Pressure and Temperature Dependence of the Longitudinal Deuterium Relaxation Times in Supercooled Heavy Water to 300 MPa and 188 K

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Flüssigkeiten / Hohe Drücke / Magnetische Kernresonanz / Transporterscheinungen / Zwischenmolekulare Wechselwirkungen

The longitudinal deuteron relaxation times T_1 in heavy water have been determined at 15.4 MHz in the temperature range from $T = 283$ K to 188 K and up to pressures of 300 MPa. Between 283 K and 200 K all isotherms exhibit pronounced maxima of T_1 in the pressure range between 150 MPa and 300 MPa. This maximum is most pronounced in the 242 K isotherm, where T_1 increases more than fourfold from 17 ms at 0.1 MPa to 73 ms at 250 MPa. The 225 MPa isobar runs at 192 K through a minimum: $T_1 = 0.5$ ms. Under the assumption of isotropic reorientation one derives from the minimum condition ($\omega_0 \cdot \tau_\theta \simeq 0.62$) the deuteron quadrupole coupling constant for D_2O to $C_{DQC} = 214 \pm 12$ kHz. The isobaric temperature dependence of the correlation times τ_θ can be described at $p \geq 200$ MPa by the VTF-equation. At $p \leq 100$ MPa τ_θ increases faster with falling temperature than predicted by the VTF-equation. In this range the isobars are best represented by an equation proposed by Speedy and Angell:

$$\tau_\theta = \tau_0 \left(\frac{T - T_s}{T_s} \right)^{-\gamma} .$$

The determination of τ_θ permits an estimate of the viscosity η and the self-diffusion coefficient D for D_2O in the supercooled range. Around $T = 190$ K and $p = 225$ MPa one gets $\eta \simeq 4$ Pa · s and $D \simeq 6 \cdot 10^{-9}$ cm²/s.

Die Spin-Gitter-Relaxationszeiten T_1 der Deuteronen in schwerem Wasser wurden bei einer Meßfrequenz von 15.4 MHz in einem Temperaturintervall von 283 K bis 188 K und Drücken bis 300 MPa bestimmt. Die Isothermen zwischen $T = 283$ K und $T = 200$ K zeigen ausgeprägte Maxima bei Drücken zwischen 150 MPa und 300 MPa. Am deutlichsten zeigt sich das Maximum in der Isotherme $T = 242$ K. Die Relaxationszeit T_1 ändert sich entlang dieser Isotherme um den Faktor 4 von 17 ms bei 0.1 MPa auf 73 ms bei 250 MPa. Die 225 MPa-Isobare durchläuft ein Minimum bei $T = 192$ K und $T_1 = 0.5$ ms. Wird isotrope Rotationsdiffusion zugrunde gelegt, so erhält man aus der Bedingung für das T_1-Minimum: $\omega_0 \cdot \tau_\theta \simeq 0.62$ ohne weitere Annahme die Deuteronen Quadrupolkopplungskonstante $C_{DQC} = 214 \pm 12$ kHz. Die isobare Temperaturabhängigkeit der Orientierungskorrelationszeit τ_θ kann bei Drücken $p \geq 200$ MPa mit der VTF-Gleichung beschrieben werden. Im Druckbereich $p \leq 100$ MPa wächst τ_θ hingegen schneller, als die VTF-Gleichung vorhersagt. Eine von Speedy und Angell vorgeschlagene Gleichung liefert eine sehr gute Beschreibung der Temperaturabhängigkeit von τ_θ in diesem Druckbereich:

$$\tau_\theta = \tau_0 \left(\frac{T - T_s}{T_s} \right)^{-\gamma} .$$

Die Bestimmung von τ_θ ermöglicht eine Abschätzung der Viskosität η und des Selbstdiffusionskoeffizienten D im unterkühlten Bereich. Bei $T = 190$ K und $p = 225$ MPa erhält man $\eta \simeq 4$ [Pa · s] und $D \simeq 6 \cdot 10^{-9}$ [cm²/s].

Introduction

Liquid water can be readily supercooled after emulsification in a mixture of cycloalkanes and an emulsifier [1]. Kanno, Speedy, and Angell [2] studied in such emulsions the pressure dependence of the homogeneous nucleation temperature T_H to 300 MPa with the result, that T_H follows the general trends observed for the melting pressure curve, except that the decrease of T_H with pressure is much steeper than the decrease

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of the $T_m(p)$-curve. Fig. 1 gives a simplified version of this part of the phase diagrams of H_2O and D_2O. The whole region between $T_m(p)$ and $T_H(p)$ given there is covered by the experiments described below.

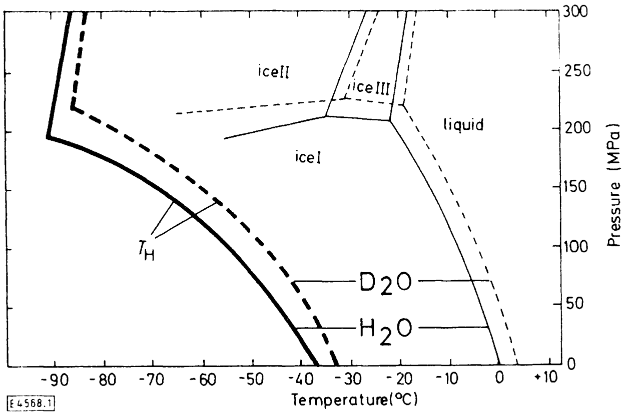


Fig. 1
Part of the phase diagrams of H_2O and D_2O showing the melting pressure curves and the pressure dependence of the homogeneous nucleation temperature T_H

In recent years a variety of physical properties of supercooled water has been studied at atmospheric pressure and these studies have revealed the unique properties of water in the metastable state [3]. Kanno and Angell [4] also succeeded in studying the compressibility of supercooled H_2O and D_2O to $T = 243$ K and pressures up to $p = 190$ MPa. The only experiments that have been extended at elevated pressures down to the respective homogeneous nucleation temperatures are to our knowledge the longitudinal proton relaxation time (T_1) studies on emulsified H_2O by the present authors [5]. In these studies it could be shown that the reorientational motions in supercooled water are slowed down by three to four orders of magnitude if water is supercooled from 270 K to 187 K.

Quantitative analysis of the proton relaxation data however is complicated, since the protons relax by dipole-dipole interaction and the relaxation rate observed is a sum of the intra- and intermolecular contributions.

These older studies are completed with the results presented here by deuterium T_1-measurements on emulsified heavy water. The deuterons of D_2O relax by quadrupole relaxation and the experimental T_1 thus contains only an intramolecular contribution. In principle it should thus be feasible to separate from an analysis of the proton and deuteron relaxation rates the intra- and intermolecular contributions to the proton T_1. However, the strong isotope effect observed, when comparing light and heavy water renders such a procedure fairly inaccurate.

The water droplets in the emulsions studied here do have an average diameter of $5 \cdot 10^{-6}$ m. It could thus be argued that in these small droplets surface effects change the behaviour of the whole aqueous phase [6]. However, previous T_1-results obtained by other authors [7–10] in the range $T_m \leq T \leq T_m + 30$ K in the bulk liquid and in emulsions as well as our own data given below do not show any systematic deviation in this region of overlap, thus proving, that the emulsification does not influence the physical properties under study.

Experimental

The spin-lattice relaxation times of the deuterons were obtained at 15.4 MHz on a Varian XL-100-15 FT-NMR spectrometer equipped with a high power pulse amplifier and interfaced to a 16 K-Varian 620-100 computer by a $\frac{\pi}{2} - T - \pi - \tau - \frac{\pi}{2}$ pulse sequence. The emulsions were contained in a high pressure glass capillary with i. d. 1.2 mm and o. d. 7 mm. Details of the high pressure equipment have been described elsewhere [11, 12]. The pressure range covered extends to 300 MPa. The applied pressure was measured by a precision Bourdon gauge (Heise, Newton, CT, USA) to ±0.5 MPa and was generated with standard $_8^1$ equipment (HIP, Erie, PA, USA). The temperatures were determined to ±0.5 K by a chromel-alumel thermocouple. The emulsions were obtained following a procedure suggested by Rasmussen and McKenzie [1]. They were prepared from triply distilled heavy water (99.75%, E. Merck, Darmstadt, BRD) emulgated in a mixture of 50% w/w methylcyclohexane and 50% w/w methylcyclopentane (E. Merck, Darmstadt, BRD). In order to stabilize the emulsions 4% w/w of an emulgator (Span65, Sorbitantristearat, Serva, Heidelberg, BRD) was 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 rigorously slashing the mixture through a stainless steel net (635 mesh, Spörl & Co., Sigmaringendorf, BRD) in a sealed glass tube. The τ_0-data were computer fitted with a standard nonlinear least squares fit program.

Theoretical

Under the conditions prevailing in our experiments the deuteron spin relaxation is dominated by its intramolecular quadrupole interaction. The time-dependence of this interaction is due to the rotational motion of the water molecules. There is no evidence for any contribution from either chemical exchange of the deuterons or from dipolar interactions. The measured spin-lattice relaxation rate $1/T_1$ of the deuterium nucleus is given in the theory of nuclear magnetic relaxation [13–15], assuming that the electric field-gradient tensor has cylindrical symmetry about the O-D bond [16, 17] by

$$\frac{1}{T_1} = \frac{3}{80}\left(\frac{e^2qQ}{\hbar}\right)^2 \{J(\omega_0) + 4J(2\omega_0)\}$$

$(e^2qQ)/\hbar$ is the deuteron quadrupole coupling constant. The spectral density functions are given by

$$J(\alpha\omega_0) = \int_{-\infty}^{\infty} G_2(\tau)\exp(i\alpha\omega_0\tau)\,d\tau$$

where $G_2(\tau)$ is the normalized correlation function of the elements of the Wigner rotation matrix of rank two [14, 15] describing the time-dependent orientation of the electric field-gradient tensor relative to the laboratory coordinate system defined by the direction of the static magnetic field. We will assume, that the motion of the molecule is isotropic and can be described by a Markov process characterized by a single correlation time τ_θ. Under these assumptions, T_1 is given by

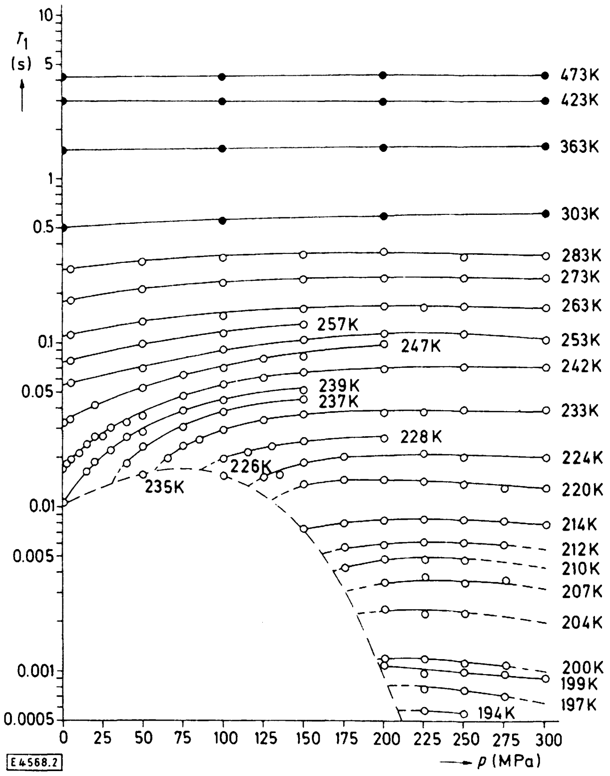
$$\frac{1}{T_1} = \frac{3}{40}\left(\frac{e^2qQ}{\hbar}\right)^2 \left\{\frac{\tau_\theta}{1 + \omega_0^2\tau_\theta^2} + \frac{4\tau_\theta}{1 + 4\omega_0^2\tau_\theta^2}\right\} \tag{1}$$

which in the extreme narrowing limit ($\omega_0^2\tau_\theta^2 \ll 1$) reduces to

$$\frac{1}{T_1} = \frac{3}{8}\left(\frac{e^2qQ}{\hbar}\right)^2 \cdot \tau_\theta \,. \tag{2}$$

Results

Fig. 2 contains the spin-lattice relaxation times of the deuterons between 283 K and 188 K and pressures up to 300 MPa. The data are also compiled in Table 1.



Comparison of our T_1-data, obtained in emulsions, with the longitudinal relaxation times T_1 by Jonas et al. [8] and DeFries et al. [9] measured in bulk liquid heavy water are within experimental error the same, corroborating the assumption that emulsification does not change the properties of the liquid water. The same holds for the atmospheric pressure results obtained in bulk and emulsified D_2O by Hindman et al. [18, 19] and our results.

Inspection of Fig. 2 shows, as has already been demonstrated [5], that the spin-lattice relaxation times in liquid water at low temperatures and low pressures behave rather anomalous compared with more normal substances like liquid ND_3 [20] and D_2S [21]. The deuteron T_1's increase with raising pressure, the increase being steepest at the lowest temperatures. This anomaly is considerably more pronounced in liquid D_2O as compared with liquid H_2O in the same temperature and pressure range. This is seen most clearly in the 239 K isotherm in D_2O, where T_1 increases by a factor ~5, whereas in the 237 K isotherm of H_2O the increase amounts only to a factor of 2.4 in the pressure range 0 – 150 MPa. In the low temperature ($T \leq 207$ K) and high pressure ($p \geq 200$ MPa) region however, water behaves like a normal viscous liquid with T_1 slightly decreasing with increasing pressure. Fig. 3 compares the 225 MPa isobars of D_2O and H_2O [5]. The minimum in the T_1-isobar, already found in H_2O, could also be detected in the case of D_2O.

Fig. 2
Pressure and temperature dependence of the longitudinal relaxation times T_1 of the deuterons in D_2O. Own results: open circles, Jonas et al. [7 – 10]: full circles

Table 1
Experimental longitudinal relaxation times T_1 (ms) of the deuterons in D_2O

p(MPa) T (K)	0,1	5	50	75	100	125	150	175	200	225	250	275	300
283	275	280	315		335		350		360		340		350
273	175	180	215		235		245		250		255		250
269	143												
264	117												
263	110	113	134		146		164		170	168	170		165
260	85												
257	76.3	78	99		115		130						
255	63												
253	54	57	70		92		104		113	116	115		105
250	42												
246	32	34.5	54	64	71	81	85		99				
243	18.6												
242	17	19.4	38	48	57		66.5		70		73		72
241	14												
239	10.3	12.2	29	38.5	45		53						
237			23.5	31	38.5		46						
235			15.5		33								
233				23.5	30	34.6	37		38	38.3	39.5		41
						130 MPa							
228					20	23.8	25.2		26.8				
224						15.5	18.8	20.5	21	21.5	20.5		20
220							13.8	15	15	14.4	13.8	13.3	13.5
214							7.4	8.1	8.4	8.5	8.4	8.3	8
212								5.72	6.0	6.25	6.2	6.0	
210								4.2	4.78	4.78	4.7		
207									3.45	3.6	3.45	3.6	
204									2.4	2.22	2.28		
202										1.75			
200									1.18	1.20	1.12	1.0	
199									1.10	0.97	1.0	0.97	0.90
197										0.79	0.77	0.72	
195										0.58	0.56		
193										0.53			
192										0.50			
190										0.55	0.62		
188										0.62			

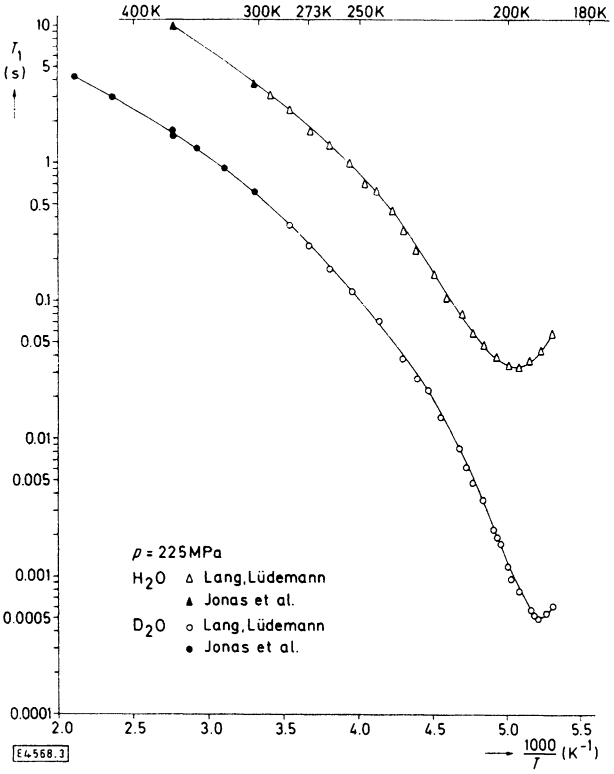


Fig. 3
225 MPa isobar of the longitudinal relaxation times T_1 of the deuterons in D_2O. For comparison the proton T_1 of H_2O [5] are included

The temperature of the minimum in D_2O is shifted by 5 K to lower temperatures ($T_{\min} = 192$ K) as compared to H_2O ($T_{\min} = 197$ K). Most unfortunately the increase of the deuterium T_1 beyond the minimum can only be measured in a short temperature interval, since it occurs in close proximity of the homogeneous nucleation temperature.

Discussion

1) Estimate of the Deuterium Quadrupole Coupling Constant (C_{DQC})

Theory predicts a minimum in Eq. (1) if $\omega_0 \tau_\theta = 0.6158$ [13, 22]. This minimum in the 225 MPa T_1-isobar can be seen in Fig. 3. Because there is no parameter left in Eq. (1) we can calculate an experimental value of the C_{DQC} without any further assumption. With $T_1 = 0.5 \pm 0.06$ msec at $T = 192$ K we get

$$\frac{e^2qQ}{h} = 214 \pm 12\,\text{kHz}.$$

Several measured or estimated C_{DQC}'s from the literature are collected for comparison in Table 2. The value obtained for the C_{DQC} is essentially the same as in the case of ice Ih. [23, 24]. This shows that the short range order in water at low temperatures must be very close to that of the crystal. As will be discussed later in this paper, the major influence of pressure is to bend the hydrogen bond angles, but changes of this angle do influence the C_{DQC} only very weakly [26]. Consequently this quantity should vary only a little in the moderate pressure range covered by our experiments.

Table 2
Comparison of the deuteron quadrupole coupling constant derived from the minimum of the $T_1(T)$-curve with data collected from the literature

D_2O	$\frac{e^2qQ}{h}$ (kHz)	η	Ref.	
Ice Ih	213.4 ± 0.3	0.112 ± 0.005	23	polycrystalline, $T = 77$ K
	213.2 ± 0.8	0.1 ± 0.002	24	single crystal, $T = 263$ K
Ice II	225.8 ± 0.3	0.127 ± 0.005	25	polycrystalline, $T = 77$ K
	219.8 ± 0.3	0.134 ± 0.005		
	226.1 ± 0.3	0.1 ± 0.005		
	220.3 ± 0.3	0.102 ± 0.005		
Ice IX	220 ± 3	0.12 ± 0.03	26	polycrystalline, $T = 77$ K
Vapour	318.6 ± 2.4	0.06 ± 0.16	27	HDO
supercooled liquid	214 ± 12		this work	$T = 192$ K, $p = 225$ MPa minimum condition of $T_1(T)$ curve isotropic reorientation
Liquid	230 ± 10		28	$\tau_\theta(^1H) = \tau_\theta(^2H)$
Liquid	208		29	$\tau_\theta(^2H) = \frac{1}{3}\tau_{diel.}$
	250			τ_{diel} with inner field correction
Liquid	258.6		18	$\tau_\theta(^2H) = \frac{1}{3}\tau_{diel}$, with inner field correction, $C_{DQC} = \text{const.}$
Liquid	230		9	Debye-equation, $C_{DQC}\,(\neq f(T)) = \text{const.}$
			8	~5% variation of C_{DQC} with density
Liquid	226 – 203		7	~10% decrease of C_{DQC} with increasing density, $C_{DQC} = \text{const.}$
Liquid	222		30	$\tau_\theta(^2H) \simeq 1.23 \cdot \tau_\theta(^1H)$
$LiCl-D_2O$ aqueous solution	230 ± 10		31	fit to Cole-Davidson distribution for τ_θ
$LiCl-D_2O$ 11 M aqueous solution	150		32	minimum condition of $T_1(T)$-curve anisotropic reorientation
THF/D_2O clathrat hydrate	215 ± 2	0.11 ± 0.01	33	$T = 37$ K
p-dioxane/D_2O clathrat hydrate	217	0.1	34	$T = 63$ K

One further comment should be made to the result obtained by Powles et al. [28]. They assumed in their analysis that the reorientational correlation times in H_2O and D_2O are the same, i. e. $\tau_\theta(^1H) = \tau_\theta(^2H)$. However, our preliminary $^{17}O - T_1$ measurements in $H_2{}^{17}O$ and $D_2{}^{17}O$ in the temperature range 243 K to 383 K and pressures up to 300 MPa show that they should transform according to the corresponding moments of inertia, i. e. the ratio of the measured ^{17}O spin-lattice relaxation times is

$$\frac{T_1(H_2{}^{17}O)}{T_1(D_2{}^{17}O)} \approx 1.3 \text{ compared to} \left(\frac{\langle I_{D_2O}\rangle}{\langle I_{H_2O}\rangle}\right)^{1/2} = 1.38\,.$$

With $\tau_\theta(^2H) = 1.3 \cdot \tau_\theta(^1H)$ their estimated value of the C_{DQC} should lower to 204 kHz which is close to our value. Different authors have claimed the C_{DQC} to be independent of temperature [9, 18] and only slightly decreasing with increasing density [8, 9, 35, 36]. We therefore assume a constant value of the C_{DQC} over the range of temperatures and pressures measured. However, with increasing temperature the $O-D...O$ distance will become larger [27, 38], and this widening of the average R_{OO}-distance must have an effect upon the C_{DQC} [16, 17, 39, 40]. It is trivial to predict qualitatively from an inspection of the results collected in Table 2 that raising the temperature should lead to an increase of the C_{DQC}. However, it is at present impossible to make any reliable quantitative estimate of this change. In the following we will therefore calculate all correlation times with the C_{DQC} derived from the T_1-minimum condition.

2) Comparison of the T_1-Minimum in the High Pressure Isobars of H_2O and D_2O

Comparing the depth of the respective minima in the H_2O and D_2O isobars offers the possibility to test the assumption underlying the interpretation of the H_2O-data in the region of the minimum of the T_1 isobar [5]. One gets for the ratio of the measured spin-lattice relaxation rates of the protons and deuterons at the corresponding minima of the 225 MPa-isobars

$$\left(\frac{1}{T_1}\right)^{H_2O}_{exp} \Big/ \left(\frac{1}{T_1}\right)^{D_2O}_{exp} = 1.56 \cdot 10^{-2}\,.$$

With $r_{HH} = 1.56$ Å and $C_{DQC} = 214$ kHz theory predicts for the ratio of the intramolecular relaxation rate of H_2O and the measured (i. e. completely intramolecular) relaxation rate of D_2O at the minimum ($\omega_0 \tau_\theta \simeq 0.6158$)

$$\left(\frac{1}{T_1}\right)^{H_2O}_{intra} \Big/ \left(\frac{1}{T_1}\right)^{D_2O}_{exp} = 1.35 \cdot 10^{-2}\,.$$

Therefore, at the minimum of the proton T_1 isobar ($p =$ 225 MPa) the intermolecular relaxation rate $\left(\frac{1}{T_1}\right)^{H_2O}_{inter}$ amounts only to about 14%, which in view of a 10% error in T_1 justifies the assumption, previously made, that almost all of the measured relaxation rate is due to intramolecular dipole-dipole interactions.

3) Temperature and Pressure Dependence of the Reorientational Correlation Times

Rotational correlation times were calculated with Eq. (2) and below 210 K with Eq. (1) and the C_{DQC} of 214 kHz derived above. Their pressure dependence reflects that of the relaxation times and in the low temperature, low pressure region shows clearly the anomalous increase in rotational mobility with raising pressure. It has been suggested, that the influence of pressure is a distortion of the hydrogen bond direction in the random hydrogen bonded network of liquid water with an accompanying weakening of the respective interaction [41]. The lower the temperature, the stronger this distortional effect of the applied pressure seems to be. This is consistent with the view that strong supercooling leads to an increased straightening of $O-H...O$-bonds in the random hydrogen bonded network and that the major effect of pressure in the low pressure region is to deform hydrogen bond angles [42, 43]. This tendency is not found at higher pressures, where water behaves like a normal viscous liquid, i. e. the molecular mobility decreases slightly with raising pressure [20]. Similar effects have been found in the case of the self-diffusion coefficient D, where diffusivity increases with

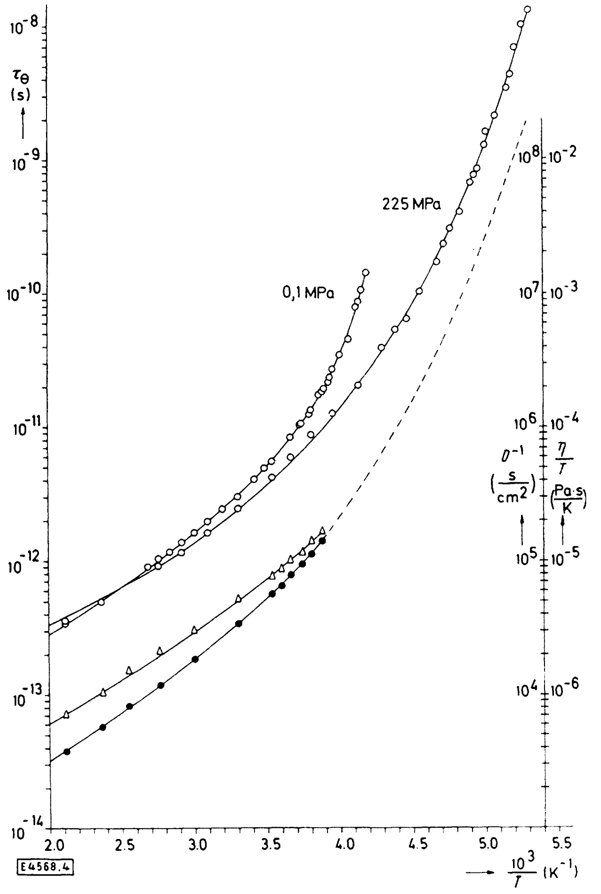


Fig. 4

0.1 MPa and 225 MPa isobars of the reorientational correlation times τ_θ (open circles). For comparison the 225 MPa isobars of D^{-1} (open triangles, D = selfdiffusion coefficient) and η/T (full circles, η = viscosity) obtained by Jonas et al. [8, 9] in the stability region of D_2O are included, together with an extrapolation of η/T to the homogeneous nucleation temperature T_H

increasing pressure as a consequence of the removal of a dominant slow component [44] and with the specific heat C_p at constant pressure which becomes insensitive to pressure at higher pressures ($p \geq 200$ MPa) [45].

At the higher pressures the temperature dependence of the reorientational correlation time is given by the VTF-equation

$$\tau_\theta = \tau_0 \cdot \exp\left(\frac{B}{T - T_0}\right) \tag{4}$$

which often describes the behaviour of viscous liquids [46, 47]. Water at pressures $p \geq 200$ MPa therefore returns to normal supercooled liquid behaviour. The temperature T_0 corresponds to an internal equilibrium low temperature limit of the liquid [47–50]. T_0 has, however, never been measured directly in the case of water because of fast crystallization occurring at the homogeneous nucleation temperature T_H. We have least squares fitted our τ_θ-data over the whole range of temperatures measured, together with data from the Refs. [7–9, 18, 19] so that in the most favorable case ($p = 225$ MPa) a temperature range extending from 473 K down to 188 K could be included. The best fit value for the ideal glass transition temperature was $T_0 = 141 \pm 2$ K in the pressure range $p = 200$ MPa – 300 MPa. At pressures below $p = 200$ MPa the parameter T_0 increases with decreasing pressure. Especially at saturation pressure the fit was much worse compared to the higher pressures. The parameter obtained by fitting τ_θ over the whole pressure range measured and temperatures from 473 K down to the respective homogeneous nucleation temperatures are collected in Table 3. The temperature dependence of τ_θ at $p = 225$ MPa and 300 MPa is plotted against $1/(T - T_0(p))$ in Figs. 5 and 6. The full line represents the VTF-equation with the parameters given in Table 3. The value of the glass transition temperature $T_0 = 141 \pm 2$ K of high pressure heavy water is close to the experimental glass transition temperature $T_g = 140$ K obtained with vapor-deposited vitreous water [45, 51] and also to that extrapolated from binary aqueous solutions, $T_g = 138 \pm 2$ K [47], but not with the $T_0 = 200$ K estimated from an analysis of

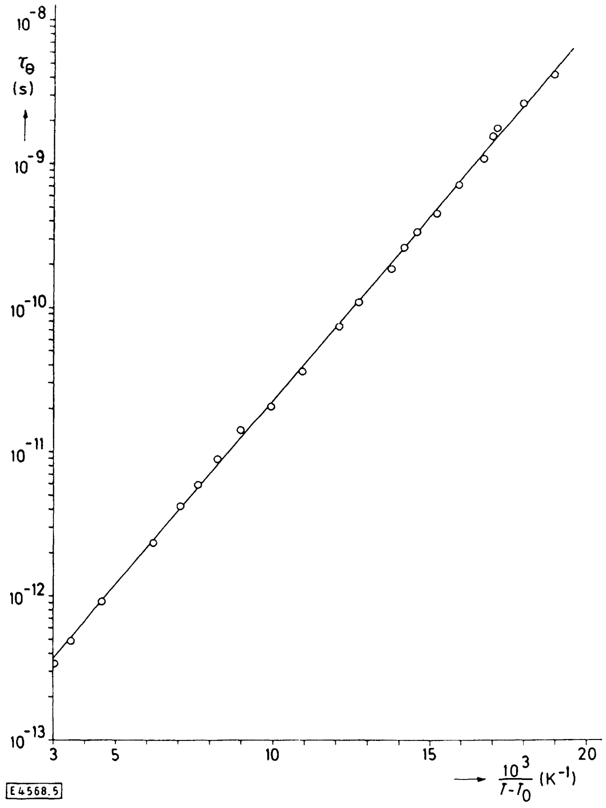


Fig. 5
Representation of the 300 MPa isobar of the reorientational correlation times τ_θ by the VTF-equation (Eq. (4)). Solid line is obtained from a least-squares fit of the data ($T_0 = 140$ K, $B = 591.3$ K, $\tau_0 = 6.26 \cdot 10^{-14}$ s)

Table 3
Parameters of the VTF-equation (Eq. (4)) obtained from the least-squares fits of the τ_θ-isobars (temperature range 473 K $\geq T \geq T_H$)

p (MPa)	T_0 (K)	B (K)	τ_0 (s)
0.1	185	373.1	$1.20 \cdot 10^{-13}$
50	165	481.5	$7.90 \cdot 10^{-14}$
100	140	640.0	$5.22 \cdot 10^{-14}$
150	133	672.5	$4.90 \cdot 10^{-14}$
200	139	604.0	$6.07 \cdot 10^{-14}$
225	141	582.3	$6.61 \cdot 10^{-14}$
250	142	563.3	$7.03 \cdot 10^{-14}$
300	140	591.3	$6.26 \cdot 10^{-14}$

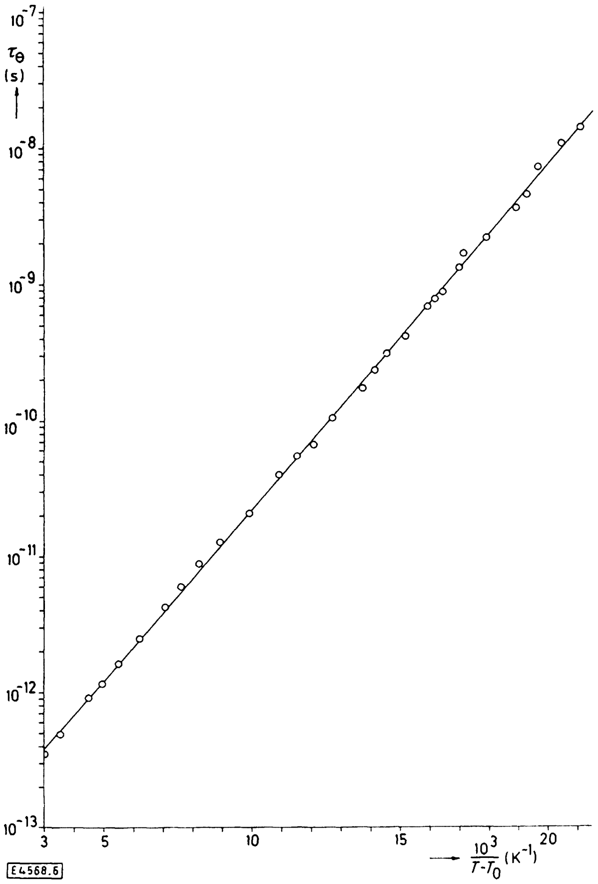


Fig. 6
Representation of the 225 MPa isobar of the reorientational correlation times τ_θ by the VTF-equation (Eq. (4)). Solid line is obtained from a least-squares fit of the data ($T_0 = 141$ K, $B = 582.3$ K, $\tau_0 = 6.61 \cdot 10^{-14}$ s)

the T-dependence of the self diffusion coefficient [52]. The preexponential factor τ_0 corresponds to a frequency of $\tilde{\nu} \approx 560\ \mathrm{cm}^{-1}$ which lies in the frequency range of the librational motions of D_2O observed in the IR and Raman spectra of heavy water [53]. These motions therefore appear to reflect the fluctuations connected with the liquid-glass transition of water. The abnormal increase of the T_0 parameter indicates that τ_0 increases in the low pressure region much faster than is predicted by the VTF-equation. This fast increase must be due to anomalous fluctuations with a much stronger temperature dependence. Thus in the low pressure region the temperature dependence of the data can only be accounted for by an equation recently proposed by Speedy and Angell [54], which gives the variation of any dynamical variable with temperature as:

$$\tau_\theta = \tau_0 \left(\frac{T - T_s}{T_s} \right)^{-\gamma} . \qquad (5)$$

The singular temperature $T_s(p)$ can, according to Angell [45] be interpreted as the boundary of the free energy surface for liquid water or as a line of metastable higher order transitions running across the free energy surface. We have least squares fitted all our τ_θ-data also with this equation. At pressures up to 100 MPa the fit was excellent, including τ_θ-values at constant pressure from 473 K down to the homogeneous nucleation temperature $T_H(p)$. In Figs. 7 and 8 τ_θ versus $(T - T_s)/T_s$ is plotted. The full line represents the best fit to Eq. (5). The best fit parameter to Eq. (5) are collected in Table 4. The 150 MPa isobar could be fitted with either Eqs. (4) or (5) with equal accuracy, whereas at higher pressures systematic deviations occurred in the fit of the data to Eq. (5). It can thus be concluded that the singular temperature T_s decreases much faster with increasing pressure than does the homogeneous nucleation temperature and that at pressures between 150 MPa and 200 MPa it falls below the glass transition temperature T_0. This indicates that the anomalous fluctuations inferred by the use of Eq. (5) are strongly suppressed with raising pressure so that at higher pressures ($p \geq 200$ MPa) the dynamics of liquid water are governed by the fluctuations connected with the liquid-glass transition. The factor τ_0 in Eq. (5) corresponds to a frequency $\tilde{\nu} \simeq 60\ \mathrm{cm}^{-1}$ which is in the region of the hydrogen bond bending motions [53]. Evidently the anomalous fluctuations grow and decay with a greater time constant and can only develop in the open hydrogen bonded network known to exist at low temperatures and low pressures in water. As the nature of the open hydrogen bonded network changes with raising pressure to closer packed forms with strongly bent bonds, these anomalous fluctuations are suppressed by fluctuations dominating the dynamic behaviour of normal viscous liquids.

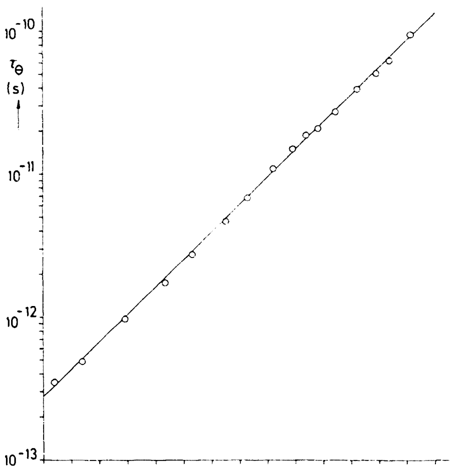


Fig. 7
Representation of the 50 MPa isobar of the reorientational correlation times τ_θ by Eq. (5). Solid line results from the least-squares fit of the τ_θ-data (T_s = 221 K, γ = 1.925, $\tau_0 = 4.23 \cdot 10^{-13}$ s)

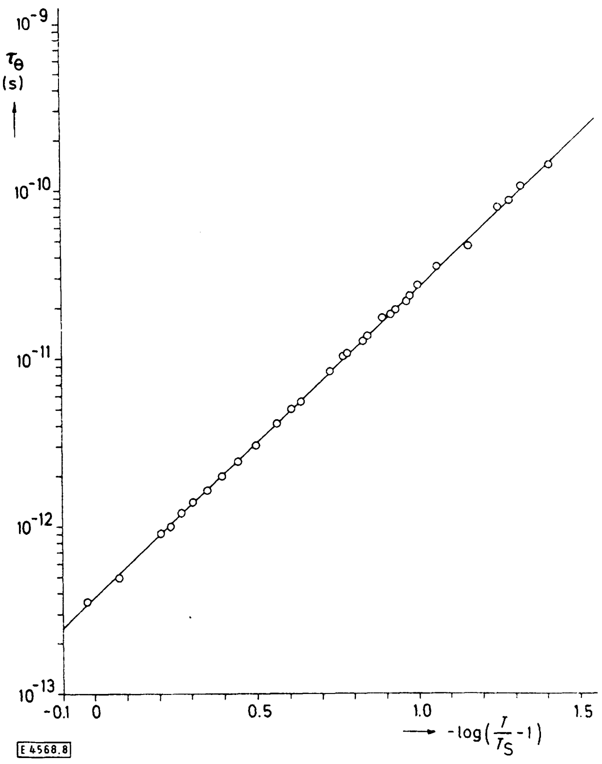


Fig. 8
Representation of the 0.1 MPa isobar of the reorientational correlation times τ_θ by Eq. (5). Solid line results from the least-squares fit of the τ_θ-data (T_s = 230 K, γ = 1.848, $\tau_0 = 3.74 \cdot 10^{-13}$ s)

Table 4
Parameters of Eq. (5) obtained from the least-squares fits of the τ_θ-isobars (temperature range 473 K $\geq T \geq T_H$)

p (MPa)	T_s (K)	γ	τ_0 (s)
0.1	230	1.848	$3.74 \cdot 10^{-13}$
50	221	1.925	$4.23 \cdot 10^{-13}$
100	207	2.172	$5.51 \cdot 10^{-13}$
150	197	2.373	$6.73 \cdot 10^{-13}$

4) Estimate of the Viscosity and the Self-Diffusion Coefficient of Water at 190 K and 225 MPa

In Fig. 4 the 0.1 MPa and 225 MPa isobars of the correlation time τ_θ are given together with the self-diffusion coefficient D and the viscosity η at 225 MPa obtained by

Jonas et al. [8, 9]. It is common practice to use the latter two physical properties in combination with τ_θ for the classification of the microdynamic behaviour of a liquid. However, there is little hope that either of the two transport coefficients can be measured for the low temperature, high pressure region of the supercooled water in the near future and the best one can do is to estimate η and D from the experimental τ_θ. If hydrodynamics can be applied, τ_θ should be proportional to $1/D$ and η/T [55]. As can be seen from an inspection of the data collected in Fig. 4 the temperature dependence of $1/D$ and η/T are not exactly parallel with each other nor parallels the τ_θ-isobar either of the two quantities. Considering the uncertainty about the correct T-dependence of the C_{DQC} the attempt to derive an extrapolation formula from the data given appears not justified. Assuming that the proportionality constant between τ_θ and $1/D$ or η/T is independent of temperature between 258 K and 188 K we can however estimate the self-diffusion coefficients and the viscosities of supercooled water at the lowest temperatures of the metastable range to $\eta \simeq 4\,\mathrm{Pa\cdot s}$ and $D \simeq 6 \cdot 10^{-9}\,\mathrm{cm^2/s}$. These figures indicate, that water does become a quite viscous liquid under these conditions, with a viscosity comparable to that of waterfree glycerol around room-temperature.

5. Conclusions

The small contribution of the intermolecular term to the dipole-dipole relaxation of supercooled water estimated from a comparison of the results obtained at the minimum of the T_1-isobars in H_2O and D_2O leads to the conclusion, that at the lowest temperatures the coordination around a central water molecule is essentially tetrahedral and that the local order of the supercooled liquid is best described by one of the low pressure phases of ice.

The increase of T_1 with pressure observed in the isotherms between 300 K and 240 K is much more pronounced for the deuterium relaxation data than for the proton results. This can only in part be explained by the compensatory effect of the intermolecular dipole-dipole relaxation contribution upon the proton T_1, which should become more efficient with increasing density. Preliminary measurements of the ^{17}O-relaxation times, which can be described completely by quadrupole relaxation and thus monitor only intramolecular contributions, in light and heavy water [56] do reveal the same trend. The major source for this difference is in our opinion that the open hydrogen bonded network characteristic of supercooled water at low pressure is, at the lowest temperatures obtainable at 0.1 MPa, more perfectly developed in D_2O than in H_2O. This conclusion is further corroborated by an inspection of the pressure dependence of the compressibility data obtained by Kanno and Angell [4] for supercooled D_2O and H_2O. At 253 K for instance, the decrease in κ_T with pressure is much more pronounced for D_2O than for H_2O. The attempts to describe the temperature dependence of the correlation times do show that the supercooled water at pressures $p \leq 100\,\mathrm{MPa}$ does reveral pronounced anomalies. τ_θ does increase faster than described by the VTF-equation and the data presented here lend considerable support to the description of the temperature dependence by Eq. (5) proposed by Speedy and Angell [54].

At pressures $p \geq 200\,\mathrm{MPa}$ water does behave like a normal supercooled liquid. The τ_θ-data are well represented by the VTF-equation and a reasonable glass temperature of $T_0 = 141 \pm 2\,\mathrm{K}$. The unique properties of water appear thus to be confined to the low temperature and low pressure region, where an open hydrogen bonded network with $O-D\cdots O$ angles close to 0 C can develop.

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Rate and Equilibrium Data for the Complex Formation of Alkali Metal Ions with the Cryptand (2,2,1) in Methanol

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Komplexverbindungen / Reaktionskinetik

The dissociation rates of complexes between alkali metal ions and the macrobicyclic ligand 4,7,13,16,21-pentaoxa-1,10-diazabicyclo-(8,8,5)-tricosane (cryptand-(2,2,1)) have been studied in methanol by stopped-flow experiments at various temperatures. The corresponding rates of formation were calculated using stability constants. Enthalpies and entropies of activation were compared with the corresponding quantities of complexation and discussed in terms of ionic size and ionic solvation. The specific dependence of decomplexation rate and stability constant on ionic radius [15] were found also for the corresponding enthalpies of activation and complexation, respectively, but the preference of Na^+ over K^+ is reversed. This fact together with the observation that the rate of dissociation of $Na(2,2,1)^+$ is enhanced by proton catalysis, led to the suggestion that the cavity radius of (2,2,1) lies between the ionic radii of Na^+ and K^+.

Die Dissoziationsgeschwindigkeit der Komplexe von Alkaliionen mit dem makrobicyclischen Liganden 4,7,13,16,21-Pentaoxa-1,10-diazabicyclo-(8,8,5)-tricosan (2,2,1) wurde in Methanol mit einem „stopped-flow"-Verfahren bei verschiedenen Temperaturen untersucht. Die Geschwindigkeitskonstante der Komplexbildung wurde aus derjenigen der Dissoziation mit Hilfe der Stabilitätskonstanten berechnet. Die Aktivierungsenthalpien und -entropien wurden mit den Reaktionsenthalpien und -entropien verglichen und die Einflüsse von Ionengröße und Ionensolvatation diskutiert. Die spezifische Abhängigkeit der Dissoziationsgeschwindigkeit und der Komplexstabilität vom Ionenradius [15] wird auch für die Aktivierungsenthalpie der Dissoziation und die Reaktionsenthalpie gefunden, jedoch mit vertauschter Reihenfolge von Na^+ und K^+. Diese Eigenschaft und die Beobachtung, daß die Dissoziationsgeschwindigkeit von $Na(2,2,1)^+$ durch Säure beschleunigt wird, lassen vermuten, daß die Größe des Hohlraumradius von (2,2,1) zwischen den Werten für die Radien von Na^+ und K^+ liegt.

Introduction

Within the continually expanding group of macrocyclic and macrobicyclic ligands which form stable complexes with metal ions, macrobicyclic diazapolyethers (cryptands) are additionally characterized by their ability to form extremely stable inclusion complexes (cryptates) with alkali and alkaline earth metal ions [1, 2] which dissociate unusually slowly. These properties facilitate a thorough investigation of complex stability [3–9] and dissociation rate constants [10–15], and, in addition, the determination of the thermodynamic functions for complex formation and for the activation process [16]. The simpler cryptands, in which the three bridges between the nitrogen atoms contain only one or two ether groups, display pronounced peak selectivities for those cations of the first or second groups of elements which are able to fill the ligand cavities, which in the complexed state are

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