

## PROTON SPIN-LATTICE RELAXATION IN PURE WATER BETWEEN 0°C AND 100°C\*)

by K. KRYNICKI

The Physics Laboratories, University of Kent at Canterbury, England.

### Synopsis

Proton spin-lattice relaxation times,  $T_1$ , at 28 MHz by a recovery from saturation, are reported for very pure water between 0 and 100°C. Our experimental  $T_1$  values for water are the longest values which have been observed. In this temperature region the most effective spin-lattice relaxation mechanism in water is by proton dipole-dipole intra- and intermolecular interactions modulated by thermal molecular motion. Measurements for water of dielectric relaxation, X ray diffraction, self diffusion, viscosity and slow neutron inelastic scattering are used in the interpretation of the proton  $T_1$  results. The intermolecular contribution to  $T_1^{-1}$  has been determined with the aid of X ray radial distribution curves and Hubbard's correction for the off-centre proton effect. There is excellent agreement between the temperature dependence of the experimental proton spin-lattice relaxation times and the reciprocals of the dielectric relaxation times. The ratio of the dielectric relaxation time to the molecular reorientation NMR correlation time is found independent of temperature and equal to 3.7 instead of the expected value, three. This result provides an evidence for a small value of the single jump angle in the Brownian reorientation of water molecules and may be accounted for by an internal field correction factor of 0.81. This compares with the value 0.69 obtained for water from the Powles formula.

§ 1. *Introduction.* Proton spin relaxation in water has been studied very extensively since the first theory and measuring methods were developed by Bloembergen, Purcell and Pound<sup>1)</sup> (hereafter referred to as BPP). For a long time, however, the relative importance of the paramagnetic effect of dissolved atmospheric oxygen on the relaxation times in liquids had not been fully appreciated. The effect was demonstrated by Chiarotti *e.a.*<sup>2)</sup> who measured the proton spin-lattice relaxation times,  $T_1$ , for several air-free liquids at 20°C and the value of 3.6 s was given for water. This value, however, clearly refers to room temperature (approx.

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\*) The experimental work was carried out in the Institute of Nuclear Physics, Cracow 23, Poland, and was a part of the author's Ph. D. thesis (Jagellonian University, 1961). The interpretation, although based on certain ideas from the thesis, is modified and revised here and is presented in the light of a recent progress in studying transport properties of water by N. M. R. and other methods.

27°C) as may be concluded from the  $T_1$  temperature dependence, reported later by Giulotto *e.a.*<sup>3)</sup> for water between  $-11^\circ\text{C}$  and  $90^\circ\text{C}$  and the interpolated value at  $20^\circ\text{C}$  was 3.05 s. The quantity  $T_1\eta/T$ , where  $\eta$  is the viscosity and  $T$ , the absolute temperature, was found to decrease with increasing temperature. Giulotto *e.a.* ascribed this to a gradually collapsing quasicrystalline structure of water.

The proton  $T_1$  and the self diffusion coefficient,  $D$ , for air-free water between 0 and  $100^\circ\text{C}$  were measured by Simpson and Carr<sup>4)</sup>. The reported  $T_1$  value at  $20^\circ\text{C}$  was 2.95 s with the maximum random error of 2%. They observed a decrease of  $T_1\eta/T$  with increasing temperature particularly above  $40^\circ\text{C}$ , whereas  $D\eta/T$  was constant within the experimental error.

The temperature dependence of the  $T_1\eta/T$  was also studied by Hennel *e.a.*<sup>5)</sup> using a highly purified air-free water sample. The interpolated  $T_1$  values between 0 and  $75^\circ\text{C}$  were later given by Hennel<sup>6)</sup> in his attempt to decide, with the aid of the BPP theory, between different forms of the internal field correction in dielectric relaxation.

The Hennel *e.a.* results, somewhat extended, were used by the author<sup>7)</sup> in a quantitative interpretation of the  $T_1$  temperature dependence. That interpretation was based on an extensive use of the available results of measurements for water, such as dielectric relaxation, X ray diffraction, self diffusion, slow neutron inelastic scattering and viscosity. The Powles internal field correction<sup>8)</sup> was used to deduce molecular reorientation correlation time,  $\tau_d$ , from the measured dielectric relaxation times. The intermolecular contributions to  $T_1^{-1}$  were evaluated with the help of the X ray radial distribution curves<sup>9)</sup> and the so-called small motion  $D$  values determined by Brockhouse<sup>10)</sup> from the broadening of the quasielastic peak obtained in inelastic scattering of slow neutrons from water. The experimental and calculated  $T_1$  values agreed well both in magnitude and temperature dependence.

However, further investigations of slow neutron scattering from water, using spectrometers of better resolution (e.g. see Larsson and Dahlborg<sup>11)</sup>), have not confirmed Brockhouse's results. In general, cold neutrons operating effectively on a short time scale from practically zero up to about  $10^{-11}$  s, allow to study very high frequency motions and diffusion mechanisms in liquids rather than to measure macroscopic diffusion coefficients.

Recently Hubbard<sup>12)</sup> pointed out that a considerable error may be made in the calculation of the intermolecular relaxation by treating all nuclear spins as being at the centres of the molecules. Hubbard's improved formula allowing for this off-centre spin effect is important for water molecules.

These facts indicate that the original evaluation of the intermolecular contribution to  $T_1^{-1}$  in water<sup>7)</sup> might be in error and thus the involved *a priori* use of the Powles internal field correction might not be justified.

There is evidence, from deuteron  $T_1$  measurements for  $D_2O^{13}$ , that such a correction may be important.

The results of proton  $T_1$  measurements for water up to the critical temperature<sup>14) 15)</sup> have confirmed that dipole-dipole intra- and intermolecular interactions provide the most effective relaxation mechanism up to at least 100°C. Moreover, the  $T_1$  values of Powles and Smith<sup>15)</sup> provided an excellent confirmation of the correctness of the earlier  $T_1$  measurements for water<sup>5) 7)</sup>. An interpolation of the results in <sup>7)</sup> and <sup>15)</sup> gives  $T_1 = 3.15 (\pm 2\%)$  at 20°C.

A revised interpretation of the  $T_1$  for water is presented. The intermolecular relaxation contribution can now be estimated to a better accuracy, thus allowing a comparison of the proton intramolecular correlation times and the measured dielectric relaxation times. The accurate interpolated  $T_1$  values, given in this paper for pure water, may be useful in other investigations, e.g. of various aqueous solutions<sup>16) 17)</sup>.

§ 2. *Theoretical.* For a liquid, whose molecules contain only two like magnetic nuclei of spin  $I = \frac{1}{2}$ , the dipolar intra- and intermolecular interactions lead to the well-known BPP formulae<sup>1)</sup>,

$$\left(\frac{1}{T_1}\right)_{\text{intra}} = \frac{3}{2}\hbar^2\gamma^4r_0^{-6}\tau_d \quad (1)$$

and

$$\left(\frac{1}{T_1}\right)_{\text{BPP}}^{\text{inter}} = \frac{3\pi^2\hbar^2\gamma\eta N}{kT}, \quad (2)$$

where the correction of Kubo and Tomita<sup>18)</sup> is introduced. Both formulae imply an extreme narrowing condition,  $\omega_r\tau_c \ll 1$ , valid for water, where  $\omega_r$  is the angular resonant frequency and  $\tau_c$ , the correlation time.  $\gamma$  is the nuclear gyromagnetic ratio;  $r_0$ , the internuclear distance within the molecule;  $N$ , the number of molecules in 1 cm<sup>3</sup> and  $k$ , the Boltzmann constant. For water, to a very good approximation, protons are the only magnetic nuclei so that  $\gamma = 2.6752 \times 10^4$  gauss<sup>-1</sup> s<sup>-1</sup>, and  $r_0 = 1.519$  Å<sup>19)</sup>. Equation (1) evaluated for water is

$$\left(\frac{1}{T_1}\right)_{\text{intra}} = 6.953 \times 10^{10}\tau_d \text{ s}^{-1}. \quad (1')$$

Formula (1) is substantially correct and may be also derived by a more general quantum theory of magnetic resonance absorption<sup>18)</sup> or by a density matrix method<sup>20)</sup>. Formula (2) is derived<sup>1)</sup> by integrating equation (1) from a closest approach distance  $d$ , assumed to be equal to the molecular diameter  $2a$ , to infinity and assuming the Stokes-Einstein relation for the self diffusion coefficient to express the translational correlation time. These are rather

rough approximations. Torrey<sup>21)</sup> made a more accurate calculation based on the solution of the translation diffusion equation, but still with the assumption  $d = 2a$ . Torrey's formula gives a  $(1/T_1)_{\text{inter}}$  value which is 4/5 of that obtained from the BPP formula (2). Hubbard<sup>12)</sup> has derived a correction to  $(1/T_1)_{\text{inter}}$  due to a molecular reorientation effect on the dipolar interaction between spins which are not at the centres of spherical molecules.

For two spin  $-\frac{1}{2}$  molecules the Torrey-Hubbard formula may, to a good approximation, be written

$$\left(\frac{1}{T_1}\right)_{\text{inter}} \simeq \frac{4\pi\gamma^4\hbar^2N}{5dD} \left[1 + 0.233\left(\frac{b}{a}\right)^2 + 0.15\left(\frac{b}{a}\right)^4\right], \quad (3)$$

where  $b$  is the distance of each proton from the centre of the molecule and  $a$  is the molecular radius. (In further discussion of (3) the equality sign will be used).

Formula (3) includes an assumption that in the liquid the distribution of molecules around a given molecule is uniform. Seiden<sup>22)</sup> pointed out that this assumption may lead to an appreciable error in the  $(1/T_1)_{\text{inter}}$  calculation and suggested the use of X ray diffraction results as an appropriate correction. This is because the probability of finding a molecule at a distance between  $r$  and  $r + dr$  from a given molecule (strictly from the scattering centre within the molecule) is given by the radial distribution function,  $4\pi\rho(r)r^2 dr$ , obtained from the X ray diffraction pattern. The function  $\rho(r)$  is, in close neighbourhood of the given molecule, characterized by a maximum which gets bigger and more pronounced with decreasing temperature. Seiden<sup>22)</sup> concluded that the radial distribution functions may be also used to calculate  $(1/T_1)_{\text{inter}}$  for polar liquids. They will be used in this paper for water.

We have

$$\frac{4\pi N}{d} = \int_d^\infty \frac{4\pi\rho(r)r^2 dr}{r^4} \simeq \int_d^{r_m} \frac{4\pi\rho(r)r^2 dr}{r^4} + 4\pi N \int_{r_m}^\infty \frac{dr}{r^2}, \quad (4)$$

so the intermolecular contribution to  $T_1^{-1}$  is of the form

$$\begin{aligned} \left(\frac{1}{T_1}\right)_{\text{inter}} &= \frac{\hbar^2\gamma^4}{5D} \left[ \int_d^{r_m} \frac{F(r) dr}{r^4} + 4\pi N \int_{r_m}^\infty \frac{dr}{r^2} \right] \times \\ &\quad \times \left[ 1 + 0.233\left(\frac{b}{a}\right)^2 + 0.15\left(\frac{b}{a}\right)^4 \right]. \end{aligned} \quad (5)$$

$r_m$  represents the upper limit of  $r$  used in X ray diffraction measurements and  $F(r) = 4\pi\rho(r)r^2$ .

Morgan and Warren<sup>9)</sup> determined the radial distribution curves, up

to  $r_m = 8\text{\AA}$ , for water at five temperatures, 1.5, 13, 30, 62 and  $83^\circ\text{C}$ , and their results were confirmed recently<sup>23</sup>). These results give the positions of the oxygen atoms in water.

For simplicity of calculation we assume that water molecules are spheres whose centres coincide with the centres of the oxygen atoms. (The O atom would be shifted by only  $0.07\text{\AA}$  from the molecule centre chosen at the centre of gravity). Then  $b$  may be identified with the O-H distance, i.e.  $b = 0.957\text{\AA}$ , whereas the radius value is  $a = 1.38\text{\AA}$ . The Hubbard correction for the off-centre proton effect amounts to 1.147. Equation (5) can now be partially evaluated to show clearly its temperature dependence

$$\left(\frac{1}{T_1}\right)_{\text{inter}} = 1.306 \times 10^{-37} D^{-1} \left[ \int_a^{8\text{\AA}} \frac{F(r) dr}{r^4} + 1.571 \times 10^8 N \right] \text{s}^{-1}. \quad (5')$$

It has been shown<sup>24) 25)</sup> that the proton  $T_1$  value for air-free water is frequency independent which excludes any contribution due to anisotropic chemical shift. The scalar coupling mechanism due to presence of a small amount (0.04%) of  $^{17}\text{O}$  was shown<sup>26)</sup> to contribute only to the spin-spin relaxation. Recent  $T_1$  measurements<sup>14) 15)</sup> for water up to the critical temperature indicate also that the spin rotation interaction does not contribute appreciably to  $T_1^{-1}$  at low temperatures except near  $100^\circ\text{C}$  where it will be estimated approximately. Therefore the experimental  $T_1^{-1}$  for air-free water is satisfactorily described by the sum of contributions given by formulae (1') and (5'), i.e.

$$\left(\frac{1}{T_1}\right)_{\text{exp}} \simeq \left(\frac{1}{T_1}\right)_{\text{intra}} + \left(\frac{1}{T_1}\right)_{\text{inter}}. \quad (6)$$

§ 3. *Experimental.* The method used for  $T_1$  measurement and some experimental details have been already described<sup>27)</sup>. This method involves three steps: (1) Saturation of the resonance signal by an intense modulation field of mixed frequencies, 50 and 30 Hz; (2) Undisturbed recovery of nuclear magnetization far enough from resonance; (3) Slow passage through resonance after complete ( $M_0$ ) or partial ( $M_t$ ) recovery of the magnetization. The whole procedure was sequenced semi-automatically and the resonance signals were recorded photographically with a mirror oscillograph. All  $T_1$  measurements were made at 28 MHz. The sample temperature was controlled within  $\pm 0.1^\circ\text{C}$  and could be measured to  $\pm 0.1^\circ\text{C}$ . The accuracy of the  $T_1$  measurement for water at a single temperature is estimated as better than  $\pm 3\%$ .

The sample was prepared from triple distilled water by prolonged boiling in a special Jena glass apparatus and subsequent sealing off under vacuum<sup>16)</sup>. Very carefully cleaned glass was used throughout. The sample tube was of

12 mm o.d. and 1 mm wall thickness and the sample volume was about 1.5 cm<sup>3</sup>.

§ 4. *Interpretation.* A. General. The experimental results are given in figure 1 as  $\log T_1$  against  $-10^3/T$  where  $T$  is the absolute temperature. These proton  $T_1$  values for H<sub>2</sub>O do not show an Arrhenius behaviour in the temperature region between 0 and 100°C in contrast to D<sub>2</sub>O for which the deuteron  $T_1$  could be described by the activation energy of 3.90 kcal/mole

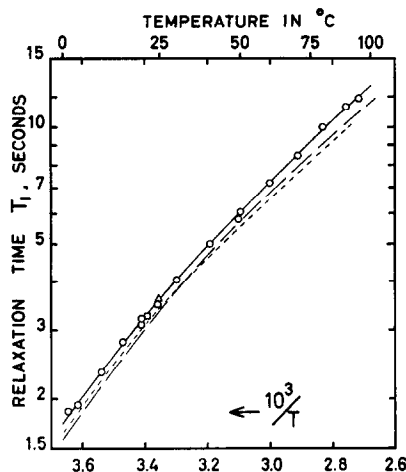


Fig. 1. Proton spin-lattice relaxation times,  $T_1$ , for air-free water as a function of temperature (○). Also given are single temperature results due to Anderson and Arnold<sup>29</sup>) (□) and to Powles and Cutler<sup>24</sup>) (Δ). The broken curves represent the interpolated values from Giulotto *et al.*<sup>3</sup>) (-----) and from Simpson and Carr<sup>4</sup>) and Hausser<sup>14</sup>) (---). The interpolated values from Powles and Smith<sup>15</sup>) almost coincide with the smooth curve.

above 40°C<sup>13</sup>). A corresponding *mean* activation energy for the proton measured  $T_1$  would be 3.68 kcal/mole above 40°C, which increases to 3.77 kcal/mole obtained from the better Arrhenius fit if one removes small spin-rotation contributions. The spin rotation contributions have been estimated approximately at several temperatures, using a procedure that was recently found successful for HCl-DCI solutions<sup>28</sup>), and amount to 0.9% and 4.4% of  $(1/T_1)_{\text{exp}}$  at 50°C and 100°C respectively.

The present  $T_1$  values are generally some 5–10% higher than most of the reported data for water<sup>3</sup>)<sup>4</sup>)<sup>14</sup>), however, they agree within  $\pm 2\%$  with the data of Powles and Smith<sup>15</sup>) if their  $\log T_1$  versus  $1/T$  graph curvature is not neglected. Two other  $T_1$  values, namely that at 21.5°C of Anderson and Arnold<sup>29</sup>) and that at 25°C of Powles and Cutler<sup>25</sup>), agree satisfactorily with the present data. The  $T_1$  values interpolated at 5°C intervals, including those extrapolated slightly from 2.1°C to 0°C and from 95.2°C

to 100°C, are given in table I. Their accuracy is better than  $\pm 2\%$  and the author believes that they represent at present the most accurate set of the proton  $T_1$  values for water.

B. Comparison of  $T_1$  with dielectric relaxation and viscosity. The big activation energy for  $T_1$  indicates that the molecular motion leading to proton spin relaxation is dominated by frictional effects<sup>30) 13)</sup>. This follows also from the temperature-dependence measurements of the dielectric relaxation time,  $T_d$ <sup>31)</sup>, which is satisfactorily described for water by the Debye relation based on Stokes hydrodynamic approach, i.e.  $T_d \propto \eta/T$ , when the hydrogen bonding is taken into consideration<sup>32)</sup>. It should be mentioned that the observations provide a single  $T_d$  for water<sup>33)</sup>. Due to molecular rigidity the motion of electric dipole moments is essentially the motion of the water molecules.

The relation between the characteristic times for molecular reorientation,  $T_d$  and  $\tau_d$ , can be expressed as

$$\frac{T_d f(\epsilon_0, \epsilon_\infty)}{\tau_d} = q. \quad (7)$$

The parameter  $q$  was shown<sup>34) 35)</sup> to vary from  $q = 3$ , when the solution of the reorientational diffusion equation may be used in the calculation of a random process correlation function (i.e. a single jump angle  $\phi_s$  is much smaller than the correlation angle  $\phi_c$ ), to  $q = 1$  when this condition is not met. We estimate by theoretical arguments<sup>35)</sup> that the ratio  $\phi_s/\phi_c \ll 1$  for water in the temperature region concerned, and hence  $q = 3$ .  $f(\epsilon_0, \epsilon_\infty)$  is the internal field correction shown by Powles<sup>8)</sup> and Glarum<sup>36)</sup> to have the form

$$f(\epsilon_0, \epsilon_\infty) = \frac{2\epsilon_0 + \epsilon_\infty}{3\epsilon_0} \quad (8)$$

which has been supported indirectly<sup>37) 8) 38) 13)</sup>.  $\epsilon_0$  is the static dielectric constant and  $\epsilon_\infty$  is the high frequency dielectric constant due to induced moments. For water, taking  $\epsilon_\infty = 5.5$ <sup>31)</sup> and  $\epsilon_0$  from recent measurements by Owen *et al.*<sup>39)</sup>,  $f(\epsilon_0, \epsilon_\infty)$  varies from 0.688 at 0°C to 0.695 at 70°C. This small temperature dependence of the  $f(\epsilon_0, \epsilon_\infty)$  makes it possible to compare directly the two measured relaxation times  $T_1$  and  $T_d$ .

The temperature dependences of the experimental  $T_1^{-1}$  and  $T_d$  agree very well as seen in table I where the product  $(T_1 T_d)^{-1}$  is constant and equal to  $3.37 \times 10^{10} \text{ s}^{-2}$  within  $\pm 3\%$ . Since it may be expected from (1'), (7) and the above discussion that  $(1/T_d) \cdot (1/T_1)_{\text{intra}}$  should be independent of temperature, one concludes from (6) that  $(1/T_1)_{\text{inter}}$  must have the same temperature dependence as  $T_d$ . This will be confirmed in § 3.C.

The  $T_1^{-1}$  may therefore be compared with  $\eta/T$  similarly to the  $T_d$ . Table I shows that  $T_1 \eta/T$  decreases continuously with increasing temperature

TABLE I

Temperature (°C)	$T_1$ (interpol.) (s)	$T_d \times 10^{12}$ (s)	$\left(\frac{1}{T_1 T_d}\right) \times 10^{-10}$ (s <sup>-2</sup> )	$\frac{T_1 \eta / T}{(T_1 \eta / T)_{20^\circ \text{C}}}$	$\frac{\eta / (T T_d)}{(\eta / (T T_d))_{20^\circ \text{C}}}$
0	1.73	17.7	3.26	1.06	1.04
5	2.07			1.05	
10	2.39	12.7	3.30	1.03	1.02
15	2.76			1.02	
20	3.15	9.56	3.32	(1.00)	(1.00)
25	3.57	8.28 <sup>α</sup>	3.46	1.00	1.01
30	4.03	7.38	3.36	0.99	1.00
35	4.50			0.98	
40	5.00	5.95	3.36	0.97	0.98
45	5.50			0.96	
50	6.03	4.84	3.42	0.95	0.98
55	6.60	4.46 <sup>β</sup>	3.40	0.95	0.97
60	7.20	4.04	3.44	0.94	0.97
65	7.81			0.94	
70	8.46			0.93	
75	9.11	3.23	3.35	0.93	0.94
80	9.80			0.92	
85	10.5			0.92	
90	11.25			0.91	
95	12.0			0.91	
100	12.75			0.90	

<sup>α</sup> = ref. 40<sup>β</sup> = ref. 41

between 0 and 100°C, as previously noted<sup>3) 5)</sup>. For other  $T_1$  results<sup>4)</sup>  $T_1 \eta / T$  was nearly constant below 40°C. Table I gives also the temperature dependence of the  $T_d^{-1}(\eta / T)$  for comparison to that of  $T_1 \eta / T$ .

*a. Relation to some models of water.* From the above comparisons it seems reasonable to explain the temperature dependence of  $T_1^{-1}$  and  $T_d$  together. Such explanation, based on the viscosity data and involving hydrogen bonding effect, exists for the  $T_d$ <sup>32)</sup>. It is often assumed that there are five different types of water molecules according to the number of hydrogen bonds which may be four, three, two, one and zero bonds. Further details depend very much on the model.

The Haggis model<sup>42)</sup>, discussed by Grant<sup>32)</sup>, assumes that the molecules can be treated as a statistical system of reacting species and that the transitions between the states are realized by the appropriate formation and breaking of the hydrogen bonds. By assuming the same probability of breaking all types of hydrogen bonds in water, the theory gives the equilibrium percentages of molecules  $n_i$  in each state at various temperatures. Four- and three-bonded molecules cannot rotate without breaking several bonds, whereas two-bonded molecules need to break only one bond to rotate. Single and one-bonded molecules can of course rotate without breaking bonds. Haggis obtained a proportionality between the experimental  $T_d^{-1}$  and the fraction of two-bonded molecules,  $n_2$ . A graph of  $\log(n_2 T_d)$



against  $10^3/T$  between 0 and 60°C is a satisfactory straight line corresponding to an activation energy of 3.2 kcal/mole. Grant<sup>32)</sup> assumed also that viscosity of water between 0°C and 100°C is directly related to the number of hydrogen bonds which are not broken and deduced the behaviour of  $\eta/(TT_a)$  in satisfactory agreement with the experiment.

It may be noted that the  $n_i$  values depend on the assumed percentage of broken bonds,  $p$ , in liquid water at 0°C. Haggis<sup>42)</sup> chose  $p = 16\%$ , but it was later<sup>40)</sup> changed to 9% and the new interpretation admitted rotating of two-bonded molecules in an unsymmetrical state. Consequently  $T_a^{-1}$  was found to be proportional to  $n_3$ . The graph of  $\log(n_3T_a)$  against  $10^3/T$  gives then an activation energy of 3.7 kcal/mole\*).

It seems difficult to work out an interpretation of the  $T_a$  and  $T_1$  for water in terms of the so-called flickering cluster model proposed by Frank and Wen<sup>43)</sup>. They considered some covalency in the hydrogen bond and a charge separation and postulated that hydrogen bonding is of a cooperative nature, i.e. several bonds are made and broken at a time. In effect there are short-lived clusters of highly hydrogen-bonded regions surrounded by single molecules. The flickering of the bond systems produces a fluctuating electric polarization since the cluster boundaries carry some electric charges. In an external field this should give a contribution to the dielectric constant and play a part in the dielectric relaxation. However, it is not clear whether the main relaxation in water can be related to such a process. The difficulty is how to estimate reliably an average lifetime  $\tau$  of the clusters. The single  $T_a$  observed<sup>33)</sup> ( $T_a = 9.6 \times 10^{-12}$  s at 20°C) might be taken as a measure of  $\tau$ , but the slow neutron inelastic scattering offers a more direct way. Recent scattering measurements<sup>11)</sup> give a value of  $1.5 \times 10^{-12}$  s for an average residence time of a water molecule at 20°C. Whether this time refers to single molecules or hydrogen-bonded ones is, however, not certain at present. For the beryllium filter technique and the values of momentum transfer used<sup>11)</sup> the neutron elementary observation time is estimated to fall in the region below  $1.5 \times 10^{-12}$  s. Further scattering experiments, possibly using still slower neutrons, will be valuable. For instance, there is a possibility that due to strong intermolecular interactions the rate of exchange between single and one-bonded molecules is greater than the flickering frequency for the whole clusters. The flickering cluster model has had some success in calculating the thermodynamic properties of liquid water<sup>44)</sup>.

C. Evaluation of the intermolecular relaxation contribution. The  $(1/T_1)_{\text{inter}}$  is evaluated from formula (5'). The integral appearing in the formula has been evaluated graphically from the radial distribution functions

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\*) Haggis e.a.<sup>40)</sup> give 3 kcal/mole for this activation energy but their graph is wrongly constructed; the same mistake was made by J. B. Hasted in "Progress in Dielectrics" vol. 3 (1961) p. 132.

$F(r)$  determined<sup>9</sup>) for 1.5, 13, 30, 62 and 83°C. From the extensive and somewhat differing literature values of the self diffusion coefficient  $D$  for water the author prefers those measured recently by Hausser<sup>25</sup>) between 20°C and 380°C with the NMR technique. These results agree with those obtained by small concentration deuterium tracers<sup>45</sup>) or for  $D_2O$ <sup>46</sup>). Above about 40°C Hausser's  $D$  values show the Arrhenius behaviour with an activation energy of 3.37kcal/mole. A criterion for the choice of the Hausser  $D$  values was their relation to  $\eta/T$ .

Table II lists the values of the parameters used in formula (5') and the values of  $(1/T_1)_{\text{inter}}$ . The latter are anticipated to have the same temperature dependence as  $T_d$  by virtue of the  $T_{1\text{exp}}$  behaviour discussed above. This is indeed the case as indicated by constancy of the expression  $(1/T_1)_{\text{inter}} \cdot (1/T_d)$  shown in the last column of table II. It appears that the  $(1/T_1)_{\text{inter}}$  contribution is somewhat temperature dependent decreasing from 45 to 40% of the  $(1/T_1)_{\text{exp}}$  when the temperature increases from 1.5 to 83°C. A corresponding density, i.e.  $N$ , decrease is only 3.0%.

TABLE II

Temperature (°C)	$D_\delta \times 10^5$ (cm <sup>2</sup> s <sup>-1</sup> )	$N \times 10^{-22}$ (cm <sup>-3</sup> )	$\left[ \int_d^{8\text{\AA}} \frac{F(r)}{r^4} dr \right] \times 10^{31}$ (cm <sup>-1</sup> )	$\left( \frac{1}{T_1} \right)_{\text{inter}}$ (s <sup>-1</sup> )	$\left( \frac{1}{T_1} \right)_{\text{inter}} \times \left( \frac{1}{T_d} \right)$ $\times 10^{-10}$ (s <sup>-2</sup> )
1.5	1.02	3.343	1.435	0.245	1.46
13	1.49	3.341	1.425	0.171	1.49
30	2.37	3.329	1.434	0.107	1.45
62	4.46	3.284	1.403	0.056	1.44
83	6.15	3.243	1.326	0.039	1.35

$\delta$  = interpolated values from ref. 25.

It should be mentioned that if the self diffusion coefficient is expressed by the Stokes-Einstein relation,  $D = kT/6\pi\eta a$ , then the Hubbard corrected formula gives the  $(1/T_1)_{\text{inter}}$  values which are only 5–10% lower than those shown in table II. However, such a procedure alters appreciably the temperature dependence of  $(1/T_1)_{\text{inter}}$ . The value of the  $(1/T_1)_{\text{inter}}$  was shown<sup>47</sup>) to be quite insensitive to the details of the translation diffusion models for water.

D. Determination of the  $\tau_d$  and  $f(\epsilon_0, \epsilon_\infty)$ . Using the  $(1/T_1)_{\text{inter}}$  values given in table II and the formulae (1') and (6) one can determine the correlation times for the dipolar intramolecular interaction,  $\tau_d$ . Small spin-rotational contributions to  $(1/T_1)_{\text{exp}}$  at higher temperatures are removed as mentioned before. In figure 2 the values of  $\tau_d$  are shown together with the measured  $T_d$  values. The ratio  $T_d/\tau_d$  is found to be nearly temperature independent and equal to about 3.7. The temperature independence of the  $T_d/\tau_d$  suggests that the single jump angle  $\phi_s$  for water molecules is indeed very

small. According to Valiev and Agishev<sup>35)</sup>  $\phi_s \propto T^{1/2}\eta^{-1}$  and so the  $\phi_s$  value is expected to increase in this temperature region by a factor of 6 which would considerably affect the ratio  $T_d/\tau_d$  if the  $\phi_s$  were big<sup>34)</sup>. Consequently,  $q = 3$  and formula (7) gives for the internal field correction  $f(\epsilon_0, \epsilon_\infty) = 0.81$ , the accuracy being estimated as  $\pm 10\%$ . This is compared with 0.69 as obtained from the Powles formula<sup>8)</sup>. In spite of some approximations the

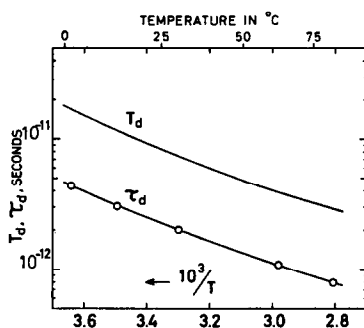


Fig. 2. Temperature dependence of the measured dielectric relaxation times,  $T_d$ , and the correlation times for dipolar intramolecular intermolecular interaction,  $\tau_d$ .

present analysis suggests that the internal field correction for water is significant and described by Powles' formula. Two older theories of internal field, developed by Lorentz and Onsager, give results which are considerably different from the present value. It may be mentioned that the Powles correction was used to explain the low value of the quadrupole coupling constant determined from the deuteron  $T_1$  measurement for liquid  $D_2O$ <sup>13)</sup>. In both cases a spherically symmetric rotation of molecules in the liquids is assumed on the basis of the single  $T_d$  observed<sup>31) 33)</sup>. This assumption contains some simplification since there are strong forces between electric dipole moments of the molecules as discussed by Némethy and Scheraga<sup>44)</sup>. It is, however, beyond the scope of this investigation to decide how much this could contribute to the difference between the theoretical and 'experimental' values of  $f(\epsilon_0, \epsilon_\infty)$ .

**Acknowledgements.** The author wishes to thank Professors H. Niewodniczański and A. Z. Hryniewicz of Jagellonian University, Cracow, Poland, for permission to publish the results of the thesis. Thanks are also due to Professor J. G. Powles for advice and encouragement.

*Note added in proof:*

Recently D. P. Stevenson (J. phys. Chem. **69** (1965) 2145), using spectral data on the vibrational and vacuum ultraviolet absorptions, concluded that the monomer species concentration in liquid water is only 0.1–1% between 24 and 92°C. If so, then (besides other implications): (1) The flickering cluster model of water could not be upheld; (2) basic 'relaxing units' in dielectric and N.M.R. relaxations would have to be one-bonded water molecules for which a small  $\phi_s$  value is very plausible; (3) slow neutron scattering from water at moderate temperatures measures an average life time

of a hydrogen bond as suggested in ref. 11. Stevenson's conclusion does not affect the interpretation of the present paper.

Received 5-7-65

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