Self-Diffusion of Water at Low Temperatures and High Pressure

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Self-diffusion coefficients obtained by the NMR spin-echo method are reported for water at temperatures below 0 °C and at pressures up to 350 MPa in the liquid region bounded by the ice I and ice III phases. The data are compared with other measurements in this region.

Measurements of the self-diffusion coefficient of water are important for the testing of the many proposed models of liquid water. Examples currently under scrutiny in the literature include the mixture model of Lammana *et al.* (1995), the percolation model of Stanley and Texeira (1980), and the stability limit conjecture of Speedy (1982) (Preilmeier *et al.*, 1987). Generally speaking, the data employed have been obtained along the saturation line rather than those obtained under high pressure, despite the fact that among the more remarkable properties of this substance are the increases in both fluidity and in the self-diffusion coefficient effected by an increase in pressure. High pressure results have been obtained by Woolf (1975, 1976) (HTO in H_2O and DTO in D_2O), Jonas and co-workers (Wilbur *et al.*, 1976; DeFries and Jonas, 1977; Lamb *et al.*, 1981) (D_2O and H_2O at high temperatures), Angell *et al.* (1976) (H_2O), Krynicki *et al.* (1980) (H_2O), Harris and Woolf (1980) (H_2O and $H_2{}^{18}O$), and Lüdemann and co-workers (Prielmeier *et al.*, 1987, 1988) (H_2O, D_2O). With the exception of Woolf's work on HTO in H_2O and DTO in D_2O, which were diaphragm cell measurements made with tritium-labeled water and were thus tracer-diffusion coefficients, the measurements listed have all been carried out by the NMR spin-echo method. The work prior to 1982 has been comprehensively reviewed by Weingärtner (1982). However, of the studies listed, only two include measurements in the subzero temperature region of the phase diagram lying between ice I and ice III (Figure 1).

Angell *et al.* (1976) used two high-pressure vessels, one of Be−Cu containing a quadrupole gradient coil wound on a Teflon former, the other a thick-walled, HF-etched, glass capillary inserted inside a second, Delrin, quadrupole coil. These coils producing the magnetic field gradient on which the NMR spin-echo method depends must be calibrated. This is normally done using fluids for which the self-diffusion coefficients are accurately known (± 0.1−0.2%), these being derived from precise tracer diffusion measurements (Tyrrell and Harris, 1984; Holz and Weingärtner, 1991). The first quadrupole coil had a calibration which varied with temperature and pressure and as the lowest calibration point available (then and now) is at 1 °C (Mills, 1973); this introduced some uncertainty in the values obtained, estimated by the authors as ±(3 to 6)%. Numerical values were not given, the results being reported only in graphical form. The capillary cell used with the second coil, which did have a temperature independent calibration, had a low sample volume with consequent low signal to noise ratios. Results obtained with this cell had an uncertainty of ±(3 to 7)%, as estimated from the graph published. The maximum pressure was 238 MPa.

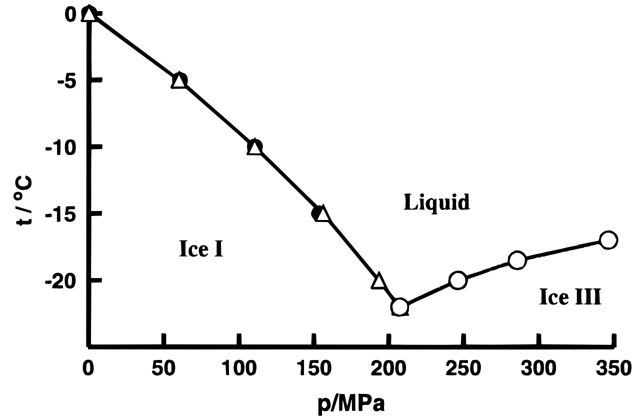

Figure 1. Partial phase diagram of water showing the ice I−ice III−liquid triple point at −22 °C, 209 MPa: (●) Bridgman, 1912; (△, ○) Henderson and Speedy, 1987.

Lüdemann's apparatus uses the etched capillary cell with gradient coils mounted outside the thermostat in which the cell is mounted (Prielmeier, 1988; Lang and Lüdemann, 1991). The calibration constant is therefore independent of the state of the sample. This group used emulsions of water in order to be able to obtain data in the supercooled regime as well as the subzero liquid. With emulsions, pulsed gradient techniques must be employed so that the measurement time is less than the time for a water molecule to traverse the micelle in which it is contained. The gradient is applied longitudinally over the cylindrical sample cell (whereas we apply it across its width, which makes it easier to obtain the necessary linearity of the magnetic field gradient across the sample). However, it is an improvement over the gradient coil system previously used which may have given rise to coil calibration factors which were temperature dependent (Lang and Lüdemann, 1991). The maximum pressure obtained in this work was 400 MPa.

As we required accurate values of the self-diffusion coefficient of water for comparison with that of water in a series of nonelectrolyte solutions at high pressures and at temperatures below that obtained in our earlier work (Harris and Woolf, 1980), we have made new measurements in this region at pressures to 350 MPa and at temperatures down to the ice I−ice III−liquid triple point (−22 °C, 209 MPa). Emulsions were not used, and so we did not attempt measurements right in the supercooled region, though some appear to lie just inside the phase boundary given by Henderson and Speedy (1987) and Bridgman (1912). These results extend the range of our original measurements which had a lower temperature limit of 4 °C and an upper pressure limit of 300 MPa and

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Table 1. Self-Diffusion Coefficients of Water

t/°C	p/MPa	$D/10^{-9}$ m^2 s^{-1}	t/°C	p/MPa	$D/10^{-9}$ m^2 s^{-1}
−21.50	209.5	0.56_4	0.06	0.1	1.13
			0.02	0.1	1.13
−19.92	201.5	0.60_3	0.08	25.5	1.17
−20.00	225.5	0.59_6	0.10	50.5	1.20
−19.89	253.5	0.59_2	−0.05	100.5	1.21
			−0.06	150.5	1.22
−14.99	156.0	0.73_8	−0.05	200.5	1.21
−14.99	200.5	0.73_3	−0.06	250.5	1.19
−14.99	251.0	0.71_8	−0.04	300.5	1.15
−14.99	300.5	0.69_6	−0.05	350.5	1.13
−14.99	350.5	0.67_1			
			5.00	0.1	1.313[a]
−9.99	102.5	0.87_3	5.00	50.0	1.37
−9.97	150.5	0.88_7	5.05	100.0	1.39
−10.00	200.5	0.87_2	5.03	199.5	1.38
−9.99	200.5	0.87_2	5.03	300.5	1.33
−9.90	250.5	0.86_6	5.00	350.0	1.29
−9.94	300.5	0.83_6			
−9.90	350.5	0.81_5	25.00	0.1	2.299[a]
			25.04	52.5	2.34
−5.00	50.5	1.00_6	25.05	100.5	2.35
−4.99	151.0	1.05_0	25.00	150.5	2.31
−4.98	200.5	1.03_3	25.05	200.5	2.29
−4.99	250.5	1.01_6	25.07	251.5	2.22
−5.00	300.5	0.99_2	25.04	300.0	2.18
−4.96	350.5	0.96_5	25.00	350.5	2.12

[a] Atmospheric pressure values from Mills (1973).

enable comparison with the pulsed gradient emulsion studies.

Experimental Section

The high-pressure NMR spin-echo apparatus has been described previously (Harris *et al.*, 1990). The steady gradient method was employed. At each state point, values obtained for constant magnetic-field gradients over a range of rf-pulse separations and at constant rf-pulse separation over a range of gradients were averaged. The rf and quadrupole gradient coils are both mounted in grooves cut in the same Macor glass former (Corning) and held in place by epoxy cement (Araldite K138). The former is contained within the Be−Cu pressure vessel employed. The sample cell used was of the Teflon bellows type (Easteal *et al.*, 1983) and is always placed in the same position within the combined rf/gradient coil fields. This is a particular advantage in this type of work.

The gradient coil was calibrated using the reference values for the self-diffusion coefficient of water established at 0.1 MPa by Mills (1973). The coil constant, averaged over 13 points, was (0.5017 ± 0.0015) T/(A m rad): the maximum deviation was 0.8%. There was no apparent temperature dependence over the range 1−45 °C, and this value was assumed to apply at lower temperatures and at high pressures.

Pressures (accuracy, ±0.5 MPa) were measured with a Heise Bourdon gauge calibrated against a Budenberg 283 dead-weight piston gauge. The hydraulic fluid was 3M FC-75, a fully fluorinated material. Temperatures (accuracy, ±0.02 K) were measured with a calibrated four-lead Pt resistance thermometer (Leeds and Northrup) inserted in the bottom closure of the pressure vessel: this is sensitive enough to detect the adiabatic changes induced when the pressure is pumped up or let down.

Results

The results are listed in Table 1. Excellent agreement was obtained at 5 and 25 °C with our older data (Harris and Woolf, 1980) which were obtained with a different gradient coil and using a glass cell with a stainless-steel bellows (Figure 2). Satisfactory agreement was obtained with the results of Angell *et al.* (1976), though their data show more scatter (Figure 3). Good agreement was obtained with the pulsed gradient emulsion results of Prielmeier *et al.* (1987, 1988) (Figure 4), except above 200 MPa at −10 °C, where their data lie about 7−9% below ours, twice the sum of the estimated experimental errors. Both sets show that the curvature of the diffusion coefficient−pressure isotherms evident in the range 0−25 °C is much more pronounced at subzero temperatures. Comparison of the isotherms in Figures 2 and 4 makes evident the trend of the maximum to higher pressures as the temperature

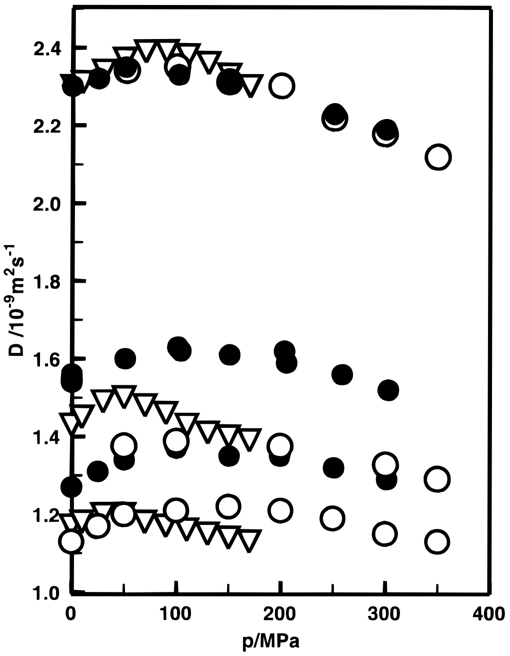

Figure 2. Comparison of the experimental self-diffusion coefficients of water with previous work above 0 °C: (○) 0, 5, and 25 °C, this work; (●) 4, 10, and 25 °C, Harris and Woolf, 1980; (▽) 2, 10, and 25 °C, Krynicki *et al.*, 1980.

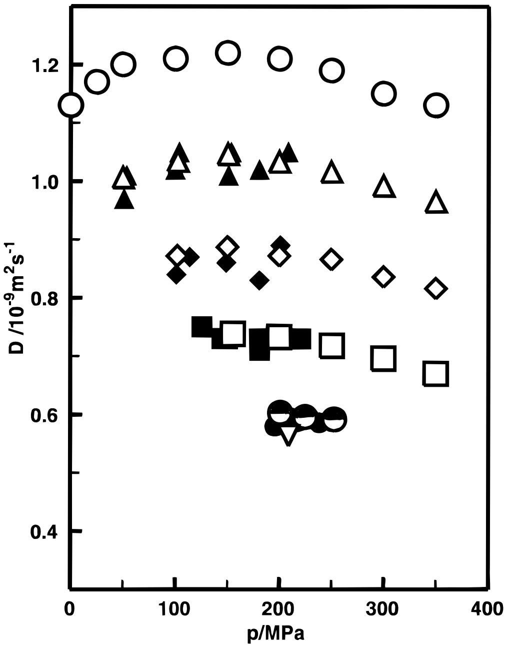

Figure 3. Comparison of the experimental self-diffusion coefficients of water with previous work below 0 °C: (○) 0 °C, (△) −5 °C, (◇) −10 °C, (□) −15 °C, (◓) −20 °C, (▽) −21.5 °C, this work; (▲) −4.4 and −5 °C, (◆) −9.3 and −10 °C, (■) −14.3 and −15 °C, (●) −20.1 °C , Angell *et al.*, 1976.

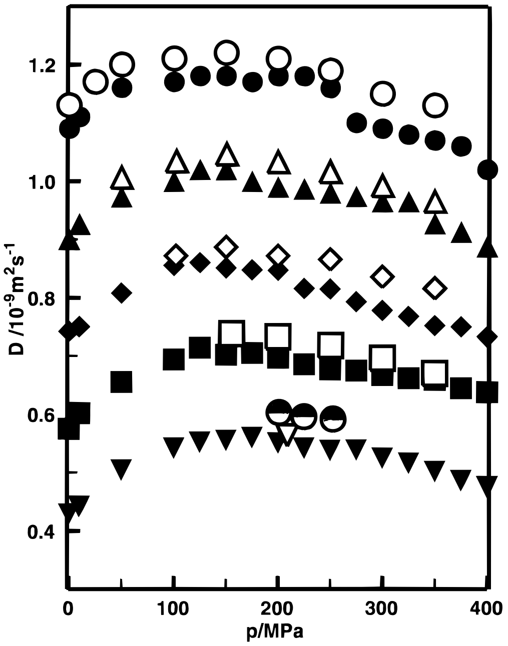

Figure 4. Comparison of the experimental self-diffusion coefficients of water with previous work below 0 °C: (open symbols) as in Figure 3; (●) 0 °C, (▲) −5 °C, (◆) −10 °C, (■) −15 °C, (▼) −21 °C, Prielmeier *et al.*, 1988.

is lowered, though the rate of change below 0 °C is fairly small.

This general agreement between data sets is encouraging given the differences in the techniques applied, particularly in regard to the ways in which the magnetic field gradient is established, with, on the one hand, a steady gradient applied normal to the sample cell axis using a coil within the pressure vessel and, on the other, a pulsed gradient produced over a much larger volume along the sample axis, using coils outside the pressure vessel.

The lowest isotherms of Krynicki *et al.* (1980) are also shown in Figure 2, but there are substantial differences between these data and those of Prielmeier *et al.* and ourselves, the results peaking at pressures lower than are found here and declining more rapidly with increasing pressure. The reasons for the differences are not clear, particularly as their 25 °C isotherm is consistent with our results. Krynicki *et al.* also used the steady gradient technique, but with Helmholtz gradient coils external to their pressure vessel. They calibrated these coils using the positions of the zeros of the echoes produced with different gradient currents and checked with an independent measurement on benzene, which was within 0.5% of the accepted value. No allowance appears to have been made for the background magnetic field inhomogeneity of the electromagnet which can give rise to systematic errors in steady gradient measurements where only the pulse separation is varied. It is preferable, where possible, to check these with constant pulse separation, variable gradient runs, where any background contribution can readily be determined. Nevertheless, there is no obvious reason why the effect of gradient inhomogeneity, if present in this case, should have been pressure dependent. It is possible that the use of mercury to separate the sample from the hydraulic fluid in the apparatus of Krynicki *et al.* may have affected the rf tuning or the gradient field as the temperature and pressure were varied and the mercury level changed in response, but this is speculation on our part. However, in view of the general agreement between our data and those of Prielmeier *et al.*, it seems likely that the results of Krynicki *et al.* (1980) are in error below 25 °C.

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