

Pressure and temperature dependence of the longitudinal proton relaxation times in supercooled water to -87°C and 2500 bar

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The longitudinal proton relaxation times T_1 of the water protons have been determined at 100.1 MHz in the temperature range from $+20$ to -87°C and up to pressures of 2500 bar. At temperatures below $+10^{\circ}\text{C}$, the T_1 isotherms exhibit a maximum at pressures between 1.5 and 2 kbar. While at $+10$ and 0°C , T_1 rises by $\sim 10\%$ from its atmospheric pressure value, this maximum becomes much more pronounced between -20 and -45°C . In this region application of pressure increases T_1 by $\sim 100\%$. The isobars at 2 kbar and above run through a minimum at -76°C , indicating that at this temperature $\omega\tau_{\theta} \approx 1$ and that the proton relaxation rate cannot be described by the extreme narrowing condition below $\sim -40^{\circ}\text{C}$. The experimental T_1 data and the τ_{θ} values derived at 2 kbar could be treated by a sum of two exponentials. While the smaller activation energies derived from this fit of 3.44 ± 0.17 kcal mole $^{-1}$ is independent of pressure, the higher activation energy decreases from 13 ± 0.65 kcal mole $^{-1}$ at atmospheric pressure to 9.3 ± 0.5 kcal mole $^{-1}$ around 1 kbar and then remains independent of pressure to 2.5 kbar. The data are qualitatively discussed in terms of a random hydrogen-bond network.

INTRODUCTION

At low temperatures, liquid water reveals anomalies in its thermodynamic and transport properties, and it may be expected that these anomalies become more pronounced in the supercooled state. Experiments in this supercooled region thus should allow conclusions about the structural features in the thermodynamically stable temperature range of the liquid.

Rasmussen and McKenzie¹ showed that water emulgated in cycloalkanes is easily supercooled down to -38°C , where homogeneous nucleation occurs under atmospheric pressure. Kanno *et al.*² found that the homogeneous nucleation temperature (T_H) of water decreases down to -92°C under application of pressure up to 2 kbar. Application of even higher pressure leads to an increase of the T_H - P curve with an initial slope of approximately 8 (K kbar $^{-1}$).

Though the emulgation technique makes the preparation of metastable supercooled liquid water rather uncomplicated, there are only a few spectroscopic techniques that can be applied to such emulsions. Among these, nuclear magnetic resonance appears the most promising. At atmospheric pressure, measurements of the longitudinal relaxation rates of the protons of water have been published by Hindman *et al.*³ for the temperature interval from -16 to $+145^{\circ}\text{C}$. Hindman *et al.*⁴ supplemented these data by studies on ^{17}O and ^2H relaxation over the temperature interval from -18 to $+178^{\circ}\text{C}$. Hindman⁵ also performed measurements of T_1 for oxygen-17 enriched water in *n*-heptane emulsions in the supercooled region down to -31°C .

Hertz and Rädle⁶ investigated the proton relaxation of water at 0, 30, and 75°C up to 3 kbar. Recently, Jonas *et al.*⁷ extended their measurements at 10, 30, and 90°C up to 9 kbar, and DeFries and Jonas¹⁹ measured T_1 in the temperature range $+10$ to -15°C and pressures up to 6 kbar. In our communication we present proton re-

laxation studies on water in the temperature range $+20$ to -87°C at pressures up to 2.5 kbar.

EXPERIMENTAL

The longitudinal relaxation times T_1 of the protons were obtained on a Varian XL-100-15-FT-NMR spectrometer interfaced to a 16 K-Varian 620-100 computer by a t_1 - 90° - t_2 - 180° - t_1 - 90° pulse sequence. The emulsions were contained in a high pressure glass capillary with i. d. 1.5 mm and o. d. 7 mm. Details of the apparatus have been described elsewhere.^{8,9}

By careful selection of the capillaries we were able to extend the experiments to pressures up to 2.5 kbar. The pressures were measured by a precision Bourdon gauge (Heise, Newton, CT) to ± 5 bar and generated with standard $\frac{1}{8}$ in. equipment (HIP, Erie, PA). The temperatures were determined to ± 0.5 K by a chromel-alumel thermocouple.

The samples were prepared with triply distilled water emulgated in a mixture of 50% w/w methylcyclohexane and 50% w/w methylcyclopentane (E. Merck, Darmstadt, BRD). To stabilize the emulsions 3% w/w of an emulgator (Span 65, Serva, Heidelberg, BRD) were added to the cycloalkanes. The components were degassed carefully on a high vacuum line by at least five freeze-pump-thaw cycles to a final pressure of 7 mPa. The emulsions were prepared by either pressing the degassed liquids with oxygen-free argon through several layers of a stainless steel net (635 mesh, Spörl & Co., Sigmaringendorf, BRD) or by rigorously slashing the mixture through a stainless steel net of the same fabric in a sealed glass tube. Inspection of the emulsions under the microscope gave an average diameter for the water droplets of $6 \mu\text{m}$.

Comparison of the T_1 values obtained in the water emulsions with the results found by other authors^{3,6,7,10,19} proved that the samples were free of oxygen.

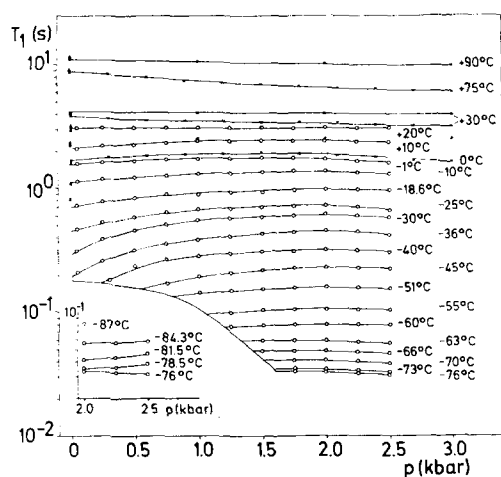


FIG. 1. Pressure and temperature dependence of the longitudinal relaxation times T_1 of the water protons. The results obtained between -76 and -87°C are shown in the insert in the lower left corner of the figure. Our results: Open circles, Hertz and Rädle⁶; crosses, Jonas *et al.*⁷; full circles, Hindman *et al.*³; full triangles, Hausser.¹⁴

The T_1 values were either determined along isotherms by raising the pressure in steps of 250 bar or along isobars by varying the temperature. Within experimental error full agreement was found in the different runs.

Especially in the vicinity of the T_H - P curve, the emulsions tend to crystallize partially. The amount of crystallization varied, presumably depending on the quality of the emulsions, from 20%–80%, as judged from the area under the water proton absorption peak. However, after a few minutes at a fixed temperature and pressure the rate of crystallization slowed down sufficiently to allow the determination of T_1 . The T_1 obtained did not depend on the degree of intensity loss. This was controlled by reheating the partially crystallized emulsion and re-determination of T_1 at higher temperatures. The T_1 data are judged reliable to $\pm 5\%$; their reproducibility was better than $\pm 3\%$.

THEORETICAL

In the case of proton T_1 in water only dipolar interactions and spin-rotation interactions must be considered. As shown by Smith and Powles,¹¹ the spin-rotation contribution to the proton relaxation rate is estimated to be 0.003 sec^{-1} at 90°C , 1 bar and even less at lower temperatures and higher pressures, and therefore can be neglected. Only the inter- and intramolecular dipolar contributions to the observed proton relaxation rate have to be taken into account:

$$\left(\frac{1}{T_1}\right)_{\text{obs}} = \left(\frac{1}{T_1}\right)_{\text{intra}} + \left(\frac{1}{T_1}\right)_{\text{inter}} \quad (1)$$

The intramolecular dipolar contribution is given by¹²

$$\left(\frac{1}{T_1}\right)_{\text{intra}} = \frac{3\gamma^4 \hbar^2}{10\tau^6} \left(\frac{\tau_\theta}{1 + \omega_0^2 \tau_\theta^2} + \frac{4\tau_\theta}{1 + 4\omega_0^2 \tau_\theta^2} \right), \quad (2)$$

where γ is the proton gyromagnetic ratio; \hbar is Planck's constant divided by 2π ; τ is the distance between the hydrogens in a water molecule; τ_θ is the reorientational

correlation time; and ω_0 is the resonance frequency of the proton. At and around room temperature, τ_θ is sufficiently small, so that $\omega_0 \tau_\theta \ll 1$. In this region, Eq. (2) reduces to

$$\left(\frac{1}{T_1}\right)_{\text{intra}} = \frac{3\gamma^4 \hbar^2}{2\tau^6} \tau_\theta \quad (3)$$

This situation is often referred to as the extreme narrowing limit; here the intramolecular relaxation rate is frequency independent. In the case, $\omega_0 \tau_\theta \geq 1$ the relaxation rate becomes frequency dependent.

The intermolecular dipolar contribution to the proton T_1 , which includes both translational and reorientational effects, can be calculated from an expression introduced by Hubbard,¹³

$$\left(\frac{1}{T_1}\right)_{\text{inter}} = \frac{6N\pi^2 \gamma^4 \hbar^2 \eta}{5kT} \left[1 + 0.233 \left(\frac{b}{a}\right)^2 + 0.15 \left(\frac{b}{a}\right)^4 \right], \quad (4)$$

where N is the number of spins per unit volume, a is the hydrodynamic radius, b is the distance of the proton from the center of the molecule, k is the Boltzmann factor, and η is the shear viscosity of the liquid. The Hubbard correction, given in brackets, is a contribution to the relaxation caused by the rotation of neighboring molecules. One should be aware that severe assumptions are made here, namely, that

- the extreme narrowing limit is at least approximately valid;
- only translational motion is taken into account;
- the distribution of molecules around a given molecule is uniform.

Similar formulas could be derived, as discussed by Krynicki,¹⁰ if the radial distribution function for water were known; but these data are lacking for supercooled water at high pressures.

RESULTS

Figure 1 contains the longitudinal relaxation times T_1 of the water protons taken at elevated pressures between $+90$ and -87°C .

Figure 1 also includes part of the results by Jonas *et al.*⁷ obtained at 90, 30, and 10°C and elevated pressures (full circles).

The isotherms by Hertz and Rädle⁶ at 75, 30, and 0°C are also given (crosses). It should be noted that the pronounced decrease of the T_1 values in the 75 and 30°C isotherms found by Hertz and Rädle is not corroborated by the data from Jonas *et al.*⁷ and our results. The 0°C isotherms by Hertz and Rädle and the data from Jonas *et al.* and DeFries and Jonas agree well with our T_1 values. Except for the differences mentioned above, our data, obtained in emulsions, are within experimental error the same as those measured in bulk liquid water. This bears out the view that the emulsification does not influence the T_1 values. The same holds for the atmospheric pressure results from Hausser¹⁴ and Hindman *et al.*³ down to the supercooled region to -16°C (full triangles). The anomalous increase of T_1 with pressure is first observed in the $+10^\circ\text{C}$ isotherm. In this isotherm

TABLE I. Experimental longitudinal relaxation times (sec) of the water protons.^a

$T \backslash P$	50	250	500	750	1000	1250	1500	1750	2000	2250	2500									
20	3.10	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1									
10	2.10	2.20	2.25	2.35	2.40	2.45	2.45	2.45	2.43	2.41	2.40									
-1	1.60	1.65	1.67	1.70	1.73	1.76	1.80	1.77	1.72	1.66	1.62									
-10	1.14	1.20	1.23	1.26	1.31	1.33	1.37	1.37	1.39	1.35	1.32									
-18.6	0.75	0.79	0.84	0.90	0.90	0.94	0.95	0.98	0.98	0.98	0.97									
-25	0.47	0.53	0.57	0.64	0.67	0.69	0.71	0.73	0.74	0.71	0.67									
-30	0.32	0.39	0.46	0.50	0.52	0.58	0.59	0.60	0.62	0.61	0.59									
-36	0.20	0.26	0.32	0.36	0.38	0.41	0.43	0.45	0.46	0.45	0.42									
-40	300 bar																			
		0.18	0.24	0.27	0.29	0.30	0.31	0.32	0.33	0.32	0.31									
-45				0.17	0.20	0.21	0.22	0.23	0.23	0.23	0.22									
-51					0.14	0.15	0.145	0.157	0.16	0.158	0.156									
-55						0.010	0.105	0.106	0.105	0.105	0.106									
-60							0.077	0.079	0.079	0.080	0.080									
-63								0.059	0.059	0.058	0.056									
-66									0.049	0.048	0.046									
-70										0.041	0.037									
-73											0.035									
-76												0.033								
-78.5													0.035							
-81.5														0.036						
-84.3															0.041					
-87																0.043				
																	0.056			
																		0.057		
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																				0.081

^aP-Pressure (bar); T=Temperature (°C).

and around 0 °C the maximum of T_1 occurs at 1.5 kbar, where T_1^{\max} is ~10% higher than the atmospheric pressure value.

In the isotherms between -25 and -40 °C this anomaly is considerably more pronounced. At -30 °C, T_1 increases by approximately 100% in the pressure region between 1 bar and 2 kbar. The occurrence of homogeneous nucleation does not allow the full isotherms to be taken at temperatures below -38 °C. In the low temperature region below -65 °C it appears, however, that water behaves like a normal liquid with T_1 slightly decreasing with pressure. Until -76 °C the values of T_1 decrease with falling temperature. A further decrease of temperature leads then to an increase of T_1 . The minimum of T_1 is best visible in the 2 kbar isobar given in Fig. 4.

DISCUSSION

As stated in the theoretical section, the contributions from intra- and intermolecular relaxation processes have to be taken into account for the explanation of the anomalous curvature of the isotherms. Since one cannot separate these two processes from proton relaxation data alone with sufficient accuracy, we abstain from a detailed analysis of the isotherms in the following and discuss only the isobars.

Two procedures have been proposed to fit the T_1 isobars in the extreme narrowing limit. Hindman³⁻⁵ used a four parameter fit in the form of two exponentials:

$$-\ln T_1 = \ln(ae^{b/T} + ce^{d/T}). \quad (5)$$

Speedy and Angell¹⁵ could fit the data with only three parameters with an equation of the form

$$T_1 = A\epsilon^\gamma \quad \text{where } \epsilon = \frac{T - T_s}{T_s}, \quad (6)$$

and suggested that T_s may correspond to the limit of mechanical stability for the supercooled liquid phase. However, in the case of the proton T_1 values, Speedy and Angell could only make use of the data at atmospheric pressure. Under this condition we could reproduce our results by the procedure proposed. However, we did not succeed in describing the T_1 values at elevated pressures with any T_s in the vicinity of the T_H - P curve. Consequently we attempted to fit our T_1 isobars in the range of the extreme narrowing limit by the procedure proposed by Hindman.

The parameters obtained from this analysis are given in Table I and Fig. 2. At atmospheric pressures the results agree closely with the data obtained by Hindman. The lower activation energy is with 3.44 ± 0.17 kcal mole⁻¹ almost independent of pressure while the higher

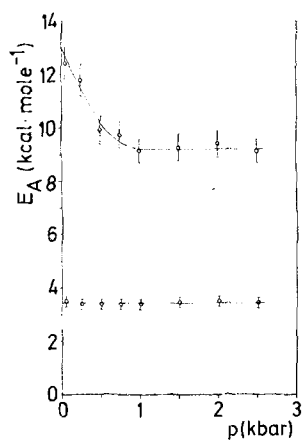


FIG. 2. Activation energies E_A obtained from the fitting of the proton T_1 isobars with two exponentials as a function of pressure.

activation energy decreases from 13 ± 0.65 kcal mole⁻¹ to 9.3 ± 0.5 kcal mole⁻¹ in the pressure range from 1 bar to 1 kbar and stays independent of pressure at 9.3 ± 0.5 kcal mole⁻¹ between 1 kbar and 2.5 kbar. As pointed out in the theoretical section, the proton relaxation times at and beneath room temperature can be described by two dipolar contributions: the intramolecular relaxation rate and the intermolecular relaxation rate.

Without additional data or assumptions it is impossible to separate these two contributions. At atmospheric pressure Hindman³⁻⁵ could use relaxation data from deuterium, and oxygen-17-enriched water samples as well as viscosity, density, and diffusion coefficient results. At elevated pressures Jonas *et al.*⁷ made use of viscosity and density data available in the region of their work and calculated the reorientational correlation time τ_θ as a function of temperature and density. There is little hope that viscosity or diffusion data can be obtained in the supercooled emulsions, therefore one has to rely on the few results available. To get some information about the motional behavior of the water molecules, we first attempted to determine τ_θ values at atmospheric pressure by computing $\rho(T)$ and $\eta(T)$ with the formulas given by Speedy and Angell¹⁴ and inserting these in Eq. (4) to

evaluate $(1/T_1)_{\text{inter}}$. Then with Eqs. (1) and (2) one can compute $\tau_\theta(T)$ at atmospheric pressure. Furthermore, τ_θ values at 2 kbar can be obtained as follows: For the minimum of the T_1 - T curve, as given for the 2 kbar isobar in Fig. 4, τ_θ can be calculated by $\omega_0\tau_\theta \approx 1$ with $\omega_0 = 6.28 \times 10^8$ (Hz) yielding $\tau_\theta = 1.6 \times 10^{-9}$ (sec). Inserting this value into Eq. (2) and taking the same proton-proton distance as used in the evaluation of the higher temperature results $r_{\text{H-H}} = 0.152$ nm gives the result that at $\sim -76^\circ\text{C}$ T_1 can within experimental error be described by the rotational intramolecular motion alone. Further τ_θ values can be taken from Jonas *et al.*⁷ or calculated from a safe extrapolation of the density and viscosity data down to -15°C . These data and the τ_θ obtained at -76°C were then also fitted by two exponentials, the parameters of which are given in Table II, and the results obtained for 2 kbar and 1 bar shown in Fig. 3. The data thus obtained have been inserted into Eqs. (2) or (3), respectively, and $(T_1)_{\text{intra}}$ determined. The result is given in Fig. 4 (dotted line).

The conclusion to be drawn is that the translational diffusion of a single water molecule decreases faster with falling temperature than the rotational motion. For a more quantitative analysis of the proton relaxation data, it is highly desirable to study the relaxation behavior of the deuterons in heavy water and of oxygen-17 enriched water emulsions in the same temperature and pressure range, since these nuclei relax by quadrupole induced relaxation processes. The latter statement holds especially for a more quantitative discussion of the isotherms between -10 and -50°C . The drastic increase in the mobility of the water molecules caused by application of pressure is rather unexpected and makes any extrapolation of the existing τ_θ data into the low pressure region hazardous.

CONCLUSIONS

First, it should be noted that the temperature dependence of T_1 at constant pressure ($P \geq 2$ kbar) runs through a minimum (at about -76°C). This is predicted

TABLE II. Parameters obtained from the fit of the isobars of the longitudinal relaxation times T_1 and for the 2 kbar isobar of τ_θ with $1/T_1$ (respectively, $\tau_\theta = a \exp(b/T) + c \exp(d/T)$).^a

Pressure (bar)	a	b	c	d
50	$(49 \leq 65 \leq 101) \times 10^{-5}$	1762 ± 88	$(0.05 \leq 0.16 \leq 0.6) \times 10^{-10}$	6229 ± 311
250	$(62 \leq 84 \leq 127) \times 10^{-5}$	1717 ± 86	$(0.11 \leq 0.35 \leq 1.2) \times 10^{-10}$	5957 ± 298
500	$(59 \leq 84 \leq 120) \times 10^{-5}$	1717 ± 86	$(5 \leq 14 \leq 39) \times 10^{-10}$	5000 ± 250
750	$(61 \leq 90 \leq 122) \times 10^{-5}$	1702 ± 85	$(6 \leq 18 \leq 47) \times 10^{-10}$	4910 ± 245
1000	$(58 \leq 82 \leq 117) \times 10^{-5}$	1712 ± 85	$(23 \leq 60 \leq 155) \times 10^{-10}$	4598 ± 230
1500	$(46 \leq 77 \leq 95) \times 10^{-5}$	1762 ± 88	$(10 \leq 33 \leq 70) \times 10^{-10}$	4683 ± 234
2000	$(43 \leq 75 \leq 102) \times 10^{-5}$	1762 ± 88	$(8 \leq 23 \leq 64) \times 10^{-10}$	4753 ± 238
2500	$(47 \leq 78 \leq 108) \times 10^{-5}$	1732 ± 86	$(13 \leq 40 \leq 166) \times 10^{-10}$	4612 ± 230
$\tau_{\theta/2}$ kbar	$(12 \leq 16 \leq 22) \times 10^{-15}$	1443 ± 72	$(0.03 \leq 0.8 \leq 2.2) \times 10^{-20}$	5074 ± 254

^aThe intervals of the a - and c values were estimated by inserting in Eq. (5) the maximum error of the parameters b and d . (It should be noted that the parameters a and c are very sensitive to even slight variations of the parameters b and d .)

by the general theory of spin-lattice relaxation in liquids.^{12,16,17} The behavior of the spin-lattice relaxation time T_1 can thus be discussed in a general way. The theory results in the following expression, already given in the theoretical section above,

$$\frac{1}{T_1} = c_1 \left(\frac{\tau_c}{1 + \omega^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega^2 \tau_c^2} \right), \quad (2')$$

where c_1 includes factors independent of frequency, temperature, and pressure. Therefore, when $\omega\tau_c \gg 1$, one has $T_1 \sim \omega^2 \tau_c$, and with $\omega\tau_c \ll 1$, $T_1 \sim 1/\tau_c$. Thus, in the region between these two extremes, T_1 runs through a minimum when $\omega\tau_c \approx 1$.

In normal liquids, T_1 falls with increasing pressure, since raising pressure causes an increase of the correlation time τ_c . As can be seen in Fig. 1, the proton T_1 in supercooled water presents this behavior only at pressures higher than 1.5 kbar and at temperatures above -76°C . It should be mentioned that this normal liquid behavior agrees with the predictions made in the BPP theory.¹⁸

Under these conditions, one has $\omega\tau_c < 1$ and $T_1 \sim 1/\tau_c$. On the contrary, in the temperature range -76 to -87°C , where $\omega\tau_c > 1$ and $T_1 \sim \tau_c$, T_1 must increase with raising pressure as observed experimentally. This is additional strong evidence that the minimum in T_1 vs T plot is real. Furthermore, we can deduce that the anomalous increase of T_1 with pressure in the range where $\omega\tau_c \ll 1$ means that initial compression leads to a faster motion of the water molecules. This can be seen from Fig. 3, where it is shown that the correlation time τ_c decreases with initial compression. Furthermore, one notes that above $+20^\circ\text{C}$ no pressure dependence of the correlation time can be noticed. In connection with the

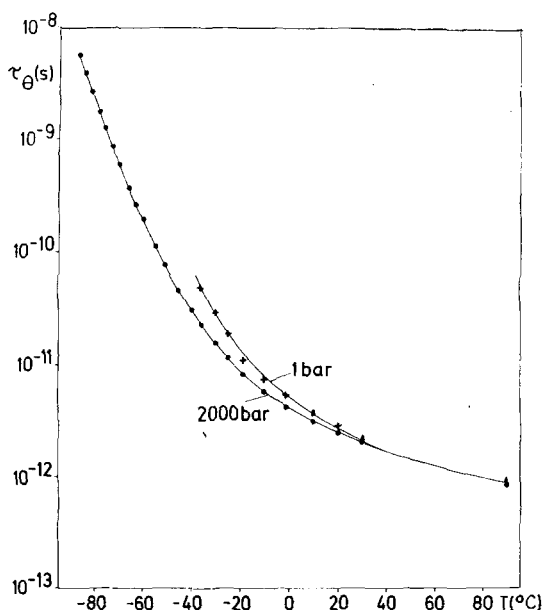


FIG. 3. Reorientational correlation times τ_θ for the intramolecular proton relaxation in water as function of temperature. \bullet , our results for the 2 kbar isobar; $+$, derived from data from Speedy and Angell as described in the text¹⁵; \blacktriangle , data from Jonas *et al.*⁷.

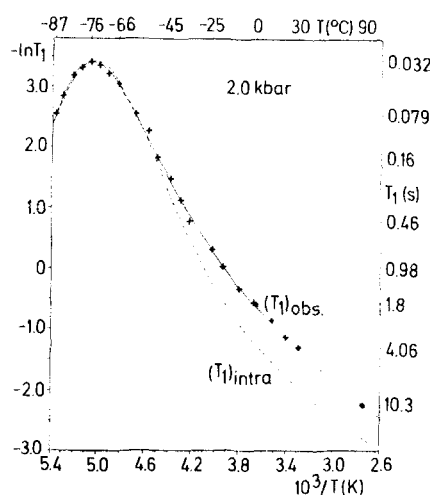


FIG. 4. 2.0 kbar isobar of the longitudinal relaxation time T_1 of the water protons. Full line: experimental relaxation times (T_1); crosses $+$: our results; diamond \diamond : results from Jonas *et al.*⁷; broken line: intramolecular relaxation times (T_1)_{intra} derived from the τ_θ results of Fig. 3. For details see text.

asymptotic behavior of Eq. (2) in the extreme narrowing limit the above statement can be obtained.

This anomalous behavior of liquid water is observed at temperatures below $+30^\circ\text{C}$ and becomes more pronounced below 0°C . Also the largest effect is obtained in the temperature range -20 to -40°C . The extension of the proton-relaxation data of water to -87°C gives considerable support to the description of the temperature dependence of either T_1 or τ_θ at constant pressure by a sum of two exponentials proposed by Hindman *et al.*³⁻⁵ The small activation energy indicates that, at high temperatures, proton spin-lattice relaxation is dominated by processes which involve the breakage of one hydrogen bond, thereby allowing the molecules to diffuse and reorient. On the other hand, the large activation energy suggests that processes where, during reorientation of the molecules, several hydrogen bonds have to be broken predominate at low temperatures. This shows that in supercooled water, a random hydrogen-bond network is fully developed at low temperatures. The decrease of the latter activation energy with increasing pressure clearly shows that initial compression disturbs the hydrogen-bond network and thus weakens the hydrogen bonds. Of course, the weakening of the hydrogen bonds facilitates the reorientation of the molecules. Therefore, the initial increase in fluidity with pressure can at least qualitatively be explained in terms of a distorted hydrogen-bond network. This view of the effect of compression on water is in agreement with the predictions from molecular dynamics calculations by Stillinger and Rahman¹⁹ and with recent results obtained by DeFries and Jonas.¹⁷

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