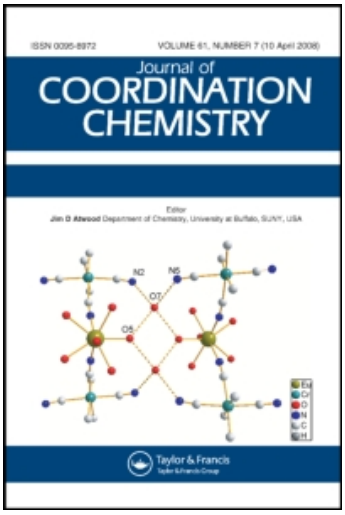

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STABILITY CONSTANTS FOR THE OXOVANADIUM(IV)-GLYCINE SYSTEM IN AQUEOUS SOLUTION

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STABILITY CONSTANTS FOR THE OXOVANADIUM(IV)–GLYCINE SYSTEM IN AQUEOUS SOLUTION

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The stability constants for the formation of various oxovanadium(IV)-glycine complexes have been measured by a combination of spectrophotometric and *p*H measurements. Evidence for the existence of monodentate and bidentate glycinatooxovanadium(IV) and bisglycinatooxovanadium(IV) complexes along with the protonated analog of the monodentate glycinatooxovanadium(IV) complex is presented. The absorption spectra, the molar absorptivities and the *p*H profiles for each of the various species are given in graphical form. The results are dicussed in terms of bonding competition between nitrogen and oxygen ligands with oxovanadium(IV).

INTRODUCTION

A number of recent papers have been concerned with the microscopic details of substitution processes in transition metal complexes.[1–6] Of particular interest is the interaction between metal ions and various amino acids in that the protonated and unprotonated forms appear to have markedly different reactivities.[7] Several reports[8–15] have appeared for glycine, which is one of the simplest amino acids, reacting with transition metal ions including nickel(II), manganese(II), chromium(II), copper(II) and zinc(II). A series of preliminary kinetic measurements[16] in this laboratory on the oxovanadium(IV)–glycine system suggested that the proposed model for the marked differences[7] in reactivities could be tested[16] if the appropriate equilibrium properties of the oxovanadium(IV)–glycine complexes were available. The purpose of this paper is to present the absorption spectra, molar absorptivities, and the stability constants for the formation of various oxovanadium(IV)–glycine complexes.

EXPERIMENTAL

The stock solution of oxovanadium(IV) was prepared by electrolytically reducing a slurry of vanadium pentoxide in perchloric acid. The reduction proceeded for about 10 hours at a platinum cathode with a potential of about 6–7 volts. The reduction was continued until vanadium(III) was detected in the solution. Small amounts of vanadium pentoxide were added and oxygen was passed through the solution to remove traces of vanadium(III). The presence of appreciable concentrations of vanadium(III) was ascertained by the reduction of iodate ion and the observation of liberated iodine. This test is sensitive to $\sim 10^{-5}$ M vanadium(III). Vanadium(V) was detected in the stock solution by the addition of iodide ion and the resulting evolution of iodine. This test is sensitive to $\sim 10^{-4}$ M vanadium(V). The final 0.6 M vanadium(IV) stock solution was 1 M in perchloric acid and gave negative tests for both vanadium(III) and vanadium(V).

The oxovanadium(IV) stock solution was analyzed by titration with standard $KMnO_4$ and compared with the optical spectrum which was determined by means of a Cary 14R recording spectrophotometer. The total acid concentration was determined by passing aliquots of the stock solution through a Dowex 50–8X cation exchange column and by titrating the eluent with standard NaOH to the phenolphthalein endpoint. The acid concentration was obtained by making corrections for the hydrogen ions released by the oxovanadium(IV).

Commercially available glycine was recrystallized several times from a water-methanol solvent. The crystals were washed with methanol and ether. The final product was oven dried at 110°C for 48 hours. Sodium perchlorate was prepared from sodium carbonate and perchloric acid by the method reported previously[17]. The concentration of the

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sodium perchlorate stock solution was determined by titrating the eluent from a Dowex 50–8X ion exchange resin with sodium hydroxide.

The *p*H of each solution was measured with a Radiometer Model 26 *p*H meter equipped with a combination glass-calomel electrode which was calibrated in the *p*H region of interest with standard Radiometer buffers. The spectrophotometric measurements were all carried out by using matched quartz cells in a Cary 14R recording spectrophotometer. The temperature was controlled by immersing the cells in water in the cell holder. The actual cell holders were maintained at constant temperature by means of an external temperature bath. The temperature was measured with a calibrated Dymec quartz thermometer and the reported temperatures were maintained to $\pm 0.0_5$°C. Individual absorbance readings were reproducible to ± 0.001 absorbance units and accurate to ± 0.003 absorbance units over the spectral range investigated.

Distilled water was prepared from a Barnsted still followed by passage through Barnsted inorganic and organic exchange columns. The resulting water was passed through an 18 inch column of glass wool and was stored in the dark.

RESULTS AND DISCUSSION

The chemical properties of the vanadium(IV) ion have been well investigated in acidic aqueous solutions.[18–26] A combination of spectrophotometric and potentiometric measurements[18] and several more recent NMR studies[19–26] indicate that in solutions containing more than 0.002 M acid vanadium(IV) exists as the oxovanadium(IV) ion, (VO^{2+}). As the hydrogen ion concentration is decreased below 0.002 M, two additional complexes are formed in solution. These species are [$VOOH^+$] and [$(VO)_2(OH)_2^{2+}$] and their concentrations are governed by the equilibria[18]

$$VO^{2+} + H_2O \underset{}{\overset{K_{m_1}}{\rightleftharpoons}} VOOH^+ + H^+$$

$$2VO^{2+} + H_2O \overset{K_{m_2}}{\rightleftharpoons} [(VO)_2(OH)_2^{2+}] + 2H^+$$

The appropriate equilibrium constants are reported in Table I. It is important to note that Rossotti and Rossotti[18] report that precipitation occurs when approximately 10% of the oxovanadium(IV) ions are hydrolyzed, but that the positions of the absorption maxima do not change.

Glycine exists in equilibrium in aqueous solution in both a protonated (H_2Gly^+) and an unprotonated (Gly^-) form and as a zwitterionic species (HGly). The equilibria between these species can be written as follows:

$$\underset{(HGly)}{H_3{}^+N{-}CH_2{-}CO_2{}^-} + H^+ \overset{K_{g_1}}{\rightleftharpoons} \underset{(H_2Gly^+)}{H_3{}^+N{-}CH_2{-}CO_2H}$$

$$\underset{(Gly^-)}{H_2N{-}CH_2{-}CO_2{}^-} + H^+ \overset{K_{g_2}}{\rightleftharpoons} \underset{(HGly)}{H_3{}^+N{-}CH_2{-}CO_2{}^-}$$

Various values for the two protonation constants of glycine have been reported in the literature[26] and these are noted to change only slightly in different ionic media. In order to be consistent however, we have chosen values[26c,d] at an ionic strength of 0.1 M KCl in that this closely approximates the concentrations used in this study. These values are recorded in Table I.

TABLE I

Stability constants for the hydrolysis of oxovanadium(IV) and glycine at 25°C

Process	*Value*	*Reference*
K_{m1}	1.0×10^{-6}	19
K_{m2}	$1.31_8 \times 10^{-7}$	19
K_{g1}	$(2.18 \times 10^2)^a$	9, 12, 27
K_{g2}	$(3.98 \times 10^9)^b$	9, 12, 27

[a] The corresponding value at 10°C is $2.45_4 \times 10^2$.
[b] The corresponding value at 10°C is $1.02_5 \times 10^{10}$.

Ballhausen and Gray[27] have reviewed the electronic structure of the oxovanadium(IV) ion. In this species, the vanadium-oxygen bond is the strongest link. Four equivalent water molecules are coordinated to the metal in a square planar arrangement[19–21] and a fifth water molecule is very weakly coordinated in an axial position. A general summary of the spectral characteristics of various oxy-ligand complexes of oxovanadium(IV) has been published.[27,28] In general, all of the complexes appear to be strikingly similar: each show one band at about 13,000 cm^{-1} (770 nm), followed by a somewhat less intense band at about 16,000 cm^{-1} (630 nm). It is important to note that $VOSO_4 \cdot 5H_2O$

which is known to have a sulfate oxygen coordinated in the equatorial position[29] has a maximum band at almost the exact same wavelength as does the aqueous VO^{2+} ion. Other complexes with ligands such as acetylacetone, ethylenediaminetetracetic acid, and oxalate, in which coordination to the oxygen-containing bidentate ligand must also occur in the equatorial positions, show only slight shifts in the positions of the maximum bands as compared to that observed for $(H_2O)_4VO^{2+}$.

The molar absorptivities for the oxovanadium(IV) ion were remeasured for this study at 760, 580 and 555 nm in solutions of 0.2 M ionic strength maintained with sodium perchlorate. These values correspond to 17.2, 4.1_0 and 2.2_2 $M^{-1}\,cm^{-1}$ at 760, 580 and 555 nm, respectively, and agree well with the values reported in the literature.[17]

Solutions of glycine show no absorption maximum in the visible region of the spectrum. Only negligibly small corrections need be made for reasonably concentrated solutions of glycine in that the molar absorptivities are less than 4×10^{-3} $M^{-1}\,cm^{-1}$ at the wavelengths of concern.

When solutions of glycine and oxovanadium(IV) are prepared below *p*H 3, the general features of the spectra are very similar to that of an aqueous oxovanadium(IV) perchlorate solution, except that at all wavelengths in the visible region, the molar absorptivities are larger. The absorbance of several oxovanadium(IV)–glycine solutions at various *p*H values are listed in Table II. The absorbance of solution increases as the glycine concentration increases and the change in absorbance parallels the change in concentration of HGly but not that of Gly^-. On this basis, we associate the change with the formation of a protonated, monodentate oxovanadium(IV)–glycine complex as is shown below:[30]

$$VO^{2+} + HGly \underset{}{\overset{K_1}{\rightleftharpoons}} VOHGly^{2+} \qquad (1)$$

The formation of this complex is not too surprising in that HGly might be expected to form relatively weak, monodentate complexes as intermediates in the formation of the corresponding bidentate-chelated complex.

Based on the differences in absorbance associated with changes in initial concentrations of glycine, oxovanadium(IV) and *p*H, it is possible to evaluate the molar absorptivity of the $VOHGly^{2+}$ complex as long as the HGly concentration is in large excess when compared with the VO^{2+} concentration. This is the case in the *p*H range 2.5–3.0 (*vide infra*).

In the solutions of oxovanadium(IV) and high concentrations of HGly, the spectrum changes only in intensity but not in the position of the peak maximum. Therefore we have concluded that the glycine oxygen is initially coordinated to the

TABLE II

Absorbances of 0.0200 M oxovanadium(IV) solutions[a] as a function of glycine concentration at 760 nm and 25°C

Glycine (M)	*p*H	[HGly] (M)	$[Gly^-]$ $M \times 10^7$	$[VO^{++}]$ $M \times 10^2$	$[VOHGly^{2+}]$[b] $M \times 10^2$	Absorbance[c] Meas.	Calc.
0.195	2.935	0.150	0.32_5	1.34	0.580	0.876	0.874
0.234	2.682	0.156	0.18_9	1.35	0.607	0.881	0.883
0.235	2.972	0.184	0.43_4	1.24	0.660	0.903	0.899
0.312	2.671	0.207	0.24_4	1.22	0.728	0.922	0.921
0.312	2.850	0.232	0.41_2	1.15	0.768	0.934	0.934
0.312	2.998	0.248	0.62_1	1.10	0.784	0.943	0.939
0.312	3.040	0.252	0.69_5	1.08	0.786	0.940	0.940
0.390	2.565	0.239	0.22_1	1.16	0.798	0.935	0.944
0.390	2.905	0.299	0.60_3	1.02	0.876	0.965	0.968
0.390	3.130	0.326	1.11	0.93_8	0.881	0.985[b]	0.970
0.390	3.212	0.334	1.37	0.90_8	0.874	0.984	0.968

[a] All measurements were made in 2.00 cm quartz cells at an ionic strength of 0.200 M maintained with $NaClO_4$. The quantities in square brackets denote species concentrations at equilibrium.

[b] Below *p*H 3.1, species other than $VOHGly^{2+}$ formed by means of additional equilibrium processed contribute less than 3% to the overall absorbance. Above *p*H 3.1, species[30] such as $VOGly^+$ and $VO(Gly)^+$ make detectable contributions and appropriate absorbance corrections need be made (*vide infra*).

[c] The calculated absorbances are based on a self-consistent non-linear least squares calculation using the appropriate equilibrium constants and molar absorptivities for the various vanadium(IV) species reported in this paper.

oxovanadium(IV) which is consistent with the electronic arguments of Ballhausen and Gray.[27] Additional support for this assignment comes from a series of experiments using the ethyl ester of glycine under conditions similar to that reported in Table II. In these experiments, no spectral changes associated with complex formation are observed and at higher *p*H values, the only observed changes appear to be associated with hydrolysis and precipitation of oxovanadium(IV).

The interference of higher order complexes at 760 nm can also be ruled out in that a continuous variation plot[31] (Job's method) shows a distinct maximum at a 1:1 ratio of VO^{2+} to HGly as can be seen in Figure 1. This assumption is further

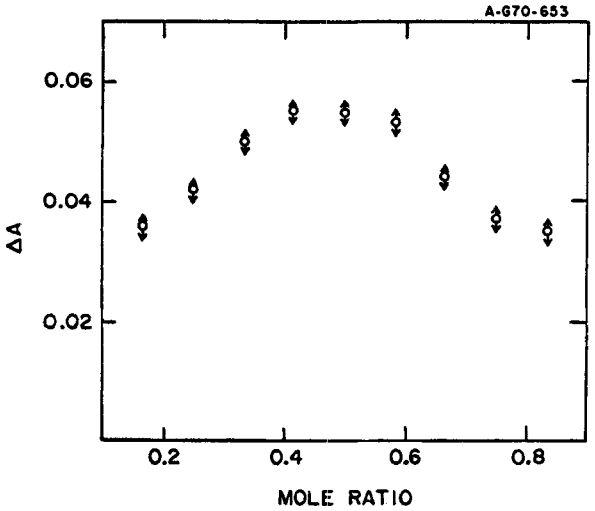

FIGURE 1 Continuous variations plot for various $[VO^{2+}]/[VO^{2+} + \text{glycine}]$ ratios at *p*H = 2.9 and 25°C.

verified in a kinetic study[16] where it is shown that the formation of this complex is first order in VO^{2+} and HGly.

Additional confirmation of these spectrophotometric data might be obtained from a series of *p*H measurements. In view of the fact that rather large glycine to vanadium(IV) ratios are required in order to suppress metal ion hydrolysis and possible concomitant precipitation of vanadium(IV) hydroxide species, *p*H titration curves are not very helpful in evaluating the equilibrium properties of the vanadium(IV)–glycine system. Thus, the results depend on a detailed evaluation of very careful spectrophotometric measurements.

An estimate of $32.5 \pm 0.5\ M^{-1}\,cm^{-1}$ was obtained for the molar absorptivity of the $VOHGly^{2+}$ species from the intercept of a graph of the apparent molar absorptivity as a function of the reciprocal of the concentration of HGly. The total absorbance of a solution under the conditions shown in Table II is primarily a function of the molar absorptivities of VO^{2+} and $VOHGly^{2+}$ and the equilibrium constants for equation 1 and the glycine protonation reactions.

By using a special subroutine of the general nonlinear least squares program,[32] it is possible to obtain an exact fit of the experimental data by minimizing the difference between the calculated and observed absorbance values. For the initial purposes of this calculation, K_{g1}, K_{g2}, K_{m2}, K_{m2} and the molar absorptivity of VO^{2+} were treated as known constants and unit weights were used for each datum point at 25°C in Table II. The final values of K_1 and the molar absorptivity for $VOHGly^{2+}$ are $2.88 \pm 0.08\ M^{-1}$ and $33.2 \pm 0.2\ M^{-1}\,cm^{-1}$, respectively[33]. The uncertainties correspond to standard deviations which are calculated directly by the program. A comparison of the measured and the calculated absorbances[33] in terms of these parameters is given in the last two columns of Table II. A corresponding set of experiments was carried out at 10°C and the calculated value of K_1 (10°C) is $3.1_7 \pm 0.1_2\ M^{-1}$.

Below *p*H 3.0, the contribution to the spectra of species other than $VOHGly^{2+}$ is less than 3.0%. As the *p*H is increased from the 3 to the 4.0 range, a marked difference appears in the spectrum and the absorbance data can not be fitted by means of a single equilibrium expression. This difference is most conspicious in the 550–600 nm region of the spectra[35] and the change in absorbance is larger at higher *p*H values. In that the concentration of Gly^- increases as the *p*H increases, it might be expected that the observed changes are associated either with direct Gly^- coordination to form $VOGly^+$ or by deprotonation of $VOHGly^{2+}$. In either case, the product would be $VOGly^+$ which would be expected to have a spectrum very similar to that observed for $VOHGly^{2+}$.

The stoichiometry for these reactions[30] is as follows:

$$VO^{2+} + Gly^- \underset{}{\overset{K_2}{\rightleftharpoons}} VO(Gly)^+ \qquad (2)$$

$$VOHGly^{2+} \underset{}{\overset{K_3}{\rightleftharpoons}} VOGly^+ + H^+ \qquad (3)$$

$$VOGly^+ \underset{}{\overset{K_4}{\rightleftharpoons}} VO(Gly)^+ \qquad (4)$$

It should be noted that equation 4 has also been

included in order to take into account direct conversion of $VOGly^+$ to $VO(Gly)^+$. Clearly, these equations are not intended to describe the pathways by which these species are formed, but only the various equilibria which must be taken into account in order to completely describe the system.[34]

Other equations which must be included for completeness are:

$$VO(Gly)^+ + Gly^- \underset{\rightleftarrows}{K_5} VO(Gly)_2 \quad (5)$$

$$VO^{2+} + Gly^- \underset{\rightleftarrows}{K_6} VOGly^+ \quad (6)$$

$$VOHGly^{2+} \underset{\rightleftarrows}{K_7} VO(Gly)^+ + H^+ \quad (7)$$

At higher pH values (> 3.0), any changes in the 760 nm peak become a complicated function of both HGly and Gly^- concentration in that each of these species are involved in equilibrium reactions with oxovanadium(IV). At relatively high concentrations of HGly, the absorbance at 760 nm becomes constant even with changes in concentration of Gly^-. This is consistent with additional equilibrium processes such as those shown in equations 2–7.

In order to evaluate the equilibrium constants K_2 and K_6 we need only consider the overall absorbance of the system which is shown by Beer's law and can be written as:

$$Abs = p\Sigma\varepsilon_i C_i = p(\varepsilon_m C_m + \varepsilon_1 C_1 + \varepsilon_2 C_2 + \varepsilon_3 C_3) \quad (8)$$

where Abs is the absorbance of the system at the appropriate wavelength, p is the path length and ε_i and C_i are the molar absorptivities and concentrations of each of the absorbing species in solution (i.e. $C_m = VO^{2+}$, $C_1 = VOHGly^{2+}$, $C_2 = VO(Gly)^+$ and $C_3 = VOGly^+$). By substituting species concentrations, in terms of the appropriate equilibrium expressions, we obtain a general equation for the absorbance at any wavelength:

$$Abs = \frac{pC}{1 + K_1[HGly] + K_2(1 + 1/K_4)\,[Gly^-]}$$
$$\{\varepsilon_m + \varepsilon_1 K_1[HGly] + K_2(\varepsilon_2 + \varepsilon_3/K_4)\,[Gly^-]\} \quad (9)$$

In this expression, C represents the total concentration of oxovanadium(IV) and the equilibrium constants K_1, K_2, and K_4 are defined in terms of equations 1, 2, and 4, respectively.[34]

The changes in the absorption spectrum with change in pH are most significant at 555 and 580 nm. At 580 nm, the values of ε_m and ε_1 can be measured independently at lower pH values. These molar absorptivities are 4.1_0 and 10.2_7, respectively. At 555 nm, the corresponding values are 2.2_2 and 6.0_3 respectively. Since $[VO(Gly)^+]$ appears to have a larger molar absorptivity than VO^{2+} and since $VOHGly^{2+}$ and $VOGly^+$ might not have very different molar absorptivities, values of K_2, and[34], ε_2 and ε_3 can be calculated directly by means of our general non-linear least squares fitting program.[32] This calculation has been carried out for the eighteen spectral measurements at two wavelengths (555 nm and 580 nm). The resulting values for the equilibrium constants are $K_2 = (1.1 \pm 0.1) \times 10^6\ M^{-1}$ and $K_4 = 1.8$. The initial glycine concentrations and the pH values are listed in Table 3 along with the measured absorbances at 555 and 580 nm. An average value of ε_2 (555 nm) $= 15.9 \pm 0.4$ and ε_2 (580 nm) $= 17.8 \pm 0.2$ is evaluated directly by the program. The fitted values of ε_3 at both wavelengths are indistinguishable from the measured values of ε_1 at the same wavelengths. The average difference between the fitted and the calculated absorbances is less than ± 0.003 absorbance units.

As a double check on the validity of this method, values of the absorbance at 760 nm were also fitted by using the final iterated value of K_2 and K_4. Thus at 760 nm the only parameters to be fitted were ε_2 and ε_3. The resulting value of ε_2 (760 nm) was 19.0 ± 0.3 and once again ε_3 was experimentally indistinguishable from ε_1 (i.e. $\varepsilon_1 = 33.2 \pm 0.2$ and $\varepsilon_3 = 33.1 \pm 0.3$). A comparison of the observed and calculated absorbances, based on these values, is shown in the last two columns of Table III. Clearly, the agreement is very good in that the average difference between the observed and calculated absorbance at 760 nm is less than 0.004 absorbance units except for the last three entries. The largest deviations are observed at the highest pH values (> 3.65) at 760 nm where small errors due to the formation of the $VO(Gly)_2$ complex are becoming increasingly important. Although the error in K_2 is substantial, an independent measure of K_2 can be obtained at higher pH values.

In the previous section, the pH was maintained around 3.5 in an attempt to minimize contributions from the bis complex, $[VO(Gly)_2]$. As the pH is increased, however, this contribution can not be neglected, as can be seen from the last 3 entries in Table III which were made above pH 3.7. The aqueous oxovanadium(IV) ion itself, in the

TABLE III

Experimental and calculated absorbances for solutions[a] containing VO^{2+}, $VOHGly^{2+}$ and $VO(Gly)^{+}$ as predominant species as a function of *p*H and glycine concentration[30]

*p*H	Glycine (M)	$[VOHGly^{2+}]$ M × 10^2	$[VOGly^{+}]$ M × 10^2	$[VO(Gly)^{+}]$ M × 10^2	Abs. (555 nm) Expt.	Abs. (555 nm) Calc.	Abs. (580 nm) Expt.	Abs. (580 nm) Calc.	Abs. (760 nm) Expt.	Abs. (760 nm) Calc.
3.551	0.390	0.789	0.147	0.266	0.234	0.232	0.352	0.352	0.995	0.994
3.412	0.595	0.980	0.132	0.240	0.239	0.239	0.365	0.367	1.046	1.052
3.560	0.595	0.912	0.173	0.314	0.259	0.257	0.384	0.384	1.046	1.046
3.541	0.682	0.959	0.174	0.316	0.263	0.261	0.391	0.390	1.061	1.062
3.410	0.780	1.06_0	0.143	0.259	0.252	0.251	0.383	0.383	1.075	1.082
3.601	0.780	0.956	0.200	0.361	0.278	0.275	0.407	0.406	1.070	1.071
3.405	1.009	1.13_0	0.151	0.273	0.258	0.260	0.395	0.397	1.105	1.108
3.556	1.009	1.04_1	0.196	0.355	0.280	0.280	0.416	0.414	1.104	1.099
3.530	1.019	1.06_2	0.188	0.340	0.277	0.277	0.412	0.411	1.107	1.100
3.557	1.019	1.04_0	0.197	0.356	0.279	0.280	0.414	0.414	1.109	1.096
3.415	1.332	1.19_2	0.162	0.293	0.269	0.272	0.411	0.411	1.134	1.132
3.550	0.595[b]	0.935	0.174	0.314	0.258	0.261	0.385	0.390	1.066	1.068
3.515	0.682[b]	0.992	0.170	0.308	0.259	0.263	0.393	0.395	1.086	1.085
3.512	0.780[b]	1.03_0	0.175	0.317	0.263	0.269	0.400	0.403	1.099	1.099
3.528	1.019[b]	1.08_2	0.191	0.346	0.283	0.282	0.415	0.419	1.129	1.121
3.831	0.780[b]	0.805	0.285	0.517	0.320	0.315	0.447	0.443	1.104	1.069[c]
3.712	1.019[b]	0.943	0.254	0.460	0.306	0.307	0.442	0.441	1.139	1.105[c]
3.782	1.019[b]	0.883	0.280	0.507	0.320	0.318	0.454	0.450	1.134	1.096[c]

[a] 0.0200 M VO^{2+} and an ionic strength of 0.200 M maintained with $NaClO_4$ and 25°C in 2.00 cm cells.
[b] 0.0204 M VO^{2+}.
[c] Since sizable contributions from the species $VO(Gly)_2$ result at *p*H values above 3.6 (*vide infra*) at 760 nm, these experiments were not used in the final evaluation of K_2 and K_4.

absence of complexing ligands, is known to be unstable at high *p*H values.[18] In the presence of high concentrations of glycine such as those reported here, even at *p*H 7, the solutions are stable for several hours and after 24 hours, only small changes are noted in the visible absorption spectra. At high *p*H values (> 5), the spectra of solutions containing oxovanadium(IV) and glycine show a peak[35] at 555 nm. This peak is also relatively sensitive to changes in *p*H as can be seen from Figure 2.

Above *p*H 5.7, the absorbance is relatively constant through the *p*H 7 range. We have assigned these conditions to the formation of the bisglycinatooxovanadium(IV) complex, $[VO(Gly)_2]$ as is shown by equation 5. At *p*H values greater than 7.0, the absorbance of the solution decreases and the solution is markedly less stable with respect to precipitation. These changes are consistent with the possibility of hydrolysis and subsequent precipitation of various oxovanadium(IV) species.

From the data at $pH > 6.5$, a value for the molar absorptivity (ε_4) for $VO(Gly)_2$ can be calculated directly. We obtain ε_4 (555 nm) = 16.0 ± 0.2 and ε_4 (580 nm) = 14.1 ± 0.3. The total absorbance at

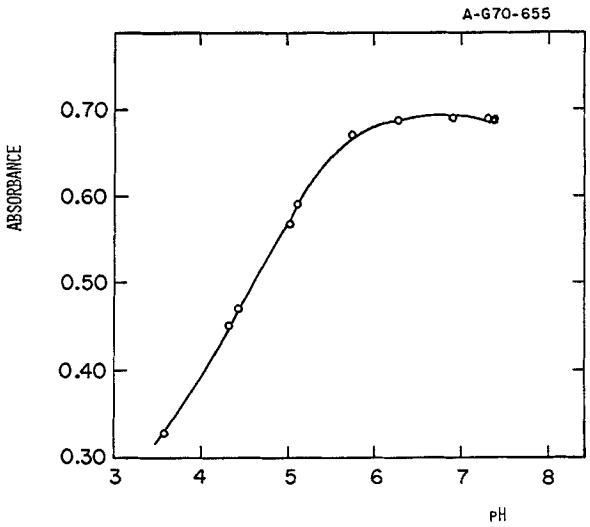

FIGURE 2 Absorbance of $VO(Gly)_2$ at 555 nm as a function of *p*H. Solution contains 0.02M VO^{+2} and 2.1M glycine at 25°C.

lower pH values once again can be described in terms of Beer's law and the various species present:

$$\text{Abs} = p(\varepsilon_m C_m + \varepsilon_1 C_1 + \varepsilon_2 C_2 + \varepsilon_3 C_3 + \varepsilon_4 C_4) \quad (10)$$

where C_4 represents the concentration of $VO(Gly)_2$ and the other symbols are as defined previously.

By measuring the absorbance at 555 and 580 nm and by fitting equation 10 in terms of the equilibrium expressions 2, 3, 4 and 5 at these two wavelengths by using the non-linear least squares program, the best values of the equilibrium constants K_4 and K_5 are obtained directly along with the concentration of each species at equilibrium. This calculation has been carried out and we obtain $K_4 = (1.8_1 \pm 0.3_5)$ and $K_5 = (5.4_1 \pm 0.6_0) \times 10^4$, and the measured absorbances can be reproduced to $\pm$ 0.003 absorbance units. These results are shown in Table IV. Under these conditions, where the concentration changes for $VO(Gly)^+$ are considerably higher than in the previous section, a more reliable estimate for K_4 is obtained which is in good agreement with our previous estimate.

Thus, it has been possible to determine values for K_1, K_2, K_4 and K_5 directly.[33] Values for K_3, K_6 and K_7 can be determined[34] from the above values in terms of equations 1–9. The errors associated with each of these values can be propagated from the errors reported for K_1, K_2, K_4 and K_5.

As a final check on the derived equilibrium constants and molar absorptivities, the species concentrations for each individual set of initial conditions were calculated[36] in terms of the various equilibrium expressions described here. The absorbance for each measurement was recalculated by summing the contributions from each of the individual species. The final results were gratifying in that the measured absorbances from all of the experiments could be reproduced[37] with an average deviation of less than $\pm$ 0.003 absorbance units.

A plot of the molar absorptivities for VO^{2+}, $VOHGly^{2+}$, $VO(Gly)^+$ and $VO(Gly)_2$ as a function of wavelength is shown in Figure 3 based on the data reported here at 25°C. Thus values for VO^{2+}, $VOHGly^{2+}$ and $VO(Gly)_2$ have been obtained by direct measurement whereas that for $VO(Gly)^+$ corresponds to a computed absorption curve.

TABLE IV

Species concentration[a] for the formation of $VO(Gly)_2$ at 25°C

pH	$[Gly^-]$ $M \times 10^4$	$[VO^{2+}]$ $M \times 10^3$	$[VOHGly^{2+}]$ $M \times 10^2$	$[VOGly^+]$ $M \times 10^2$	$[VO(Gly)^+]$ $M \times 10^2$	$VO(Gly)_2$ $M \times 10^2$	Absorbance (555 nm) Expt.	Calc.
4.015[b]	0.0248	5.78	1.59	0.861	1.56	0.212	0.893	0.893
4.158[b]	0.0346	4.63	1.28	0.962	1.74	0.330	0.956	0.958
4.359[b]	0.0551	3.20	0.884	1.06	1.91	0.578	1.047	1.049
4.528	0.0839	0.890	0.254	0.448	0.810	0.372	0.476	0.474
4.585[c]	0.0956	0.792	0.226	0.454	0.822	0.431	0.489	0.493
4.325[d]	0.113	0.589	0.362	0.400	0.724	0.450	0.487	0.487
4.555[e]	0.117	0.608	0.227	0.427	0.773	0.497	0.495	0.497
4.672	0.117	0.623	0.178	0.437	0.791	0.507	0.501	0.499
4.920	0.207	0.309	0.088	0.383	0.693	0.785	0.533	0.538
5.045[f]	0.274	0.253	0.0714	0.415	0.750	1.13	0.672	0.668
5.039[e]	0.357	0.142	0.0529	0.303	0.549	1.07	0.571	0.572
5.011[d]	0.0552	0.0710	0.0438	0.235	0.425	1.290	0.600	0.600
5.531[e]	1.105	0.0218	0.0081	0.144	0.261	1.58	0.619	0 618
4.510	0.0805	0.928	0.264	0.448	0.811	0.357	0.467	0.470

[a] All solutions contain 0.0200 M VO^{2+} and 1.019 M glycine initially unless otherwise noted. The measurements were made in 2.00 cm cells at an ionic strength of 2.00 M maintained with $NaClO_4$.
[b] 0.0490 M VO^{2+}.
[c] 0.02039 M VO^{2+}.
[d] 2.180 M glycine.
[e] 1.332 M glycine.
[f] 0.0241 M VO^{2+}.

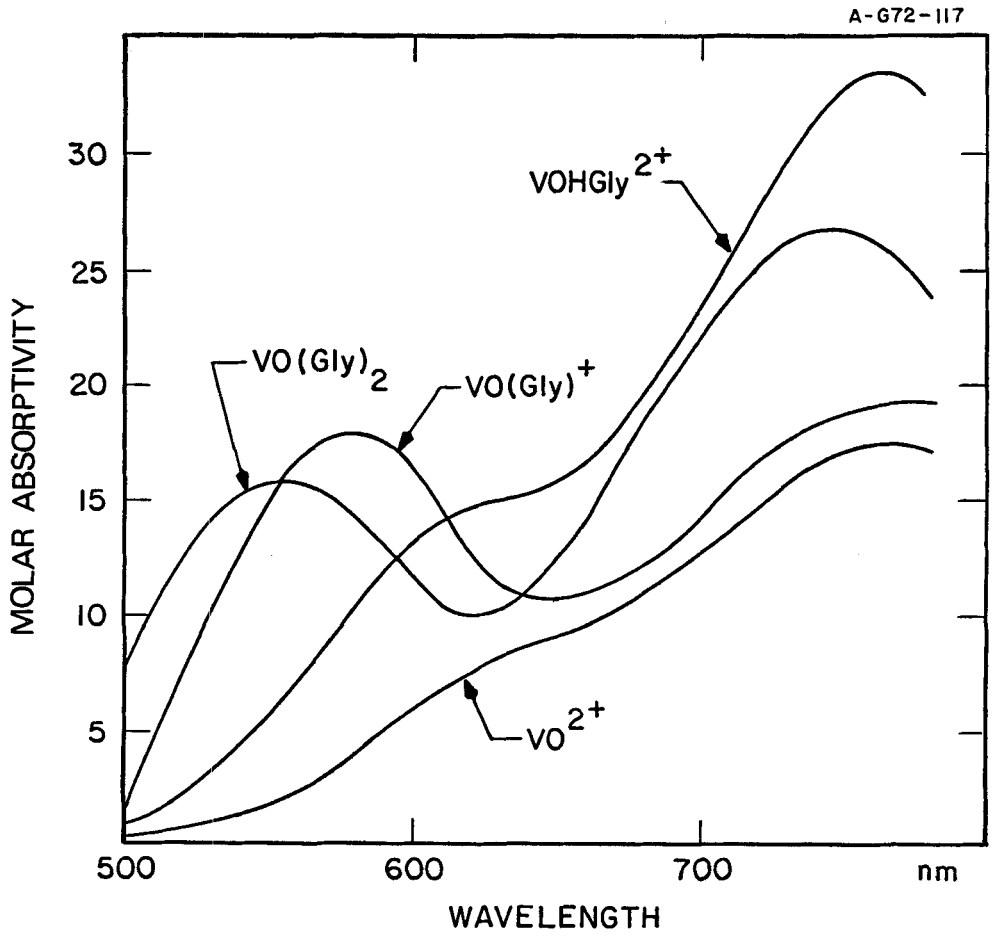

FIGURE 3 Molar absorptivity for various vanadium(IV)-glycine species as a function of wavelength at 25°C.

SUMMARY

A series of spectrophotometric and *p*H measurements of various mixtures of acidic solutions of oxovanadium(IV) and glycine has been used to systematically evaluate the equilibrium processes. The system is characterized by the following equilibria at 25°:

$VO^{2+} + HGly \leftrightarrows VOHGly^{2+}$	$K_1 = 2.88 \pm 0.08$	(1)
$VO^{2+} + Gly^- \rightleftarrows VO(Gly)^+$	$K_2 = (1.1 \pm 0.1) \times 10^6$	(2)
$VOHGly^{2+} + \rightleftarrows VOGly^+ + H^+$	$K_3 = (5.3_0 \pm 0.9) \times 10^{-5}$	(3)
$VOGly^+ \leftrightarrows VO(Gly)^+$	$K_4 = 1.8_1 \pm 0.3_5$	(4)
$VO(Gly)^+ + Gly^- = VO(Gly)_2$	$K_5 = (5.4_1 \pm 0.6_0) \times 10^4$	(5)
$VO^{2+} + Gly^- \rightleftarrows VOGly^+$	$K_6 = (6 \pm 1._3) \times 10^5$	(6)
$VOHGly^{2+} - \rightleftarrows VO(Gly)^+ + H^+$	$K_7 = (9.6 \pm 1._5) \times 10^{-5}$	(7)
$H^+ + HGly \leftrightarrows H_2Gly^+$	$K_{g_1} = 2.18 \times 10^2$	(8)[26]
$H^+ + Gly^- \leftrightarrows HGly$	$K_{g_2} = 3.98 \times 10^9$	(9)[26]
$VO^{2+} + H_2O \leftrightarrows VOOH^+ + H^+$	$K_{m1} = 1.0 \times 10^{-6}$	(10)[18]
$2VO^{2+} + 2H_2O \leftrightarrows [(VO)_2(OH)_2{}^{2+}] + 2H^+$	$K_{m2} = 1.31_8 \times 10^{-7}$	(11)[18]

A graph of the relative concentrations of each of the species present in a solution containing oxovanadium(IV) and 1.0 M glycine is given in Figure 4 as a function of *p*H. These concentrations are based on the equilibrium constants shown below.

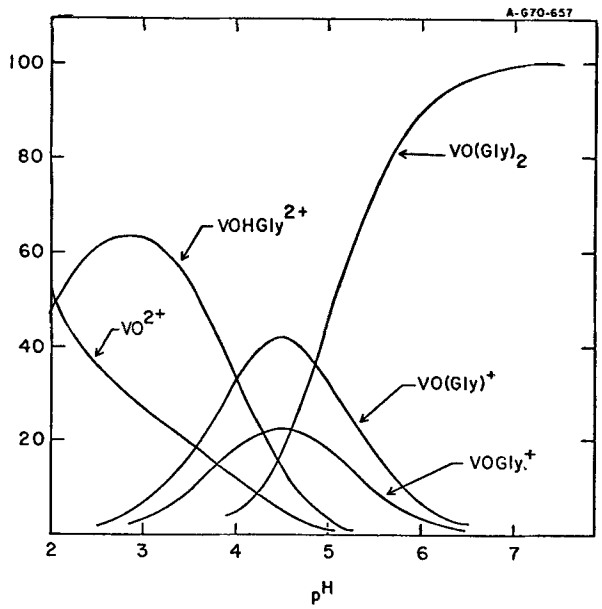

FIGURE 4 Relative concentration of various species for the VO^{2+}-glycine system with 1.00 M glycine at an ionic strength of 0.2 M as a function of *p*H.

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30. The monodentate form of HGly when coordinated to oxovanadium(IV) will be represented in this paper as $VOHGly^{2+}$. The bidentate or chelated form of Gly^- will be contained in brackets. Thus the chelated form of the monodentate Gly^- complex with oxovanadium(IV) will be represented as $VO(Gly)^+$. In a similar fashion, the bisglycinatooxovanadium(IV) complex, in which both glycines are chelated, will be represented as $VO(Gly)_2$.
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32. A description of the algorithm of the computer program is given in the Los Alamos publication LA-2367 and addenda. In this non-linear least squares program which uses the method developed by Gauss, the square of the differences between the observed and calculated dependent variable is minimized. Each individual data point is given unit weights. A modified Fortran(IV) version of this program is presently available from Gilbert Gordon at the University of Iowa.
33. Minor contributions from additional species such as $VOGly^+$ and $VO(Gly)^+$ which were present at less than the 2–3% level were taken into account in the final calculation by using the appropriate equilibrium constants for these species as estimated in this paper

(*vide infra*). Thus, the reported values were obtained by means of a reiterative technique and correspond to a self-consistent set of equilibrium constants, molar absorptivities and associated errors.

34. For example, the direct formation of $VO(Gly)^+$ from VO^{2+} and Gly^- is highly unlikely in that most probably, this reaction must occur stepwise. An independent evaluation of K_4 by kinetic techniques results in a value of 1·8. Clearly, the equilibrium constants are interrelated. For example, $K_2 = K_1K_3K_4K_{g1}$, $K_3 = K_2/K_1K_4K_{g1}$, $K_6 = K_2/K_4$ and $K_7 = K_3K_4$.
35. The spectra of the chelated glycine complexes ($VO(Gly)^+$ and $VO(Gly)_2$)) show marked differences from the monodentate complexes. The appearance of peak maxima at 555 and 580 nm (18,200 and 17,200 cm^{-1}) is not inconsistent with differences anticipated for nitrogen coordination in the formation of the chelated complexes.
36. In addition to using our programs for calculating species concentrations from the appropriate equilibrium expressions, we also used the Fortran (IV) program of D. D. Perrin and I. G. Sayce, *Talanta* **14**, 833 (1967). Identical results were obtained with both programs.
37. In this context it should be noted that the hydrolyzed oxovanadium(IV) species, $VOOH^+$ and $[(VO_2(OH)_2^{2+}]$ are present in very low concentration throughout this study and the maximum contribution by the sum of both species is always less than 1 %.