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THE p, T, c DEPENDENCE OF DEUTERIUM SPIN–LATTICE RELAXATION TIMES IN UNDERCOOLED $NaCl/D_2O$ AND NaI/D_2O SOLUTIONS

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Nuclear magnetic relaxation time measurements are well suited to monitor orientational and positional fluctuations of water molecules in solutions. Hence the dependence of deuteron spin–lattice relaxation rates on pressure ($p \leqslant 225$ MPa), temperature ($180 \leqslant T \leqslant 283$ K) and composition (NaCl: $c \leqslant 5$ m, NaI: $c \leqslant 9.5$ m) are reported in undercooled $NaCl/D_2O$ and NaI/D_2O solutions over wide ranges of the external variables. The anomalous increase of molecular mobility upon compression, observed in neat undercooled water becomes less pronounced with increasing salt concentration until the pressure dependence reverts to normal behaviour at the edge of the glass forming composition range. This behaviour is qualitatively different from the recently studied systems LiCl– and $MgCl_2$–D_2O. In the presence of network breaking agents like hydrostatic pressure and/or ionic solutes molecular motions can be slowed down upon cooling sufficiently for the relaxation rates to exhibit a maximum and to become frequency dependent. Within a recently developed motional model a detailed account of orientational fluctuations of water molecules can be given and conclusions are drawn regarding the influence of structure and composition on molecular motions.

1. Introduction

In liquid water at low temperatures structural correlations develop within the random, transient hydrogen-bonded network with increasing correlation length and with a slowing down of orientational and positional fluctuations of water molecules [1,2]. These cooperative phenomena are most pronounced in the deeply undercooled metastable phase. Hydrostatic pressure and/or ionic solutes may be considered network breaking agents which act to suppress long-ranged density–density correlations and shift the low-temperature limit of the metastable phase, set by the homogeneous nucleation temperature T_H, to increasingly lower temperatures [1]. Eventually nucleation may become kinetically impossible, hence the solutions freeze to an amorphous solid at the glass transition T_g [3].

In undercooled liquids molecular motions may be slowed down sufficiently that probes such as nuclear magnetic resonance can yield specific information concerning structure and dynamics. Nuclear magnetic relaxation rates of deuterium nuclei are well suited to monitor orientational fluctuations of water molecules. In neat water these diffusive modes of molecular motions are isotropic [4], but dissolved ions induce a motional anisotropy [5–7] for adjacent water molecules. The perturbing influence of the ion on molecular motions and local structures in the H-bond network depends mainly on the charge density and the mean residence time of coordinated water molecules. These molecular motions slow down strongly upon cooling and the mean residence times increase. In this slow motions regime the relaxation rates become sensitive to the form of the spectral density function $g(\omega)$, which is the Fourier–Laplace transform of the time-correlation function $G(t)$ characterizing orientational fluctuations of water molecules. Thus more detailed information about diffusive modes of molecular motions may possibly be gathered. Also parameters may be deduced characterizing the average local structure in the solutions.

Continuing our systematic study about the influence of simple ionic solutes upon water dynamics in the undercooled metastable phase [6–11], we report in this investigation deuteron (^2H) spin–lattice relaxation times in undercooled $NaCl/D_2O$ solutions in the concentration range $0.1 \leqslant c \leqslant 5$ m and in undercooled NaI/D_2O solutions in the concentration range $0.1 \leqslant c \leqslant 9.5$ m. The temperature has been varied be-

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tween room temperature and the respective homogeneous nucleation temperature $T_H(c, p)$. The pressure has been raised to 225 MPa.

2. Experimental

To prevent heterogeneous nucleation upon cooling all salt solutions had to be prepared as emulsions [12,3]. Prior to use all salts have been dried under vacuum and stored over P_2O_5 on a vacuum line for 48 h. The solutions were prepared from a stock solution of the anhydrous salt (Merck, Darmstadt, FRG) and triply distilled D_2O (99.75%, Merck, Darmstadt). Emulsions were prepared by mixing equal amounts of the salt solution with a mixture of methylcyclohexane (24 wt%), methylcyclopentane (24 wt%) and the surfactant sorbitanetristearate (Span 65, 2 wt%). Before mixing all components had to be degassed by at least five freeze–pump–thaw cycles to remove dissolved oxygen. The mixing was done in a glove bag under an argon atmosphere by pressing the mixture through a stainless steel net within a syringe. Finally the emulsion had to be filled in the strengthened glass cells [13]. In the case of NaI the whole procedure had to be done in the dark and only analytic grade MCH could be used.

All T_1 experiments were performed with the inversion recovery pulse sequence (Freeman–Hill modification) on a Varian XL-100 spectrometer at 15.35 MHz. The 225 MPa isobars of the 0.6 and the 3 m $NaCl/D_2O$ solution and the 9.5 m NaI/D_2O solution could also be measured at 46.07 MHz on a Bruker MSL 300. The relaxation times are considered reliable to $\pm 10\%$. The temperatures have been measured with a miniature chromel–alumel thermocouple (Philips, Kassel, FRG) and are accurate to ± 1 K. The pressure has been measured with a precision bourdon gauge (Heise, Connecticut, USA) to ± 0.5 MPa.

3. Results and discussion

3.1. Effect of pressure and ionic solutes upon molecular motions

In cold water spin–lattice relaxation times, T_1, increase upon isothermal compression due to a larger motional freedom of the water molecules [14]. Upon cooling the sample towards the low-temperature limit $T_H(c, p)$ of the undercooled liquid phase, the mobility increase with pressure becomes most pronounced [1,2]. This demonstrates the retardation of orientational fluctuations by the highly directional H-bond interactions which are fully developed in the random, transient H-bond network of liquid water at low temperatures [15,16]. Hence reducing thermal excitations of the network exaggerates the influence of weak interactions upon structure and dynamics and may help in unraveling details of molecular motions. The greater ease of rotation under high pressure results from strongly distorted H bonds due to unfavorable relative orientations in concordance with a more efficient packing of next-nearest neighbours. Nearest neighbour correlations are largely unchanged by pressure [17–20]. In consequence, hydrostatic pressure acts as a network breaking agent which reduces the average size of patches with largely undistorted H-bond interactions [15,20]. A lower limit for the average structural correlation times characterizing the buildup and decay of these density–density correlations is given by the orientational correlation times because reorientational motions inititate the breakup of the hydrogen-bonded patches within the network [21].

Ionic solutes distort the H-bond network in a quite different fashion. They tend to orient adjacent water molecules in a specific way [22–24], thereby reducing their ability to participate in H-bond interactions with neighbouring water molecules in favorable orientations. The higher the charge density of the ions is, the stronger are the orientational and motional constraints on coordinating water molecules and the longer are their mean residence times in preferred orientations in the coordination shell [25]. Strongly interacting ionic solutes also retard molecular motions of water molecules in their immediate vicinity as becomes obvious from a decreasing T_1 with increasing solute concentration. A striking feature in these solutions of strongly hydrating ions is the fact, that in the low-temperature, low-pressure range (undercooled phase) T_1 increases upon addition of solutes (see fig. 3 below) implying an increasing average mobility of water molecules in this state.

In contrast with hydrostatic pressure ionic solutes represent a more local perturbation of the H-bond

network. Still, both hydrostatic pressure and ionic solutes may be regarded largely equivalent as network breaking agents which suppress long-ranged structural correlations in liquid water [3,6–11] and shift the low-temperature limit of the undercooled phase (T_H) to lower temperatures.

Under the combined influence of both perturbations the anomalous pressure effect is seen to diminish with increasing salt concentration (see figs. 1 and 2) until it vanishes for compositions $R \leqslant 16$ (R = mole D_2O/mole salt) in both NaCl and NaI solutions. It is interesting to note that the unusual increase of T_1 with solute concentration in the undercooled phase reaches its maximum just at the same composition. This striking concentration effect upon the average mobility in deeply undercooled solutions is seen to diminish with increasing pressure and finally disappears at high pressure again underlining the close correspondence of pressure and ionic solutes as network perturbing agents.

Closely analogous observations have been described for the solutions $LiCl/D_2O$ [6,8] and $MgCl_2/D_2O$ [11]. In both systems the mobility ceased to increase upon compression whenever a composition was reached where, after accounting for proper coordination numbers of the hydration shells of the strongly hydrating cations (Li: 6, Mg: 16), insufficient water molecules were left to form large enough patches with largely undistorted H-bond interactions which could cause a sizable pressure effect [6]. Remarkably the corresponding concentrations represent the edge of the glass forming composition range in these solutions. This seems to be the case in NaCl solutions also as glass transitions could be observed for $c > 2.7$ m ($R \approx 16$) although at pressures $p > 100$ MPa only [3]. An important conclusion drawn from these considerations was the notion that water bridging must become important in these highly concentrated solutions, i.e. the anions are coordinated on average to the hydration spheres of the cations and are not hydrated separately by the few bulk water molecules left [6–11,26]. At still higher concentrations the relaxation rates then remained independent of pressure (up to 250 MPa), i.e. compression does not seem to influence much the dynamic properties of the hydration waters of strongly hydrating cations [6,11].

The present systems $NaCl/D_2O$ and NaI/D_2O behave in a somewhat different manner, as is illustrated in fig. 3. The relaxation times decrease upon compression in solutions with composition $R \leqslant 12$. This is especially pronounced in the system 9.5 m NaI/D_2O, corresponding to a composition $R = 5.25$. Although the average coordination number of sodium cations is known to be six [27–31], and though the mean residence times of water molecules adja-

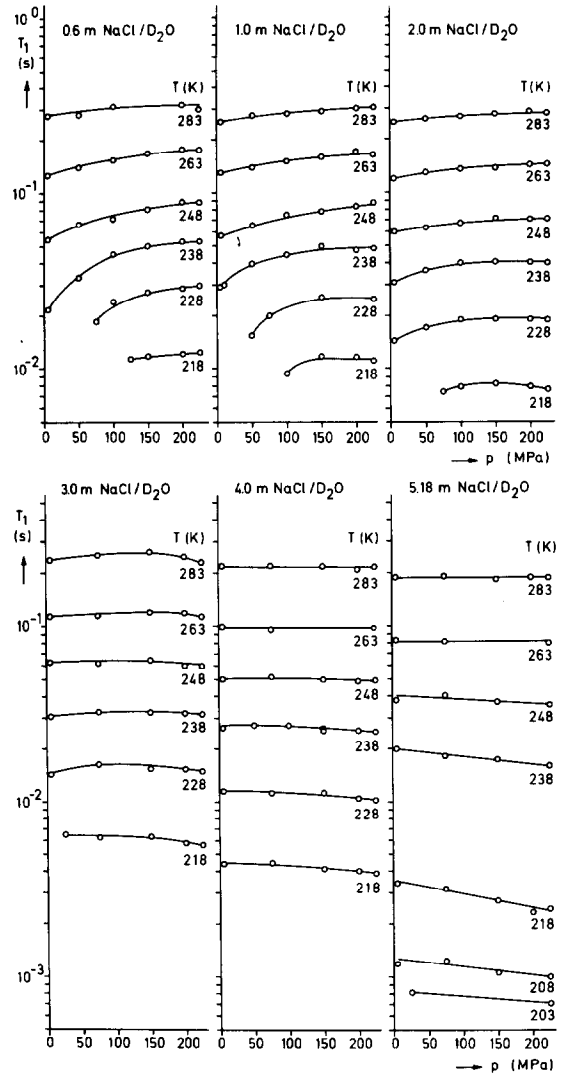

Fig. 1. Isothermal pressure dependence of the deuteron spin–lattice relaxation time T_1(^{2}H) in undercooled $NaCl/D_2O$ solutions at all concentrations investigated. (The compositions R corresponding to the concentrations c (molal) given in the figure may be found in table 1.)

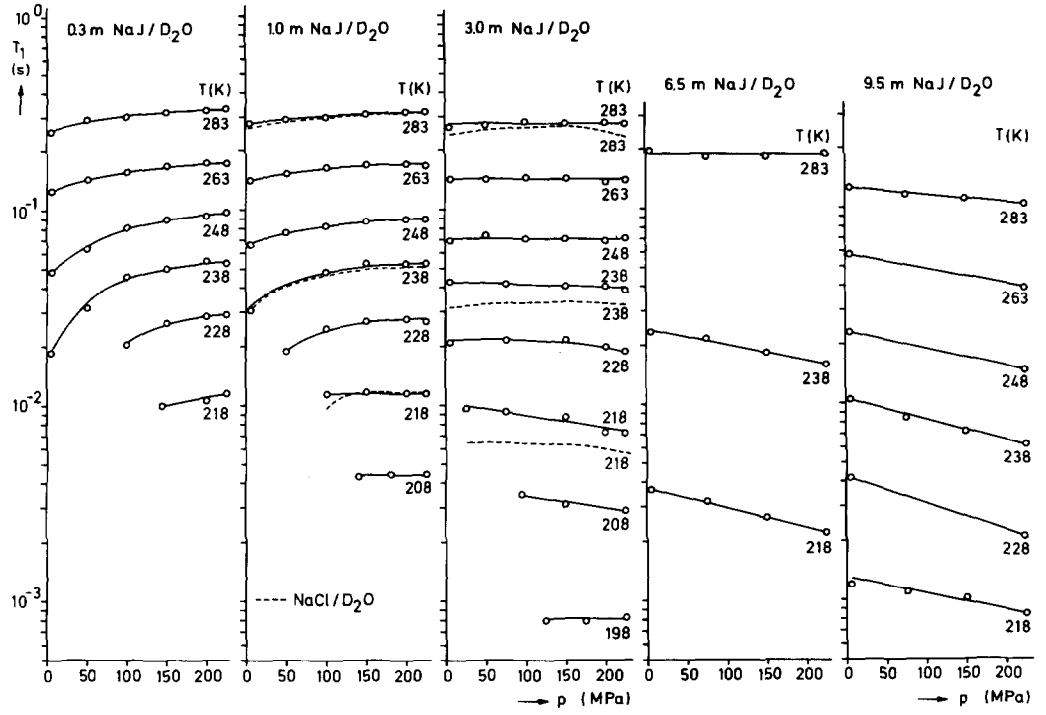

Fig. 2. Isothermal pressure dependence of the deuteron spin–lattice relaxation time $T_1(^2H)$ in undercooled NaI/D_2O solutions at all concentrations investigated. Broken lines give corresponding $T_1(^2H)$ in NaCl/D_2O solutions.

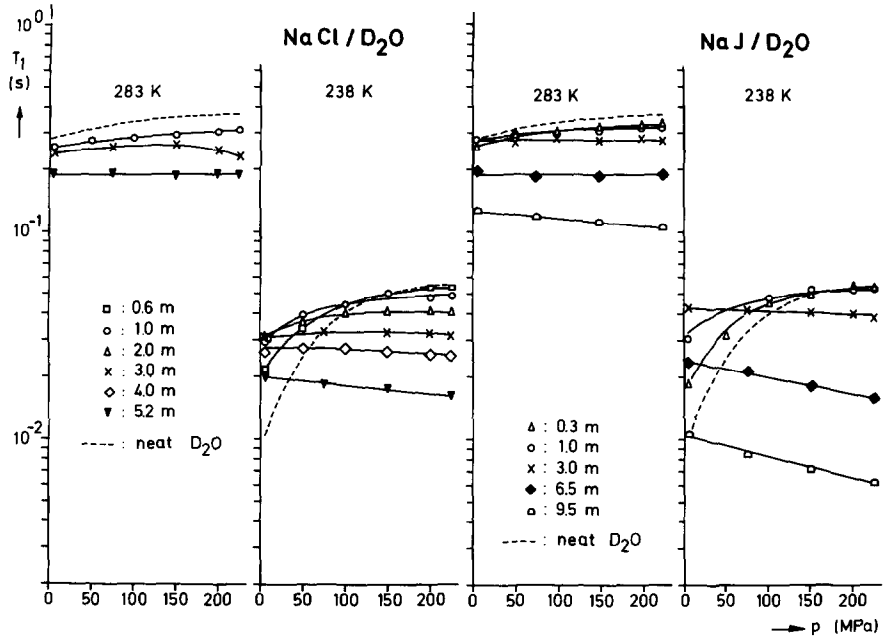

Fig. 3. Comparison of $T_1(^2H)$ isotherms in NaCl- and NaI–D_2O solutions at two temperatures corresponding to the thermodynamically stable (283 K) and undercooled metastable (238 K) phase.

cent to Na^+ are believed to be longer than for water molecules beneath Cl^- [32], these molecules cannot be considered to form a well-defined hydration shell of the Na^+ cations. This is because the negative pressure effect on the mobility of these hydration waters implies that Na^+ interacts less strongly with water than Li^+ and Mg^{2+}. Of course this is a consequence of the smaller charge density of Na^+ compared with Li^+ and Mg^{2+}. It is interesting, that computer simulations [28] lead to the conclusion, that the geometrical arrangement of the hyration shells around Na^+ remained practically unchanged upon compression. Thus, local dynamics seem to be much more sensitive to pressure than average local structures in these systems.

3.2. A motional model for the cationic hyration water

Under high pressure a relaxation rate maximum can be observed at low temperatures in the whole composition range. At low pressure it may be observed in highly concentrated electrolyte solutions only. In this slow motions regime the relaxation rates become sensitive to details of the molecular motions. A more quantitative discussion of the dynamics of water molecules in these solutions can then be given in terms of a motional model [6–11] developed recently to deduce a form of the spectral density function $g(\omega)$ for water molecules adjacent to strongly hydrating cations which is consistent with structural information available from scattering experiment [22–24]. The model decomposes the orientational fluctuations of the water molecules into small amplitude librations about their mean orientation. These fast torsional oscillations are superimposed onto anisotropic fluctuations around the local director with correlation time τ_i. It may be expected from electrostatic considerations that fluctuations around the director are less strongly hindered than those about any perpendicular axis. Hence, to keep the model simple with a minimum of adjustable parameters, only these least hindered fluctuations are taken into account. In addition to these internal modes there is an isotropic tumbling of the molecules around the ion with correlation time τ_r. Also chemical exchange [5,33] between hydration sites and bulk sites must be accounted for because the mean residence time τ_{ex} of the water molecules adjacent to Na^+ is comparable with the average correlation time in the hydration shell [32].

3.3. The relaxation rate of the hydration water

The model yields the following expression for the deuteron relaxation rate of the hydration water [6,10,11]:

$$(R_1)_{hyd} = \tfrac{3}{20}\pi^2[(\chi_{eff})^2/\omega_0][\tfrac{1}{4}(3\cos^2\beta_{DF}-1)^2 \times F(\omega_0\tau_0) + 3\sin^2\beta_{DF}\cos^2\beta_{DF}F(\omega_0\tau_1) + \tfrac{3}{4}\sin^4\beta_{DF}F(\omega_0\tau_2)], \quad (1)$$

with

$$F(\omega\tau) = 2g(\omega\tau) + 8g(2\omega\tau), \quad (2)$$

$$g(m\omega\tau) = \omega\tau/[1+(m\omega\tau)^2], \quad (3)$$

$$1/\tau_0 = 1/\tau_r + 1/\tau_{ex}, \quad (4a)$$

$$1/\tau_1 = 1/\tau_0 + 1/\tau_i, \quad (4b)$$

$$1/\tau_2 = 1/\tau_0 + 4/\tau_i. \quad (4c)$$

The slower modes of motion provide the main contribution to $g(\omega)$, whereas the effect of the fast torsional oscillations can be incorporated into an effective, librationally averaged quadrupole coupling constant [4,6,7],

$$\chi_{eff} = \left(\sum |\langle D_{02}(\Omega_{FI})\rangle|^2\right)^{1/2}\chi \approx \tfrac{1}{2}[3\langle\cos^2\beta_{FI}\rangle - 1]\chi. \quad (5)$$

β_{FI} is the angle between the z axis of the instantaneous principal frame of the electric field gradient tensor (I) and the equilibrium orientation of the OD bond (F) in the quasi-static local configuration. β_{DF} relates this equilibrium orientation of the OD bond to the local director frame (D). In most salt hydrates [34] the water molecules possess a tetragonal orientation, i.e. their dipole moment vector is tilted away from the local director by 54° roughly. Hence β_{DF} has been calculated accordingly. Anyhow, β_{DF} does not change much in going form a tetragonal to a trigonal orientation, rendering the ^2H T_1 fairly insensitive to the average orientation of the water molecules in the hydration shell [10].

These expressions imply that timescale separation pertains between the torsional and the diffusive

modes, that the anisotropic diffusive mode with correlation time τ_i and the isotropic tumbling mode with correlation time τ_r are statistically independent, that the mean residence time τ_{ex} is at least of the order of the correlation times and that the interaction is completely randomized on exchange [33].

3.4. Slow motions and non-Debye relaxation

Also an exponential decay of the component orientational correlation functions for times $t > \tau_r, \tau_i$ is implied by eq. (3), though non-exponential correlation functions [35,36] are commonly observed in undercooled liquids. These functions are often represented as a superposition of (sometimes infinitely many) exponential relaxation functions as within the current two-mode approximation, implying (many) parallel relaxation paths or as a stretched exponential emerging from a hierarchy of relaxation processes [36,37]. The spectral density functions $g(\omega)$ entering the relaxation rate expression (eq. (1)) are Fourier–Laplace transforms of these correlation functions. However, it is only in the slow motions regime at low temperatures that the form of the functions $g(\omega)$ becomes essential and details of the underlying dynamical processes may be deduced (see fig. 4). Unfortunately we could not reach low enough temperatures in those cases where measurements at two frequencies ($\omega_0 = 15.35$ and 46.07 MHz) could be performed to extract the frequency dependence of $g(\omega)$ in the slow motions regime, i.e. to detect expected deviations from the familiar Debye ω^{-2} dependence. This is because the low-temperature limit of the experiments was set by the deuteron NMR glass transition where the inverse of the correlation time becomes less than the quadrupole coupling constant. As far as data in the dispersion regime could be gathered, they are compatible with a Debye behaviour, i.e. the minimum in the relaxation time curve $T_1(T_{min})$ scales with the Larmour frequency ω_0.

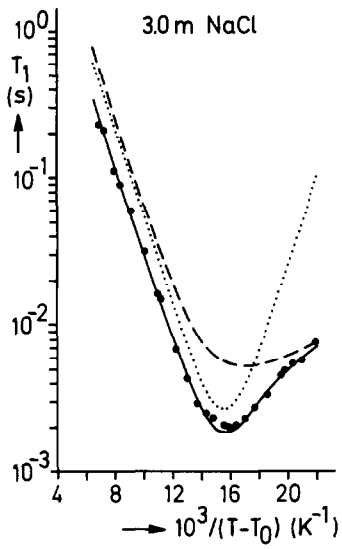

Fig. 4. Modified Arrhenius diagram of the isobaric ($p = 225$ MPa) temperature dependence of the deuteron spin–lattice relaxation time $T_1(^2H)$ of a 3 m $NaCl/D_2O$ solution. Dotted curve represents bulk water contribution and broken curve hydration water relaxation time according to eq. (8). ($T_0 = 137$ K.)

3.5. Slow motions and non-Arrhenius temperature dependence

Another characteristic feature of undercooled liquids is the non-Arrhenius temperature dependence of structural relaxation times and other dynamic variables [2,6–11,35–43]. This feature is clearly visible in figs. 5 and 6 which show the isobaric temperature dependence of the ^2H relaxation times in NaCl and NaI solutions for all compositions R investigated. It is a consequence of collective fluctuations and can be accomodated by a *VTF* law [44–46] which represents the temperature dependence of dynamic properties in most dense liquids above their glass transition rather well. A characteristic feature of the glass transition is that equilibrium correlation functions remain short ranged near T_g [43]. This should be of relevance also for aqueous solutions of simple electrolytes under high pressure or at high solute concentrations as both network breaking agents reduce the correlation length of density correlations. Hence the temperature dependence of the tumbling around the ion and of exchange processes may be represented in a highly disturbed H-bond network by

$$\tau_0 = \tau_{00} \exp[B/(T - T_0)], \qquad (6)$$

with T_0 the temperature of global motional arrest. It corresponds to calorimetric glass transition temperatures in the limit of very small cooling rates [47].

To determine T_0 for a solution of composition R

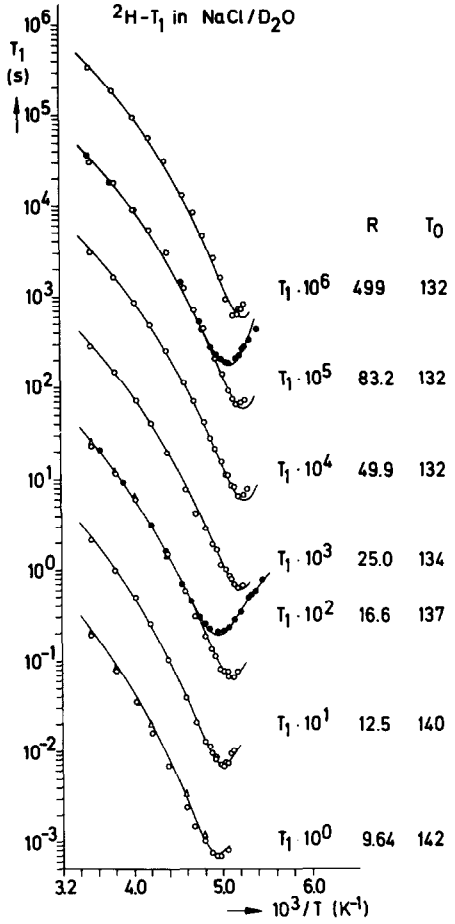

Fig. 5. Isobaric (p=225 MPa) temperature dependence of the deuteron spin–lattice relaxation time $T_1(^2H)$ for all compositions R (mole D_2O/mole salt) investigated. T_0 represents ideal glass transition temperature according to eq. (6). (○, $\omega/2\pi$ = 15.35 MHz, ●, $\omega/2\pi$ = 46.07 MHz.)

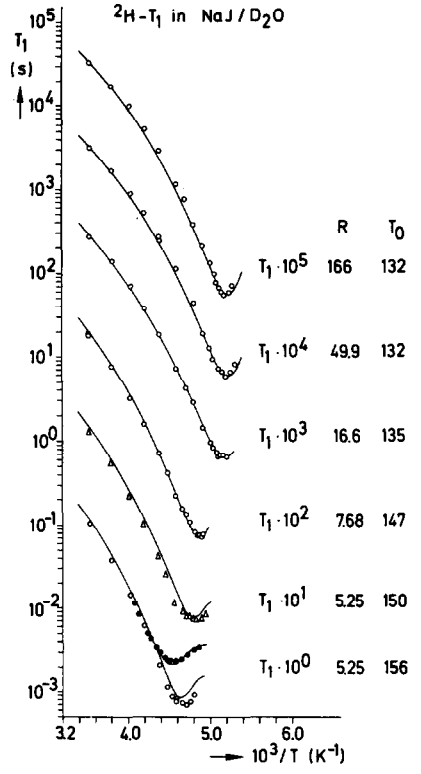

Fig. 6. Isobaric (p=225 MPa) temperature dependence of the deuteron spin–lattice relaxation time $T_1(^2H)$ for all compositions R investigated. (○, $\omega/2\pi$=15.35 MHz; △, $\omega/2\pi$=15.35 MHz, p=5 MPa; ●, $\omega/2\pi$=46.07 MHz.)

an empirical correlation between experimentally determined glass transition temperatures T_g and the temperature T_{min} of minimal relaxation times, observed in the systems LiCl/D_2O [6,8] and $MgCl_2$/D_2O [8,11], has been used in these studies to correlate T_0 and T_{min}. This empirical relation will be assumed to hold generally in undercooled salt solutions. Thus the composition dependence of $T_{min}(R, \omega = \text{constant})$ served to predict $T_0(R)$, compiled in table 1. Fig. 7 shows the composition dependence of the resulting $T_0(R)$ in NaCl– and NaI–D_2O solutions in relation to $MgCl_2$– and LiCl–D_2O solutions. Contrary to the latter systems only very few experimental glass transition temperatures T_g are reported for NaCl solutions at pressures $p > 100$ MPa and concentrations $c > 2.7$ m [3] and no such data exist for NaI solutions. It is of interest that the substitution of the Cl^- by the I^- anion leads to a small reduction ($\approx$3 K) of T_0. Thus the latter is determined by both cations and anions.

The abovementioned rule taken for granted, a modified Arrhenius diagram, ln T_1 versus $(T - T_0)^{-1}$, reveals that the slope parameter B is identical to that in neat D_2O (4) under high pressure and is independent of concentration as has been observed in aqueous LiCl and $MgCl_2$ solutions also.

In the slow motions regime severe deviations from a *VTF*-type behaviour become obvious as fig. 4 illustrates. The high-field (B=7 T) data in figs. 5 and 6 seem to indicate a turnover to an Arrhenius behav-

Table 1
Compilation of temperatures of minimal T_1 and related ideal glass transition temperatures T_0 for all compositions R investigated in $NaCl/D_2O$ solutions

	c (mol/kg)	R (mol D_2O/mol salt)	$\omega/2\pi$ (MHz)	$T_{min}\pm 2$ (K)	$T_0\pm 2$ (K)
$NaCl/D_2O$	0.1	500.0	15.35	192	132
	0.6	83.2	15.35	192	132
			46.07	197	
	1.0	50.0	15.35	192	132
	2.0	25.0	15.35	194	134
	3.0	16.7	15.35	197	137
			46.0	202	
	4.0	12.5	15.35	200	140
	5.2	9.6	15.35	202	142
NaI/D_2O	0.3	166.7	15.35	192	132
	1.0	50.0	15.35	192	132
	3.0	16.7	15.35	195	135
	6.5	7.7	15.35	206	147
	9.5	5.3	15.35	214	156
			46.07	217	

iour of the relaxation time curve. This behaviour resembles the splitting off of a second mode as in secondary relaxation pocesses. As the global motional modes should slow down strongly at these low temperatures local modes must take over and dominate the relaxation. Thus, according to the current motional model, the local anisotropic mode is considered to constitute a thermally activated process with its concomitant Arrhenius temperature dependence

$$\tau_i = \tau_{i0} \exp(E_a/kT) . \qquad (7)$$

Because of the torsional oscillations τ_{i0} should correspond to the inverse of an average librational frequency. From experimental determinations of the frequency of the band maximum of the primary hydration water component in aqueous sodium halide solutions [48] the corresponding τ_{i0} are calculated and are compiled in table 2.

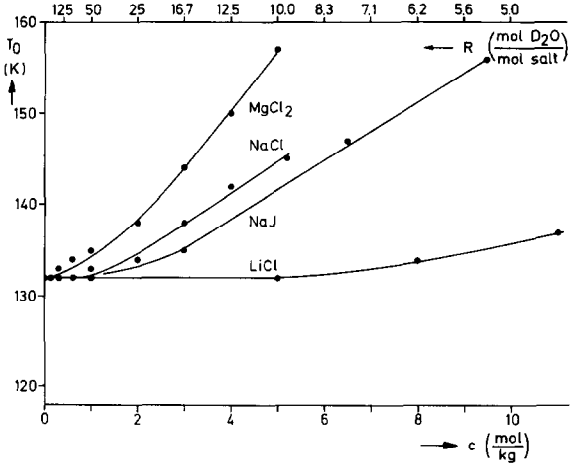

Fig. 7. Comparison of the composition dependence of the ideal glass transition temperature $T_0(R, p=225$ MPa). ($MgCl_2$: ref. [11], LiCl: ref. [10].)

3.6. The two-site approximation

Because the exchange between hydration sites and bulk sites is fast ($T_1 > \tau_{ex}$), an average relaxation time can be observed only. It will be calculated within a two-state approximation [49] as a mole-fraction weighted average according to

Table 2
Compilation of model parameters entering eqs. (4)–(8) for $NaCl/D_2O$ and NaI/D_2O. The corresponding parameters for the system $LiCl/D_2O$ are given for comparison

	NaCl	NaI	LiCl [a]
τ_{00} (ps)	0.120	0.085	0.200
τ_{i0} (ps)	0.062	0.069	0.080
E_a (kJ/mol)	18.70	18.70	19.80
B_r (kJ/mol)	5.72	5.72	5.72
χ_{eff} (kHz)	192	201.2	192
n_h	6 ($c \leqslant 4$ m)	6 ($c \leqslant 3$ m)	6 ($c \leqslant 8$ m)
	5 ($c \leqslant 5.2$ m)	4 ($c = 6.5$ m)	4.55 ($c = 11$ m)
		3 ($c = 9.5$ m)	

[a] Taken from ref. [10].

$$R_1(T, p, R) = \frac{n_h}{R}(R_1)_{hyd} + \frac{R - n_h}{R}(R_1)_{bulk}, \qquad (8)$$

with n_h the dynamic hydration number of the cations. Of course, both rates R_1 have to be calculated at the same reduced temperature ($T - T_0(R)$) pertaining to the respective composition R of the solution because the clusters of hydrated cations and bulk water molecules are in dynamic equilibrium. The small influence of the anions upon the bulk water dynamics is incorporated simply into the proper Kauzmann temperature T_0 [50] for the solution of composition R. It is for this reason that the relaxation rates of bulk water and neat water differ if compared at the same temperature. Hence both rates are not equal as is often assumed in the literature.

3.7. Estimate of the model parameters

Before applying the model to the experimental data it has to be eplained how those parameters in eqs. (1) and (8), that cannot be obtained from other sources, can be estimated from the experimental data. To this end the 3 m NaCl solution investigated at 46.07 MHz has been chosen because the lowest temperatures could be reached there.

The strong non-Arrhenius temperature dependence already indicates that, according to the current motional model, the relaxation time curve $T_1(T)$ in the fast motions regime, i.e. at medium undercooling, is dominated almost completely by the tumbling mode τ_0. Hence τ_{00} in eq. (6) can easily be estimated from T_1 data at high temperatures where the local anisotropic mode does not contribute to the relaxation significantly. In consequence of a shorter mean residence time of water molecules adjacent to Na^+ cation, τ_{00} turns out to be smaller than in the case of Li^+. Furthermore a significant anion effect is seen in this parameter which may be traced back to a further reduction of the mean residence time on replacing the Cl^- by the I^- anions.

Now, according to the *VTF* temperature dependence the relaxation rate should slow down strongly at low temperatures. This strong slowing down is, however, hidden behind the much weaker Arrhenius temperature dependence of the local anisotropic mode which becomes the faster process at low temperatures and dominates the relaxation in the slow motions regime. The relaxation time curve $T_1(T)$ should then display an Arrhenius temperature dependence. As fig. 4 illustrates (see hydration water relaxation time curve), because pronounced deviations from a *VTF* behaviour appear at low temperatures only, data well below T_{min} are necessary to extract reliable apparent activation energies E_a opposing anisotropic fluctuations around the local director.

To do so χ_{eff} (see eq. (1)) has to be known. It may be calculated from the relaxation rate maximum $R_1(T_{min})$ predicted by eqs. (1) and (8) and corroborated experimentally in all solutions investigated. In NaCl solutions $\chi_{eff}(^2H)$ is slightly smaller than found in neat D_2O as expected from theoretical calculations [51]. A similar reduction has been observed also in $LiCl–D_2O$ solutions [10] indicating that Na^+ causes a comparable distortion of adjacent water molecules. However, substitution of Cl^- anions by the larger I^- anions yields $\chi_{eff}(^2H)$ as in neat water suggesting that,

due to the higher charge density, Cl^- anions polarize the hydration water molecules also. Because the electric field gradient at the deuterium nucleus depends inversely on the OD distances [51–53], a reduction of χ_{eff} indicates an increased OD bond length resulting from the polarization of water molecules squeezed between cations and anions or from larger mean squared librational amplitudes [28].

Except for the local barriers E_a all other model parameters have been extracted from the experimental data directly or obtained from other sources as explained above. The former have been determined from a non-linear least-squares fit (NAG E04FCF) of eqs. (1) and (8) to the T_1 data of the 3 m solution obtained at 46.07 MHz. The dynamic hydration number n_h in eq. (8) has been chosen in accordance with the coordination numbers as deduced from computer simulations and scattering experiments, i.e. $n_h = 6$. A least-squares fit with n_h as a second adjustable parameter gave $n_h = 6.4$ in good agreement with computer simulation results [28]. In the case of the NaI solutions measurements at 46.07 MHz could only be performed for the 9.5 m solution. The slope on the low-temperature side is consistent with an activation energy E_a as obtained for NaCl solutions, though further data are necessary to resolve any anion effect on this parameter. The full curve in fig. 4 represents the calculated relaxation time curve demonstrating good overall agreement with the experimental data. Also the component relaxation time curves corresponding to bulk and hydration water are drawn (see eq. (8)). They illustrate that in dilute and moderately concentrated solutions, corresponding to mole-fraction weights $n_h/R < 0.5$ roughly, the locus of the minimum as well as the form of the $T_1(T)$ curve is largely determined by the bulk water contribution. It also demonstrates that above T_{min} hardly any influence of the local anisotropic mode can be seen in the relaxation time curve.

3.8. Average relaxation rate and dynamic hydration number

Having determined all parameters for the hydration water relaxation rate (eq. (3)), the two-state approximation (eq. (8)) may be used to calculate the relaxation time isobares ($p = 225$ MPa) for all solutions of composition R with the parameters given in table 2 if the appropriate Kauzmann temperatures T_0 are inserted. Figs. 5 and 6 demonstrate that the model correctly reproduces the isobaric ($p = 225$ MPa) T, ω dependence of the relaxation times for all compositions up to saturation. But to obtain that agreement the dynamic hydration number n_h had to be reduced in the most concentrated solutions as indicated in table 2. Note that this is different from the systems $LiCl/D_2O$ and $MgCl_2/D_{21}O$ where the hydration number n_h could always be taken as equal to the coordination number known from structural data. A reduction of the hydration number is certainly due to the breakdown of the dynamic equivalence of the water molecules comprising the less well-defined hydration shell of the sodium cations. As much higher concentrations can be reached in the system NaI/D_2O, the necessary reduction of n_h is more pronounced. It should be noted that the same level of agreement could not be obtained by adjusting τ_{00}, corresponding perhaps to a changing exchange lifetime τ_{ex}, and keeping n_h unchanged. In effect, reducing the dynamic hydration number in eq. (8) at high concentrations enhances the number of water molecules which display bulk water dynamics leading to a less broad and deeper minimum in the relaxation time curve. This is tantamount to saying that, on average and on a timescale set by the correlation times, less water molecules are strongly perturbed by the cations at high concentrations. But as the hydration shell becomes less well defined and contact ion-pairing effects become important the current simple dynamical model certainly must become inappropriate.

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