

Pressure dependence of NMR proton spin-lattice relaxation times and shear viscosity in liquid water in the temperature range -15 – 10°C *

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The NMR proton spin-lattice relaxation times T_1 and shear viscosities have been measured as functions of pressure in the temperature interval -15 – 10°C . At low temperatures the low pressure boundary of the experiments is ice I, whereas ice V represents the high pressure extreme of our measurements. The initial compression at all temperatures covered in our study results in higher motional freedom of water molecules so that the pressure dependence exhibits a minimum in viscosity and a maximum in T_1 . This is a consequence of significant distortion of the hydrogen bond network due to compression which also seems to weaken the hydrogen bonds. Further compression leads to restricted motional freedom due to increased packing of the molecules. This anomalous behavior of spin-lattice relaxation and shear viscosity with compression is more pronounced at lower temperatures since the hydrogen bond network is better developed at lower temperatures. In agreement with our earlier data covering the 10 – 90°C temperature range, we find that compression under isothermal conditions distorts the random hydrogen bond network, leading to diminished coupling between the rotational and translational motions of water molecules. The data indicate that the Debye equation describes the relationship between the reorientational correlation time and shear viscosity at constant volume but is not applicable to describe the density effects on water reorientation. In general, pressure and temperature have parallel effects on many dynamic properties at temperatures below 40°C and pressures below 2 kbar, whereas at higher temperatures and pressures their effects are just the opposite. Hard core repulsive interactions become more important than the directional interactions of hydrogen bonding at high compression.

I. INTRODUCTION

Our earlier high pressure NMR studies^{1,2} of liquid water have demonstrated that the most interesting behavior of various transport and relaxation properties with compression occur at temperatures of 10° and 30°C . Taking advantage of the phase diagram of water as shown in Fig. 1, we decided to measure shear viscosity η and the NMR proton spin-lattice relaxation time T_1 under experimental conditions of P and T denoted by the shaded area in Fig. 1. The temperature range studied was -15° to 10°C , and highest pressure was 6 kbar. According to our best knowledge, the measurement of self-diffusion of water to 2380 bar and to -20°C as reported by Angel *et al.*⁴ represents the only other high pressure study of water transport properties at low temperatures. However, there have been numerous experiments dealing with various properties of supercooled water at atmospheric pressure.⁵⁻⁹

There are several purposes of our study: first, to find whether the anomalous behavior of proton T_1 and shear viscosity with initial compression of liquid water is also present at temperatures below 0°C ; second, to confirm whether the Debye equation is valid under isochoric conditions in this temperature range and whether change in density causes this relationship to fail. Third, by studying T_1 and η under experimental conditions where the extremes at low and high pressures are the ice I and ice V we hope to gain more information about the dynamic structure of water at low temperatures. Another motivation was the finding of our earlier study¹ that compression diminishes the coupling between the rotational and translational motions of water molecules due to changes in the hydrogen bond

network. We were interested in whether water exhibits similar behavior at temperatures below 0°C .

II. EXPERIMENTAL

A. NMR measurements

The high pressure, pulsed NMR spectrometer used is described elsewhere.¹⁰ The high pressure was generated with Enerpac handpumps and was measured with a Heise bourdon pressure gauge with an estimated accuracy of ± 0.05 kbar. Pressure was transmitted to the titanium pressure vessel using CS_2 as the pressurizing fluid. The Lauda K-70R Ultra-Kryomat was used to cool the sample via methanol circulating through a jacket surrounding the pressure vessel. The temperature of the sample was measured with a copper/constantan thermocouple placed inside the pressure vessel near the water sample. The sample was kept within $\pm 0.2^{\circ}\text{C}$ of the nominal temperature.

The spin-lattice relaxation times were measured using the 180° – τ – 90° sequence to an estimated accuracy of $\pm 3\%$ with an automated system. The NMR spectrometer was run by a PDP/8 computer which was interfaced with the pulse programmer, Fabritek 1074 computer averager, and the RF transmitter. Optimization of pulse lengths and phase as well as measurement of T_1 was done automatically by the computer as described in detail elsewhere.¹¹

B. Viscosity

The viscosity of water was measured using a rolling ball viscometer as described previously.¹² The viscometer was calibrated using the 10°C , 0–6 kbar data of

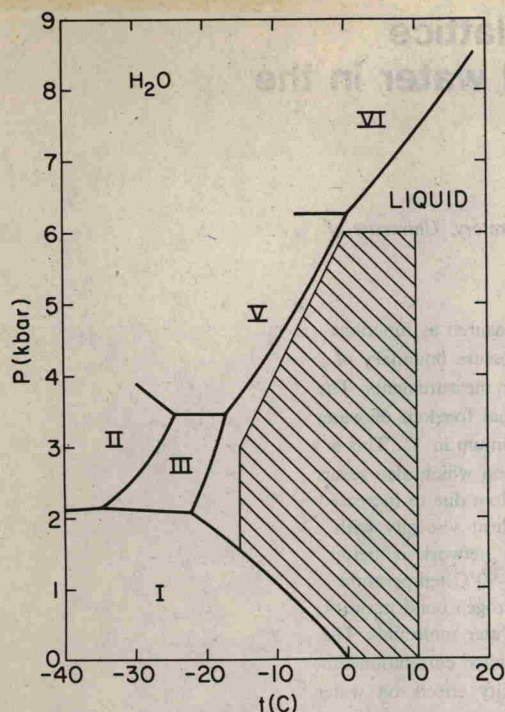


FIG. 1. Phase diagram for H₂O (Ref. 3). The range of pressures and temperatures of our measurements denoted by shaded area.

Harlow.¹³ The viscosities have an estimated accuracy of $\pm 2\%$.

C. Sample preparation

Samples of distilled deionized water were degassed in quartz tubes by the freeze-pump-thaw technique. The liquid was then loaded into the Pyrex tube-stainless steel bellows sample cell in an oxygen-free argon glove box.

III. RESULTS AND DISCUSSION

The experimental shear viscosities and proton spin-lattice relaxation times are given in Table I. The results of shear viscosity measurements are shown in Fig. 2. The η values of water at 2.2 °C reported by Bett and Cappi¹⁴ are included in Fig. 2 as a check of the accuracy of our η vs pressure dependence. Their values appear between our 0° and 5° C values, and the agreement is excellent. Hindman⁷ used a double exponential form of a rate expression to fit the measured viscosities in H₂O by various authors. Since points below 0 °C represent supercooled data, we have plotted them as 1 bar values. They are in good agreement with extrapolated values of our measurement of individual isotherms. It is interesting to note that Bruges and Gibson's¹⁵ expression which correlated viscosity vs pressure data above 0 °C can be successfully used to predict viscosities at temperatures below 0 °C. Our experimental viscosities agree well with those calculated by the correlation equations as given by Bruges and Gibson. One finds agreement at 0° and -5 °C to within 1%; at -10 °C, 2%; and at -15 °C, 3%. Since the equation is based on viscosities at temperatures

above 0 °C, it is not surprising that the deviation of predicted values from the experimental ones increases with decreasing temperature.

The spin-lattice relaxation times of H₂O are shown in Fig. 3. The low temperature, supercooled values measured by Hindman *et al.*⁶ are shown on the plot as 1 bar points. They agree very well with our measure-

TABLE I. Experimental shear viscosities and spin-lattice relaxation times T_1 in liquid water.^a

t (°C)	P (kbar)	ρ (g/cm ³) ^b	η (cP)	T_1 (sec)
10°	0.001	1.000	1.30	2.35
	1	1.042	1.27	2.52
	1.22	1.050	1.27	2.55
	2	1.078	1.29	2.59
	2.79	1.100	1.34	2.58
	3	1.106	1.36	2.57
	4	1.131	1.46	2.48
5°	4.83	1.150	1.58	2.40
	5	1.154	1.60	2.38
	6	...	1.77	...
0°	0.001	1.001	1.53	2.00
	1	1.043	1.44	2.21
	1.19	1.050	1.44	2.23
	2	1.079	1.46	2.27
	2.75	1.100	1.51	2.23
	3	1.107	1.54	2.22
	4	1.133	1.67	2.14
-5°	4.77	1.150	1.78	2.07
	5	1.155	1.83	2.04
	6	...	2.03	...
-10°	0.001	1.000	(1.80) ^c	(1.69)
	1	1.044	1.64	1.92
	1.17	1.050	1.64	1.93
	2	1.080	1.65	1.96
	2.69	1.100	1.72	1.93
	3	1.109	1.76	1.92
	4	1.135	1.90	1.84
-15°	4.68	1.150	2.02	1.77
	5	1.157	2.09	1.74
	6	...	2.31	...
-20°	1	1.045	1.91	1.61
	1.14	1.050	1.91	1.63
	2	1.081	1.92	1.68
	2.63	1.100	1.98	1.66
	3	1.111	2.03	1.64
	4	1.137	2.21	1.55
	4.57	1.150	2.35	1.49
-25°	5	1.160	2.45	1.44
	1	(1.046)	2.29	(1.36)
	1.11	1.050	2.27	(1.38)
	2	1.083	2.26	1.45
	2.55	1.100	2.33	1.43
	3	1.114	2.43	1.40
	4	1.140	2.68	1.29
-30°	4.38	1.150	(2.80)	(1.24)
	1	(1.047)	(2.77)	(1.08)
	1.08	(1.050)	(2.75)	(1.09)
	2	1.085	2.71	1.18
	2.48	1.100	2.80	1.18
	3	1.116	2.96	1.14

^aValues obtained by best-fit of experimental data.

^bReference 24.

^cValues in parentheses denote extrapolated values.