K. Zare, P. Lagrange, J. Lagrange, J. Chem. Soc. Dalton Trans. (1979) 1372.
- [33] P. Lagrange, M. Schneider, J. Lagrange, J. Chim. Phys. 95 (1998) 2280.
- [34] J.R. Kula, Anal. Chem. 38 (1966) 1382.