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Nuclear magnetic resonance studies of supercooled aqueous electrolyte solutions

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Abstract. The dynamic properties of water molecules coordinated to simple ions (alkali and alkali-earth halides) and hydrophobic ions (tetraalkylammonium (TAA) halides) in supercooled solutions have been investigated with NMR. The study of spin–lattice relaxation rates and self-diffusion coefficients as functions of temperature, pressure, Larmor frequency and concentration reveals characteristic features of molecular motions close to the low-temperature limit of the metastable phase (percolation transition and glass transition) and provides certain details of the local arrangement of water molecules in the coordination sphere of these ions. The intramolecular flexibility of the alkyl chains of the hydrated TAA cations has been investigated also. The dynamics of the methyl group reorientation provide a sensitive probe of structural differences in these solutions.

1. Introduction

Nuclear magnetic relaxation studies provide valuable information about rotational and translational diffusion of water molecules and ions in undercooled electrolytes. In metastable water at low temperatures, hydrogen bonding interactions dominate the dynamic structure of the random transient H-bond network [1]. Hence molecular motions become highly cooperative close to the low-temperature limit of the metastable phase (the percolation transition [2] and glass transition [3]). Dissolved atomic ions disturb the local structure and alter the molecular motions of coordinated water molecules in a characteristic fashion depending on the charge density and the state of the H-bond network. Molecular ions with apolar groups, such as tetraalkylammonium (TAA) ions, allow the competing influence of the Coulomb effect of the charge density, the hydrophobic effect of the apolar surface and the H-bond interactions upon the dynamic structure of the network to be studied. Also the dependence of the intramolecular flexibility of the alkyl chains of the hydrated cations upon the mode of hydration (coulombic versus hydrophobic) may be investigated. In particular the dynamics of the methyl group reorientation provide a sensitive probe of structural differences in the hydration layer.

2. Hydration water dynamics

In the random transient H-bond network, molecular motions occur on two largely separated time scales [4]. Hindered translations and rotations can be approximated as

quasi-lattice vibrations (QLVs) which, however, are strongly damped at high temperatures. At low temperatures they superimpose onto the slower translational and rotational diffusive modes. Because of time scale separation both may be considered statistically independent.

A specific motional model of reorientational fluctuations of water molecules coordinated to simple atomic ions has been developed [5–7] in accord with the extensive knowledge of the average local ion–water arrangement provided by neutron and x-ray scattering [8] as well as by computer simulations [9].

Local structural features are less well known in the case of aqueous solutions of TAA cations [10]. Also, because of competing coulombic, hydrophobic hydration and hydrogen bonding interactions, hydration water dynamics must become much more involved. Hence the simple one-dimensional diffusion model to represent the anisotropic fluctuations around the local director [7] must be altered in favour of a more general, although less specific, correlation function such as a Cole–Davidson distribution of correlation times. Both the two-step model [11] and the model-free approach [12] may be useful also. The latter model may also be used to describe the internal flexibility of the alkyl chains of the TAA ions.

3. Aqueous solutions of simple atomic ions

3.1. Reorientational dynamics in the fast-motion regime

Orientalional fluctuations of water molecules in metastable electrolyte solutions may be investigated conveniently through ^2H spin–lattice relaxation rates $R_1(^2\text{H})$. In the fast-motion regime ($\omega\tau \leq 1$) these rates reflect an average rotational mobility of water molecules only. At low temperatures the rapid completion of the H-bond network hinders molecular motions strongly [13]. Ionic solutes and/or hydrostatic pressure disrupt the H-bond network and hence facilitate molecular motions. This is reflected by an increase in the spin–lattice relaxation time $T_1(^2\text{H})$ which is proportional to an average rotational correlation time of the water molecules. Hydrostatic pressure changes the structure of the transient network with low thermal excitations from a state characterized by large patches with strong linear H bonds towards a highly disordered structure with weak, bent or disrupted bonds. Dissolved atomic ions disturb the network only locally, depending on the charge density [14].

Weakly hydrating ions (low charge density) always increase the average mobility of the water molecules irrespective of the state of the H-bond network, although the effect is less pronounced at high pressures. Ions with a high charge density impose strong orientational constraints upon coordinated water molecules and hence disrupt the surrounding well developed H-bond network and increase the average mobility. This effect obviously must reach a maximum at a composition where only hydration water molecules are left. Often this concentration corresponds to the edge of the glass-forming composition range [15]. With a highly distorted network, ion–dipole interactions dominate over weak H-bond interactions and cause a slowing down of the average orientational mobility of water molecules. Except for F^- , cations induce a much more pronounced alteration of the dynamic structure of the network than do simple anions [14].

3.2. Reorientational dynamics in the slow-motion regime

A strongly distorted H-bond network (high pressure and high solute concentration) is very reluctant to nucleate a crystalline phase, and hence very low temperatures may be

reached [1]. Molecular motions are slowed down strongly and the spin–lattice relaxation rate curves $R_1(T, p, \omega)$ become sensitive to details of the orientational fluctuations. They have been discussed in terms of the two-site two-mode approximation introduced in section 2 [16]. The overall tumbling of the molecules becomes highly cooperative, exhibiting characteristic power-law or VTF temperature dependences [17] with the corresponding ideal glass transition temperatures T_0 deduced from $R_1(T)$ -curves. An increase in T_0 upon addition of salt reflects a slowing down of cooperative tumbling modes, whereas a decreasing T_0 reflects increasing molecular mobility. These results suggest that the effect of ionic solutes upon orientational and positional fluctuations is determined mainly by their effect on T_0 .

In the slow-motion regime ($\omega\tau \geq 1$), spin–lattice relaxation rates slow down less strongly than would be expected from a VTF temperature dependence. At these low temperatures, local anisotropic modes with an Arrhenius temperature dependence seem to dominate the relaxation [18]. Close to their respective low-temperature limits, dense metastable liquids often exhibit a non-exponential relaxation of structural fluctuations [19].

Large deviations from an ω^{-2} Lorentzian dependence of the hydration water relaxation $R_1(T, p, \omega)$ have been observed in LiCl solutions close to their calorimetric glass transition temperature T_g . They could be well represented by a Cole–Davidson distribution of tumbling correlation times [14].

4. Aqueous solutions of hydrophobic ions

Aqueous solutions of TAA ions are model systems to investigate the effect of different modes of hydration (coulombic versus hydrophobic) upon the dynamic structure of the H-bond network and the internal flexibility of the solute molecules. With increasing length of the alkyl chains the charge density decreases, diminishing the importance of ion–dipole interactions, and the apolar surface increases, promoting hydrophobic hydration structures in the immediate neighbourhood. However, it is still unclear how long the alkyl chains have to be for the hydrophobic hydration phenomenon to dominate over coulombic ion–dipole forces in controlling the dynamic structure of the surrounding network [10, 20].

4.1. Dynamics of the water molecules

Orientalional fluctuations of water molecules coordinated to tetramethylammonium (TMA^+) ions show a temperature dependence characteristic of strongly hydrating atomic ions. If the H-bond network is strongly perturbed because of thermal excitations (high T) or hydrostatic pressure, these ions reduce the average mobility of water molecules. At low temperatures, however, H bonds slow down reorientational fluctuations stronger than ion–water interactions, thus enhancing the average mobility, as may be seen in figure 1. If these ions were to induce ‘clathrate-like’ transient structures, then one might expect a continued further reduction in the average mobility upon addition of solute down to the lowest temperatures. Further a regular behaviour is seen with increasing solute concentration with no anomaly as seemed to be indicated by recent neutron scattering data [10] which suggested a switching between different modes of hydration with increasing concentration. The diffusion coefficients of water molecules and cations also do not show any anomaly in their concentration dependences. Comparing the

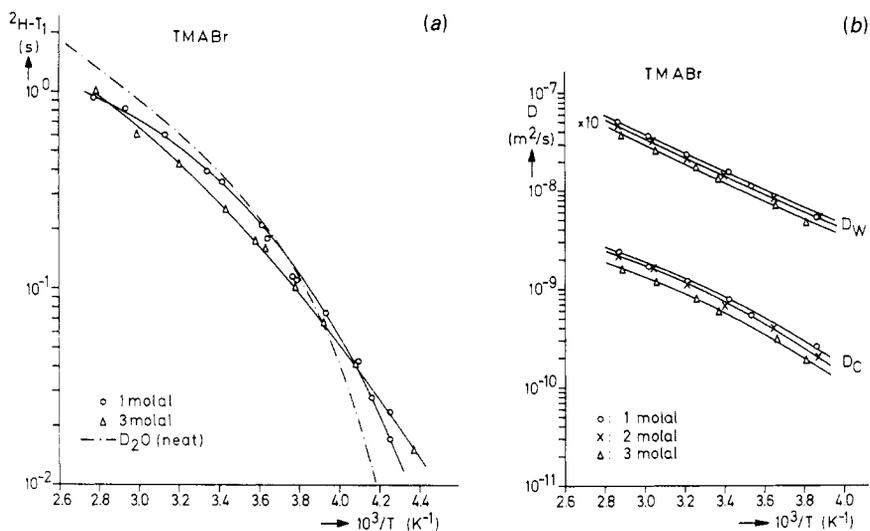


Figure 1. (a) Arrhenius diagram of the deuterium spin-lattice relaxation time $T_1(^2\text{H})$ in metastable TMA Br-D₂O solutions. (b) Corresponding Arrhenius diagram of the self-diffusion coefficients D_w of the water molecules and self-diffusion coefficients D_c of the TMA⁺ cations.

hydration water dynamics of TMA, tetrapropylammonium (TPrA) and tetrabutylammonium (TBuA) cations, the larger ions reduce the average mobility at all temperatures investigated.

4.2. Internal flexibility of the cations

Proton relaxation rates of the different CH_n groups of the alkyl chains in these ions have been investigated also. These rates mainly reflect internal reorientations about C—C bonds as well as the overall tumbling of the whole ions. Again the methyl group relaxation rates do not indicate any change in the mode of hydration with concentration.

In TPrA⁺ and TBuA⁺ solutions the relaxation rates decrease with increasing distance of the CH_n group from the central nitrogen atom. This, of course, reflects the increasing internal flexibility along the alkyl chain. In both systems, relaxation rate maxima could be observed; hence molecular motions could be followed into the slow motions regime (figure 2). Attempts to reproduce these relaxation rate curves with the model-free approach discussed in section 2 failed in the case of the α -CH₂ relaxation for any value of the generalized order parameter. This is because the maximum dipolar relaxation rate is proportional to $R_{1,\text{max}} \propto (r_{\text{HH}})^{-6}$ and is underestimated with H—H distances taken from the literature ($r_{\text{HH}} = 0.178 \text{ nm}$ [21]). Only with a reduction in the H—H distance were we able to reproduce $R_{1,\text{max}}$ as is shown in figure 2. Further the methyl group relaxation rates were overestimated with $r_{\text{HH}} = 0.178 \text{ nm}$; hence librational averaging must be taken into account to reduce the maximum relaxation rate.

Further these methyl group reorientations provide a sensitive probe of the state of the surrounding H-bond network and hence reflect changes in the mode of hydration as may be seen in figure 3. To a first approximation the slow overall molecular tumbling mode does not contribute to the methyl group relaxation rate $R_1(\text{CH}_3)$ which thus

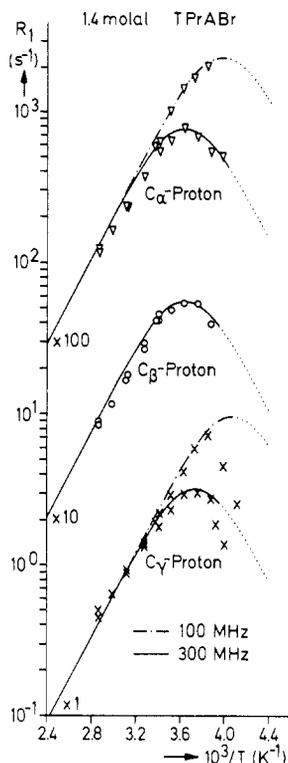


Figure 2. Proton spin-lattice relaxation rates R_1 of the alkyl chain CH_n groups in metastable 1.4 M TPrABr- D_2O solutions. The α - CH_2 group is closest to the nitrogen atom.

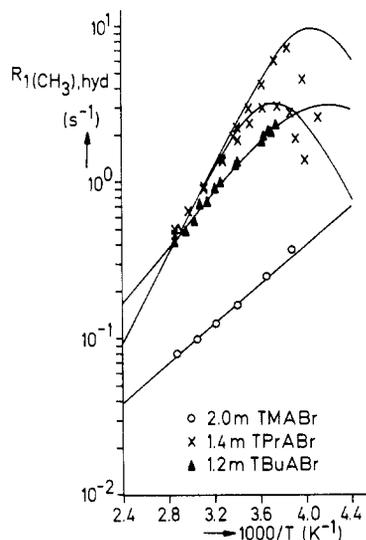


Figure 3. Arrhenius diagram of the relaxation rate R_1 of the methyl protons in metastable TMABr-, TPrABr- and TBuABr- D_2O solutions.

monitors the fast anisotropic internal reorientation only. This internal mode is slowed down considerably in going from TMA⁺ to TPrA⁺ but becomes faster in TBuA⁺ again. This may reflect a change in the mode of hydration from the essentially coulombic hydration of TMA⁺ and TPrA⁺ to the hydrophobic hydration of TBuA⁺ ions dissolved in water.

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