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O¹⁷ Nuclear Magnetic Relaxation in Aqueous
Solutions of Diamagnetic Metal Ions

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ABSTRACT

Measurements are reported on the transverse relaxation of oxygen-17 of water in solutions of diamagnetic electrolytes. For the 2+ ions it is shown that the effective correlation time for the quadrupole relaxation of waters in the first coordination sphere is appreciably shorter than the tumbling time for the hydrated ion. The data can be explained if the waters rotate randomly around the metal-oxygen axis in a time short compared to the tumbling time of the hydrated ion. This intramolecular rotation lowers considerably the effective quadrupole coupling. The model implies that corresponding effects should be present in proton and deuterium relaxation in water and evidence is cited which is consistent with this prediction.

INTRODUCTION

The nuclear magnetic relaxation of oxygen-17 of water is brought about by quadrupole coupling interrupted through the tumbling of the water molecules.¹ When diamagnetic ions are added to the water, the tumbling time of waters in the immediate vicinity of the ions would be expected to be lengthened considerably, thereby increasing the rate of relaxation. The experimental effect is considerably smaller than might be anticipated. This note deals with possible explanations of this observation.

In solutions of diamagnetic salts the O^{17} nuclei may be considered to reside in two different environments, i.e., the bulk water, and the coordination spheres of the cations and anions. If there is fast exchange of H_2O between these environments, a single nuclear magnetic resonance of O^{17} is observed, which corresponds to the average of the resonances in the different environments. Half the line width at half height of this resonance, $\delta\omega$, expressed in radians per second, is equal to the reciprocal of the apparent transverse relaxation time, T_2 .

For purposes of presentation of the data we will write:

$$\delta\omega = \frac{1}{T_2} = \frac{1}{T_{2H_2O}} + \frac{1}{T_{2d}} \quad (1)$$

where T_{2H_2O} is defined as the transverse relaxation time of pure water, and $1/T_{2d}$ represents how much the presence of the diamagnetic ions changes the line width compared to pure water.

The O^{17} nuclear relaxation in pure water is given by Eq. (2).^{1,2}

$$\frac{1}{T_2} = \frac{3}{40} \frac{2I+3}{I^2(2I-1)} \left(1 + \frac{\xi^2}{3}\right) \left(\frac{eQq}{h}\right)^2 \tau_c \quad (2)$$

I is the nuclear spin quantum number, ξ the asymmetry parameter, Q the nuclear quadrupole moment, q the electric field gradient, and τ_c the correlation time. It is the correlation time τ_c which is expected to increase significantly for waters bound to ions in the solution, thus broadening the resonance.

EXPERIMENTAL

The O^{17} nmr experiments were done at 8.134 Mc with equipment described previously.³ Water enriched to 11% in O^{17} was obtained from Oakridge National Laboratories. Acidified solutions of the metal ions were obtained by dissolving reagent grade perchlorate salts or oxides in solutions of $HClO_4$ in O^{17} enriched water. The line width of the O^{17} resonance was measured at two or three different metal ion concentrations in the range 0.5 to 2.0 m. No measurable effect on the O^{17} resonance was observed on changing the $HClO_4$ concentration between 0.1 and 2.0 m.

RESULTS AND DISCUSSION

The experimental data are summarized in Table I. For all the metal ions listed the exchange of water between the first coordination sphere and the bulk water is fast (column 4 of Table I). It appears that only

small relaxation effects arise from the presence of Li^+ , Na^+ , Ca^{2+} , and ClO_4^- ions in the solution. In the concentration range studied the resulting line-broadening corresponds to ca. 10% or less of $1/T_{2\text{H}_2\text{O}}$. Appreciable line-broadening was observed in solutions of Mg^{2+} and Cd^{2+} perchlorates. For all the metal ions studied T_{2d} seems to be essentially independent of temperature. The data for Li^+ , Na^+ , and Mg^{2+} at 25° agree quite well with those reported by Fister and Hertz⁴ for various Li^+ and Na^+ salts, and for MgCl_2 .

In order to analyze the data in more detail it is necessary to adopt a simplified model. It will be assumed that the correlation time of Eq. (2) is proportional to the viscosity, for all environments. This approximation, while rough, should not invalidate the conclusions to be drawn later. With this assumption Eq. (1) becomes

$$\frac{\eta^\circ \delta\omega}{\eta} = \frac{1}{T_{2\text{H}_2\text{O}}} + \frac{1}{T_{2d}^\circ} \quad (3)$$

where $1/T_{2d}^\circ$ is the hypothetical contribution the diamagnetic ions would make to the line width if the viscosity of the solution, η , were equal to that of pure water, η° . With this assumption it is seen from the values of $1/(mT_{2d}^\circ)$ in Table I that for all the ions studied the effects are small relative to the bulk water line width, which is 156 rad sec^{-1} at 25°.

For the 1:1 electrolytes the smallness of the line broadening could be attributable to a short exchange lifetime of the coordinated waters.⁵ For the 2:1 electrolytes the water-metal ion interactions should be much

Table I.

Line Broadening of O^{17} Resonance
of Water by Electrolytes at 25°

	$\frac{1}{mT_2^d}$, rad sec ⁻¹ m ⁻¹ (a)	k (25°) (b) sec ⁻¹	$\frac{1}{mT_2^d}$
LiClO ₄	10	$> 10^8$	2
NaClO ₄	8	$> 10^8$	5
Ca(ClO ₄) ₂	8	$> 10^8$	-17
Mg(ClO ₄) ₂	52	1×10^5	4
Cd(ClO ₄) ₂	44	2×10^8	~5

(a) In the concentration range 0.5 to 2.0 m. The symbol m designates moles per 1000 grams of water. For comparison the value of $\frac{1}{T_2^{H_2O}}$ at 25° is 156 rad sec⁻¹.

(b) From Reference 6; k is the first order rate constant for the elimination of a water molecule from the first coordination sphere of the cation.

stronger and it is shown for Mg^{2+} and Cd^{2+} (Table I)⁶ that the exchange lifetimes are long compared to the rotational correlation times. It will be shown below that large effects would be expected for the +2 ions if the correlation time were determined by the rotation of the hydrated ion.

The contributions from the perchlorate ions, as judged by the 1:1 electrolyte results, appear to be small, and in the model given below it will be assumed that the relaxation behavior of waters coordinated to perchlorate ions is the same as that of the bulk water.

The quadrupole coupling constant and asymmetry parameter for O^{17} in gaseous HDO have been determined by Stevenson and Townes.⁷ Transforming their values to the principal axis system⁸ in H_2O^{17} one obtains for the x, y and z components of the tensor -9.83, 2.91 and 6.91 Mc/sec, respectively, where the water molecule is placed in the X-Y plane with the Y axis bisecting the HOH angle. There is evidence⁷ that the quadrupole coupling of O^{17} decreases somewhat in going to the liquid state; we will use the tensor for the gaseous molecule because the tensor components are not known for the liquid and a water attached to a metal ion does not necessarily behave more like a liquid water molecule than a gaseous one.

When the O^{17} comes close to a charged ion there is a contribution to the second derivative of the electric potential at the oxygen nucleus from the field of the charged ion. For the waters in the first coordination sphere of Mg^{2+} this is estimated to give quadrupole coupling components of -0.4 and 0.2 Mc/sec along the Mg-O bond and at right angles to it, respectively. If there is an appreciable Sternheimer antishielding

correction⁹ these values could be of opposite sign and conceivably larger, but there is no simple way to estimate the correction. The other ions of Table I should give smaller corrections than magnesium ion. In what follows it will be found that the observed relaxations are much smaller than expected. It seems unlikely that the above electrostatic contribution could fortuitously produce a large reduction in relaxation for all of the ions to be discussed and therefore this possible explanation will be ignored.

The effect of Mg^{2+} , Cd^{2+} and Ca^{2+} ions on the overall line width can be estimated from Eq. (2) if one knows the quadrupole coupling of 0^{17} in the first coordination sphere and the correlation time τ_c . As mentioned above, the former will be assumed to be the same as for gaseous H_2O , and τ_c is calculated assuming that the first coordination sphere waters are restricted in their motions to the tumbling of the entire hydrated metal ion. What is probably a lower limit for the rotational correlation time of the latter can be estimated from the Stokes-Einstein equation¹⁰

$$\tau_r = \frac{4\pi a^3 \eta}{3kT} \quad (4)$$

where η is the viscosity and r is the radius of the hydrated sphere which will be taken to be the sum of the ionic radius of the metal ion, the ionic radius of oxygen, and the Van der Waals radius of the oxygen. The calculated values of τ_r at 25° are 3.8 , 4.9 and 5.0×10^{-11} sec. for Mg^{2+} , Cd^{2+} and Ca^{2+} respectively. The value for Mg^{2+} agrees well with the value determined for Mn^{2+} , which has a similar size, by a dispersion measurement.¹¹ The contribution to $1/(T_{2d}^\circ)_m$ from this source will be

$$\frac{f_M}{m} \left(\frac{1}{T_{2M}^0} - \frac{1}{T_{2H_2O}} \right) \quad (5)$$

where $1/T_{2M}^0$ is the line width of O^{17} in the first coordination sphere of the cations calculated by Eq. (2) and f_M is the mole fraction of waters in the first coordination sphere of the cations. Assuming the coordination numbers to be 6, 8 and 8, the calculated values of (5) at 25° are 4, 7 and 7×10^2 rad sec⁻¹ m⁻¹ for Mg^{2+} , Cd^{2+} and Ca^{2+} respectively. These numbers are much larger than the observed values of $1/(T_{2d}^0 m)$ in Table I. The uncertainties in these calculations can hardly account for the discrepancies.

Fister and Hertz⁴ have interpreted similar data in terms of the structure forming and structure breaking effects of the different ions on the solvent water molecules. Indeed, if there were a large structure breaking effect outside of the first coordination sphere of the divalent ions which almost exactly balanced the large relaxation contribution of the first coordination sphere waters, the data could be accounted for. Such a fortuitous cancellation is unlikely. Rather the model assumed for the quadrupole relaxation of the first coordination sphere waters of the cations is suspect.

In the above model the water was taken to be rigidly bound to the metal ion. It is plausible, however, that the water molecules rotate about the metal-oxygen bond more rapidly than the whole complex tumbles. Because of the particular values of the quadrupole tensor of O^{17} in the water molecule the effect of intramolecular rotation about the metal-oxygen

axis can be quite large. If the model is chosen which has the metal oxygen bond lying in the plane of the water molecule and bisecting the HOH angle, rotation about the M-O bond that is much more rapid than tumbling of the hydrated ion averages the x and z components of the tensor to yield -1.45, 2.90 and -1.45 Mc/sec for the x, y and z components respectively. As a consequence the value of $1/T_{2M}$ of Eqs. (2) and (5) is reduced by a factor of 12 for a given τ_r . If the plane of the water molecule is tilted relative to the M-O axis, this factor becomes smaller. If the rapid rotation is accompanied by a variable tilting of the M-O axis out of the plane of the water molecule, the factor will be greater. Thus rapid internal rotation of the waters of the hydrated complex can severely reduce the O^{17} quadrupole relaxation. It seems likely that this phenomenon is responsible for the relatively small experimental values of $1/T_{2d}^o$.

Other evidence for this effect can be adduced. In the interpretation of O^{17} relaxation in solutions of vanadyl ion it was necessary to invoke this type of motion for second coordination sphere waters.¹² The direct observation¹³ of the line width of O^{17} of the six waters in the first coordination sphere of Al^{3+} permits calculation of a value of the correlation time of 3.2×10^{-11} sec, if the quadrupole coupling of the O^{17} is taken to be the same as in gaseous water. Using the measured viscosity of 4.1×10^{-2} poise at 25° and a radius of $3.31 \text{ \AA}$ one predicts from Eq. (4) a value of τ_r of 1.5×10^{-10} sec. This is probably an underestimate of τ_r because of the use of the first coordination sphere radius whereas the translational mobility of Al^{3+} indicates a larger effective size. The discrepancy between the experimental τ_c and the calculated τ_r

is presumed to be due to rotation of the waters about the Al-O axis.

It is interesting that the effect is observed for such a highly charged ion as Al^{3+} where the strong binding of the waters is evidenced by their slow exchange.¹³

To make a precise analysis of the phenomenon one would need the orientation of the water molecules, a more precise knowledge of the O^{17} quadrupole coupling tensor of the attached waters, and the rotational correlation time for the hydrated ion. These quantities are not presently available. Were they available it would be possible to determine the correlation time for rotation of the water about the M-O axis. Shimizu¹⁴ has developed the necessary equation for the case of quadrupole coupling with zero anisotropy, but the large anisotropy of O^{17} in water limits the applicability of his formula.

If rotation of the water molecules about the M-O axis of hydrated metal ions is of importance in O^{17} quadrupole relaxation, the effect of this motion should also be observed in the relaxation of protons and deuterium of H_2O , HOD and D_2O . Proton nuclear relaxation comes primarily from intramolecular dipole-dipole coupling. It can be shown that rapid rotation of the water about the M-O axis will reduce the dipole-dipole relaxation to $1/4$ of the isotropic tumbling value, regardless of the angle made by the M-O axis with the bisector of the HOH angle, assuming of course that the protons stay equidistant from the metal ion. If one treats the data on protons in MgCl_2 solution in Table I of Fister and Hertz⁴ according to Eq. (3), a limiting value of $1/(T_{1d} \cdot m)$ of $0.236/T_{1\text{H}_2\text{O}}$ is obtained. If all of this value is attributed to enhanced relaxation in the first coordination sphere of Mg^{2+} , Eq. (5) gives $1/T_{2M}^\circ$

as $3.2/T_{1_{H_2O}}$. This value is again very small so that it seems necessary once again to invoke rotation of the complexed water about the Mg-O axis. A closer analysis is not attempted because of the complication of inter-molecular proton interactions of the water molecules in each environment.

From the data of Hertz and Zeidler⁵ for the longitudinal relaxation of deuterium in D_2O solutions of $CaCl_2$, one finds $1/T_{1_M} = 1.1/T_{1_{D_2O}}$. Again the small effect of the metal ion implies that there is a much faster correlation time than the tumbling time of the hydrated ion. Calculation shows that the partial averaging of the quadrupole tensor¹⁶ by rapid rotation about the symmetry axis of the water molecule should greatly reduce the quadrupole relaxation of deuterium.

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