NEW RESULTS OF HIGH-PRESSURE NMR STUDIES ON SUPERCOOLED WATER AND AQUEOUS ELECTROLYTE SOLUTIONS

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Abstract

Nuclear magnetic relaxation rate measurements at different frequencies are reported in supercooled light and heavy water and supercooled aqueous LiCl solutions. It is shown that measurements in the dispersion regime, where the relaxation rates are frequency dependent, are essential for gathering detailed information about the nature of reorientational motions of the water molecules. The orientational fluctuations of water molecules are decomposed into fast librational oscillations and slower diffusional motions. In supercooled water the latter are found to be nearly isotropic. Adjacent to a cation, the orientational fluctuations of water molecules are described by fast librations superimposed on to anisotropic diffusional reorientations within the coordination sphere. In addition the hydration complex is assumed to tumble around isotropically. The motional models account well for the observed T,ω dependence of the relaxation rates.

1 INTRODUCTION

Long-range structural correlations develop within the random, transient hydrogen-bonded network of liquid water (Angell 1983). 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-range density–density correlations and turn supercooled water into a normal viscous liquid.

In supercooled liquids molecular motions may be slowed down sufficiently so that probes such as nuclear magnetic resonance (NMR) 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 (about 1 ps) than the timescale of the NMR experiment (Larmor period about 100 ns) rendering the information contained in the relaxation times rather limited. If, however, the liquid can be coerced into supercooling, molecular motions are slowed down and their timescale becomes comparable with the observing frequency of the NMR experiment. Nuclear magnetic relaxation times then become frequency dependent and more specific information

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about the molecular motions may be obtained. Measurements in this dispersion region are essential for a better understanding of the dynamics of the liquid phase.

2 RELAXATION RATE DISPERSION IN SUPERCOOLED WATER

Deuterium (^{2}H) relaxation rate dispersion in supercooled D_2O under high pressure (p = 225 MPa)

At a pressure of 225 MPa D_2O emulsions can be undercooled to about −90 °C and spin–lattice and spin–spin relaxation rates have been obtained at these temperatures and three frequencies (Lang *et al* 1984). The relaxation rates are given by

$$\begin{aligned} 1/T_1 &= (3\pi^2/20)\ \chi^2_{\text{eff}}\ F_2(\omega_0,\tau) \\ 1/T_2 &= (3\pi^2/20)\ \chi^2_{\text{eff}}\ F_2'(\omega_0,\tau) \end{aligned} \tag{1}$$

where

$$\begin{aligned} F_2(\omega_0,\tau) &= 2\ g(\omega_0) + 8\ g(2\omega_0) \\ F_2'(\omega_0,\tau) &= 3\ g(0) + 5\ g(\omega_0) + 2\ g(2\omega_0) \end{aligned}$$

and

$$g(m\omega_0) = \tau/[1 + (m\omega_0\tau)^2]$$

with χ the deuterium quadrupole coupling constant and $g(m\omega_0)$ the spectral density of reorientational modes m at the observing frequency ω_0. These modes can be decomposed into fast librations about a mean orientation superimposed on to slower isotropic diffusional reorientations characterised by an orientational correlation time τ. The slower mode of motion provides the main contribution to $g(\omega_0)$, whereas the effect of the fast oscillations can be incorporated into an effective, librationally averaged, quadrupole coupling constant

$$\chi_{\text{eff}} = \Gamma\chi \simeq (\sum_m |\langle D^2_{0m}(\Omega_{IF})\rangle|^2)^{1/2}\ \chi \tag{2}$$

where Γ is a motional averaging factor, $D_{0m}(\Omega_{IF})$ is an element of the rotation matrix which relates (I) the principal axis system of the field gradient tensor of the molecule to (F) the equilibrium orientation of the OD bond in the quasistatic network. The T dependence of the correlation time τ_2 is assumed to follow the Vogel–Tamman–Fulcher (VTF) equation (Angell and Smith 1982)

$$\tau = \tau_0 \exp[B/(T - T_0)]. \tag{3}$$

The model parameters have been obtained by a least squares fit to the spin–lattice relaxation times obtained at three different frequencies (figure 1). The same parameters provide a good description of the T,ω dependence of the spin–spin relaxation times T_2. It is worth mentioning that only in the dispersion region can correlation times be obtained directly from the ratio T_1/T_2.

Proton (^{1}H) spin–lattice relaxation rate in supercooled H_2O and $H_2{}^{17}O$ under high pressure (p = 200 MPa)

The protons are relaxed mainly via a dipole–dipole interaction mechanism. The total rate measured in H_2O consists of an intramolecular and an intermolecular rate

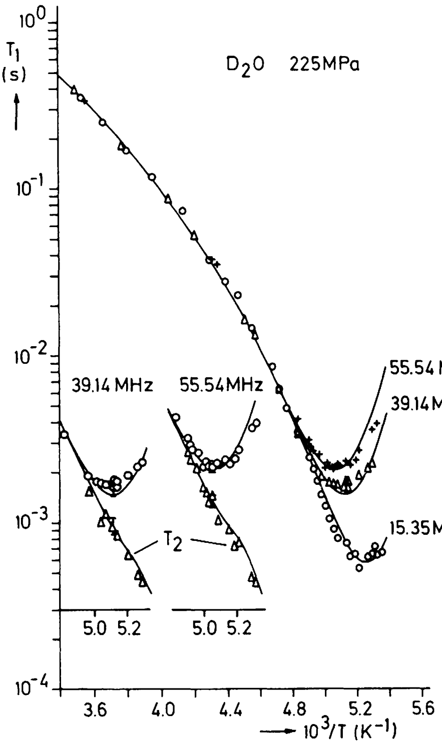

Figure 1. Deuterium spin–lattice (T_1) and spin–spin (T_2) relaxation times. The full curves show dependence of T_1 and T_2 according to equation (1). For best-fit parameters see table 1.

which cannot be separated easily by the common $^1H/^2H$ replacement because of the large dynamic isotope effect in liquid water. However, in $H_2{}^{17}O$ the ^1H–^{17}O dipolar interaction provides an additional intramolecular relaxation. The total rate measured in $H_2{}^{17}O$ is thus given by

$$\frac{1}{T_1}\,(H_2{}^{17}O) = \frac{1}{T_1}\,(H_2{}^{16}O) + X\frac{1}{T_1}\,({}^1H\text{–}{}^{17}O) \qquad (X = 0.51) \tag{4}$$

with

$$\frac{1}{T_1}\,({}^1H\text{–}{}^{17}O) = K'\left(\frac{\Gamma}{<r_{OH}^3>}\right)^2 f(\omega_{^1H},\omega_{^{17}O},\tau)$$

$$f(\omega_{^1H},\omega_{^{17}O},\tau) = \tfrac{1}{3}\tilde{g}(\omega_{^1H} - \omega_{^{17}O}) + \tilde{g}(\omega_{^1H}) + 2\tilde{g}(\omega_{^1H} + \omega_{^{17}O}) \tag{5}$$

$$K' = \frac{7}{2}\left(\frac{\mu_0}{4\pi}\gamma_{^1H}\gamma_{^{17}O}\hbar\right)^2$$

Figure 2 shows the relaxation times obtained in $H_2{}^{17}O$ (51%) and $H_2{}^{16}O$ at two frequencies. Subtracting both rates $1/T_1(H_2{}^{17}O) - 1/T_1(H_2{}^{16}O)$ the intramolecular rate $1/T_1({}^1H - {}^{17}O)$ has been obtained and is shown in figure 3 for the highest frequency ($\omega({}^1H)/2\pi = 360$ MHz).

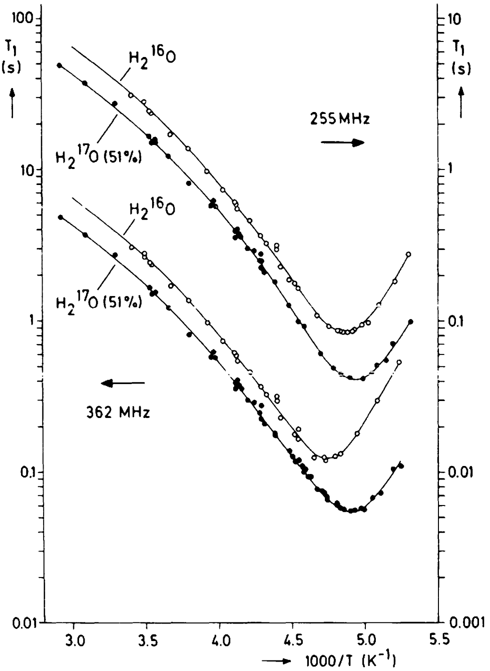

Figure 2. Proton spin–lattice (T_1) relaxation times obtained in H_2O and $H_2{}^{17}O$ (51% enriched).

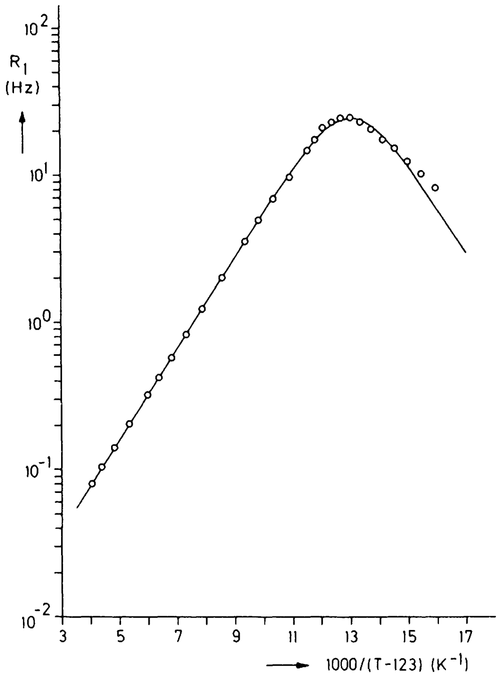

Figure 3. Intramolecular proton spin–lattice relaxation rate ($1/T_1(^1H-^{17}O)$). The curve shows the T dependence according to equation (5). For best-fit parameters see table 1.

Again we decompose the reorientational modes into fast librations superimposed onto a slower overall tumbling of the molecules. The slower tumbling motion determines the spectral density at the observing frequency. The fast oscillations average out part of the dipolar interaction and lead to a librationally averaged coupling strength approximating to $(\Gamma/\langle r_{OH}^3\rangle)^2$.

The motional averaging factor Γ is given by the same expression as in the case of D_2O. The T dependence of the correlation time is described by the VTF equation (3). The model parameters are again obtained from a least squares fit and the result is shown in figure 3 as the line drawn through the data. The parameters obtained in light and heavy water are given in table 1. The motional averaging factor is expected to exhibit an isotope effect due to the larger librational amplitude in light water. It can be estimated if the librations are treated as harmonic oscillations and if Γ is approximated by

$$\begin{aligned} \Gamma &\simeq (1-3\langle\theta^2\rangle)^{1/2} \\ \langle\theta^2\rangle &= \frac{1}{2}\frac{\hbar}{I\omega_1}\coth\left(\frac{h\omega_1}{2kT}\right) \simeq \frac{1}{2}\frac{\hbar}{I\omega_1} \qquad \text{if } T \leqslant 200\text{ K.} \end{aligned} \tag{6}$$

Hence $\Gamma(D_2O)/\Gamma(H_2O) = 0.87/0.82 = 1.06$ resulting in a static bond length $r_{OH} = 0.985$ Å. The pre-exponential factors τ_0 correspond to librational frequencies, hence they should scale as the square root of the moment of inertia of D_2O and H_2O. This is indeed obtained, as was observed earlier with the ^{17}O relaxation in $D_2{}^{17}O$ and $H_2{}^{17}O$ (Lang and Lüdemann 1982).

Table 1. Least squares fit parameters for D_2O (equation (1)) and H_2O (equation (5)).

	τ_0(s)	B(K)	T_0(K)	$\chi(^2H)$(kHz)	$r_{OH}\Gamma(^1H-^{17}O)^{-1/3}$(Å)
D_2O	4.98×10^{-14}	687.6	132	201	—
H_2O	3.61×10^{-14}	732.2	123	—	1.055

Although this analysis yielded reasonable parameters the frequency dependence of equation (5) is at odds with the experimental results so far obtained at the lower frequencies. We are at present unable to give any sensible explanation for this discrepancy. Furthermore, in spite of the apparent success of the proposed model, a close inspection of figures 1 and 3 reveals that the relaxation times vary somewhat less dramatically with temperature close to the homogeneous nucleation temperature. This is indicative of a slight anisotropy of the tumbling motion. Unfortunately the interference of the nucleation event prohibits the collection of data at even lower temperatures which seem necessary to obtain reliable parameters within an anisotropic motional model.

3 DEUTERIUM RELAXATION RATE DISPERSION IN SUPERCOOLED LiCl–D_2O SOLUTIONS

Deuterium relaxation rates have been obtained in LiCl–D_2O solutions of composition $R \equiv$ (moles D_2O/moles salt):4.55–166.7 (Lang and Lüdemann 1985). In dilute solutions emulsification and application of hydrostatic pressure was necessary to obtain the degree of supercooling required to reach the dispersion region. In the glass-forming composition range $R<10$ the relaxation rates are independent of pressure ($p<225$ MPa) and low temperatures can be obtained easily.

Baianu *et al* (1978) investigated the local structure of aqueous glasses of LiCl–D_2O ($R = 2$–10) by solid state NMR and concluded that the random network consists basically of $Li^+(D_2O)_4Cl^-$ clusters with the excess water incorporated as interstitial clusters. They suggested that the average local structure in the liquid state 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 molal 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 average structure of the coordination sphere of the Li^+ cation has been deduced from neutron scattering work on LiCl–D_2O solutions by Enderby and Neilson (1981). The water molecules 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_2O molecule from the radial direction of about 52° in concentrated solutions. The orientational fluctuations of the water molecules can be decomposed as described in the following. The molecules execute small-amplitude librations about their mean orientation. These fast oscillations are superimposed onto an internal motion which is described as a one-dimensional diffusion of the molecules about the direction connecting the cation with the oxygen nucleus. The tilt angle is fixed to $\theta = 52°$. In addition to these internal modes the hydration complex is assumed to tumble around isotropically. The model leads to the following expression for the relaxation rate of the hydration water:

$$\left(\frac{1}{T_1}\right)_{\mathrm{hyd}} = \frac{3\pi^2}{20}\chi^2_{\mathrm{eff}}\{0.082\ \mathrm{F}(\omega_o,\tau_r)+0.366\ \mathrm{F}(\omega_o,\tau_1)+0.552\ \mathrm{F}(\omega_0,\tau_2)\} \qquad (7)$$

with

$$F(\omega_o,\tau) = 2\tilde{g}(\omega_0,\tau) + 8\tilde{g}(2\omega_o,\tau)$$

$$\tilde{g}(m\omega_o,\tau) = \tau/1+(m\omega_o\tau)^2$$

and

$$\frac{1}{\tau_1} = \frac{1}{\tau_r} + \frac{1}{\tau_i} \qquad \frac{1}{\tau_2} = \frac{1}{\tau_r} + \frac{4}{\tau_i}.$$

An analogous equation holds for $(1/T_2)_{\mathrm{hyd}}$ with $F(\omega_o,\tau)$ replaced by $F'(\omega_0,\tau)$ as given in equation (1).

χ_{eff} is the librationally averaged deuterium quadrupole coupling constant. Since this constant is not altered by the presence of a Li^+ cation adjacent to a water molecule (Cummins *et al* 1985) we can use the librationally averaged coupling constant of neat D_2O (see table 1). The T dependence of the overall tumbling motion is described by the VTF equation, for the internal motion a simple Arrhenius behaviour is assumed:

$$\tau_r = \tau_{r0}\exp\left(\frac{B}{T-T_0}\right) \qquad \tau_i = \tau_{i0}\exp\left(\frac{E_a}{kT}\right). \qquad (8)$$

T_0 can be estimated from the known glass temperature of the system ($T_0 = 137$ K), the parameter B has been taken as obtained in neat D_2O.

The remaining model parameters (τ_{r0}, τ_{i0}, E_a) have been obtained by a least squares fit of equation (7) to the experimental spin–lattice relaxation rates measured at two frequencies (see table 2). Figure 4 shows the experimental data and the resulting best-fit curve. Preliminary spin–spin relaxation times are also shown together with the T dependence predicted by the model.

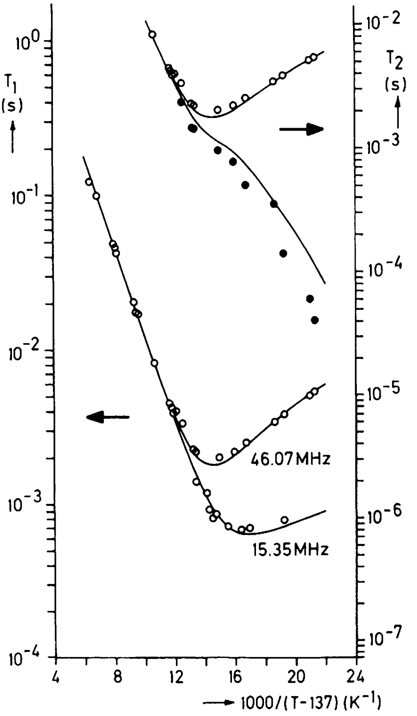

Figure 4. Deuterium spin–lattice (T_1) and preliminary spin–spin (T_2) relaxation times in a LiCl–D_2O solution of composition R = 4.55. The curves show T,ω dependence of T_1 and T_2 according to equation (7). Best-fit parameters are given in table 2.

Table 2. Least squares fit parameters for the hydration water in LiCl–D_2O solutions (equation (7)).

τ_{r0}(s)	τ_{i0}(s)	E_a/k_B(K)	E_a(kJ mol^{-1})
1.62×10^{-13}	1.89×10^{-13}	2251	18.72

Until now only the dynamics of the water molecules hydrating the Li^+ cations in the $Li^+(D_2O)_4Cl^-$ clusters have been considered. If the average local structure of liquid LiCl–D_2O solutions is closely related to the local structure of the corresponding glasses it should be possible for R>4.55 to describe the relaxation rates by (Boden and Mortimer 1978)

$$\frac{1}{T_1}(T,p,R) = \frac{4.55}{R}\left(\frac{1}{T_1}(T)\right)_{\text{hyd}} + \frac{R-4.55}{R}\left(\frac{1}{T_1}(T,p)\right)_{\text{bulk}} \tag{9}$$

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 $(T - T_0(R))$

of the actual solution of composition R. Replacing $(1/T_1)_{\mathrm{bulk}}$ by $(1/T_1)_{D_2O}$ as obtained in neat D_2O at $p = 225$ MPa, equation (9) 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 ($4.55 \leqslant R \leqslant \infty$) as is shown in figure 5. Two remarks are in order here. First it was observed that the minimum temperature T_{min} in the $T_1(T)$ curve has an identical composition dependence to the experimental glass temperature T_g. This suggests that the influence of ionic solutes upon the T dependence of T_1 at high pressure is determined mainly by its effect on T_0. Hence T_0 has been altered with changing

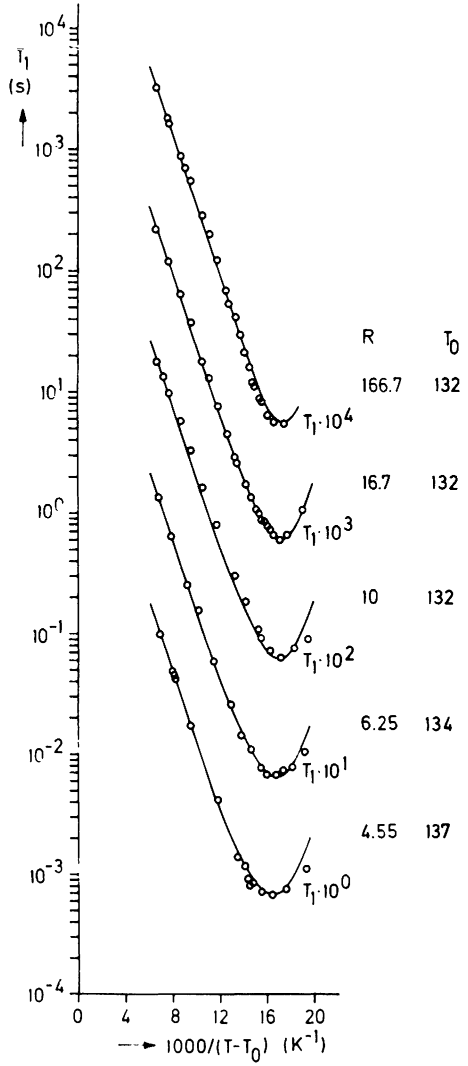

Figure 5. Deuterium spin–lattice (T_1) relaxation times in LiCl–D_2O solutions of composition R. The curves show T dependence of T_1 according to equations (9, 7 and 1).

composition in accord with the variations seen in T_{min}. Second, in a modified Arrhenius diagram ($T_1 \leftrightarrow (T-T_0)^{-1}$) all curves exhibit an identical slope on the high-temperature side of the minimum, thus $B \equiv B$ (D_2O). At these temperatures $T_1(T)$ is dominated by the overall tumbling motion and it is only at low temperatures ($T < T_{\mathrm{min}}$), in the dispersion regime, that the internal mode severely influences the T dependence of T_1. Hence measurements in the dispersion regime are essential to gather information about the internal mode.

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