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Diffusion and Nuclear Spin Relaxation in Water*

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The diffusion coefficient and the spin lattice relaxation time of protons in ordinary water have been measured in the temperature range 0–100°C using nuclear magnetic resonance free precession techniques. Unlike previous diffusion measurements, the present values describe the diffusion of protons rather than foreign isotopes introduced as tracers. To within the experimental error the Stokes-Einstein relation adequately describes the relative temperature dependence of viscosity and diffusion, but above the vicinity of 40°C the spin lattice relaxation does not follow the viscosity in the predicted manner.

THE self-diffusion coefficient D and the spin lattice relaxation time T_1 of protons in water have been measured[1] over the temperature range 0–100°C using nuclear magnetic resonance free precession techniques.[2] A water sample 7 mm in length was sealed in a Pyrex tube having a 3-mm inner diameter. The paramagnetic dissolved oxygen was removed by flushing the sample several times with helium gas. The helium was then evacuated and the sample sealed in equilibrium with its own vapor.

Values of T_1 were measured for 53 points in the above temperature range and D was measured for 29 points. The estimated maximum random error is 2% for the T_1 data and 7% for the D data. The estimated maximum systematic error in the D data is 3%. No estimate of the maximum systematic error in the T_1 data has as yet been made. Five possible smooth curves have been drawn through the D data and four such curves through the T_1 data. The mean of the values read from these curves at each 5° interval is shown in Table I. The mean deviation for the values read from the D curves is 3% and from the T_1 curves is 0.5%.

The values of D given in Table I are the first directly measured values for proton diffusion in water as a function of temperature. The literature contains values of deuteron, triton, and O^{18} tracer diffusion over the

temperature range 0 to 50°C.[3] The values for these three isotopes differ at a given temperature by as much as 25%. Our proton values lie at the low end of this range. Our value for T_1 near room temperature is about 35% higher than the value given by Benedek and Purcell,[4] about 20% lower than that of Chiarotti, Cristiani, and Guilotto,[5] and 6% lower than that of

TABLE I. Oxygen-free water.

T (°C)	$D \times 10^5$ (cm^2/sec)	T_1 (sec)	$\frac{D\eta}{T}\bigg/\left(\frac{D\eta}{T}\right)_{25°C}$	$\frac{T_1}{D}\bigg/\left(\frac{T_1}{D}\right)_{25°C}$	$\frac{T_1\eta}{T}\bigg/\left(\frac{T_1\eta}{T}\right)_{25°C}$
0	0.97	1.59	1.00	1.04	1.03
5	1.16	1.88	0.99	1.02	1.02
10	1.36	2.20	0.98	1.02	1.01
15	1.58	2.55	0.98	1.02	1.00
20	1.85	2.95	0.99	1.01	1.00
25	2.13	3.37	1	1	1
30	2.46	3.82	1.02	0.98	1.00
35	2.79	4.30	1.02	0.97	1.00
40	3.14	4.76	1.03	0.96	0.99
45	3.52	5.27	1.04	0.95	0.98
50	3.94	5.77	1.05	0.93	0.97
55	4.37	6.78	1.06	0.91	0.96
60	4.82	6.81	1.06	0.89	0.95
65	5.30	7.36	1.07	0.88	0.94
70	5.78	7.91	1.07	0.86	0.93
75	6.27	8.49	1.07	0.86	0.92
80	6.81	9.10	1.08	0.84	0.91
85	7.26	9.70	1.07	0.84	0.90
90	7.75	10.30	1.06	0.84	0.89
95	8.20	10.95	1.05	0.84	0.88
100	8.65	11.55	1.03	0.84	0.87

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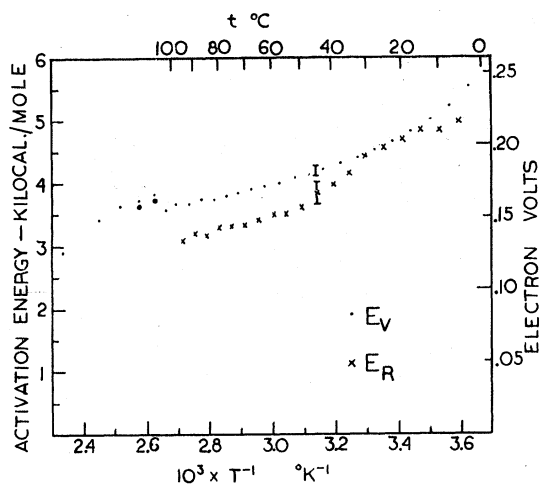
FIG. 1. The activation energy E_R for T_1 is indicated with the crosses and the activation energy E_V for T/η is indicated with the dots. Typical estimated maximum errors are indicated by the two vertical lines. The larger solid circles indicate alternate points related to discrepancies between the two sources of viscosity data.

Anderson and Arnold.[6] Brown[7] has measured T_1 for large samples at low fields obtaining close agreement with Anderson and Arnold.[6] Our measurements at 2000 gauss and 7000 gauss have revealed no field dependence. It was first suggested by Brown[8] that the lower values for our small sample may be due to relaxation at the surfaces. We are initiating measurements as a function of the surface-to-volume ratio to determine any effect of surface relaxation.

If one assumes (a) the Bloembergen-Purcell-Pound[9] theory of nuclear spin relaxation in liquids, (b) the

Stokes relationship between viscosity η and the rotational correlation time, and (c) the Stokes-Einstein relationship between viscosity and the translational self-diffusion coefficient, one expects the following relationships:

$$T_1 \propto D \propto \frac{T}{\eta} \propto e^{-E/RT}.$$

The three activation energies are predicted to be equal and are denoted by E. The last three columns of Table I contain ratios illustrating the relative temperature dependence of T_1, D, and T/η. Since the viscosity data[10] have an estimated maximum error of 0.1%, and if one temporarily assumes no temperature dependence for the unknown systematic error in the T_1 data, the estimated maximum errors of the ratios in the last three columns of Table I are 7%, 9%, and 2%, respectively. Thus the ratios of $D\eta/T$ would indicate that to within the experimental error the Stokes-Einstein relationship adequately describes water. But the ratios of $T_1\eta/T$, with smaller experimental error, indicate that T_1 does not follow η as predicted. This is similar to a result of Benedek and Purcell[4] who made measurements as a function of pressure. A major deviation from the predicted relationships appears to begin at about 40°C. It is of interest to note that this is near a minimum in the heat capacity at constant pressure[11] and an inflection point in the magnetic susceptibility.[12] This deviation can also be described by assuming different temperature-dependent activation energies E_R and E_V for T_1 and T/η. The activation energies calculated from our data on the basis of this assumption are shown in Fig. 1.

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