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Magnetic Resonance Studies of Ion Solvation. The Hydration of the Vanadyl(IV) Ion[1]

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The hydration of the vanadyl(IV) ion in aqueous solution was investigated by ^{17}O nmr spectroscopy. The solvent resonance line width and shift were studied. It was possible to distinguish between two kinds of water molecules: the equatorially coordinated water molecules with a residence time of $\tau_{M,eq} = 1.35 \times 10^{-3}$ sec, the number of which was determined by the method of molal shifts and found to be four, and other molecules giving rise to a shift of the solvent water peak. This shift may be rationalized as being due to the rapidly exchanging axial water molecule with an ^{17}O hyperfine coupling constant $A/h = 2.06 \times 10^6$ Hz or due to interactions with molecules beyond the first coordination sphere. Discussing the contribution of a rapidly exchanging axial water molecule to the observed solvent line broadening, it appeared that its residence time should be of the order of 10^{-11} sec. $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the exchange reaction of the equatorial water molecules are 13.3 kcal/mole and -1.5 eu, respectively.

Introduction

The vanadyl(IV) ion, being one of the most stable biatomic ions, has drawn considerable chemical and theoretical interest and recently its chemistry has been comprehensively reviewed.[2]

Although it is generally accepted that the VO^{2+} ion exists in aqueous solution as a hydrated species, the actual composition of the aquo ion has not been determined. On the basis of the crystal structure of $VOSO_4 \cdot 5H_2O$ it is anticipated that the first coordination shell of the vanadyl(IV) ion in solution is composed of four equatorially bound water molecules in a plane with the vanadium atom and a fifth axially bound water molecule, positioned *trans* to the oxygen atom of the ion, perpendicular to this plane.[3]

It has been demonstrated, in a number of recent articles, that oxygen-17 magnetic resonance spectroscopy is most suitable for studying metal ion aquo complexes in solution.[1,4-8] Methods have been developed for the determination of hydration numbers[6,7] and for studying the kinetics of ligand exchange.[5] We present here the results of an investigation, in which these methods have been applied in an attempt to elucidate the composition of the first hydration sphere of the vanadyl(IV) ion in solution. This ion offers a definitely asymmetric water coordination sphere and its study seems to be of importance in relation to the first hydration shell of Ni^{2+}, in which four water molecules have recently been characterized and which may also be asymmetric.[1]

Theory of Methods

The basic relations for the determination of coordination numbers and for studying the kinetics of ligand exchange are often used and well known in the literature, but for convenience they are summarized below.

Nuclear magnetic resonance methods for the study of ion solvation take advantage of the fact that nuclei of ligands bound to paramagnetic ions experience large chemical shifts (relative to the uncomplexed ligand molecules) owing to the scalar hyperfine interaction between the unpaired electrons of the central ion and the ligand nuclei. The magnitude of this shift, $\Delta\nu_M$, is given by[9]

$$\Delta\nu_M/\nu = A(\gamma_e/\gamma_N)[S(S+1)/3kT] \tag{1}$$

where ν is the Larmor frequency, γ_e and γ_N are the magnetogyric ratios of the electron and the nucleus, respectively, h is the Planck constant, k is the Boltzmann constant, S is the resultant spin angular momentum (in $\hbar$ units), T is the absolute temperature, A/h is the electron nuclear hyperfine coupling constant (in hertz).

In aqueous solutions of paramagnetic ions two distinct ^{17}O nmr absorptions, for the coordinated and noncoordinated water, will be present provided that the mean residence time, τ_M, of a water molecule in the first hydration shell meets the requirement

$$\tau_M > (2\pi\Delta\nu_M)^{-1} \tag{2}$$

On the other hand, if

$$\tau_M < (2\pi\Delta\nu_M)^{-1} \tag{3}$$

one average signal will be observed, the chemical shift of which (relative to pure water) is given by

$$\delta_{H_2O} = K\frac{m_M}{m_{H_2O}} \tag{4}$$

where m_x is the number of millimoles of species x and $K = n\Delta\nu_M$, n being the coordination number of the ion.[10]

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[1] Previous paper in this series: D. Fiat, presented at XIVth Colloque Ampere, Ljubljana, 1966; to be published in "Magnetic and Electric Resonance and Relaxation," North-Holland Publishing Co., Amsterdam, 1967.

[2] J. Selbin, *Chem. Rev.*, **65**, 153 (1965).

[3] C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

[4] J. A. Jackson, J. F. Lemons, and H. Taube, *J. Chem. Phys.*, **32**, 553 (1960).

[5] T. J. Swift and R. E. Connick, *ibid.*, **37**, 307 (1962).

[6] R. E. Connick and D. Fiat, *ibid.*, **39**, 1349 (1963).

[7] M. Alei and J. A. Jackson, *ibid.*, **41**, 3402 (1964).

[8] R. E. Connick and D. Fiat, *ibid.*, **44**, 4103 (1966).

[9] N. Bloembergen, *ibid.*, **27**, 595 (1957).

[10] It is readily seen that if conditions 2 and 3 could be achieved, *e.g.*, by change of temperature, then by measuring $\Delta\nu_M$ and δ_{H_2O} the coordination number, n, could be obtained. This was one of the methods used to determine the coordination number of the nickel(II) ion.[1]

Determination of Coordination Numbers.—If to a solution of paramagnetic ions (M) characterized by condition 3 and eq 4 is added a quantity ($m_{M'}$) of other ions (M′), in the first coordination sphere of which water molecules spend a mean time $\tau_{M'} > 2\pi(\Delta\nu_{M'} - \delta_{H_2O})$, another line, due to these molecules, will appear in the ^{17}O nmr spectrum. Even if not observable, the presence of this line may be inferred and quantitatively accounted for by measuring the chemical shift in absence (δ_{H_2O}) and in presence (δ'_{H_2O}) of the ion M′. The number of millimoles of water molecules free to exchange with the coordination sphere of the paramagnetic ions (condition 3) being m'_{H_2O}, one has

$$\delta'_{H_2O} = K\frac{m_M}{m'_{H_2O}} \tag{5}$$

Combining eq 4 and 5, the simple relation

$$m'_{H_2O} = \frac{\delta_{H_2O} m_{H_2O}}{\delta'_{H_2O}} \tag{6}$$

is obtained, where the quantities on the right-hand side are known or measurable. The coordination number (n') of the ion M′ is then readily calculated

$$n' = \frac{m_{H_2O} - m'_{H_2O}}{m_{M'}} \tag{7}$$

This "molal shift" method has been introduced by Alei and Jackson[7] and has successfully been applied for the determination of hydration numbers of diamagnetic[6,7,11] as well as of paramagnetic[1] metal ions. It has recently been found that the ^{17}O nmr absorption of water experiences sizable shifts in the presence of diamagnetic 1:1 electrolytes.[12] Therefore, we wish to point out that utilizing this method corrections should be applied to the measured chemical shifts to account for the presence of other ions, both cations and anions, in order to obtain accurate values for the shifts governed by eq 4 and 5.

Kinetics of Ligand Exchange.—The effect of paramagnetic ions on the ^{17}O nmr line width of water has been investigated in detail by Swift and Connick.[5] Considering dilute solutions the relaxation rate $1/T_{2p}$ due to the presence of paramagnetic ions is given by the following equations for the corresponding limiting cases

a. $$(2\pi\Delta\nu_M)^2 >> T_{2M}^{-2},\ \tau_M^{-2};\quad T_{2p}^{-1} = P_M/\tau_M \tag{8}$$

where T_{2M} and P_M are the nuclear relaxation time and the molar fraction of the molecules in the first coordination sphere. The relaxation rate is governed by the rate of chemical exchange of water molecules between the hydration sphere and the solvent in bulk.

b. $$\tau_M^{-2} >> (2\pi\Delta\nu_M)^2 >> (T_{2M}\tau_M)^{-1};\quad T_{2p}^{-1} = P_M\tau_M(2\pi\Delta\nu_M)^2 \tag{9}$$

The determining factor here is the rate of relaxation through the change in the precessional frequency ($\Delta\nu_M$).

c. $$T_{2M}^{-2} >> (2\pi\Delta\nu_M)^2,\ \tau_M^{-2};\quad T_{2p}^{-1} = P_M/\tau_M \tag{10}$$

This result is identical with eq 8, although the limiting condition here is different.

d. $$(T_{2M}\tau_M)^{-1} >> T_{2M}^{-2},\ (2\pi\Delta\nu_M)^2;\quad T_{2p}^{-1} = P_M/T_{2M} \tag{11}$$

In this case the controlling factor is the relaxation rate of a nucleus in the first coordination sphere.

The rate constant, $1/\tau_M$, of the first-order ligand-exchange reaction is temperature dependent and is given by

$$1/\tau_M = (kT/h)\exp[-(\Delta H^{\ddagger}/RT) + (\Delta S^{\ddagger}/R)] \tag{12}$$

Where $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the enthalpy and entropy of activation, respectively. It is seen that T_{2p} in cases a, b, and c will be temperature dependent according to eq 12 but will be (at first approximation) temperature independent in case d.

Cases a and c represent the situation of exchange broadening (with increasing temperature) before the collapse of the nmr absorptions for the coordinated and noncoordinated water molecules. The narrowing (with increasing temperature) of the average line is characterized by eq 9 (case b).

The relaxation rate, T_{2M}^{-1}, of a nucleus in the first coordination sphere of a paramagnetic ion, assuming $(2\pi\nu_e)^2\tau_e^2 >> 1$, is given by[13]

$$\frac{1}{T_{2M}} = \frac{7}{15}S(S+1)\frac{\gamma_N{}^2g^2\beta^2}{r^6}\tau_c + \frac{1}{3}S(S+1)\left(\frac{A}{\hbar}\right)^2\tau_e \tag{13}$$

Where τ_c and τ_e are the correlation times, g is the electron g factor, β is the Bohr magneton, and r is the distance between the nucleus and the electrons. The first term is the contribution of the dipolar interaction, and the second, of the electronic–nuclear hyperfine interaction. The correlation time in the hyperfine term is related to the electron relaxation time, T_{1e} (assuming $T_{1e} = T_{2e}$), and to the residence time of a nucleus in the first sphere by

$$1/\tau_e = 1/T_{1e} + 1/\tau_M \tag{14}$$

It can be shown that, owing to the large hyperfine coupling constants observed for ^{17}O nuclei in the first coordination sphere of transition metal ions, this contribution to T_{2M}^{-1} is the dominant one and that the dipolar term may usually be neglected.[5,8]

Experimental Section

Vanadyl(IV) sulfate pentahydrate of Purum grade obtained from Fluka AG was used throughout this study. It was analyzed by volumetric titration with $KMnO_4$ and was found to contain 4.06×10^{-3} mole of $VOSO_4$/g, the remaining assumed to be crystallization water (18.78×10^{-3} mole/g). Aqueous $VO(ClO_4)_2$ and $VOCl_2$ were prepared by precipitation of the sulfate using the corresponding barium salt.

Oxygen-17-enriched (*ca.* 2 atom %) water, analyzed by mass

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(11) D. Fiat and R. E. Connick, *J. Am. Chem. Soc.*, **88**, 4754 (1966).

(12) Z. Luz and G. Yagil, *J. Phys. Chem.*, **70**, 554 (1966).

(13) I. Solomon, *Phys. Rev.*, **99**, 559 (1955); I. Solomon and N. Bloembergen, *J. Chem. Phys.*, **25**, 261 (1956); N. Bloembergen, *ibid.*, **27**, 572 (1957).

spectrometry, was obtained from the isotope separation plant of this institute.

The nmr measurements were performed using a Varian DP-60 spectrometer operating at 8.13 MHz and equipped with the Model V-4340 variable-temperature probe accessories. Chart calibrations were done by the usual audio-frequency modulation method, the frequency being continuously monitored by an electronic counter.

The line-width temperature dependence of a 0.32 *m* acidified solution of $VOSO_4$ was determined in the interval 25–100°. The derivative of the absorption mode was recorded using a 20-Hz sinusoidal modulation and corrections were applied to account for modulation broadening of the lines (assumed to be of Lorentzian shape).[14]

Chemical shifts were measured (at ambient temperature, *ca.* 300°K) of samples contained in spherical bulbs and were referred to external pure H_2O. By this procedure susceptibility effects are practically eliminated. For the coordination number determination the shifts due to Dy^{3+} in absence and presence of $VO(ClO_4)_2$ were measured in a similar manner.

Solutions of $Dy(ClO_4)_3$ were prepared by dissolving a weighed amount of Dy_2O_3 (Fluka, Puriss) in analyzed concentrated perchloric acid and then diluting with ^{17}O-enriched water.

Results

The temperature dependence of the transverse relaxation time T_{2p} is presented in Figure 1. The values of $1/T_{2p}$ were obtained from the apparent relaxation rates by subtracting the relaxation rate in absence of paramagnetic species.[5]

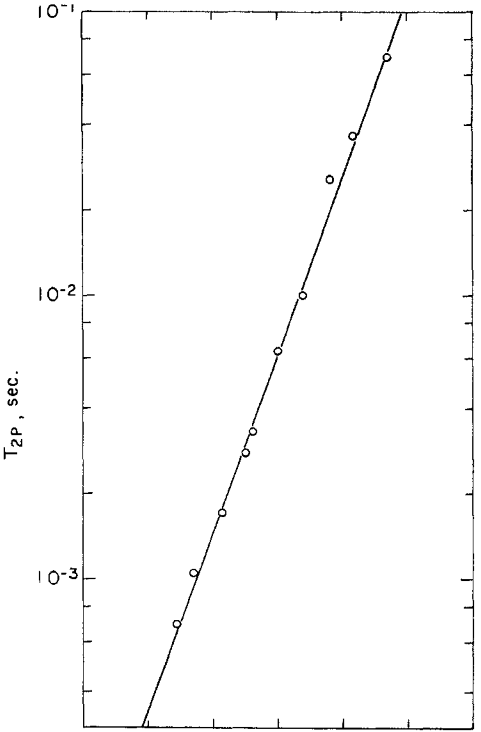

Figure 1.—The temperature dependence of log T_{2p} for a 0.32 *m* $VOSO_4$ acidified solution.

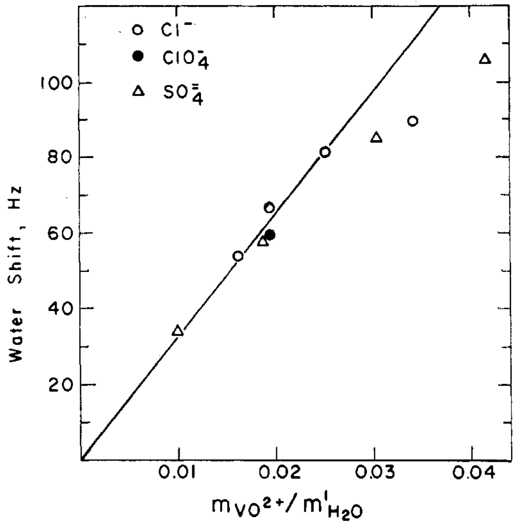

Figure 2.—Water chemical shifts *vs.* the ratio of millimoles of vanadyl(IV) ions to those of noncoordinated water molecules.

The water chemical shifts resulting from the presence of vanadyl(IV) ions are plotted in Figure 2 as a function of the ratio of the number of millimoles of vanadyl(IV) ions ($m_{VO^{2+}}$) to that of noncoordinated water ($m'_{H_2O} = m_{H_2O} - 4m_{VO^{2+}}$). To obtain these shifts from the measured values, corrections were applied to account for the presence of anions and other electrolytes (acids in this case).[12] For this purpose the water chemical shifts due to $(NH_4)_2SO_4$ were measured and found to be −4.5 Hz/*m*.

The pertinent data for the determination of the hydration number of the vanadyl(IV) ion are summarized in Table I.

TABLE I

DATA FOR THE HYDRATION NUMBER OF VANADYL(IV)

$m_{VO^{2+}}$	$m_{Dy^{3+}}$	m_{H^+}	m_{H_2O}	δ, Hz	δ', Hz	n
0.852	0.481	0.320	58.41	1400	1452	3.9
0.903	0.392	0.285	56.54	1170	1226	3.7

An average shift of 3000 ± 3 Hz was obtained for a 1 *m* solution of $Dy(ClO_4)_3$ in good agreement with previously reported values.[7] The chemical shift actually measured for the composite vanadyl(IV)–dysprosium(III) solution is δ. It was corrected to account for the shifts due to the vanadyl(IV) paramagnetic species (Figure 2) and the perchloric acid.[12] The value of δ' thus obtained was then used for the calculations. The number of millimoles of noncoordinated water is given by

$$m'_{H_2O} = 1.665 \times 10^4 \frac{m_{Dy^{3+}}}{\delta'}$$

where the above-mentioned value of the molal shift due to dysprosium(III) is used and $m_{Dy^{3+}}$ is the number of millimoles of dysprosium(III). The hydration numbers listed in the last column of Table I were calculated using eq 7.

Discussion

An analysis of the line-width temperature dependence results (see Figure 1) according to the above-mentioned limiting cases reveals that in the temperature interval studied the relaxation rate, T_{2p}^{-1}, due to the presence of the paramagnetic vanadyl(IV) ions is governed

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[14] H. Wahlquist, *J. Chem. Phys.*, **35**, 1708 (1961).

by the rate of chemical exchange of water molecules between the solvation shell and the solvent in bulk. In order to meet the limiting conditions of case a the hyperfine coupling constant should be $A/h < 3.4 \times 10^5$ Hz, whereas for case c it should be $A/h > 3.4 \times 10^5$ Hz. For these estimates the value of 3×10^{-9} sec was taken for the electron relaxation time.[15] In view of the known ^{17}O hyperfine coupling constants, which are of the order of 10^7 Hz,[5,8] it is likely that case c describes the actual situation in vanadyl(IV) solutions. However, the derivation of the parameters for water exchange is independent of this differentiation and it is possible to show that, if either of the two conditions $\tau_M^{-1} < T_{2M}^{-1}$ or $\tau_M^{-1} < 2\pi\Delta\nu_M$ is fulfilled, T_{2p}^{-1} will have the form of eq 8 (10).

It is seen that at room temperature the chemical exchange is slow enough that two distinct nmr absorptions should be present: one unshifted (relative to pure water) signal corresponding to the bulk water and a second due to the water molecules in the vanadyl(IV) aquo complex. It is practically impossible to observe the latter owing to the long (of the order of 10^{-9} sec) relaxation time of the vanadium unpaired electron,[15] which through the scalar coupling mechanism is the correlation time for nuclear relaxation. However, its presence may be inferred and quantitatively accounted for by measuring the chemical shifts caused by another suitably chosen[4,7] paramagnetic ion, *e.g.*, dysprosium(III), in the presence and absence of VO^{2+} ions.[16] Measurements on solutions containing the vanadyl(IV) ions yield the value 3.8 ± 0.2 for the hydration number, the uncertainty arising primarily from the relatively large error in chemical shift measurements of the broad lines. The coordination number, 4, thus obtained and the kinetic parameters (see Table II) derived from the temperature dependence of the line width are assigned to the four equatorially bound water molecules.

TABLE II

PARAMETERS FOR WATER EXCHANGE FROM THE FIRST COORDINATION SPHERE OF VO^{2+}

$\tau_{M,eq}$ (at 300°K)	1.35×10^{-3} sec
$\Delta H^{\ddagger}_{eq}$	13.3 ± 0.3 kcal/mole
$\Delta S^{\ddagger}_{eq}$	-1.5 ± 1 eu

It was mentioned above that the nmr signal of the bulk solvent should be unshifted. Nevertheless a small but measurable and significant chemical shift relative to pure water was observed (Figure 2). A plausible origin of such a shift seems to be *via* the scalar hyperfine coupling of an oxygen-17 nucleus of a rapidly exchanging water molecule, apparently the axial one, and the unpaired electron of the vanadyl(IV) ion. It is seen from Figure 2 that the linear relationship predicted by eq 4 is obeyed at least for low concentrations. From the slope one has $\Delta\nu_M = 3.25 \times 10^3$ Hz. Using eq 1 the hyperfine coupling constant A/h is readily calculated and found to be 2.06×10^6 Hz.

A question now arises: What will be the contribution of the exchange reaction of this molecule to the observed ^{17}O line width? This contribution should be of either of the types described by cases b and d. Using the upper limit, $\tau_{M,ax} \leqslant 4.9 \times 10^{-5}$ sec, obtained from condition 3 and T_{2M}^{-1} calculated with $A/h = 2.06 \times 10^6$ Hz, it can be shown that the limiting conditions of case d are fulfilled. In this case T_{2p}^{-1} is proportional to T_{2M}^{-1} and is independent of temperature, at first approximation. For the vanadyl(IV) solution under study this contribution to T_{2p}^{-1} should have been 7.2×10^2 sec^{-1}. However, the experimental values of T_{2p}^{-1} are in the range 10–10^3 sec^{-1} and they clearly obey an exponential law of the form of eq 12. It was assumed, in the above calculations, that the electron relaxation time is the correlation time characteristic of the hyperfine interaction. Having an electron relaxation time as long as 3×10^{-9} sec, the correlation time of this interaction may be the residence time of a water molecule in the first coordination sphere, provided that $\tau_{M,ax} << 3 \times 10^{-9}$ sec. In this case the observed shift may be due to the axial water molecule, but in order to neglect the contribution to the observed line width of the exchange reaction of this molecule, its residence time (at 300°K) has to be as short as 10^{-11} sec.

The value of the ^{17}O hyperfine coupling constant, which is smaller by about an order of magnitude than values known[5,8] for the hydrates of other transition metal ions, and the very short residence time suggest that the axial water molecule in $VO(H_2O)_5^{2+}$ is weakly bound, the overlap between the corresponding vanadium and water oxygen bonding orbitals being small. A similar conclusion has been reached in a recent infrared spectral study.[17]

Another origin for the observed ^{17}O chemical shift of aqueous solutions containing vanadyl(IV) ions may be *via* interactions involving water molecules beyond the first coordination sphere. Interactions of a similar type have been invoked to account for the shifts observed in solutions of Cr^{3+}, the first coordination shell of which is composed of six water molecules of a residence time of several hours.[18] Drawing the similarity further on, the deviation of the shift from linearity, when ploted *vs.* the concentration (see Figure 2), implies that at high concentrations part of the water molecules of the "second sphere" may be removed and replaced, perhaps by anions. However, the exact nature of this interaction is, at present, unclear.

Conclusions

The evidence presented here lends support to the intuitively adopted structure of the pentaaquovanadyl(IV) ion in solution.[3] The existence of four molecules in the first coordination sphere is demonstrated and the kinetic parameters for the corresponding

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(15) G. P. Vishnevskaya and P. G. Tishkov, *Dokl. Akad. Nauk SSSR*, **142**, 841 (1962).

(16) Anticipating data of a forthcoming communication on the hydration and complexation of the dysprosium(III) ion, it is convenient to point out at this stage that using this method the presence of anions other than perchlorate should be avoided.

(17) I. P. Lipatova, *Dokl. Akad. Nauk SSSR*, **164**, 849 (1965).

(18) M. Alei, *Inorg. Chem.*, **3**, 44, (1964).

ligand-exchange reaction are derived. The fifth axial water molecule seems to be weakly bound and has to have a residence time of the order of 10^{-11} sec.

While this work was almost completed a proton and deuterium relaxation study of vanadyl(IV) sulfate solutions appeared, in which rate constants for hydrogen exchange of the order of 1.0×10^4 sec^{-1} were reported.[19] Neglecting contributions of the exchange reactions of the axial water molecule, the authors conclude that the hydrogen lifetime in the first coordination shell of the VO^{2+} ions is determined by chemical proton exchange processes (protolysis) of the equatorial water molecules and that the residence time of a whole water molecule should be greater. These conclusions are confirmed by the present results.[20]

Acknowledgment.—We wish to thank Professor S. Alexander for his kind interest and helpful discussions.

(19) R. K. Mazitov and A. I. Rivkind, *Dokl. Akad. Nauk SSSR*, **166**, 654 (1966). This article may serve as a key to previous literature on proton relaxation in vanadyl(IV) solutions.

(20) NOTE ADDED IN PROOF.—We wish to acknowledge a recent exchange of preprints with K. Wüthrich and R. E. Connick [*Inorg. Chem.*, **6**, 583 (1967)]. They have measured ^{17}O relaxation in solutions of vanadyl(IV) perchlorate and obtained results which are in good agreement with those reported here.

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Nuclear Magnetic Resonance Relaxation of Oxygen-17 in Aqueous Solutions of Vanadyl Perchlorate and the Rate of Elimination of Water Molecules from the First Coordination Sphere

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An investigation was made of the temperature dependence of the transverse nuclear relaxation time T_2 for O^{17} in aqueous vanadyl perchlorate solutions in the range 5–170°. In the major part of this temperature region the relaxation due to the influence of the VO^{2+} ions was found to be controlled by the rate of exchange of water molecules between the first coordination sphere of the metal ions and the bulk of the solution. Values for the rate constant and the activation energy of the water exchange and for the constant which describes the scalar coupling between VO^{2+} and the O^{17} nuclei of the coordinated water molecules have been established. The rate of the water exchange was found to be slow compared to the rates found in corresponding experiments with other doubly charged metal ions. This indicates that the high positive charge of V^{4+} is an important factor not only in the formation of the vanadyl group but also in the bonding of the water molecules in the first coordination sphere. Additional relaxation effects are observed at low temperatures. It is shown that these effects are most likely explained by interactions of the vanadyl ion with O^{17} in water molecules loosely coordinated outside the first coordination sphere.

In aqueous solutions of paramagnetic metal ions a certain number of water molecules are coordinated to each metal ion. Because of the magnetic interactions between the paramagnetic ions and the magnetic moments of the O^{17} nuclei of these coordinated water molecules, the transverse nmr relaxation time of these oxygens is greatly decreased. For dilute solutions of the metal ion only a single resonance can be observed which corresponds to that of the bulk water modified by the exchange of water molecules in and out of the coordination spheres of the metal ions.

The property observed is the line width of the resonance. Half the width at half-height, $\delta\omega$, expressed in radians per second, is related to the apparent transverse relaxation time T_2 by

$$\delta\omega = 1/T_2 \tag{1}$$

The line width arises from the relaxation of the bulk O^{17} nuclei that would occur in the absence of paramagnetic ions, *i.e.*, $1/T_{2H_2O}$, and the contribution from the paramagnetic ions, $1/T_{2p}$, as given by

$$\frac{1}{T_2} = \frac{1}{T_{2H_2O}} + \frac{1}{T_{2p}} \tag{2}$$

Analysis of $1/T_{2p}$ in terms of the properties of the dissolved paramagnetic ions has been used in earlier studies to evaluate the water exchange rate and various parameters which characterize the relaxation in aqueous solutions of a series of 3d metal ions.[1] In the present paper the application of the nmr technique to the study of aqueous vanadyl perchlorate solutions is described.

I. Theory

The shape of the nmr spectrum of a chemically stable system is described by the Bloch equations.[2] A modification of the Bloch equations by McConnell[3] which includes the possibility of chemical exchange has been extended by Swift and Connick[1] to the conditions present in dilute aqueous solutions containing paramagnetic metal ions. They found that the effect

(1) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).
(2) F. Bloch, *Phys. Rev.*, **70**, 460 (1946).
(3) H. M. McConnell, *J. Chem. Phys.*, **28**, 430 (1958).