

Multinuclear Spin-Lattice Relaxation Studies of Undercooled Aqueous Potassium Fluoride Solutions Under High Pressure

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High Pressure / Liquids / Spectroscopy, Nuclear Magnetic Resonance / Transport Properties

In this investigation we report ^2H , ^1H and ^{19}F spin-lattice relaxation (SLR) rate experiments performed in undercooled aqueous KF-solutions of concentration $c \leq 12$ molal under an external pressure of $p \leq 225$ MPa. The relaxation rate curves of the various nuclei are consistently interpreted with a two mode – two site approximation of the dynamic structure of the H-bond network in these ionic solutions. The local arrangement of water molecules coordinated to an F^- -anion can be obtained from Fluor-19 relaxation rate curves and is found to correspond to an almost linear ion-water configuration. This finding is in accord with predictions from theory and computer simulations and corrects earlier findings from other NMR experiments.

Introduction

Spin-lattice relaxation time (T_1) measurements are directly related to molecular motions ($\approx G(t)$) in liquids. As the latter are fast on the time-scale of the NMR-experiment, performed under ambient conditions, details of the molecular dynamics are hidden behind an integral correlation time $\tau_{av} \approx \int G(t)dt$. If, however, the liquids can be forced into supercooling, molecular motions slow down strongly. Relaxation times then depend on the form of the spectral density function $g(\Omega) \approx \int G(t) \exp(i\Omega t)dt$, monitoring details of orientational and positional fluctuations in the liquid [1, 2].

In recent investigations [3–8] the influence of alkali- and alkali earth halides upon molecular motions of water molecules in undercooled aqueous solutions under hydrostatic pressure has been studied. The smaller cations (Mg^{2+} , Li^+ ,

Na^+) in these solutions are generally considered to exert the stronger influence upon orientation and dynamics of adjacent water molecules compared to the larger anions (Cl^- , Br^- , I^-). The potassium and cesium halide solutions represent borderline cases in this respect, hence show the least pronounced indications of a motional anisotropy and exhibit strongly composition dependent hydration numbers. The presently investigated aqueous KF solutions represent an example, where the anion F^- is known to have hydration characteristics similar to Li^+ . Hence the anion F^- may be considered to interact strongly with water and the weaker interaction of the K^+ cation may then be almost neglected.

Aqueous electrolyte solutions, emulsified in a cycloalkane/surfactant mixture, can be undercooled to 180 K and below (depending on the solute concentration), if hydrostatic pres-

sure is applied [2]. In this investigation we report ^3H , ^1H and ^{19}F spin-lattice relaxation (SLR) experiments performed in aqueous KF solutions of concentration $c \leq 12$ molal under an external pressure of $p \leq 225$ MPa. Deuteron (^2H) relaxation rates monitor orientational fluctuations only, whereas proton (^1H) and fluor (^{19}F) relaxation rates depend on orientational and positional fluctuations of the spin bearing particles. The latter relaxation rates also depend on the relative distance of the particles, hence information about the average local structure of the hydration sphere of the F^- anion may possibly be gathered.

Experiment

The solutions were prepared from a stock solution of the anhydrous salt (Merck, Darmstadt, Suprapur) and H_2O which has been drawn from a Milli-Q-unit equipped with prefilter-, carbon-, ion exchanger- and ultrafiltration cartridges and a Millistak GS filter (Millipore, Eschborn, BRD). In case of the D_2O solutions, the salt has been dissolved in D_2O (99.75% Merck, Darmstadt), dried under vacuum at 313 K and stored over P_2O_5 on a vacuum line for 48 h. After repeating this procedure four times, the desired concentration has been prepared by adding the proper amount of water. Emulsions have been prepared by mixing equal amounts of the salt solution with a mixture of methylcyclohexane (MCH), methylcyclopentane (MCP) and a small amount of the surfactant sorbitanetriscarate (Span 65). The ^{19}F - T_1 measurements in D_2O solutions are very sensitive for any contamination of the sample with ^1H nuclei because of the much stronger dipole interaction of ^{19}F with ^1H . Therefore heavy water with a deuterium enrichment of 99.95% has been used. The cycloalkanes (MCH, MCP) have been dried over a molecular sieve and the surfactant Span 65 has been dissolved repeatedly in D_2O to remove all exchangeable protons. The salt has been dried at 470 K on a vacuum line for 4 h. To further reduce the effect of paramagnetic impurities on T_1 [9], a small amount (0.1 wt-%) of the gelating compound Titriplex IV has been added to the solution.

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 box 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 high pressure glass cells [2] on a vacuum line.

All T_1 experiments were performed with the inversion recovery pulse sequence on a Varian XL-100 (^1H : 100 MHz, ^{19}F : 95.7 MHz, ^2H : 15.35 MHz) and on a Bruker MSL 300 (^1H : 300 MHz, ^{19}F : 282.7 MHz, ^2H : 46.07 MHz) multipurpose solid-liquid spectrometer. 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.

The Effect of Pressure and Ionic Solutes Upon the Dynamics of the H-bond Network

In cold water structural correlations develop within the random, transient H-bond network with increasing correlation length and with a slowing down of structural fluctuations [10, 11]. These cooperative phenomena become most pronounced close to the low temperature limit T_H of the undercooled phase. Dynamic properties of water molecules, related to these structural fluctuations, then display a dynamic scaling behaviour according to [12]

$$R_1 \approx \tau \approx (T - T_s)^{-\beta}, \quad \beta \approx 1.7 - 2.5 \quad (1)$$

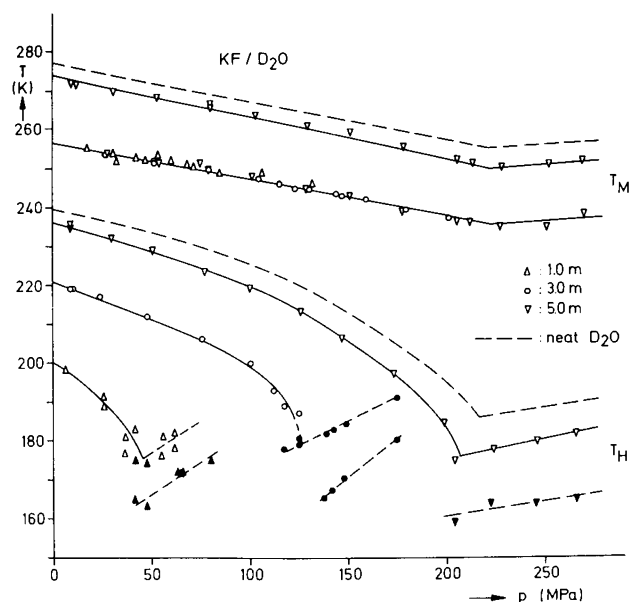


Fig. 1
Pressure dependence of the homogeneous nucleation temperature T_h of $\text{KF}/\text{H}_2\text{O}$ solutions at different concentrations

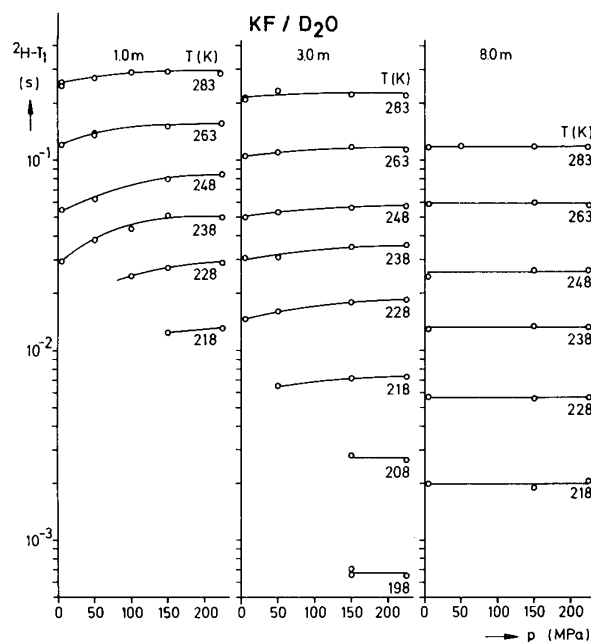


Fig. 2
Pressure dependence of deuterium spin-lattice relaxation time isotherms at various concentrations

with the scaling temperature T_s a few degrees below T_H . The latter is a strongly varying function of hydrostatic pressure and solute concentration as may be seen in Fig. 1. Ionic solutes and hydrostatic pressure may thus be considered network breaking agents which strongly perturb long-range structural correlations. Hydrogen bonds hinder molecular motions strongly. The effect of network breaking agents is to facilitate molecular motions in the perturbed H-bond network. Fig. 2 shows that $T_1(^2\text{H}) \approx D_{\text{rot}}$ increases upon initial compression demonstrating that reorientational fluc-

tuations of water molecules become less hindered. Also $T_1(^2\text{H})$ increases upon addition of ionic solutes in the undercooled phase at low pressure (Fig. 3). These effects can be understood easily in terms of an increasing distance $(T - T_s)$ from the scaling temperature $T_s(c, p)$, which is a strongly decreasing function of pressure and solute concentration.

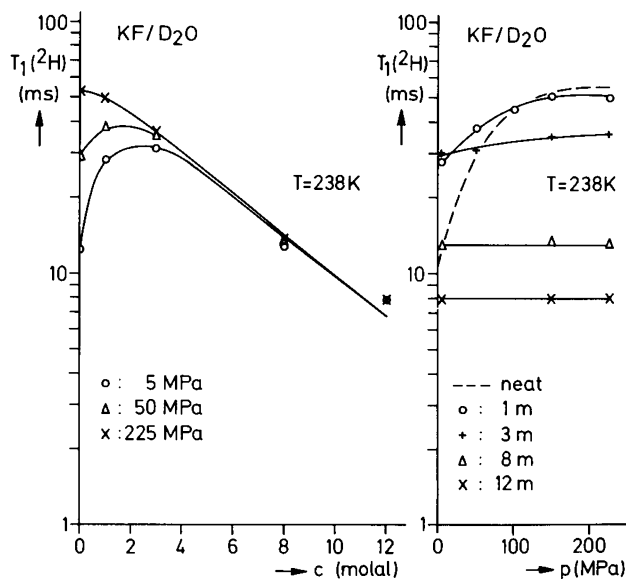


Fig. 3

Comparison of the effect of pressure and/or ionic solutes on the average rotational mobility ($\approx T_1(^2\text{H})$) of water molecules in undercooled KF/D₂O solutions

Under the combined influence of both network breaking agents these effects obviously must become less pronounced. At sufficiently high concentrations the solutions contain only water molecules hydrating the cations with almost no bulk water present. These molecules are forced into close packing by strong electrostrictive forces. Their average orientation, dictated mainly by coulomb forces, inhibits optimal H-bond interactions. Hence, the random H-bond network is strongly disrupted and modest hydrostatic pressures may exert only a minor influence upon molecular reorientations. Therefore the relaxation rates are found independent of pressure up to 225 MPa in these concentrated solutions.

Motional Model and Related Relaxation Rates

The Two-Mode Approximation

A quantitative discussion of the dynamics of water molecules in aqueous electrolyte solutions will be given in terms of a motional model, which is simple, consistent with the average local structure of ionic solutions [13, 14] and accounts for the most prominent features of the relaxation time curves in various undercooled alkali- and earthalkali halide solutions investigated so far [2–8]. The model considers water molecules adjacent to an ion to execute small-amplitude librations superimposed onto anisotropic orientational fluctuations about the local director (ion-oxygen direction).

In addition the molecules diffuse around the ion and exchange occurs between hydration sites and bulk sites. Two correlation times enter the model, namely

$$\tau_i = \tau_{i0} \exp(E_a/kT) \quad (2)$$

to characterize the local anisotropic mode and

$$\tau_0 = (1/\tau_r + 1/\tau_{ex})^{-1} = \tau_{00} \exp(B_{or}/(T - T_0)) \quad (3)$$

to account for overall tumbling and exchange processes. τ_0 is considered to correspond to an attempt frequency for barrier crossing and is set equal to the inverse of an average librational frequency [15].

Information about the average local structure of ionic solutions, i.e. the relative orientation and distance of water molecules in contact with an ion, may be obtained from neutron and X-ray scattering experiments [13, 16], computer simulations [14] or, less straightforwardly, from NMR experiments [2, 17].

Water molecules coordinated to cations are generally oriented with their protons pointing away from the cation. Concerning simple anions experiment [13, 16, 18–20] and theory [14, 21–28] favour a linear anion-water arrangement with one proton pointing towards the anion. This configuration has been questioned, however, with recent NMR experiments [9], which seem to indicate a bifurcated orientation of water molecules in contact with F[−] anions. The present experiments strongly suggest an almost linear configuration in accord with computer simulation results.

The Relaxation Rates of the Hydration Water

Pertinent expressions for the hydration water relaxation rate have been worked out for electric quadrupole interactions mediating the SLR of the deuterons (²H) [2] and for magnetic dipole interactions dominating the SLR of the protons (¹H) and the fluorine (¹⁹F) nuclei [2]. They will be summarized for the discussion to follow.

a) Deuterium Spin-lattice Relaxation Rate

$$R_1(^2\text{H}) = (1/2)(R_1(^2\text{H}_1) + R_1(^2\text{H}_2)) \quad (4)$$

$$\begin{aligned} (R_{1,or})_{hyd} = & C_{Q,or} [((3 \cos^2 \beta_{DF} - 1)/2)^2 F(\Omega_0 \tau_0) \\ & + 3(\sin \beta_{DF} \cos \beta_{DF})^2 F(\Omega_0 \tau_1) \\ & + (3/4)(\sin \beta_{DF})^4 F(\Omega_0 \tau_2)] \end{aligned} \quad (5)$$

with $C_{Q,or} = (3(\pi \Gamma_{eff})^2/20\Omega_0)$, Γ_{eff} is the quadrupole coupling constant averaged over the librations and β_{DF} is the angle between the equilibrium orientation of the OD-bond (F) and the local director frame (D) (see Fig. 4). The $F(\Omega\tau)$ refer to the usual combinations of the rotational spectral density functions $g(\Omega)$ [29] with τ_0 , τ_1 and τ_2 representing combinations of the correlation times τ_r , τ_i and τ_{ex} appropriate to the current motional model [2]. As both deuterons are not equivalent concerning β_{DF} , R_1 has to be averaged over both positions (²H₁: $\beta_{DF} = 38^\circ$, ²H₂: $\beta_{DF} = 66.5^\circ$).

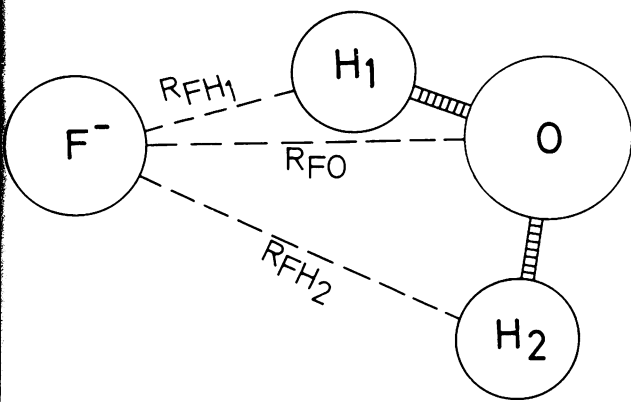


Fig. 4
Average orientation of a water molecule in the hydration shell of a F^- anion. Corresponding to a disturbed linear configuration

b) Fluor-19 Spin-lattice Relaxation Rate ($I = {}^{19}\text{F}$)

The dominant interaction mediating the SLR of the ${}^{19}\text{F}$ nucleus of the F^- anion is the dipolar coupling to the ${}^1\text{H}$ or ${}^2\text{H}$ magnetic moments of the surrounding water nuclei. This interaction is modulated by orientational fluctuations of the water molecules comprising the hydration shell of F^- with the average internuclear distances remaining constant within the time span of the relevant correlation times. It is also modulated by positional fluctuations of water molecules outside the primary hydration layer. Hence the total rate may be written as [1]

$$(R_1)(I, S) = (R_{1,\text{or}})(I, S) + (R_{1,\text{pos}})(I, S) \quad (6)$$

with I, S representing ${}^{19}\text{F}$ ($I = 1/2$) and ${}^1\text{H}$ ($S = 1/2$) or ${}^2\text{H}$ ($S = 1$) respectively. Cross-relaxation effects due to a coupling of spin systems I and S [2, 19] have been neglected in Eq. (6), as relaxation time measurements of the spin system I while irradiating the spin system S with a strong rf-field yielded identical results within the limits of accuracy given above. That cross-relaxation effects may be neglected has been demonstrated already in a thorough investigation of nuclear Overhauser effects in aqueous KF solutions under ambient conditions [19].

Within the current two-mode approximation ($R_{1,\text{or}}$) is given by Eq. (5) with the appropriate, librationaly averaged, dipolar coupling factor

$$C_{\text{D,or}} = (1/5)(\gamma_I \gamma_S h / 2\pi)^2 S(S+1) (\mu_0 / 4\pi \Sigma \langle r_{IS} \rangle^{-3})^2 \quad (7)$$

and the pertinent combinations of rotational spectral density functions $g(\Omega_I)$ and $g(\Omega_I \pm \Omega_S)$ [29]. Of course, β_{DF} now relates the equilibrium orientation of the internuclear separation r_{IS} to the local director frame. In the disturbed linear configuration one proton is much closer ($R_{\text{FH1}} = 0.181$ nm) to the fluorine anion than the other one ($R_{\text{FH2}} = 0.250$ nm). Due to the r^{-6} dependence of the dipolar coupling factor on distance, the contribution from the dipolar interaction with the more distant proton spin to the ${}^{19}\text{F}$ relaxation may be neglected. This simplification immediately implies that,

according to the motional model applied, the local, anisotropic mode does not contribute to the ${}^{19}\text{F}$ relaxation.

The translational propagator representing the positional fluctuations is assumed to obey a force-free diffusion equation with reflecting boundary conditions [30, 31]. Any pair-correlation effects will be neglected. The corresponding rate is given by

$$(R_{1,\text{pos}})(I, S) = C_{\text{D,pos}} F(\Omega_I, \Omega_S, \tau_d) \quad (8)$$

with

$$C_{\text{D,pos}} = (2\pi/5)(\gamma_I \gamma_S h \mu_0 / 8\pi)^2 \cdot S(S+1)(N_s \cdot \tau_d / d_{IS}^3) \quad (9)$$

and $F(\Omega\tau)$ representing the corresponding combination of translational spectral density functions [29]. The correlation time for translational diffusion τ_d may be expressed by

$$\tau_d = (d_{I-S})^2 / D_{\text{rel}}(I-S) = \tau_{0,IS} \cdot \exp(B/(T-T_0)) \quad (10)$$

with

$$D_{\text{rel}}(I-S) = D_{\text{self}}(I) + D_{\text{self}}(S) \quad (11)$$

the sum of the self-diffusion coefficients of the particles on which the spins I and S reside.

c) Proton Spin-lattice Relaxation Rate ($I = {}^1\text{H}$)

The SLR of the water protons is also dominated by the dipolar coupling to other protons as well as to the ${}^{19}\text{F}$ nuclei of the F^- anion. The orientational contribution ($R_{1,\text{or}})(I, S)$ to the hydration water relaxation rate is composed of a dipolar coupling of the two protons within a water molecule and the dipolar coupling of the n_h protons with the central F^- anion. It is given by Eq. (5) with the proper substitutions for $C_{\text{D,or}}$ and $F(\Omega\tau)$. The contribution ($R_{1,\text{pos}})(I, S)$ summarizes the effect of fluctuating proton-proton and proton-fluorine distances upon the relaxation rate of the hydration water protons due to relative translations of water molecules outside the primary hydration layer. It is also given by Eq. (8) with the appropriate substitutions understood.

Estimate of Model Parameters and Data Evaluation

To estimate the parameters of the relaxation rate expressions given above, it will be assumed that all water molecules of the 12 m KF solution, corresponding roughly to a composition (moles water/mole salt) $R = 4$, may be considered to be coordinated to the F^- anion on the time scale of the relevant correlation times. With this assumption the parameters of the hydration water relaxation rate may be deduced from the experimental data.

a) Deuterium Relaxation Rates

Recent investigations [2] showed, that the composition dependence of the kinetic localization temperature T_0 is reflected in the respective temperature T_{min} (T_{max}) of the minimum (maximum) of the relaxation time (rate) curve $T_1(T, R)$

($R_1(T, R)$). This empirical correlation could be established in all solutions with known calorimetric glass transitions T_g [3, 5] and proved useful in predicting T_0 in all other cases studied so far, where no T_g data yet exist. The glass temperatures T_0 estimated from the corresponding T_{\min} are compiled in Table 1.

Table 1
Compilation of model parameters entering the hydration water relaxation rate expressions

	$\tau_{(0)}$ (ps)	$\tau_{(1)}$ (ps)	E_a (kJ·mol ⁻¹)	B (kJ·mol ⁻¹)	Γ_{eff} (kHz)
H ₂ O	0.200	0.047	21	5.46	
D ₂ O	0.200	0.065	21	5.09	185
	R_{HH} (nm)	R_{HF} (nm)		d_{HH} (nm)	d_{HF} (nm)
H ₂ O	0.156	0.181	0.250	0.28	0.35
c (molal)	1	3	8	12	
T_0 (H ₂ O) (K)	127	130	137	144	
T_0 (D ₂ O) (K)	134	137	144	152	
$N_{\text{H}} \cdot 10^{28}$ (m ⁻³)	6.10	6.40	6.30	6.10	
$N_{\text{F}} \cdot 10^{28}$ (m ⁻³)	0.06	0.19	0.51	0.73	
$\tau_{0,\text{HF}}$ (ps)	0.75	0.89	1.23	1.33	
$\tau_{0,\text{DF}}$ (ps)	0.80	0.95	1.30	1.44	
$\tau_{0,\text{HH}}$ (ps)	0.39	0.47	0.66	0.71	
n_{H}	5	5	5	4	

From the graph $\ln R_1$ versus $(T - T_0)^{-1}$ the apparent activation energy B_{or} can be obtained immediately. It turned out to be slightly smaller than in the other alkali halide solutions, where B_{or} was found to correspond to the slope parameter in neat D₂O.

The preexponential factor τ_{00} of Eq. (3) can be estimated from data in the fast motions regime ($\Omega\tau \ll 1$, $T > T_{\min}$). It turned out to be rather insensitive to variations of τ_i in line with earlier findings that the local, anisotropic mode does, at least within the current motional model, not contribute significantly to the relaxation in the fast motions regime. The librational averaged quadrupolar coupling constant Γ_{eff} can be estimated from the maximal rate $R_1(T_{\max})$ observed. It is found $\approx 5\%$ smaller than in neat D₂O corresponding to an increased OD-bond length of the hydration water [32, 33].

The average angle β_{DF} between the OD-bond direction and the local director orientation is calculated in accord with a slightly disturbed linear configuration of the anion-water arrangement as has been found appropriate with computer simulations [27] and neutron scattering results in case of Cl⁻ hydration [13]. Both OD-bonds of a water molecule have different orientations with respect to the local director in the disturbed linear configuration, giving $(\beta_{\text{DF}})_1 = 38^\circ$ and $(\beta_{\text{DF}})_2 = 66.5^\circ$ respectively.

The apparent activation energy E_a of the local anisotropic mode has been obtained from a non-linear least squares fit (NAG E04FCF) of Eq. (5) to the high field ($B_0 = 7$ Tesla) $^2\text{H} - T_1$ data of the 12 m KF/D₂O solution.

All model parameters thus obtained are compiled in Table 1.

b) ^{19}F and ^1H Relaxation Rates in D₂O and H₂O

To be consistent, the parameters of the motional model for the hydration water dynamics deduced from the ^2H relaxation time data must, except for possible isotope effects, also be applicable for the orientational fluctuations contributing to the ^{19}F and the ^1H relaxation rates. But as positional fluctuations also contribute, the parameters entering the corresponding rate ($T_{1,\text{pos}}$) have to be estimated too.

The internuclear distances r_{IS} of the interacting nuclei have been taken from computer simulation results [21]. The corresponding angles β_{DF} measuring the orientation of r_{IS} relative to the local director have again been calculated in accord with a disturbed linear configuration.

Also the distances of closest approach d_{1-5} may be taken from partial radial pair distribution functions calculated with MC or MD methods [21].

Only a rough estimate of the number density of interacting spins N_s outside the hydration sphere can be given as experimental densities are lacking for the system under consideration. The value given in Table 1 is calculated from measured densities of a 1 m KF/H₂O solution [35]. To account for the density increase with pressure these densities have been corrected by a factor giving the ratio of densities at high (200 MPa) and low (0.1 MPa) pressure in a NaCl solution [36]. Further N_s had to be assumed independent of temperature. This is not a major limitation in view of the strong non-Arrhenius T -dependence of $D(T)$ assumed to be described by a VTF-equation (Eq. (3)) also.

Experimental self-diffusion coefficients of the water molecules D_{H} and the fluorine anions D_{F} are known at $T = 298$ K only [37]. Hence, again a rough estimate must suffice. From Eq. (10) the corresponding correlation time for translational diffusion may be calculated at $T = 273$ K. The temperature dependence of τ_d will be assumed to follow a VTF-law also. The composition dependence of τ_d is then reflected in the corresponding dependence of the temperature of global motional arrest $T_0(R)$.

Isotope effects upon glass transition temperatures (T_g , T_0) are also well documented [38–40]. According to the correlation of T_{\min} and T_0 , any possible isotope effect should show up as a shift of T_{\min} in H₂O compared to D₂O. But any shift of T_{\min} or equivalently T_{\max} is especially hard to detect because of the complicated form of the T_1 -minimum or equivalently R_1 -maximum in H₂O. Actually a shallow and a pronounced maximum occur, which correspond to terms $(\Omega_{\text{F}} + \Omega_{\text{H}})\tau \approx 1$, $\Omega_{\text{F}}\tau \approx 1$ and $(\Omega_{\text{F}} - \Omega_{\text{H}})\tau \approx 1$ respectively. Because $\Omega_{\text{F}} \approx \Omega_{\text{H}}$, the latter condition can be satisfied with much longer correlation times τ only, which occur at lower temperatures and cause the second, pronounced maximum. The shallow maximum of the R_1 curve in H₂O corresponds to the maximum in D₂O. The corresponding T_0 has been shifted by 7 K to lower temperatures compared to heavy water in accord with the known isotope effect in pure water [2].

With the parameters thus estimated and compiled in Table 1, the relaxation rate curves of the 12 m solutions have been calculated. They are drawn as solid lines in Figs. 7 and 8.

The Two-site Approximation

Because of fast ($\tau_{\text{ex}} \ll T_1$) chemical exchange between bulk and hydration sites, an average relaxation rate can only be obtained. It is calculated within a two-site approximation as a mole-fraction weighted average of the relaxation rates measured in the 12 m solution $(R_1)_{\text{hyd}}$ and in neat D_2O and H_2O $(R_1)_{\text{bulk}}$ respectively.

$$(R_1)(T, R, p) = (n_h/R)(R_1)_{\text{hyd}} + (1 - n_h/R)(R_1)_{\text{bulk}} \quad (12)$$

This approximation may be verified by the experimental data alone without the need to calculate the respective hydration and bulk water relaxation rates. However, both rates have to be taken at equal reduced temperatures $(T - T_0(R))$ pertaining to the solution with composition R , since the clusters of hydrated anions and bulk water are in dynamic equilibrium.

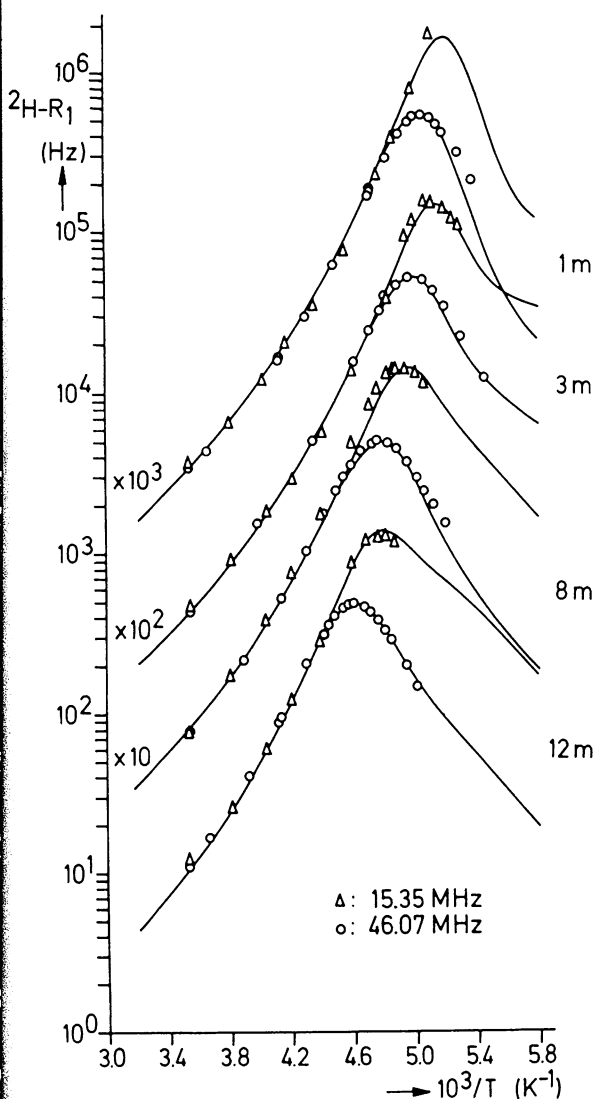


Fig. 5
Isobaric ($p = 225$ MPa) temperature dependence of deuterium spin-lattice relaxation rates in $\text{KF}/\text{D}_2\text{O}$ solutions at the concentrations given. Full lines correspond to relaxation rate curves as calculated with the two-site, two-mode approximation as discussed in the text

The dynamic hydration number n_h may be taken from computer simulation results. The corresponding numbers vary from $n_h = 4-6$, with a preference for an octahedral hydration shell.

The corresponding relaxation rate curves $R_1(T, R, p = 225 \text{ MPa})$ so calculated are drawn as solid lines in Figs. 5 to 8.

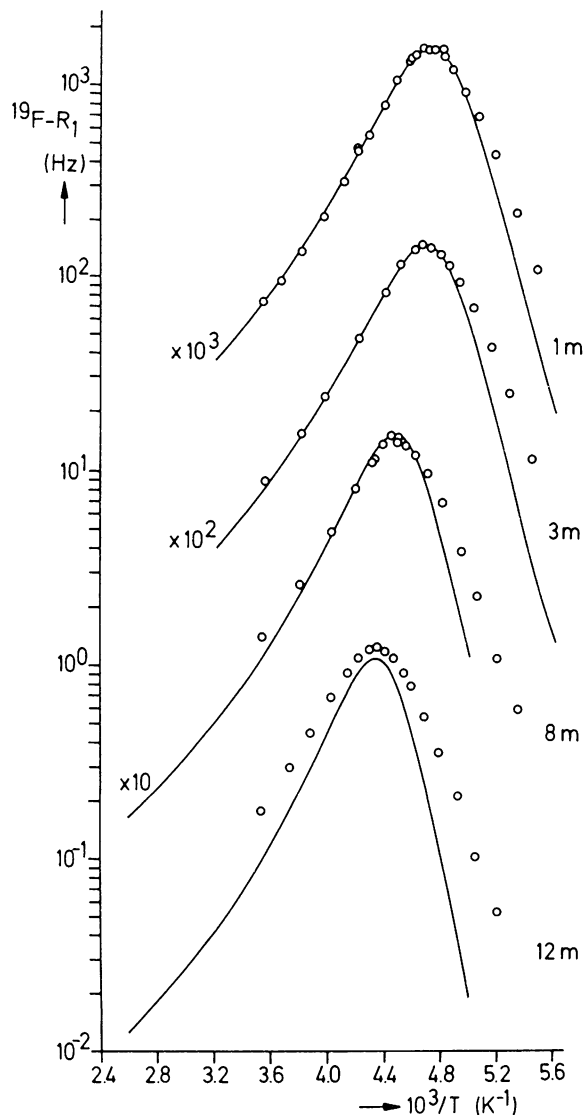


Fig. 6
Isobaric ($p = 225$ MPa) temperature dependence of Fluor-19 spin-lattice relaxation rates in $\text{KF}/\text{D}_2\text{O}$ solutions at the concentrations given. Full lines correspond to relaxation rate curves calculated with the two-site, two-mode approximation as discussed in the text

Discussion

In undercooled liquids molecular motions may be slowed down sufficiently so that probes such as nuclear magnetic resonance can yield specific information concerning structure and dynamics. Spin-lattice relaxation rates are well suited to monitor orientational and positional fluctuations of water molecules. In neat water these diffusive modes of molecular motions are isotropic [41-45], but dissolved

ions induce a motional anisotropy for adjacent water molecules. This motional anisotropy is accounted for in the simple motional model applied to interpret the temperature, composition and frequency dependence of experimental relaxation time curves of various nuclei in several aqueous electrolyte solutions in a way consistent with the local structure of these solutions as deduced from partial radial pair distribution functions. The latter may be obtained with scattering experiments or computer simulations.

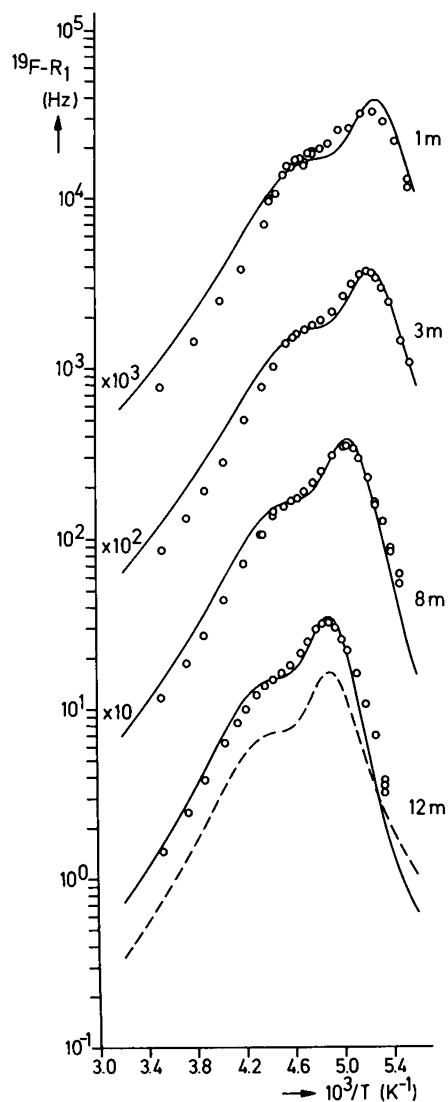


Fig. 7
Isobaric ($p = 225$ MPa) temperature dependence of Fluor-19 spin-lattice relaxation rates in KF/H₂O solutions at the concentrations given. Full lines correspond to relaxation rate curves calculated with the two-site, two-mode approximation as discussed in the text. The broken line gives the corresponding rate curve as calculated with the symmetric arrangement

a) Deuterium Spin-lattice Relaxation and Orientational Fluctuations

Undercooled liquids generally display strongly non-Arrhenian temperature dependences of transport and relaxation coefficients [46–49]. This feature is clearly visible in

Fig. 5. It is a consequence of cooperative structural rearrangements (β -process in glass-forming liquids) and may often be accommodated by a VTF-equation [50–52] (see Eq. (3)) signifying a kinetic localization phenomenon. The corresponding temperature of structural arrest T_0 is reflected in the temperature T_{\min} (T_{\max}) of the relaxation time (rate) curve.

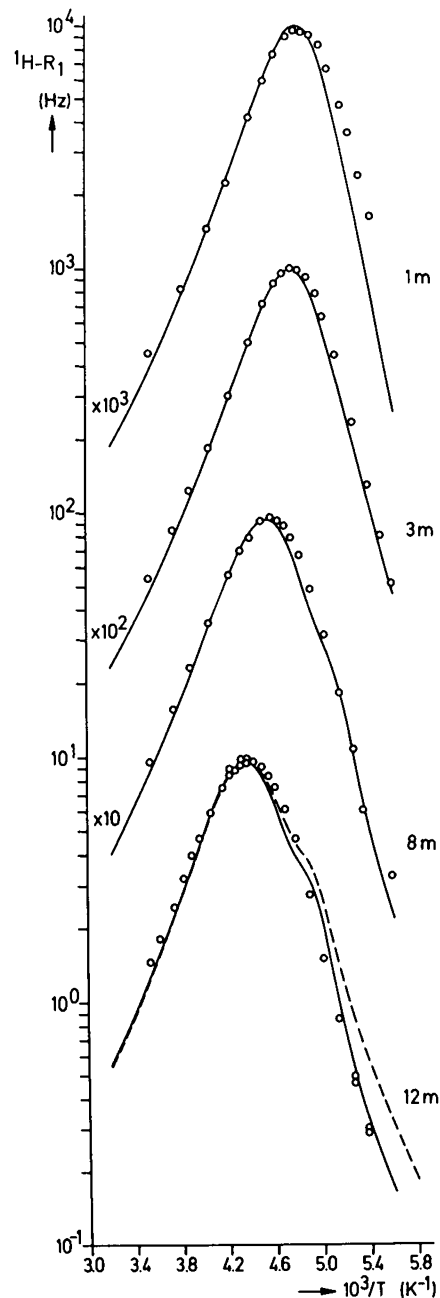


Fig. 8
Isobaric ($p = 225$ MPa) temperature dependence of proton spin-lattice relaxation rates in KF/H₂O solutions at the concentrations given. Full lines correspond to relaxation rate curves calculated with the two-site, two-mode approximation as discussed in the text

Fig. 9 compares the glass temperature $T_0(R)$ in the alkali-halide/heavy water solutions as deduced from the composition dependence of $T_{\min}(R)$ of the corresponding relaxation

time curves $T_1(T, R, p = 225 \text{ MPa})$. An interesting facet of this diagram is the observation that the sign of the slope dT_0/dR correlates with the common classification of these salts as structure makers and structure breakers. This is not only true for the cations, but also for the anions as a comparison of the T_0 -values of the present KF solutions with the other potassium halide solutions shows. The diagram also demonstrates that T_0 is largely determined by those ions which impose the stronger structural and motional constraints upon nearby water molecules.

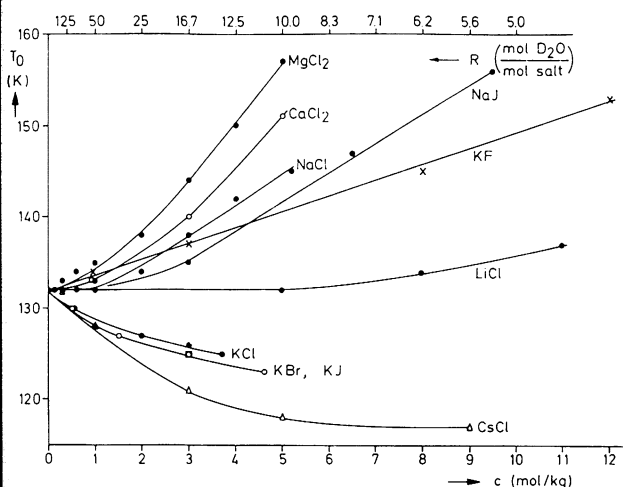


Fig. 9
Compilation of the ideal glass transition temperatures T_0 deduced from deuterium relaxation rate curves obtained in metastable ionic solutions of concentration c (mol/kg)

At the maximum of the relaxation rate curves the relevant microscopic correlation times τ become comparable to the inverse of the observing frequency $2\pi/\Omega_0$ (Larmor period). This transition from the fast motions regime ($\Omega\tau \ll 1$) to the slow motions regime ($\Omega\tau \gg 1$) becomes independent of the composition R if all tumbling modes, which are certainly related to structural fluctuations in the system, are scaled by T_0 , as the correlation between T_{\min} and T_g suggests [3, 5].

In the slow motions regime, however, the tumbling and exchange processes are predicted to slow down strongly on approach of T_0 according to the VTF-law. But the ^2H relaxation rates vary much less with falling temperature. In fact, they seem to display an Arrhenius dependence at low temperatures ($T < T_{\max}$). This feature very much resembles the splitting off of a secondary relaxation commonly observed in glass-forming liquids [46]. Within the current two-mode approximation the β -process is identified as the local anisotropic mode within the hydration shell. Because it is a thermally activated process, an Arrhenius dependence of τ_i seems natural. The corresponding apparent activation energy E_a is comparable with rotational barriers within the hydration shells of lithium- and sodium cations [7].

b) Fluor-19 Spin-Lattice Relaxation in D_2O and H_2O Solutions

The ^{19}F relaxation rates in D_2O have been calculated utilizing the correlation times appropriate to the ^2H relaxation

times. Orientational fluctuations have been calculated assuming a linear anion-water configuration in accord with computer simulation results and theoretical calculations showing the dominance of H-bond interactions. In case of the Cl^- anion this local structure could be determined with neutron scattering experiments. Because of the vanishingly small contribution ($\approx 1\%$) of the more distant deuteron of a water molecule within a linear anion-water configuration, the local anisotropic mode does not contribute to the ^{19}F relaxation. Hence only those modes related to global structural rearrangements within the system contribute. Their temperature dependence has been represented by the VTF-equation and leads one to expect a strong decrease of R_1 with falling temperature in the slow motions regime. This expectation is corroborated by the experimental $^{19}\text{F} - R_1$ data which decrease much more strongly than the corresponding $^2\text{H} - R_1$ data, where the local anisotropic mode dominates the relaxation in the slow motions regime.

Concerning the local ion-water arrangement, recent NMR experiments led to conflicting results favouring a symmetrical arrangement due to dominating ion-dipole interactions. Because $^2\text{H} - R_1$ data cannot distinguish between both configurations, the parameters τ_{00} and E_a have been determined also with β_{DF} corresponding to the symmetrical configuration. These parameters have in turn been used to calculate the orientational contribution to the $^{19}\text{F} - R_1$ in D_2O . For a nearly linear arrangement the corresponding rate ($R_{1,\text{or}}$) almost accounts for the total rate observed leaving only a minor contribution due to relative translational diffusive motions. The symmetric configuration gives a much smaller contribution from rotational modes implying a substantial contribution from relative translations, which however would afford unphysically large number densities. Hence only the disturbed linear anion-water configuration is in accord with the amplitude and the shape of the relaxation rate spectra presented. The ^{19}F relaxation rate curves drawn in Fig. 6, it should be remembered, have been calculated with the model parameters obtained from the ^2H relaxation rate curves. Hence the motional model is internally consistent.

The ^{19}F relaxation rates in H_2O have been calculated also after suitable changes in the parameters τ_{i0} , B_{or} and T_0 . These alterations should account for the dynamic isotope effect well known in pure water [2]. Hence τ_{i0} and B_{or} have been scaled by the ratios $(\tau_{i0}(\text{D}_2\text{O})/\tau_{i0}(\text{H}_2\text{O})) = 1.38$ and $(B_{\text{or}}(\text{H}_2\text{O})/B_{\text{or}}(\text{D}_2\text{O})) = 1.07$, whereas $T_0(\text{H}_2\text{O}) = T_0(\text{D}_2\text{O}) - 7 \text{ K}$ has been shifted in accord with the difference in zero point energies in light and heavy water. The structure on the relaxation rate curve $R_1(^{19}\text{F} - ^1\text{H})$ arises from contributions to the spectral density function at $(\Omega_{\text{F}} + \Omega_{\text{H}})$ and $(\Omega_{\text{F}} - \Omega_{\text{H}})$ respectively. These terms differ by a factor of ≈ 30 because the Larmor-frequencies of the ^{19}F - and ^1H nuclei are close together.

Fig. 7 also shows the relaxation rate curve calculated with the parameters appropriate to the symmetric configuration. The resulting relaxation rates are clearly too small. This is due to the $(r_{\text{FH}})^{-6}$ -dependence of the ^{19}F -relaxation rate on the F-H distance. The latter is much larger (0.23 nm) in

the symmetric configuration than in the almost linear (0.18 nm) arrangement. These results convincingly demonstrate that the experimental ^{19}F relaxation rates are very sensitive to the local arrangement of the water molecules hydrating the fluoride anion and that they are well reproduced with an almost linear configuration. The concentration dependence of the relaxation rate curves $R_1(T, c, p = 225 \text{ MPa})$ is also in close correspondence with the simple two site approximation as is demonstrated in Figs. 6 and 7.

c) Proton Relaxation in $\text{KF}/\text{H}_2\text{O}$ Solutions

Proton spin-lattice relaxation rates $R_1(^1\text{H})$ of the hydration water molecules have been calculated for a disturbed linear configuration and a symmetric configuration. The parameters, compiled in Table 1, correspond to those used to calculate the ^{19}F relaxation rate curve in the system $\text{KF}/\text{H}_2\text{O}$.

$^1\text{H}-^1\text{H}$ and $^1\text{H}-^{19}\text{F}$ dipolar interactions contribute to $R_1(^1\text{H})$. Because of the shorter distance $r_{\text{HH}} = 0.156 \text{ nm}$ compared to $r_{\text{HF}} = 0.181 \text{ nm}$ and the larger gyromagnetic ratio of the protons the $^1\text{H}-^1\text{H}$ coupling dominates the relaxation rate. A weak shoulder on the low temperature side of the relaxation rate curve $R_1(^1\text{H})$ is still observable. It corresponds to the pronounced maximum of the ^{19}F relaxation rate curve $R_1(^{19}\text{F})$ and is due to a contribution $g(\Omega_{\text{H}} - \Omega_{\text{F}})$ to the spectral density function, as discussed above. With decreasing concentration the total proton relaxation rate is, of course, dominated completely by $^1\text{H}-^1\text{H}$ interactions, hence the structure on the average relaxation rate curve disappears.

Also because of the dominance of $^1\text{H}-^1\text{H}$ couplings, the difference in the relaxation rate curves corresponding to a disturbed linear configuration or a symmetric configuration is not especially pronounced. Only on the low temperature side of the relaxation rate curve, in the slow motions regime, may both configurations be distinguished. The larger relaxation rate in case of the symmetric configuration is due to a contribution from the local anisotropic mode with its weaker Arrhenius temperature dependence. This mode dominates the temperature dependence in the slow motions regime but does not contribute to the relaxation in case of the linear configuration. The strong decrease of the relaxation rates $R_1(^1\text{H})$ in the slow motions regime, however, is well in accord with expectations predicted by the VTF-equation (Eq. (3)). Again the relaxation rate curve $R_1(^1\text{H})$ calculated with the disturbed linear configuration is in better agreement with the experimental data than the symmetric arrangement.

Conclusions

^2H , ^1H and ^{19}F spin-lattice relaxation rates of undercooled aqueous KF -solutions have been presented as a function of concentration ($c \leq 12 \text{ m}$), temperature ($T \geq 180 \text{ K}$) and pressure ($p \leq 225 \text{ MPa}$). Under ambient conditions F^- -anions reduce the average mobility of water molecules but facilitate molecular motions in the metastable states. This behaviour is similar to the influence of strongly coordinating alkali cations and contrasts the effect of the other halide

anions upon the dynamic structure of the H-bond network in these ionic solutions. Under high pressure the H-bond network is strongly disturbed and the dynamic structure of the metastable solutions is dominated by cooperative fluctuations characteristic of liquids close to their respective glass transition. The influence of dissolved ions upon the dynamics of the random, transient H-bond network is determined mainly by their effect on the ideal glass transition temperature T_0 . The slope $[dT_0(c)/dc]_{p=225 \text{ MPa}}$ serves to distinguish ions with positive and negative hydration characteristics unambiguously. Also under high pressure relaxation rate spectra of all nuclei could be obtained over a large range of correlation frequencies. From a consistent description of the amplitude and the shape of these spectra the local anion-water arrangement could be obtained. It is dominated by H-bond interactions and corresponds to an almost linear configuration in accord with theoretical predictions and computer simulations and corrects conclusions drawn from earlier NMR experiments.

The authors wish to thank Prof. Lüdemann for supporting this work and for many stimulating discussions. The expert technical help of S. Heyn, R. Knott, and E. Tremel made this work feasible. Financial support by the DFG is gratefully acknowledged.

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