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NMR Relaxation Studies in Solutions of Transition Metal Complexes. VI. Equilibria and Proton Exchange Processes in Aqueous Solutions of VO^{2+}–glycine System

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The equilibria in aqueous solution of the VO^{2+}–glycine system has been studied by pH-metry in very high ligand excess, to avoid the hydrolysis of vanadyl ions. The complexes VOG^{+}, VOG_2, $VOGH^{2+}$, VOG_2H^{+} and $VOG_2H_{-1}^{-} = VOG_2(OH)^{-}$ are dominating in the system; their formation constants are given. The formation of complexes $VOGH_{-1} = VOG(OH)$, $VOGH_{-2}^{-} = VOG(OH)_2^{-}$ and $(VO)_2G_2H_{-2} = (VO)_2G_2(OH)_2$ have also been detected. It is stated that the $VO_2G_2(OH)_2$ is not the only binuclear (polynuclear) complex in the system; the composition of the other polynuclear complexes, however, cannot be stated unambiguously because of their very low concentrations.

The rate constants of the proton exchange between the bulk water and the different complexes have been determined by measuring the T_2 relaxation time of the water protons. In contrast to the oxalate, and some other vanadyl complexes, the rate constant decreases by the decrease of the number of water molecules remaining in the first coordination sphere of the vanadyl ion. The exceedingly high proton exchange rate constant for the $VOG_2(OH)^{-}$ mixed hydroxo complex is interpreted as being due to the direct proton exchange between the bulk water and the coordinated OH group.

Introduction

The equilibria in aqueous solutions of vanadyl complexes have been studied thoroughly by different experimental methods [1]. The data in the literature, however, are rather contradictory. The soft character of the VO^{2+} ion was stated by Ramakrishna *et al.* [2] by comparing the stability constants of the complexes formed with thiosalycilic and salycilic acids, although Chatt and Ahrland [3] as well as Pearson [4] classified the vanadyl ion as a typical hard acid. This classification is supported by the comparative equilibrium studies of Napoli [5].

Reeder and Rieger [6] interpreted the stability of the VO^{2+} α-OH-carboxylic and α-SH-carboxylic acids as due to the formation of coordinative σ and π bonds. From this they concluded that the VO^{2+} ion cannot form stable complexes with ligands containing no electron pair for π-bonding (amines, aminoacids). At the same time several authors reported the formation of stable complexes with ligands containing an amine donor group [7–11].

The difficulty in the pH-metric investigation of the VO^{2+}–N-donor ligands is that the de-protonation of the N-donors in general takes place in alkaline medium, thus relatively high pH is necessary to achieve an appropriate free ligand concentration for complex formation. At pH > 4 however the hydrolysis of the vanadyl ion takes place. This problem led Tomiyasu and Gordon [9] to the conclusion: "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, pH-titration curves are not very helpful in evaluating the equilibrium properties of the vanadium(IV)–glycine system".

It seems almost a general belief that the use of pH-titration methods should be restricted to comparatively low (from 1:1 to 20:1) ligand-to-metal concentration ratios. The work of Ciavatta *et al.* [12], who studied the nickel(II)–glycine system in 1 *M* glycine medium is an exception. Recently we have published a paper [13] dealing with the possibility and accuracy of pH-metric equilibrium studies at very high ligand-to-metal concentration ratios. The most important conclusion was that if the complex formation takes place in a pH region where the protonation of the ligand does not have significant buffer effect, then even 250–500 fold ligand excess can be used to study the complex formation processes pH-metrically. Taking into account the pK values of glycine (~2.3 and ~9.6), this criterium is fulfilled in the VO^{2+}–glycine system.

The exchange reactions taking place in the system have been studied by Tomiyasu and Gordon [14] by measuring the line broadening of the $-CH_2-$ protons

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of glycine. The activation parameters derived from the temperature dependence of the line broadening indicated a second order exchange reaction, but the line broadening was found to be almost independent of the glycine concentration.

Our preliminary simultaneous measurements on the line broadening of $-CH_2-$ and H_2O protons indicated that the relaxation time of the water protons is much more sensitive to the change of the composition and pH of the solution than that of the $-CH_2-$ protons. Thus, the aim of our present work was to study the VO^{2+}–glycine system in high ligand excess pH-metrically, and to interpret the NMR relaxation results in solutions which are known from the equilibrium point of view.

Experimental

The methods and equipments described in Part V [18] were used for the preparation of $VO(ClO_4)_2$ stock solution and for the pH and T_2 relaxation time measurements. REANAL glycine was purified by recrystallization from ethanol–water mixture. The composition of the initial solutions used for pH-metric and NMR titrations are given in Tables I, II.

TABLE I. Composition of the Initital Solutions Used for pH Titrations.[a]

No.	T_H^o	T_L^o	T_M^o	Number of exp. points
1	0.3269	0.2997	0.0100	25
2	0.5267	0.4955	0.0100	34
3	0.7266	0.6994	0.0100	45
4	0.4289	0.3996	0.0128	29
5	0.7590	0.7285	0.0134	47
6	0.5254	0.5003	0.0071	46
7	0.9257	0.9006	0.0071	50
8	0.6276	0.6004	0.0100	48
9	0.7277	0.7005	0.0100	60
10	0.9278	0.9006	0.0100	49
11	1.1279	1.1007	0.0100	47
12	0.9299	0.9006	0.0128	53
13	1.1300	1.1007	0.0128	45
14	0.8972	0.8660	0.0164	69
15	1.1011	1.0841	0.0142	49
16	0.3222	0.3002	0.0028	35
17	0.9226	0.9006	0.0028	40
18	0.0175	0.0101	0.0101	17
19	0.0276	0.0201	0.0101	18
20	0.0427	0.0352	0.0101	22
21	0.0578	0.0503	0.0101	24
22	0.0652	0.0503	0.0203	34
23	0.0130	0.0101	0.0040	8
24	0.0382	0.0352	0.0040	8
25	0.0401	0.0251	0.0203	24
26	0.0501	0.0352	0.0203	26

[a]The solutions were titrated by 1.007 *M* NaOH.

TABLE II. Composition of the Initial Solutions Used for NMR Titrations.

No.	T_H^o	T_L^o	T_M^o	Number of exp. points
1	0.5072	0.5024	0.00648	31
2	2.0155	2.0095	0.00810	45
3	0.7117	0.7033	0.0113	47
4	1.5191	1.5071	0.0162	35
5	1.2200	1.2057	0.0194	38
6	1.0095	1.0048	0.00648	45
7	0.2541	0.2512	0.00405	27

The ionic strength of all of the solutions was adjusted to 1 *M* $(Na)ClO_4$. The total glycine concentration of the different solutions changed in the range of 0.01–1.1 *M*, *i.e.* its medium effect cannot be neglected. The dependence of the pK values on the total glycine concentration is seen in Fig. 1. There may be two reasons for a change in the observed pK:

i) a change in the activity coefficients, *i.e.* the standard state is no longer constant;

ii) a change in the diffusion potential between the calomel electrode (filled with saturated sodium chloride solution) and the solution studied, as a consequence of the change in the total glycine concentration.

In case i) the two pK values would change differently, because the changes in charge in the two protonation processes are basically different. In case ii), however, parallel changes would be expected and were found. Thus it may be concluded that there is no change in the standard state even if the concentrations of the supporting electrolyte and the neutral (zwitterion) form of the ligand are comparable. The change of the diffusion potential, however, should be

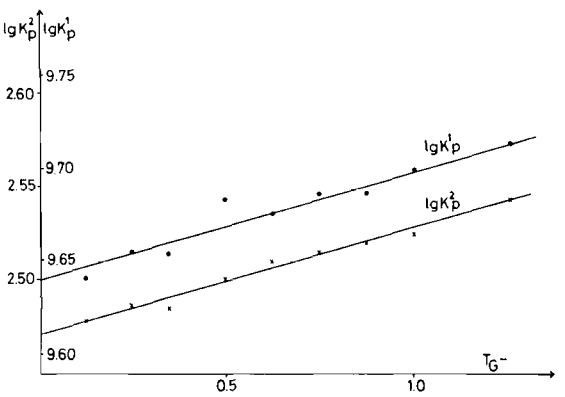

Fig. 1. The calculated protonation constants of glycine as a function of the total glycine concentration. I = 1.0 *M* $NaClO_4$, 25 °C.

$$K_p^1 = \frac{[HG^{\pm}]}{[H^+]\,[G^-]} \quad ; \quad K_p^2 = \frac{[H_2G^+]}{[H^+]\,[HG^{\pm}]}$$

taken into account when the vanadyl–glycine system is studied. For this, we have used pKs extrapolated to $T_L \to 0$, and have corrected the measured pH with an appropriate factor read directly from Fig. 1. This procedure and the calibration of the electrode system according to Irving *et al.* [15] made it possible to convert the directly read pH to $-\log[H^+]$, which was used throughout this work to evaluate titrations.

Results and Discussion

Equilibrium Studies

Titrations No. 1–17 in Table I were carried out at high ligand excess, thus no precipitation was observed until pH ~ 8.5. The titration curves were first transformed into formation curves, to see whether complex formation can be described as stepwise processes. Figure 2 shows a formation curve calculated from titration No. 15. The dashed lines are the formation curves which are obtained if ±0.01 pH unit error is assumed. In the pH range of $4.93 < pH < 7.50$, ±0.01 pH error causes ±0.01 error in the $-\log[L]$, and there is no deviation in the $\bar{n}$ values. In the lower and higher pH range however the formation curve is rather uncertain, because the buffer effect of the protonation processes becomes comparable with the buffer effect of complex formation. It follows from Fig. 2 that the formation processes between $1.3 < \bar{n} < 2.3$ could be studied in high ligand excess with acceptable precision. Thus, to get information on the beginning of the complex formation, some titrations were also carried out at comparable ligand-to-metal concentration ratios (titrations No. 18–26 in Table I). In this case however, the titrations could be done without precipitation only up to pH ~ 4. The formation functions could be given from these titrations only up to $\bar{n} \sim 0.3$–0.4. Their deviation at different ligand to metal concentration ratios indicated the effect of the hydroxo and protonated complex formation.

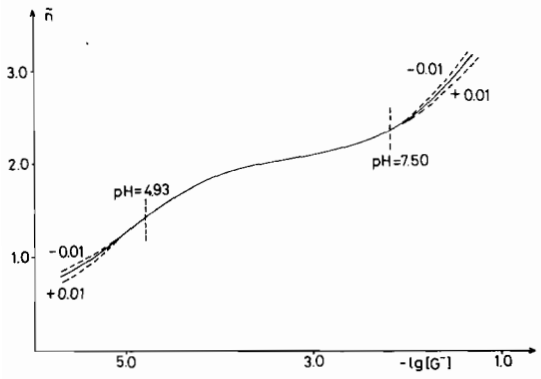

Fig. 2. Calculated formation curve from titration No. 15 in Table I. Full line: calculated from the measured pH. Dashed lines: calculated from the measured ±0.01 pH.

Three of the formation functions calculated at high ligand excess are seen in Fig. 3. It is seen that the curves are deviating from each other; moreover, the inflection points are significantly different from $\bar{n} = 2$, but the higher the ligand concentration, the nearer the inflection point to $\bar{n} = 2$. This suggests the presence of polynuclear species, which are most probably formed through OH bridging ligand(s).

For a computer calculation of the equilibria existing in the system, our own program [16, 17] was used, assuming different equilibrium models. A systematic search for the composition and stability of the complexes formed in the system led to the results collected in Table III.

From the results of the systematic search and from the data in Table III, the following conclusions can be drawn:

– The dominating complexes in the system are the VOG^+, $VOGH^{2+}$, VOG_2, VOG_2H^+ and $VOG_2H_{-1} = VOG_2(OH)^-$. Their stability constants can be calculated with acceptable standard deviations.

– The $VOGH_{-1}$, $VOGH_{-2}$ and $(VO)_2G_2H_{-2}$ complexes are formed in relatively low concentration: their presence is not questioned, but their stability constants are rather uncertain.

– The $(VO)_2G_2H_{-2}$ species is not the only binuclear (polynuclear) complex, the presence of some others should be assumed to get an acceptable fit of the experimental data, but even their composition cannot be stated safely.

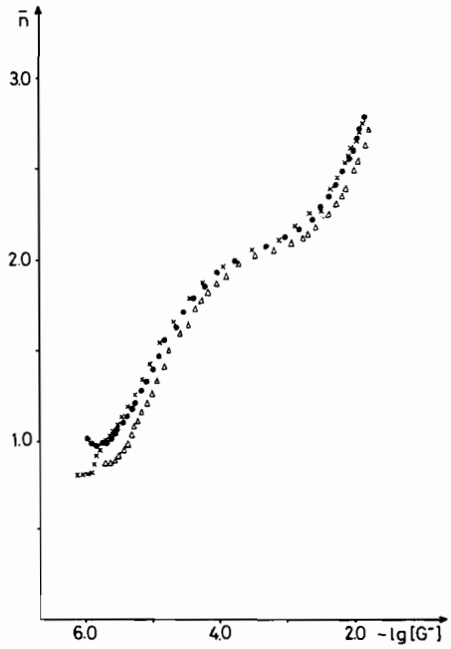

Fig. 3. Calculated formation functions at different ligand to metal concentration ratios. X-X-X Titration No. 3 in Table I. o - o - o Titration No. 12 in Table I. Δ - Δ - Δ Titration No. 11 in Table I.

TABLE III. Composition and Formation Constants of the Species Formed in the VO^{2+}–Glycine System, Assuming Different Equilibrium Models. For comparison, the results of Tomiyasu and Gordon [9] are also given.

$$\beta_{VO_xL_yH_z} = \frac{[VO_xL_yH_z]}{[VO^{2+}]^x[L^-]^y[H^+]^z}$$

Species	lgβ					
	Model I	Model II	Model III	Model IV	Present work (accepted)	[9]
H_2G^+			12.11[a]		12.11	11.94
$HG^{\pm}$			9.64[a]		9.64	9.60
VOH^+_{-1}			−6.07[a]		−6.07	−6.0[b]
$(VO)_2H^{2+}_{-2}$			−6.59[a]		−6.59	−6.88[b]
VOG^+	6.51 ± 0.03	6.51 ± 0.03	6.51 ± 0.03	6.51 ± 0.03	6.51 ± 0.03	6.23 ± 0.05
$VOGH^{2+}$	10.81 ± 0.03	10.81 ± 0.03	10.81 ± 0.03	10.81 ± 0.03	10.81 ± 0.03	10.06 ± 0.02
VOG_2	11.80 ± 0.03	11.80 ± 0.03	11.84 ± 0.03	11.84 ± 0.03	11.82 ± 0.05	10.96 ± 0.06
VOG_2H^+	16.61 ± 0.03	16.61 ± 0.03	16.64 ± 0.03	16.63 ± 0.03	16.63 ± 0.04	–
$VOG_2H^-_1$	4.11 ± 0.04	4.08 ± 0.04	4.15 ± 0.03	4.12 ± 0.04	4.10 ± 0.06	–
$VOGH_{-1}$	1.43 ± 0.09	1.43 ± 0.09	1.16 ± 0.29	1.19 ± 0.26	1.3 ± 0.3	–
$VOGH^-_2$	−6.30 ± 0.12	−6.19 ± 0.09	−6.43 ± 0.19	−6.27 ± 0.12	−6.3 ± 0.3	–
$(VO)_2G_2H_{-2}$	4.94 ± 0.24	4.91 ± 0.26	5.20 ± 0.19	5.16 ± 0.21	5.1 ± 0.4	–
$(VO)_2G_2H^-_3$	−1.80 ± 0.08	–	−1.73 ± 0.08	–	?	–
$(VO)_2G_3H^-_2$	–	7.95 ± 0.08	–	8.01 ± 0.08	?	–
$(VO)_2GH^+_2$	–	–	−0.72 ± 0.24	−0.75 ± 0.27	?	–
Average deviation of the volume of titrant (cm^3)	3.2×10^{-3}	3.3×10^{-3}	3.1×10^{-3}	3.2×10^{-3}		

[a]Determined from independent measurements [13, 18]. [b]Accepted from ref. 23.

– No VOG^-_3 complex is formed in the system. If its formation is assumed, as well as that of $VOG_2H^-_1$, then the program continuously decreases its formation constant and concentrations become unrealistically low. If formation of this complex is assumed instead of that of $VOG_2H^-_1$, then the average deviation in the volume of the titre is one order of magnitude higher than acceptable.

– Taking into account the basically different experimental methods, the agreement of our results and those of Tomiyasu and Gordon is satisfactory. Dominating complexes detected in our work are the VOG_2H^+ and $VOG_2H^-_1$. $VOG_2H^-_1$ is formed in that pH region (pH > 6.5) which was not studied by Tomiyasu and Gordon in detail. Thus the only significant deviation is the formation of VOG_2H^+ detected by us. This difference can be explained as follows. As was proved by Tomiyasu and Gordon, the visible spectrum of the VO^{2+} ion and that of the $VOGH^{2+}$ are different only in their intensity: no new band appears. Presumably a similar relation is valid for the spectrum of VOG^+ and VOG_2H^+, thus these species cannot be distinguished from spectrophotometric data only. The difference in the equilibrium model may explain the *ca.* tenth of log unit difference in the constants determined from spectrophotometric and from pH-metric measurements.

For the illustration of the equilibrium relations, Fig. 4 and 5 show the concentration distribution of the complexes formed at high and at low ligand-to-metal concentration ratios respectively.

To sum up, it can be stated that the VO^{2+} ion forms relatively stable complexes with glycine, and Cu^{2+} is the only 3d metal ion which forms significantly more stable complexes.

Relaxation Studies

Figure 6 shows the concentration distribution and the change of the normalized relaxation rate as a function of pH in case of titration No. 2 in Table II. It is seen in Fig. 6 that the relaxation rate is slightly decreasing in the pH range where the VOG_2 complex is formed. Opposite change of the relaxation rate was observed in the VO^{2+}–oxalic acid system [18] and for some other complexes [21, 22]. There is a sharp increase of the relaxation rate as the pH is raised,

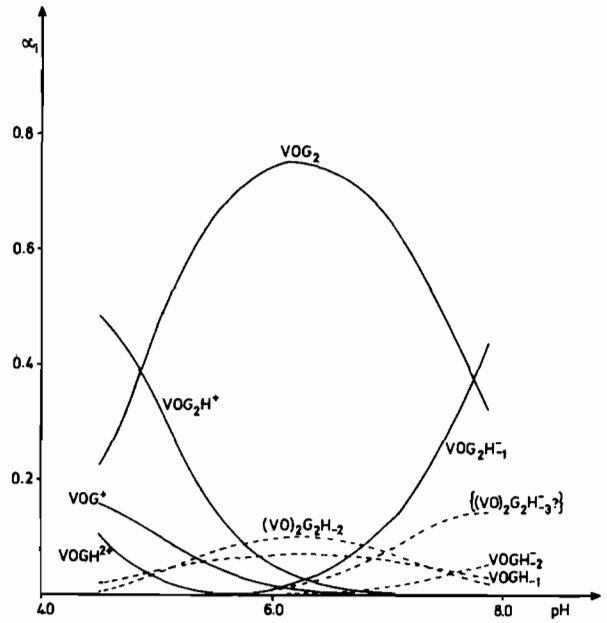

Fig. 4. Concentration distribution of the complexes formed in the VO^{2+}–glycine system at high ligand to metal concentration ratio. Titration No. 15 in Table I.

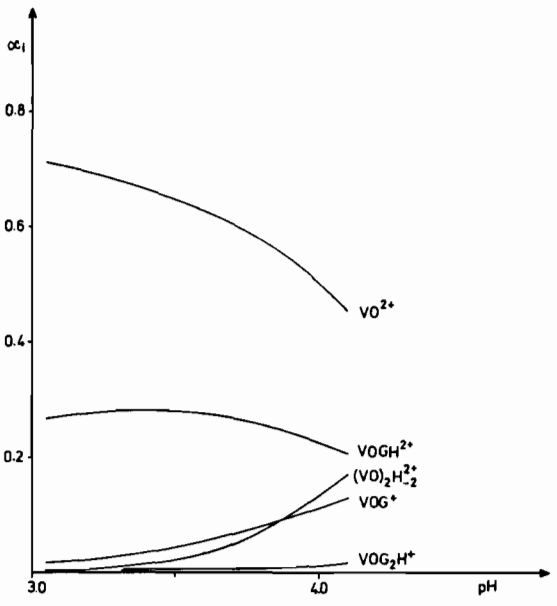

Fig. 5. Concentration distribution of the complexes formed in the VO^{2+}–glycine system at comparable ligand to metal concentration ratio. Titration No. 20 in Table I.

which is parallel with the formation of $VOG_2H^-_1$ complex; thus this may be assigned to a direct effect. The increase of the relaxation rate with increasing temperature—studied in some separate samples—indicated that the relaxation is exchange-controlled in the whole pH range.

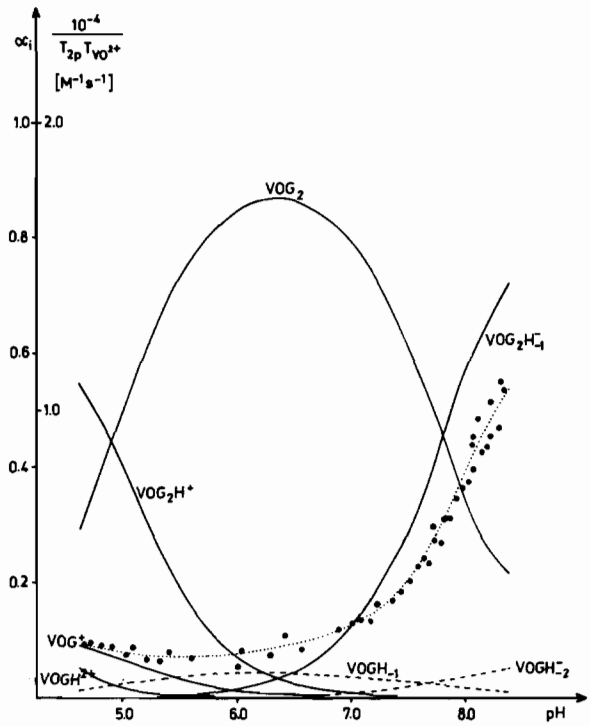

Fig. 6. Concentration distribution and the change of the relaxation rate (dotted) line as a function of pH. Titration No. 2 in Table II.

Figure 6 suggests that the relaxation rate is a linear function of the concentration of the different complexes formed in the system:

$$1/T_2^{meas} - 1/T_{2,0} = 1/T_{2p} = \Sigma r_i c_i$$

where: r_i = the molar relaxation coefficient, c_i = the concentration of the i-th metal containing species, $T_{2,0}$ = the relaxation time in the absence of vanadyl complexes.

A systematic search for the best fit of the data led to the following results:

$$r_{VO^{2+}} = (1.6 \pm 0.1)10^3\ M^{-1}\ s^{-1},$$

$$r_{VOG^+} = (0.9 \pm 0.4)10^3\ M^{-1}\ s^{-1},$$

$$r_{VOG_2} = (1.1 \pm 0.1)10^3\ M^{-1}\ s^{-1},$$

$$r_{VOGH^{2+}} = (3.2 \pm 0.3)10^3\ M^{-1}\ s^{-1},$$

$$r_{VOG_2H^+} = (3.7 \pm 0.2)10^3\ M^{-1}\ s^{-1},$$

$$r_{VOG_2H^-_1} = (1.46 \pm 0.02)10^4\ M^{-1}\ s^{-1}$$

The inclusion of other species in the calculation did not improve the average fit (3.5%) of the experimental data, and led to unrealistic (negative) parameters in some cases. Thus their contribution to the overall relaxation rate is negligible.

Because of the exchange control, the molar relaxation coefficients can be transformed into the appropriate first order rate constants of the

$$VO_xG_yH_z(HOH) + \overset{*}{H}OH \rightleftharpoons VO_xG_yH_z(\overset{*}{H}OH) + HOH$$

$$k_i = 2[H_2O]\,r_i = 108r_i$$

reactions (the water concentration in 1 *M* $NaClO_4$ is 54 *M*). The rate constants calculated are collected in Table IV. For comparison, the appropriate rate constants given for the VO–oxalic acid and VO^{2+}–malonic acid systems are also given in Table IV. From the data of Table IV, the following conclusions can be drawn:

– The rate constant for the VOG^+ complex is rather uncertain, mainly because of its low concentration. It may be safely stated, however, that the rate constant is less than that in the case of the oxalic or malonic acid complexes. This relation indicates that the labilizing effect of glycine for the remaining water molecules is less than that of the oxalate or malonate, in accordance with the difference of the charges.

– The rate constant for the VOG_2 complex is also less in the case of glycine than in case of oxalic or malonic acids, but much higher than to be assigned to the water molecule remaining in the fifth axial position. Thus a similar intramolecular rearrangement of the VOG_2 complex which was illustrated in a previous paper [18] should be assumed to interpret the proton exchange rate constant.

– A similar reasoning to that which was given in part V [18] may be applied to interpret the high rate constants for the protonated complexes $VOGH^{2+}$ and VOG_2H^+.

– The most important difference between the results for the glycine and the dicarboxylic acids is that the proton exchange from the $VOmal_2H_{-1}$ complex could not be detected, while this complex has the highest proton exchange rate constant among the species formed in the VO^{2+}–glycine system. It should be taken into account that six different dynamic processes may be responsible for this datum:

$$VOG_2 + OH^- \rightleftharpoons VOG_2OH^- \quad (a)$$

$$VOG_2(HOH) + \overset{*}{O}H^- \rightleftharpoons VOG_2(HO\overset{*}{H}) + OH \quad (b)$$

$$VOGOH + G^- \rightleftharpoons VOG_2OH^- \quad (c)$$

$$VOGOH + \overset{*}{G}^- \rightleftharpoons VO\overset{*}{G}OH + G^- \quad (d)$$

$$VOG_2\overset{*}{O}H^- + HOH \rightleftharpoons VOG_2OH^- + \overset{*}{H}OH \quad (e)$$

$$VOGOH(R\text{-}\overset{*}{N}H_2) + HOH \rightleftharpoons VOGOH(R\text{-}NH_2) + HO\overset{*}{H} \quad (f)$$

$(R\text{-}NH_2 = G^-)$

Taking into account the equilibrium constants of the different processes, the second order rate constant for the reactions (a) and (b) would be much higher than the diffusion-controlled limit, thus their effect cannot be significant. For processes (c) and (d), the magnitude of the second order rate constant would be higher than 10^8. Such a high ligand exchange rate constant has only been detected for some copper(II) complexes where the Jahn–Teller inversion explains the lability. This explanation is not probable for the VO^{2+} complexes. Process (f) means the opening of one of the chelate rings at the $-NH_2$ end; a fast proton exchange between the bulk water and the $-NH_2$ group before rearrangement. Process (e) means a fast rearrangement of the hydrogen bond formed between the coordinated OH and a bulk water molecule.

Although both processes are conceivable, process (e) seems to be the more probable one. To prove this, some relaxation measurements were carried out on the VO^{2+}–nitrilotriacetic acid systems. It is well known from the literature [6, 19, 20] that only VOL^- complex is formed in the system up to pH ~ 5; the pK of the complex is about 6.5. A very sharp increase of the relaxation rate was observed in this system in this pH range, the first order rate constant calculated for the $VOLH_{-1}$ complex is 2×10^6 s^{-1}. Because the nitrilotriacetate ligand does not contain exchangeable protons on its nitrogen atom, only a process similar to (e) may explain its high proton

TABLE IV. First Order Rate Constants of the Proton Exchange between the Bulk Water and the Different Paramagnetic Species.

	$k(s^{-1})$		
Species	$L = ox^{2-}$	$L = mal^{-2}$	L = glycine
VOL	$(1.85 \pm 0.15)10^5$	$(1.85 \pm 0.15)10^5$	$(1.0 \pm 0.5)10^5$
VOL_2	$(2.30 \pm 0.12)10^5$	$(1.55 \pm 0.05)10^5$	$(1.2 \pm 0.1)10^5$
VOLH	–	$(1.43 \pm 0.12)10^6$	$(3.5 \pm 0.3)10^5$
VOL_2H	–	–	$(4.1 \pm 0.3)10^5$
VOL_2H_{-1}	–	–	$(1.60 \pm 0.03)10^6$

exchange rate constant, and probably this is also the dominating exchange reaction in the VO^{2+}–glycine system.

Acknowledgements

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