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Measurements are reported on the transverse relaxation of oxygen-17 of water in solutions of diamagnetic electrolytes. For the \( \text{Fe}^{2+} \) 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 \(^{17}\)O 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 \(\text{H}_2\text{O}\) between these environments, a single nuclear magnetic resonance of \(^{17}\)O 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:

\[
\delta \omega = \frac{1}{T_2} = \frac{1}{T_{2\text{H}_2\text{O}}} + \frac{1}{T_{2\text{d}}}
\]  

(1)

where \(T_{2\text{H}_2\text{O}}\) is defined as the transverse relaxation time of pure water, and \(1/T_{2\text{d}}\) represents how much the presence of the diamagnetic ions changes the line width compared to pure water.
The $^{17}$O nuclear relaxation in pure water is given by Eq. (2).\textsuperscript{1,2}

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

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

**EXPERIMENTAL**

The $^{17}$O nmr experiments were done at 8.134 MHz with equipment described previously.\textsuperscript{3} Water enriched to 11\% in $^{17}$O 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 $^{17}$O enriched water. The line width of the $^{17}$O 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 $^{17}$O 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 $1/T_2^{H_2O}$. Appreciable line-broadening was observed in solutions of Mg$^{2+}$ and Cd$^{2+}$ perchlorates. For all the metal ions studied $T_2^d$ 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 Hertz 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

$$\frac{\eta^o}{\eta} \frac{\delta \omega}{\omega} = \frac{1}{T_2^{H_2O}} + \frac{1}{T_2^d}$$

where $1/T_2^d$ is the hypothetical contribution the diamagnetic ions would make to the line width if the viscosity of the solution, $\eta$, were equal to that of pure water, $\eta^o$. With this assumption it is seen from the values of $1/(mT_2^d)$ 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. For the 2:1 electrolytes the water-metal ion interactions should be much
Table I.

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

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$\frac{1}{mT_2^d}$, rad sec $^{-1}$ m$^{-1}$</th>
<th>$k$ (25°) (b) sec$^{-1}$</th>
<th>$\frac{1}{mT_2^d}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiClO$_4$</td>
<td>10</td>
<td>$&gt;10^8$</td>
<td>2</td>
</tr>
<tr>
<td>NaClO$_4$</td>
<td>8</td>
<td>$&gt;10^8$</td>
<td>5</td>
</tr>
<tr>
<td>Ca(ClO$_4$)$_2$</td>
<td>8</td>
<td>$&gt;10^8$</td>
<td>-17</td>
</tr>
<tr>
<td>Mg(ClO$_4$)$_2$</td>
<td>52</td>
<td>$1x10^5$</td>
<td>4</td>
</tr>
<tr>
<td>Cd(ClO$_4$)$_2$</td>
<td>44</td>
<td>$2x10^8$</td>
<td>~5</td>
</tr>
</tbody>
</table>

(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) 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 $^{17}$O in gaseous HDO have been determined by Stevenson and Townes. Transforming their values to the principal axis system in $H_2O^{17}$ one obtains for the x, y and z components of the tensor -9.83, 2.91 and 6.91 Me/sec, respectively, where the water molecule is placed in the X-Y plane with the Y axis bisecting the HOH angle. There is evidence that the quadrupole coupling of $^{17}$O 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 $^{17}$O 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 Me/sec along the Mg-O bond and at right angles to it, respectively. If there is an appreciable Sternheimer antisielding
correction\textsuperscript{9} 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\textsuperscript{2+}, Cd\textsuperscript{2+} and Ca\textsuperscript{2+} ions on the overall line width can be estimated from Eq. (2) if one knows the quadrupole coupling of \( Q \) in the first coordination sphere and the correlation time \( \tau_c \). As mentioned above, the former will be assumed to be the same as for gaseous \( \text{H}_2\text{O} \), and \( \tau_c \) 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 equation\textsuperscript{10}

\[
\tau = \frac{4\Pi a^3 \eta}{3kT}
\]

where \( \eta \) 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 \( \tau_r \) at 25\textdegree are \( 3.8, 4.9 \) and \( 5.0 \times 10^{-11} \) sec. for Mg\textsuperscript{2+}, Cd\textsuperscript{2+} and Ca\textsuperscript{2+} respectively. The value for Mg\textsuperscript{2+} agrees well with the value determined for Mn\textsuperscript{2+}, which has a similar size, by a dispersion measurement.\textsuperscript{11} The contribution to \( 1/(\tau_{c,m}) \) from this source will be
where \( \frac{1}{T^2_M} \) is the line width of \( ^{17}O \) 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 \( 7 \times 10^2 \) rad sec\(^{-1}\) m\(^{-1}\) for Mg\(^{2+}\), Cd\(^{2+}\) and Ca\(^{2+}\) respectively. These numbers are much larger than the observed values of \( 1/(T^2_d m) \) in Table I. The uncertainties in these calculations can hardly account for the discrepancies.

Fister and Hertz 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 \( ^{17}O \) in the water molecule the effect of intramolecular rotation about the metal-oxygen bond...
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 $\tau_r$. 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 $^{17}$O quadrupole relaxation. It seems likely that this phenomenon is responsible for the relatively small experimental values of $1/T_{2d}$.

Other evidence for this effect can be adduced. In the interpretation of $^{17}$O relaxation in solutions of vanadyl ion it was necessary to invoke this type of motion for second coordination sphere waters\(^{12}\). The direct observation\(^{13}\) of the line width of $^{17}$O of the six waters in the first coordination sphere of Al\(^{3+}\) permits calculation of a value of the correlation time of $3.2 \times 10^{-11}$ sec, if the quadrupole coupling of the $^{17}$O is taken to be the same as in gaseous water. Using the measured viscosity of $4.1 \times 10^{-2}$ poise at $25^\circ$ and a radius of $3.31$ Å one predicts from Eq. (4) a value of $\tau_r$ of $1.5 \times 10^{-10}$ sec. This is probably an underestimate of $\tau_r$ 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 $\tau_c$ and the calculated $\tau_r$
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 $^{17}O$
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. Shimizu$^{14}$ has developed the necessary equation for the case
of quadrupole coupling with zero anisotropy, but the large anisotropy
of $^{17}O$ 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 $^{17}O$ 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
Hertz$^4$ according to Eq. (3), a limiting value of $1/(T_{\text{d}}^1)m$ of $0.236/T_{\text{d}}^1$$_{H_2O}$
is obtained. If all of this value is attributed to enhanced
relaxation in the first coordination sphere of Mg$^{2+}$, Eq. (5) gives $1/T_{\text{d}}^1$$_{H_2O}$
as \( 3.2/T_{1}^{1} \) \( _{\text{H}_{2}O} \). 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 Zeidler\(^5\) for the longitudinal relaxation of deuterium in \( D_{2}O \) solutions of \( \text{CaCl}_2 \), one finds \( 1/T_{1} = 1.1/T_{1}^{1} \) \( _{\text{D}_{2}O} \). 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 tensor\(^{16}\) by rapid rotation about the symmetry axis of the water molecule should greatly reduce the quadrupole relaxation of deuterium.

Acknowledgment. This work was supported under the auspices of the United States Atomic Energy Commission.
REFERENCES

9. R. M. Sternheimer, Phys. Rev., 84, 244 (1951); 86, 316 (1952); 95, 736 (1954).
10. Reference 2, pp. 300, 313.
15. Fister and Hertz discussed qualitatively the effect of this intramolecular rotation but apparently thought it unimportant. As a consequence, their lifetimes of waters in the first coordination sphere of Li⁺ and Na⁺ are questionable. It is to be noted that their lifetimes are defined to be three times greater than is customary.
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