p,T,c-Dependence of ^2H Spin-Lattice Relaxation Rates in Supercooled $LiCl$-D_2O Solutions

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Long-ranged structural correlations develop within the random, transient hydrogen-bonded network of liquid water at low temperatures and cause characteristic anomalies in the physical properties of supercooled water. Hydrostatic pressure suppresses these anomalies and turns liquid water into a normal viscous liquid. The addition of salt-is considered another mean to suppress long-ranged density-density correlations, hence the pressure-, temperature and composition dependence of deuterium (^2H) spin-lattice relaxation times (T_1) is reported for supercooled $LiCl$-D_2O solutions over a large range of concentration ($c \leq 11$ molal), pressure ($p \leq 226$ MPa) and temperature (180 K $\leq T \leq$ 283 K). The anomalous pressure dependence of the spin-lattice relaxation times becomes weaker with increasing salt concentration

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and vanishes at the edge of the glass forming region ($c \gtrsim 5$ molal) of these solutions. In the presence of network-breaking agents like hydrostatic pressure ($p \approx 225$ MPa) or ionic solutes ($c \gtrsim 5$ molal) the molecular motions can be slowed down sufficiently for the relaxation rate $1/T_1$ to become frequency dependent and to exhibit a maximum, the composition dependence of which is also studied. Detailed account of the p,T,c-dependence of the reorientational motions of D_2O molecules is given and conclusions are drawn regarding the influence of structure and composition on molecular motions.

Introduction

In recent years the idea has been put forward that in pure liquid water at low temperatures long-ranged structural correlations develop within the random, transient hydrogen-bonded network with increasing correlation length as implied by the behaviour of thermodynamic response functions [1] and with a slowing down of structural fluctuations as implied by the behaviour of transport and relaxation properties [2]. These cooperative phenomena are most pronounced in the supercooled range. Hydrostatic pressure or ionic solutes may be considered as network-breaking agents which act to suppress long-ranged density-density correlations and turn supercooled water into a normal viscous liquid. An experimental consequence of the study of supercooled liquids is the slowing down of molecular motions so that probes such as nuclear magnetic resonance can yield specific information concerning structure and dynamics. Nuclear magnetic relaxation time measurements bear directly upon the nature of molecular motions, which in liquids are generally far more rapid ($\sim 10^{-12}$ s) than the timescale of the NMR experiment ($\sim 10^{-7}$ s) rendering the information contained in the relaxation times rather limited. If, however, the liquid can be coerced into supercooling, molecular motions can under favorable circumstances be slowed down sufficiently and their time scale becomes comparable with the Larmor period of the nucleus under investigation.

There have been many magnetic resonance investigations of aqueous electrolyte solutions [3, 4]. These studies have been restricted mostly to limited temperature ranges, dilute solutions and ambient pressure. Only very few NMR investigations have been conducted under high hydrostatic pressure [5, 6], and only recently the glassforming ability of sufficiently concentrated aqueous electrolyte solutions [7–10] has been used to explore molecular motions over a wide range of temperatures with relaxation time measurements [11–15]. However, we are not aware of any investigation encompassing a large range of all three experimental variables p, T and c.

In this and subsequent papers we will present the results of NMR studies of molecular motions in the supercooled liquid state for a variety of aqueous electrolyte solutions. Herein, we report the p, T, c-dependence of the ^2H nuclear relaxation rate of D_2O in supercooled emulsions of $LiCl$-D_2O solutions (0.3–11 molal, 283–180 K, 0–225 MPa). The dependence of the reorientation rates of D_2O molecules on temperature, pressure and composition allow conclusions to be drawn regarding the influence of structure and the glass transition upon molecular motions.

Experimental

Solutions with composition R = 500, 166.67, 50, 16.67, 10.0, 6.25 and 4.55 ($R = n(D_2O)/n(LiCl)$) were prepared from a stock solution of the anhydrous salt (Merck, Darmstadt, Suprapur, paramagnetic impurities < 1 ppm) and D_2O (99.96%, Merck, Darmstadt). Emulsions were prepared as described earlier [16, 17] after the samples have been degassed by at least five freeze-pump-thaw cycles to remove dissolved oxygen. During the experiments the emulsions were contained in high pressure glass capillaries. The whole high pressure assembly has been described earlier [18, 19].

The relaxation times of the deuteron were obtained at 15.35 MHz on a Varian XL-100-15 FT-NMR spectrometer interfaced to a 16 K Varian 620-L 100 computer and equipped with a high power pulse amplifier. Spin lattice relaxation times have been measured by a $\frac{\pi}{2} - T - \pi - \tau - \frac{\pi}{2}$ pulse sequence with a typical pulse length of 64 µs for the 180° pulse.

The T_1 measurements are accurate to ± 5% at higher temperatures ($T \geq 220$ K) and ± 10% at the lowest temperatures. The temperatures are reliable to ± 1 K. The pressure measured with a precision Bourdon gauge (Heise, Newton, CT), is accurate to ± 0.5 MPa and was generated in standard (1/8") equipment (HIP, Erie, PA).

Results

Deuterium (^2H) spin-lattice relaxation times (T_1) have been obtained of $LiCl$-D_2O solutions with composition: $4.55 \leq R \equiv \frac{n(D_2O)}{n(LiCl)} \leq 166.7$ in the pressure range: s.p. $\leq p \leq 225$ MPa and at temperatures: $180\text{ K} \leq T \leq 283$ K. Two additional solutions with composition R = 500 and 50 have been investigated at saturation pressure (s.p.) only. Depending on composition and pressure the

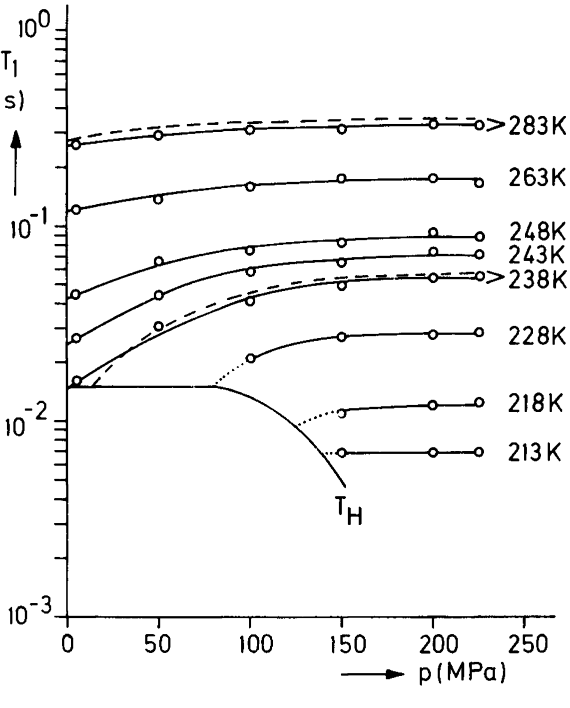

Fig. 1
Deuterium (^2H) spin-lattice relaxation time ($T_1(p,T)$) in a $c = 0.3$ molal $LiCl$-D_2O solution; – – – ^2H-T_1 in neat D_2O [16]; T_H-homogeneous nucleation temperature in a 0.3 molal $LiCl$-D_2O solution extrapolated from $T_H(p)$ in neat D_2O [58] and $T_H(c)$ at 0.1 MPa as obtained in [10] with $\Delta = T_H(0.1\text{ MPa}, c = 0) - T_H(0.1\text{ MPa}, c = 0.3)$ kept constant

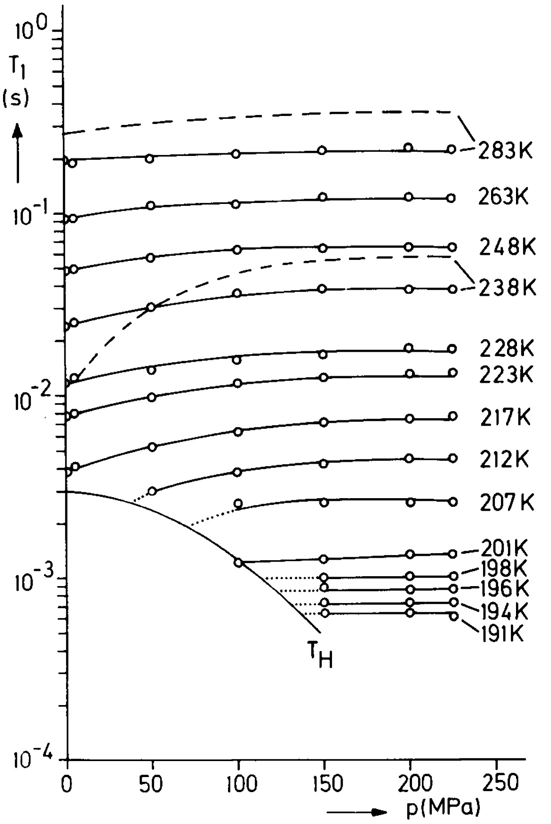

Fig. 2

Deuterium (^{2}H) spin-lattice relaxation time ($T_1(p,T)$) in a $c = 3$ molal LiCl-D$_2$O solution; — — — ^{2}H-T_1 in neat D$_2$O [16]; T_H-homogeneous nucleation temperature extrapolated as explained in Fig. 1

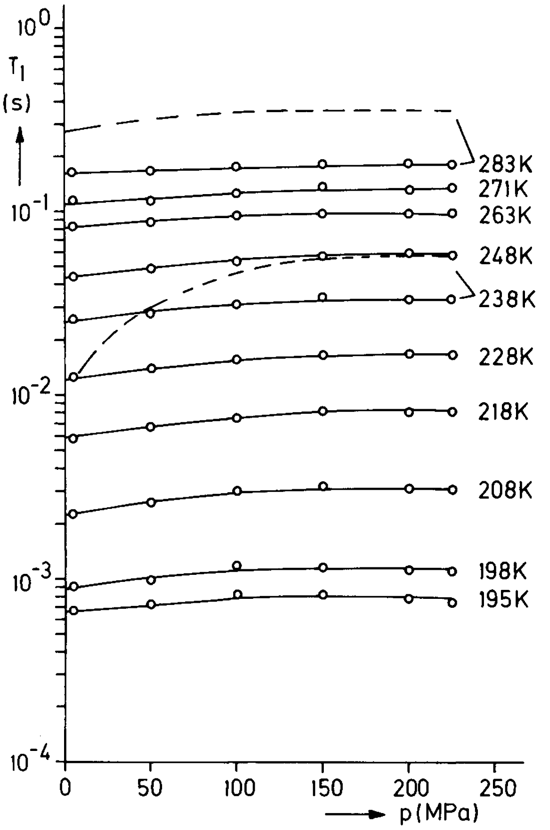

Fig. 3

Deuterium (^{2}H) spin-lattice relaxation time ($T_1(p,T)$) in a $c = 5$ molal LiCl-D$_2$O solution; — — — ^{2}H-T_1 in neat D$_2$O [16]

lowest temperature attainable was limited by the onset of homogeneous nucleation at a temperature $T_H(R,p)$. Figs. 1–3 show the isothermal pressure dependence of T_1 for the 0.3 m, 3 m and 5 m solutions. Besides decreasing with falling temperature, the relaxation time T_1 also decreases with increasing concentration in the normal liquid range at all pressures studied (compare the 283 K isotherms for example). Deeply undercooled solutions exhibit a quite different behaviour. Compared to neat D$_2$O [2, 16] at a given temperature a longer relaxation time T_1 is observed in the aqueous solutions at low pressure whereas at high pressure the ambient temperature behaviour is reconstituted. Another interesting feature to be discussed later is the anomalous positive pressure dependence of T_1. If compared at equal temperature it is seen to become progressively weaker with increasing salt concentration until it vanishes for concentrations $c \gtrsim 5$ molal. Thus this anomaly is not only shifted to lower temperatures, but is suppressed completely for compositions $R < 10$ in the temperature range investigated.

In solutions with composition $R \leq 10$ and in more dilute solutions ($R > 10$) under high pressure ($p = 225$ MPa) the dispersion region ($\omega_0\tau \approx 1$) could be reached where the spin-lattice relaxation times exhibit a minimum (see Fig. 4) and become frequency dependent. Table 1 collects the minimal T_1 ($T_1^{\min}$), the corresponding minimum temperatures $T_{\min}$ and the glass transition temperatures T_g [9, 10]. The temperatures $T_{\min}$ and T_g possess an identical composition dependence (see Fig. 5). An implication of this observation will be discussed later.

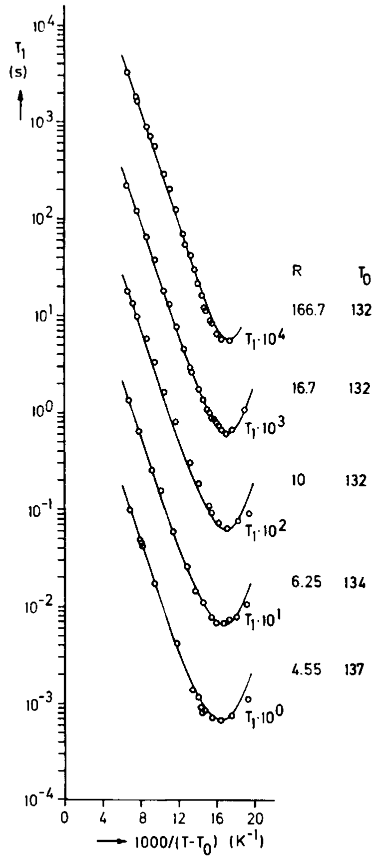

Fig. 4

Modified Arrhenius diagram of the isobaric ($p = 225$ MPa) temperature dependence of ^{2}H-T_1 at various compositions R (mole D$_2$O/mole salt);
T_0-ideal glass temperature according to the VTF-law (Eq. (11));
— The curves drawn have been calculated with Eqs. (9) and (11) inserted into Eq. (12) and the parameters given in Table 2

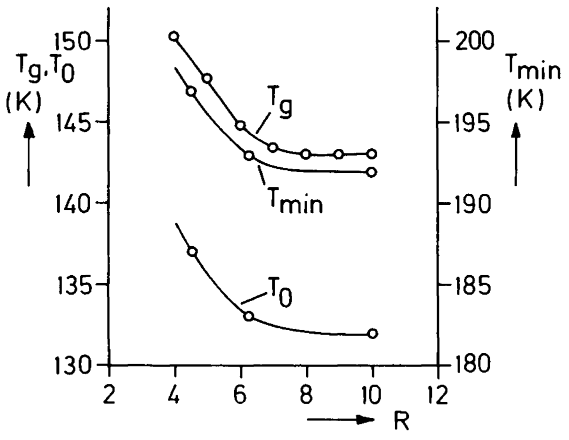

Fig. 5
Composition dependence of the glass transition temperature T_g as taken from Ref. [9], of the temperature T_{min} of the minimal spin-lattice relaxation time and of the ideal glass temperature T_0 used in the VTF-law (Eq. (11))

Table 1
Composition (R) dependence of the minimal deuterium (^{2}H) spin-lattice relaxation time T_1^{min} obtained at the temperature T_{min} and of the glass transition temperature T_g

c (molal)	0.3	3	5	8	11
R (mole D$_2$O/mole salt)	166.7	16.7	10	6.25	4.55
T_1^{min} ± 10% (ms)	0.54	0.62	0.65	0.67	0.70
T_{min} ± 2 (K)	192	192	192	194	197
T_g ± 1 (K)$^{a)}$			143	145	149

$^{a)}$ Taken from Ref. [9].

Theory

Baianu et al. [20], investigating the local structure of aqueous glasses of LiCl · RH$_2$O ($R \equiv n$(water)/n(salt): 2 – 10), concluded that the random network consists basically of Li$^+$(H$_2$O)$_4$Cl$^-$ clusters with the excess water incorporated as interstitial clusters and suggested that the average local structure in the liquid state of aqueous LiCl · RD$_2$O solutions in the same composition range is closely related to the local structure of the glassy state. We will follow this suggestion and will take advantage of the fact that the 11 m solution corresponds to a composition of 4.55 water molecules per LiCl unit. We consider these molecules to belong to the hydration sphere of the Li$^+$-cation and first seek a model description of the dynamics of water molecules hydrating the Li$^+$-cation. The parameters of the model will be obtained from a least squares fit of the ^{2}H-T_1 in the 11 m LiCl-D$_2$O solution. This approach abstains from an explicit consideration of the small influence [3] of the Cl$^-$-anions upon the dynamics of the water molecules in the Li$^+$(H$_2$O)$_4$Cl$^-$ clusters though it is certainly contained in the parameters obtained from the curve fitting excercise. In constructing a motional model of the dynamics of water molecules hydrating the cations we will rely on structural information about aqueous LiCl solutions available in the literature. From neutron scattering work on LiCl-D$_2$O solutions of Enderby and Neilson [21 – 26] the structure of the coordination sphere of the Li$^+$-cation and the Cl$^-$ anion has been deduced. According to these results the water molecules in the coordination sphere of the cation are oriented on the average with one of the lone-pair orbitals of the oxygen atoms pointing almost radially towards the cation, leading to a deviation of the dipole moment vector of the D$_2$O molecule from the radial direction of about 52° in concentrated solutions (c = 10 molal). In more dilute solutions the tilt angle decreases to ~ 40°. Adjacent to a Cl$^-$-anion a water molecule orients one of its OD-bonds radially towards the anion. Similar conclusions have been reached by Baianu et al. [20] with solid state NMR methods applied to glasses of concentrated aqueous LiCl solutions, with proton magnetic relaxation studies of 6 m aqueous LiI solutions [14] and with computer simulations of LiCl dissolved in model water [27 – 29]. Concerning dynamical information available, NMR experiments of Hertz's group [3, 30] and computer simulations [31 – 34] made clear that, at least in the case of strongly hydrated ions such as Li$^+$, there must be an internal motion of the water molecules in the hydration sphere and that the lifetime of the hydration sphere is long compared to reorientational correlation times of the water molecules. Furthermore it has been deduced from NMR relaxation studies of various aqueous alkali chloride solutions [3] that the separate influence of the Cl$^-$ anion upon the dynamics of water molecules is much smaller than the corresponding influence of strongly hydrated cations. Similar conclusions concerning the coordination sphere of Cl$^-$-anions may be drawn from computer simulations [29, 34]. Thus seeking a model description, we can decompose the orientational fluctuations of the water molecules hydrating the cation as follows [19, 36a]: The molecules execute small amplitude librations about their mean orientation. The internal motion is described as a one-dimensional diffusion of the molecule about the direction connecting the cation with the oxygen nucleus. The dipole moment vector is tilted away from this direction by an angle θ = 52° in highly concentrated solutions. In addition to these internal modes the hydration complex is assumed to tumble around isotropically.

The deuterium spin-lattice relaxation rate is given in the theory of nuclear magnetic relaxation [35] by

$$\frac{1}{T_1} = \frac{5\pi^2}{20}\left(\frac{eQ}{h}\right)^2 \{2J(\omega_0) + 8J(2\omega_0)\} \tag{1}$$

with eQ the deuteron quadrupole moment. The spectral density functions at the observing frequency ω_0 are given by

$$J(m\omega_0) = \int_0^\infty G(\tau)\exp(\mathrm{i}m\omega_0\tau)\,\mathrm{d}\tau \tag{2}$$

with [3] $G(\tau) = \langle R_0^{\mathrm{L}*}(\tau) R_0^{\mathrm{L}}(0)\rangle$ the time correlation function of the zeroth component of the irreducible electric field gradient (efg) tensor expressed in the laboratory frame. The elements of the efg-tensor are constant in a molecule fixed principal axis system of the efg-tensor. The transformation from the laboratory frame to the principal axis system can be effected with the Wigner rotation matrix which is a function of the Euler angles specifying the transformation [37]. With our motional model in mind the transformation is conveniently performed via two intermediate frames. Thus we introduce the following axis systems: the laboratory frame (L), a frame (D) whose z-axis lies along the line connecting the cation with the oxygen nucleus, a frame (F) whose z-axis describes the equilibrium orientation of the OD-bond in the hydration sphere and the molecule-fixed principal frame (I) whose z-axis lies along the instantaneous OD-bond. With these transformations, which are time-dependent because of molecular reorientations, the efg autocorrelation function becomes

$$\begin{aligned} G(\tau) = \langle &\sum_{mm'} D^{(2)*}_{\mathrm{o},-m}(\Omega_{\mathrm{LD}},\tau)\, D^{(2)*}_{-m,-m'}(\Omega_{\mathrm{DF}},\tau)\, D^{(2)*}_{-m',\mathrm{o}}(\Omega_{\mathrm{FI}},\tau) \\ &\cdot \sum_{nn'} D^{(2)}_{\mathrm{o},-n}(\Omega_{\mathrm{LD}},\mathrm{o})\, D^{(2)}_{-n,-n'}(\Omega_{\mathrm{DF}},\mathrm{o})\, D^{(2)}_{-n',\mathrm{o}}(\Omega_{\mathrm{FI}},\mathrm{o})\,\varrho_0^2\rangle \end{aligned} \tag{4}$$

where it has been assumed, that the efg-tensor is axially symmetric ($\eta \equiv (q^{\mathrm{I}}_{xx} - q^{\mathrm{I}}_{yy})/q^{\mathrm{I}}_{zz} \cong 0$ – this should be a good approximation because $\eta \simeq 0.1$ in both the solid and the gas phase of water) with $\varrho_0 = \sqrt{\frac{3}{2}}\,eq^{\mathrm{I}}_{zz}$ the largest principal component of the efg-tensor.

Assuming the the overall tumbling is isotropic, we can factorize the correlation function into

$$G(\tau) = G_{\mathrm{rot}}(\tau) \cdot G_{\mathrm{int}}(\tau) \tag{5}$$

where $G_{\mathrm{rot}}(\tau) \equiv \frac{\delta_{mn}}{5}\exp(-\tau/\tau_{\mathrm{r}})$ describes the overall reorientation.

As the librations are fast compared to the internal diffusive reorientation of the molecule about the Li^+-O direction, we can factorize the correlation function $G_{\mathrm{int}}(\tau)$ also [19, 36]. Because the librations decay on a much shorter timescale than the diffusive reorientations, they should be uncorrelated for times greater than the diffusive correlation times. Hence, using the general property of time correlation functions $\lim_{t \to \infty} G_{\mathrm{AB}}(t) = \langle A \rangle \langle B \rangle$, we finally obtain:

$$G(\tau) = \frac{3}{10}(eq^{\mathrm{I}}_{zz})^2 \exp(-\tau/\tau_{\mathrm{r}}) \sum_{mm'n'} (-1)^{-m} \cdot \langle D^{(2)}_{mm'}(\alpha_{\mathrm{D}}(t), \beta_{\mathrm{DF}}, \mathrm{o})\, D^{(2)}_{-m-n'}(\alpha_{\mathrm{D}}(\mathrm{o}), \beta_{\mathrm{DF}}, \mathrm{o}) \rangle \cdot \langle D^{(2)}_{m'\mathrm{o}}(\Omega_{\mathrm{FI}}) \rangle \langle D^{(2)}_{-n'\mathrm{o}}(\Omega_{\mathrm{FI}}) \rangle . \tag{6}$$

Describing the internal reorientation within a one-dimensional diffusion model (38) gives

$$G(\tau) = \frac{3}{10}(eq^{\mathrm{I}}_{zz})^2 \exp(-\tau/\tau_{\mathrm{r}}) \sum_{m} \exp(-m^2 t/\tau_{\mathrm{int}}) \cdot \left| \sum_{m'} d^{(2)}_{mm'}(\beta_{\mathrm{DF}}) \langle D^{(2)}_{m'\mathrm{o}}(\Omega_{\mathrm{FI}}) \rangle \right|^2 . \tag{7}$$

To simplify this expression further we assume an at least threefold symmetry of the librations around the Z_{F}-axis to obtain our final expression for the correlation function

$$G(\tau) = \frac{3}{10} e^2 q^2_{\mathrm{eff}} \exp(-\tau/\tau_{\mathrm{r}}) \cdot \left\{ \frac{1}{4}(3\cos^2\beta - 1)^2 + 3\sin^2\beta\cos^2\beta \exp(-\tau/\tau_i) + \frac{3}{4}\sin^4\beta \exp(-4\tau/\tau_i) \right\} \tag{8}$$

where

$$\frac{3}{2} e^2 q^2_{\mathrm{eff}} \equiv \frac{3}{2}(eq^{\mathrm{I}}_{zz})^2 \cdot \left(\frac{1}{2}(3\langle \cos^2\theta \rangle - 1) \right)^2 .$$

Iserting Eq. (8) into Eqs. (1) and (2) the spin-lattice relaxation rate of the water molecules hydrating the cation is obtained as

$$\left(\frac{1}{T_1}\right)_{\mathrm{hyd}} = \frac{3\pi^2}{10}\left(\frac{e^2 q_{\mathrm{eff}} Q}{h}\right)^2 \cdot \left\{ 0.082 \left[\frac{\tau_{\mathrm{r}}}{1 + (\omega_0 \tau_{\mathrm{r}})^2} + \frac{4\tau_{\mathrm{r}}}{1 + (2\omega_0 \tau_{\mathrm{r}})^2} \right] + 0.366 \left[\frac{\tau_1}{1 + (\omega_0 \tau_1)^2} + \frac{4\tau_1}{1 + (2\omega_0 \tau_1)^2} \right] + 0.552 \left[\frac{\tau_2}{1 + (\omega_0 \tau_2)^2} + \frac{4\tau_2}{1 + (2\omega_0 \tau_2)^2} \right] \right\} \tag{9}$$

with $\frac{1}{\tau_1} = \frac{1}{\tau_{\mathrm{r}}} + \frac{1}{\tau_i}, \frac{1}{\tau_2} = \frac{1}{\tau_{\mathrm{r}}} + \frac{4}{\tau_i}$ and the, librationally averaged, deuterium quadrupole coupling constant (DQC) [19, 39]

$$\frac{e^2 q_{\mathrm{eff}} Q}{h} = \frac{e^2 q^{\mathrm{I}}_{zz} Q}{h} \cdot \frac{1}{2}(3\langle \cos^2\theta \rangle - 1). \tag{10}$$

The question whether or not the electric field gradient eq at the site of the deuterium nucleus is altered substantially by the presence of a Li^+-cation adjacent to a water molecule has been negated recently in a thorough theoretical investigation by Cummins et al. [39]. Hence we will use the librationally averaged DQC of neat D_2O as obtained recently [19].

Discussion

In pure liquid water at low temperatures long-ranged structural correlations develop within the random, transient hydrogen-bonded network with increasing correlation length and with a slowing down of structural fluctuations as the temperature approaches the Speedy-Angell temperature T_{s} which is close to but below the homogeneous nucleation temperature T_{H} [2, 40, 41]. Hydrostatic pressure or ionic solutes may be considered as network-breaking agents which act to suppress long-ranged density-density correlations and turn supercooled water into a normal viscous liquid. Collective configurational fluctuations, characteristic of viscous liquids close to their glass transition temperature T_{g}, then dominate the dynamics of supercooled water.

The most direct indication of the influence of hydrostatic pressure upon the topology of the liquid is the depression of T_{H} with increasing pressure [1, 40]. It has been shown recently by Angell et al. [8, 10] that the same phenomenon is observed with increasing salt concentration in aqueous electrolyte solutions. In the system LiCl-water with composition $R \lesssim 10$ homogeneous nucleation becomes kinetically impossible because $T_{\mathrm{H}} < T_{\mathrm{g}}$ [10]. Around $R \simeq 10$ nucleation, though possible, fails to occur [10]. Thus for compositions $R < 10$ LiCl-water solutions are glassforming [7, 9, 10]. The average local structure of the LiCl-RD$_2$O solutions is assumed to be related to the glasses which form at low temperatures and composition $R \leq 10$ [20]. Their structural elements are $Li^+(D_2O)_4Cl^-$ clusters with the excess water incorporated in between. A description of the reorientational dynamics of the hydration water is needed before the dynamical behaviour of the bulky water clusters can be related to neat water.

In many amorphous systems [42–44] the T-dependence of dynamic quantities is well described with the Vogel-Tammann-Fulcher (VTF) law [44, 45].

$$\tau_{\mathrm{x}} = \tau_{\mathrm{xo}} \exp\left(\frac{B}{T - T_0}\right) \quad \mathrm{x} = \mathrm{r}, \mathrm{i} \tag{11}$$

with the ideal glass transition temperature T_0. In recent work on supercooled D_2O under high pressure [19] the isobaric T-dependence of the orientational correlation time τ_{w} could be described also by the VTF-equation with $T_0 = 132$ K at $p = 225$ MPa. This leads to the suggestion that the T-dependence of T_1 in the various LiCl-D$_2$O solutions under high pressure may follow the VTF-law also. In order to estimate T_0 in supercooled LiCl-D$_2$O solutions T_0 ($p = 225$ MPa) is assumed to be independent of composition for $R \gtrsim 10$ and to parallel the composition dependence of T_{g} ($p = 0.1$ MPa) obtained in solutions with $R \lesssim 10$. This is supported by the observation (see Table 1) that T_{min} is independent of composition for $R \geq 10$ and shifts to higher temperatures by the same amount as T_{g} changes with composition for $R < 10$ (Fig. 5).

Hence in Fig. 4 the ^{2}H-T_1 obtained at $p = 225$ MPa and different concentrations are plotted in a modified Arrhenius diagram versus $1/(T\text{-}T_0(c))$. The VTF law is obeyed in all solutions and at temperatures $T > T_{\min}$ the slope of all curves is identical. In this temperature range the extreme motional narrowing $(\omega_0\tau)^2 \ll 1$ prevails with $1/T_1 \sim \tau \sim \exp(B/(T-T_0(c)))$. Thus the apparent activation energy $k_B \cdot B$ at $p = 225$ MPa is independent of concentration. This implies that under high pressure the effect of composition upon the temperature dependence of T_1 (c, p, T) is dominated by its effect on $T_0(c, p)$.

If we describe the temperature dependence of the correlation times τ_r and τ_i for the hydration water by the VTF-equation [11] and assume that all water present in the 11 molal solution belongs to the hydration sphere of the cation we can fit our T_1 data in this solution to Eq. (9) to obtain the two unknown constants τ_{ro}, τ_{io} since we know the constant B and the librationally averaged DQC from the study of neat D_2O [19] and we can estimate T_0 from Fig. 5. The corresponding parameters of best fit are included in Table 2. In this way a simple description of the reorientational dynamics of water molecules hydrating the Li^+-ions is obtained. The ratios $\tau_{ro}/\tau_{wo} \simeq 14$ and $\tau_{io}/\tau_{wo} \simeq 4$ indicate that the orientational mobility of the water molecules is slowed down substantially in the immediate neighbourhood of a Li^+-cation. In the extreme motional narrowing regime $((\omega_0\tau_x)^2 \ll 1, x = r, i, w)$ an average orientational correlation time for the hydration water can be calculated

$$\tau_{av} = \tau_{av,o} \cdot \exp\,(B/T\text{-}T_0))$$

$$\begin{aligned} \tau_{av,o} &= \tau_{ro} \cdot [0.082 + \tau_{io}(0.366(\tau_{ro} + \tau_{io})^{-1} \\ &\quad + 0.552(4\tau_{ro} + \tau_{io})^{-1})] \\ &\simeq 0.14\,(\mathrm{ps}) \text{ with } \tau_{ro} = 0.70\,(\mathrm{ps}),\ \tau_{io} = 0.21\,(\mathrm{ps}). \end{aligned} \tag{11a}$$

The ratio $\tau_{av,o}/\tau_{wo} \simeq 0.14\,(\mathrm{ps})/0.05\,(\mathrm{ps}) \simeq 2.8$, calculated at equal reduced temperatures, is a direct measure of the slowing down of orientational fluctuations and is in good agreement with estimates available in the Refs. [3, 30, 32]. From the ratio $\tau_{ro}/\tau_{io} \simeq 3.3$ the internal reorientation of the water molecules is seen to be roughly three times faster than the overal tumbling motion. From τ_{av} a time constant corresponding to the reorientation of a vector fixed in the molecule and more directly related to rotational motions is estimated to $\tau_{\text{tumb}} = 3\tau_{av,o}\exp(\frac{B}{T\text{-}132}) \simeq 46$ (ps) at $T = 278$ K and is of the same order of magnitude as the lifetime of a water molecule in the hydration sphere, which is ~ 33 (ps) at $T = 278$ K [34]. Thus the concept of a well-defined hydration complex moving as a dynamic entity on a picosecond timescale is meaningful.

Until now only the dynamics of the water molecules hydrating the Li^+-cations in the $Li^+(H_2O)_4Cl^-$ clusters have been considered. For the water clusters in more dilute solutions with composition $R > 4.55$ Baianu et al. [20] and Boden and Mortimer [13] suggested that the average local

Table 2
Parameters of best fit for the T-dependence of the orientational correlation times τ_r, τ_i of the hydration water according to the VTF-equation (A) and of the orientational correlation time τ_w of the water clusters according to the Speedy-Angell equation (B)

A

$\tau_{ro} = 0.70$ (ps) $\tau_{io} = 0.21$ (ps)

All other parameters in Eq. (11) have been taken as obtained in Ref. [19] ($\tau_{wo} = 0.05$ (ps), $B = 687.6$ (K)).
T_0 has been estimated as explained in the text.

B[a])

			B1[b])				B2[c])			B3[d])	
c(molal)	p(MPa)	γ[e])	τ_{wo}(ps)	T_s(K)	T_0(K)	SQ[f])	τ_{wo}(ps)	T_s(K)	SQ[f])	T_0(K)	SQ[f])
0.1	0.1	1.85	0.43	228.7	146	0.0016	0.43	228.7	0.0016	146	0.33
0.3	5	1.87	0.46	225.7	145	0.0082	0.48	225.7	0.0091	145	0.16
0.3	50	1.93	0.54	217.9	138	0.0024	0.55	218.0	0.0027	138	0.016
0.3	100	2.11	0.64	205.4	134	0.0013	0.67	207.0	0.017	134	0.0026
0.3	150	2.37	0.80	195.4	132	0.0025	0.80	195.7	0.027	132	0.017
0.3	200	–	–	–	–	–	–	–	–	131	0.018
1.0	0.1	1.85	0.54	220.0	142	0.0095	0.60	222.1	0.020	142	0.15
3.0	0.1	1.85	1.02	208.1	137	0.072	1.29	208.3	0.17	137	0.036
3.0	5	1.87	0.98	207.6	137	0.0048	1.21	208.2	0.069	137	0.025
3.0	50	1.93	0.99	203.8	135	0.038	1.17	203.9	0.074	135	0.054
3.0	100	2.11	1.22	193.6	133	0.15	1.45	194.2	0.21	133	0.064
3.0	150	2.37	1.52	187.0	132	0.40	1.57	187.0	0.43	132	0.074
3.0	200	–	–	–	–	–	–	–	–	132	0.050
5.0	5	–	–	–	–	–	–	–	–	132	0.16
5.0	50	–	–	–	–	–	–	–	–	132	0.073
5.0	100	–	–	–	–	–	–	–	–	131	0.057
5.0	150	–	–	–	–	–	–	–	–	130	0.069
5.0	200	–	–	–	–	–	–	–	–	130	0.073

[a]) The T-dependence of τ_r and τ_i was assumed to follow the VTF-law Eq. (11) with the parameters given in part A except for the glass-temperature T_0.
[b]) T_0 has been used with Eq. (11) in $(1/T_1)_{\text{hyd}}$ of Eq. (12) as obtained in fit B3.
[c]) $T_0 = 132$ K held constant.
[d]) T-dependence of τ_w assumed to follow Eq. (11) with $B = 687.6$ K and $\tau_{wo} = 0.05$ (ps).
[e]) γ has been assumed independent of concentration, values obtained in neat D_2O (16) used.
[f]) SQ = sum of sqaures of residuals $R_i(x)$ with $R(x) = \ln T_1 - \ln f^{-1}(x), f(x)$ as calculated in Eq. (12) x-Parametervector.

structure of liquid aqueous LiCl-D_2O solutions is closely related to the local structure of the corresponding glasses, hence for $R > 4$ it should be possible to describe the relaxation rates by [13]

$$\frac{1}{T_1}(T,p,R) = \frac{4}{R}\left(\frac{1}{T_1}(T,p)\right)_{\text{hyd}} + \frac{R\text{-}4}{R}\left(\frac{1}{T_1}(T,p)\right)_{\text{bulk}} \tag{12}$$

provided the values chosen for the relaxation rates of the hydration water $(1/T_1)_{\text{hyd}}$ and the bulk water $(1/T_1)_{\text{bulk}}$ correspond to the reduced temperature $(T\text{-}T_0(c,p))$ of the actual solution. Since we assume $(1/T_1)_{\text{hyd}} \equiv (1/T_1)_{11m}$ we use 4.55 instead of 4 in Eq. (12).

Replacing $(1/T_1)_{\text{bulk}}$ by $(1/T_1)_{D_2O}$, as obtained in neat D_2O at p = 225 MPa, Eq. (12) provides, without any further adjustable parameters, a very good description of the temperature dependence of the deuterium relaxation rates at p = 225 MPa for all intermediate compositions ($4.55 \le R \le \infty$) (see Fig. 4). Thus the influence of ionic solutes upon the T-dependence of T_1 at high pressure is determined mainly by its effect on T_0. Once the random, transient hydrogen-bonded network has been distorted sufficiently by the application of high hydrostatic pressure ($p > 200$ MPa) no further influence of an equivalent network-breaking agent such as monovalent ionic solutes upon the dynamics of the bulky water clusters is seen. In particular, no indications of structural transitions, observed in the ^{2}H and ^{7}Li relaxation rates at room temperature and ambient pressure of LiCl solutions at $R \simeq 10$ [46, 47] are seen as the solutions under high hydrostatic pressure are diluted. The model accounts for the most prominent features of the $T_1(T,c)$ curves in the dispersion region, i.e. the depth of the minimum in $T_1(T)$, the increase in T_1^{min} with concentration, the broadening of the minimum and the shift in T_{min} to higher temperatures for $R < 10$, without invoking a distribution of correlation times. The results should not be interpreted to mean that, for example, in the 8 molal solution, which corresponds to a composition R = 6.25, the water molecules not belonging to the hydration sphere behave like neat water dynamically. That Eq. (12) works well in this solution is due to the small contribution (~ 27%) of the second summand in Eq. (12). In the 5 molal solutions the weighting of both summands is about equal and it may be concluded that a cluster of ~ 5 water molecules exhibits, under high pressure, an average dynamical behaviour similar to neat D_2O under the same conditions. This lends support to the hypothesis [48] that the average local structure of the glass and the corresponding liquid are closely related and that the excess water is arranged in interstitial clusters [20] and does not form a separate hydration shell around the Cl^- ions. Otherwise the good agreement obtained in setting $(1/T_1)_{\text{bulk}} \simeq (1/T_1)_{\text{ncat}}$ is hardly understandable. The solutions with R = 10 showed an, albeit small, anomalous pressure effect in T_1, which arises from the destruction of locally ordered, low density patches with almost linear hydrogen bonds. A total of ~ 5 water molecules is probably the smallest cluster able to build up these patches and this is about the size of the interstitial cluster in a solution of composition R = 10.

The question arises whether Eq. (12) will be applicable to more dilute solutions ($R \ge 10$) in the low pressure regime and how to describe the temperature dependence of $(1/T_1)_{\text{bulk}}$. In this context a correlation between the possibility of homogeneous nucleation and the anomalous positiv pressure dependence of T_1 is worth mentioning. The pressure dependence becomes weaker with increasing salt concentration until for $R < 10$ T_1 is independent of pressure. Hence the anomalous pressure dependence of T_1 disappears as soon as T_H is depressed below T_g. In supercooled D_2O [2, 16, 17] it has been found that the temperature dependence of the orientational correlation time of the water molecules at low pressure is less well described by the VTF-equation. Instead, following a proposal by Speedy and Angell [41], a fractional power law

$$\tau_w = \tau_{wo}\left(\frac{T\text{-}T_s}{T_s}\right)^{-\gamma} \tag{13}$$

was more suitable. Fitting the isobaric T-dependence of various static and dynamic response functions to this fractional power law, $T_s(p)$ has been found only a few degrees below the homogeneous nucleation temperature $T_H(p)$ [2, 40]. The meaning of T_s is a matter of great concern and different interpretations have been offered in the literature. Whether it is given the meaning of a mechanical stability limit as in Speedy's conjecture [49] or a percolation threshold, as in Stanley and Teixeira's proposal [50], is assigned to it, the

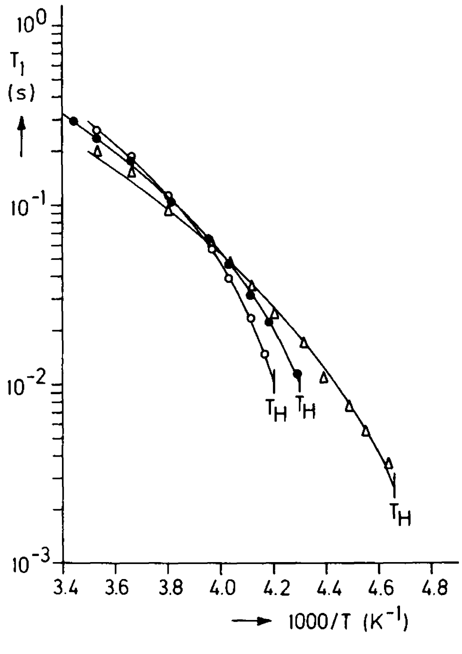

Fig. 6
Isobaric (p = 0.1 MPa) temperature dependence of the deuterium (^{2}H) spin-lattice relaxation time T_1 in solutions with composition R = 500 (○), 50 (●), 16.7 (△);
- The curves have been calculated with Eqs. (9) and (13) inserted into Eq. (12). The corresponding parameters are given in Table 2.

T_H-homogeneous nucleation temperature taken from Ref. [10]

physical mechanism envisaged is the cooperative clustering of highly structured, low density patches the nature of which is yet unclear although various possibilities have been proposed [41, 49–52].

To apply Eq. (12) to solutions of composition $R > 10$ at low pressure ($p \leq 150$ MPa) Eq. (13) was used for the temperature dependence of the orientational correlation time τ_w of bulk water. The exponent γ was assumed to be independent of concentration equal to the values obtained in neat D_2O. τ_{wo}, T_0 and T_s were treated as parameters in an unconstrained nonlinear least squares fit (N.A.G. EO4FCF) of Eqs. (9) and (12) to the T_1-isobars. In view of the recent conclusions of MacFarlane and Angell [53] that $T_g >$ 160 K in amorphous solid water it is unlikely that T_0 is as low as $\sim$ 132 K at ambient pressure, accordingly it has been considered as a free parameter. Table 2 contains the parameters of best fit and Fig. 6 shows a few T_1-isobares at ambient pressure. A least squares fit with τ_{wo} and T_s as the only parameters and with T_0 fixed at 132 K gave τ_{wo} and T_s almost in agreement with those obtained above although the fit was better in the former case.

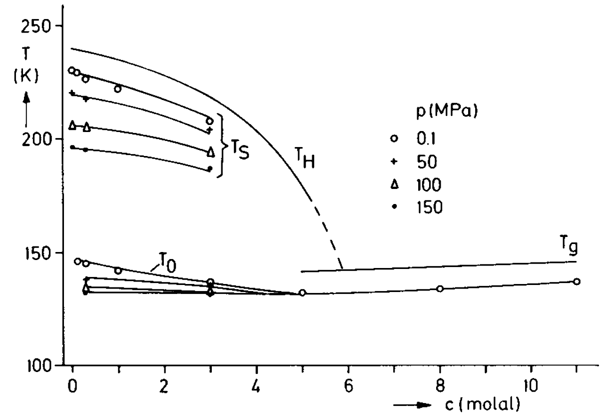

Fig. 7
Concentration dependence of the Speedy-Angell temperature T_s and the ideal glass temperature T_0 at constant pressure; T_H-homogeneous nucleation temperature taken from Ref. [10]; T_g-glass transition temperature taken from Refs. [9, 10]

The isobaric concentration dependence of T_s parallels roughly the one determined for T_H ($p = 0.1$ MPa) by C. A. Angell et al. [10] (see Fig. 7) except that it appears to be weaker at higher pressure. This follows from the observation that the positive p-dependence of T_1 vanishes gradually when the concentration increase to $c = 5-6$ molal. The p-dependence of T_H is only known for a 1 m LiCl-solution [8]. It is similar to the p-dependence of T_H in pure water albeit at lower temperatures. $T_s(p)|_c$ closely follows the $T_H(p)$ curve for neat D_2O up to $p = 150$ MPa (see Fig. 8) with a weaker p-dependence at higher concentrations. This is a consequence of the fact that the anomaly becomes suppressed with the addition of network-breaking agents. The use of the Speedy-Angell relation (Eq. (13)) may thus yield artificially high T_s-values, especially at higher concentrations and high hydrostatic pressure. The increase of the prefactor τ_{wo} with salt concentration (see Table 2) indicates that the dynamical behaviour of the water clusters changes with the addition of network-breaking agents even if compared at equal reduced temperatures T-$T_s(c,p)$. In this range the density fluctuations possess a much larger correlation length than at high pressure and it is plausible that the presence of network-breaking agents is reflected in the dynamical state of the water clusters. The ideal glass temperature T_0 is found to decrease with concentration and pressure until it becomes independent of concentration in the range $c \leq 5$ molal at high hydrostatic pressure and independent of pres-

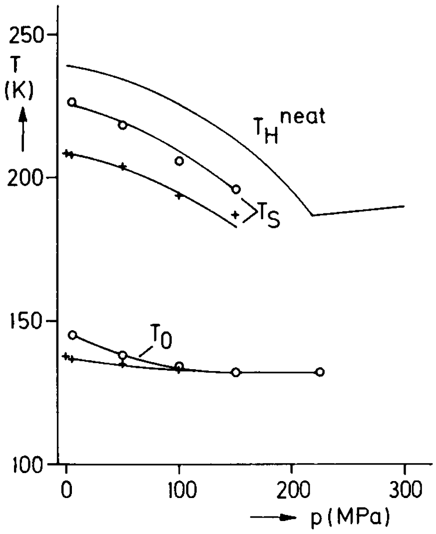

Fig. 8
Pressure dependence of the Speedy-Angell temperature T_s and the ideal glass temperature T_0 at constant concentration (0.3 m (○), 3 m (+));
T_H-homogeneous nucleation temperature

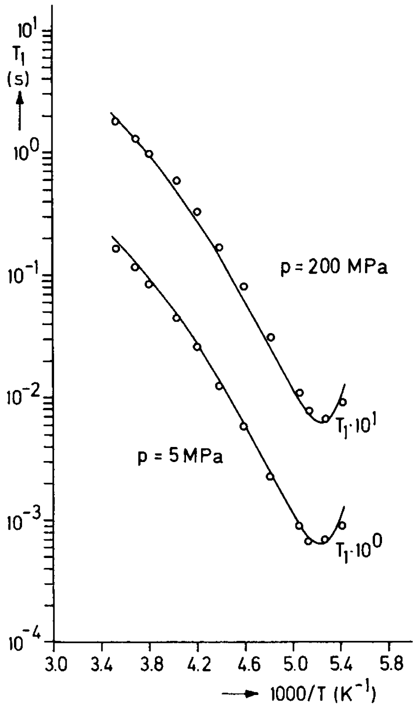

Fig. 9
Isobaric T-dependence of ^{2}H-T_1 in a LiCl-D_2O solution with composition $R = 10$. The curves drawn are calculated with Eq. (9) and Eq. (11) inserted into Eq. (12) and the parameters given in Table 2

sure for compositions $R < 10$. As the T_1-isobars are almost flat in the pressure range between ca. 150 MPa to 225 MPa, any attempt to fit these isobars yields similar parameters. On the other hand the VTF-equation description can be applied to these isobars almost as successfully as for the 225 MPa isobars without adjusting any parameters. This is best seen for the 5 molal solution (Fig. 9), where only a weak p-dependence is found and consequently all the isobars can be described with Eq. (11) and Eq. (12) with $T_0 = 132$ K to good approximation. This indicates that one has to consider Eqs. (11) and (13) as limiting cases which describe the dominant T-dependence at high and low pressures respectively. At intermediate pressures some combination of both T-laws [54–57] may be more appropriate but a total of up to six unknown parameters would result.

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