

Vibrational dynamics and structural relaxation in aqueous electrolyte solutions in the liquid, undercooled liquid and glassy states

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Summary

In very concentrated aqueous electrolyte solutions, the competition between dipolar and ionic forces and most of the system properties, are finely monitored by the concentration. For LiCl , RH_2O (R being the number of water moles per mole of salt) two domains of concentration exist around even hydration numbers $R = 6$ and $R = 4$, which can be reversibly undercooled from the liquid to the glassy state. At other concentrations, for $R < 12$, metastability is achieved only in a restricted temperature range.

The collective behaviour as well as individual atomic motions, have been studied by neutron inelastic scattering in the metastable state of LiCl , $6\text{H}_2\text{O}$ and LiCl , $4\text{H}_2\text{O}$ down to the glass transition.

The study of the structural relaxation by neutron spin echo (NSE) allows us to show that the temperature dependence of the response of the system follows a scaling relation with a cross-over at a phase transition present in the liquid phase.

Increasing hydrodynamic interactions in a liquid is certainly the best manner to analyse the intrinsic and microscopic correlations into the system. So the various motions, collective, relaxational, individual and their coupling can be revealed by approaching glass formation conditions.

LiCl , RH_2O (or LiCl , RD_2O) is one of the most suitable system because **by changing R** (the number of water molecules per molecule of salt) we change **strongly the nature of the medium and by using isotopic substitution on Li^+ , Cl^- , D** we can differentiate the dynamics of the various atoms or ions.

Changing R gives the possibility to analyse two types of liquids : the first one, for $R > 6$ is **intrinsically inhomogeneous**, and described by a regular mixture of pure water and the hydrate LiCl , $6\text{H}_2\text{O}$ (1). The second one, for $R < 6$ is a mixture in which the **competitions between dipolar forces and coulombic forces** are finely monitored.

In this paper, we **summarize** some recent analysis of different kinds of dynamical responses which lead to some questions on their **non linear behaviour**.

The **total dynamical responses** of the electrolyte LiCl, 6H₂O and LiCl, 4H₂O have been analyzed between 0.3 meV and 120 meV, i.e. in a domain of frequencies covering collective vibrational response and individual motion of ions.

1. Dynamical structure factor.

From the **dynamical structure factor** $S(q, \omega)$ measured with the IN 6 instrument (ILL, Grenoble) at a resolution of 80 μeV , for LiCl, R H₂O (with $R=6$), two types of informations can be derived :

(i) - the **frequency distribution** $G(E)$ ($E=\hbar\omega$) (extracted as in ref (3) , neglecting the incoherent contribution to the scattering), which permits an analysis of the characteristic frequencies (2) which define this low energy "vibrational network" (3).

(ii) - The **central mode**, i.e diffusive processes from the quasi elastic behaviour around $E=0$.

A - In the frequency distribution, three **fundamental modes** of the H-bonded network dominate : bending at 7 meV, **restricted translational motion** or **stretching** at 23 meV, and **restricted rotational motion** or **libration** at 85 meV (see figure 1). The identification of these modes has been made by comparison with experiment on pure water (2) (10) .

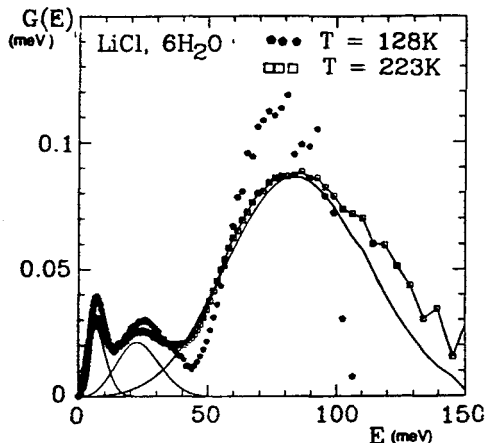


Fig. 1. Generalized density of states obtained for LiCl, 6H₂O in the glassy and liquid states and assignments of the principal bands for the liquid state (see 2).

The **influence of temperature** on the different modes has been followed in this disordered system down to the **non ergodic situation** ($T < 142$ K for LiCl, 6H₂O). (Fig. 2)

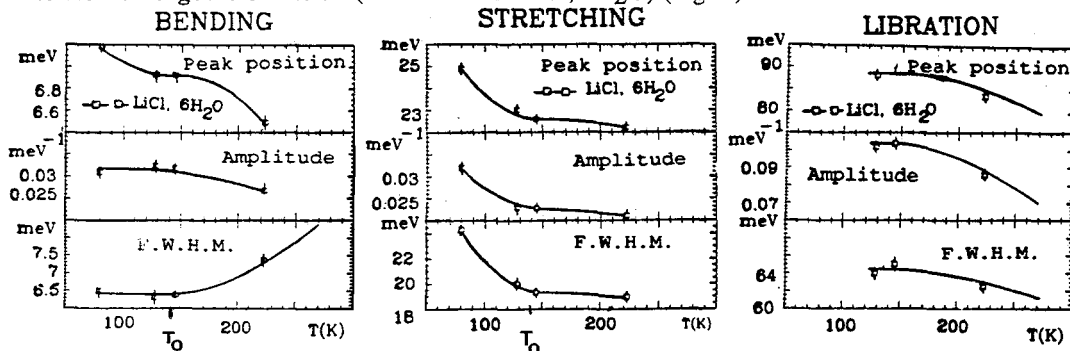


Fig. 2. Evolution of the three fundamental bands characterizing the bending, stretching, librational motions assigned to H bonded H₂O in LiCl, 6H₂O versus temperature.

- The **broadening of the bending motion** which is large in the liquid state is correlated to the **existence of different microscopic dynamical configurations**. This mode has a significant assymetry towards high energies which increases with temperature, giving some support to a **delocalization of the excitations or a fluctuating coupling between different microscopic configurations** (12)

- Among these modes, **stretching** is the **most influenced by the glass transition** or equivalently by T_0 i.e the lowest temperature limit of liquid metastability(2) However the limited range of energy that we were able to reach, does not permit us to fully analyze the low temperature behaviour for librational modes. There is another temperature of interest which is characteristic of a **third order phase transition** in the liquid(quoted by T_p = peritexy at 207 K). It appears that the **stretching mode is nearly temperature independant in the low temperature supercooled liquid** for $T_0 < T < T_p$. This temperature range is characterized by additional microscopic configurations (hydration 5) compared to those of the room temperature liquid.

B - **Quasi elastic data**, i.e. the **central mode**, permits to obtain informations on the individual motion of H or D in H_2O and D_2O . At the **composition R=6**, the system is **molecular** and although there is no correct diffusion's analysis of the different elements Li^+ , Cl^- and H_2O , the trends

give $D_{Li^+} < D_{Cl^-} < D_{H_2O}$ at $25^\circ C$ (4)

• The **proton delocalization** due to vibrations is deduced from the Debye Waller component. It is obtained from the total quasielastic intensity, I and is shown in fig. 3a and fig. 3b for $LiCl, 6H_2O$ and $LiCl, 4H_2O$.

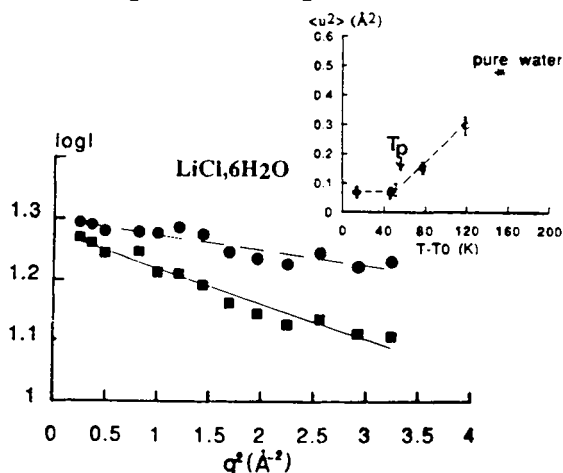


Fig. 3 a. Debye-Waller factor measured by QENS for $LiCl, 6H_2O$ in the liquid ($\blacksquare$) 223 K and in the super-cooled liquid ($\bullet$) 192 K

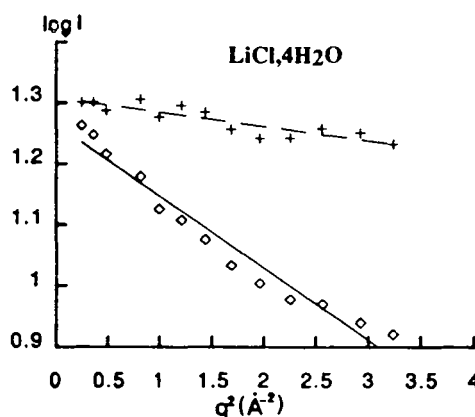


Fig. 3b. Debye-Waller factor measured by QENS for $LiCl, 4H_2O$ in the liquid state ($\diamond$) 275 K and in the supercooled liquid state ($+$) 210 K

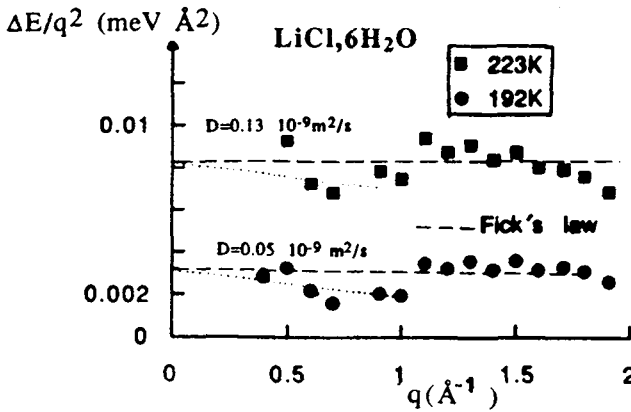
Insert : Mean square displacement of H_2O in $LiCl, 6H_2O$ and in $LiCl, 4H_2O$ in liquid and super-cooled liquid versus $(T - T_0)$, T_0 being the lowest temperature limit of the liquid metastability.

* Proton delocalization in pure water (11)

The mean square displacement obtained for H_2O in $\text{LiCl}, 6\text{H}_2\text{O}$ and $\text{LiCl}, 4\text{H}_2\text{O}$ and referred to T_0 , lowest temperature limit of the metastability (10) is temperature dependent in the liquid state and nearly temperature independent in the supercooled liquid.

This effect is induced by a restricted translational motion due to interactions of H_2O with Li^+ and Cl^-

- The diffusion coefficient of H_2O can be obtained from $S(q, \omega)$ and compared to the ordinary diffusion law (5). As a matter of fact, the diffusion can be coupled to the hydrodynamics of the medium, the coupling being function of the kinematic viscosity D_T , according to $\delta = D / (D + D_T)$ (5). The q dependence of the half width of the central mode given in fig.4 for $\text{LiCl}, 6\text{H}_2\text{O}$ permits to obtain diffusion coefficient in agreement with literature (4).



The narrowing of the central mode for all q values inferior to $q_{\text{max}} (\approx 1.9 \text{ Å}^{-1})$ confirms the coupling of this mode with hydrodynamics (6).

Fig. 4. FWHM of $S(q, \omega)$ divided by q^2 for $\text{LiCl}, 6\text{H}_2\text{O}$ at different temperatures above and below T_p .

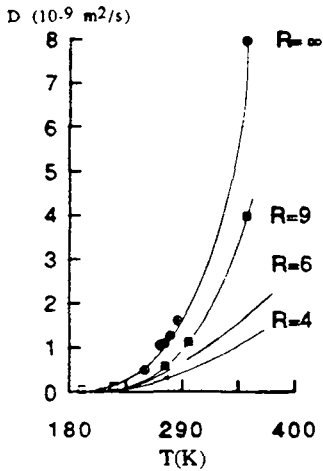


Fig. 5. H_2O diffusion coefficient evolution with temperature in $\text{LiCl}, R\text{H}_2\text{O}$ for various R .

- The H_2O diffusion coefficient obtained in this molecular system, for $R = 6$ and $R = 4$ permits to confirm the strong influence of the solvation on the dynamics of H_2O when $R \leq 6$ (fig 5)

2. Relaxational behaviour.

The relaxational behaviour has been obtained on an "adequate" range of time (10^{-12} sec. to 10^{-9} sec) by NSE experiment performed on IN11 at ILL(9) on LiCl, $6D_2O$ at $q = q_{\max} = 1.9 \text{ \AA}^{-1}$, $q_{\max}$ being the momentum transfer of the main peak of the structure factor at room temperature.

We deduce from this data (7), the evolution of the **characteristic relaxational time τ_{NSE}** which can be compared to the one obtained from viscosity (8) (fig. 6). Two scaling laws (10) give the evolution of τ , with two characteristic temperatures of the system : lowest limit of the metastability T_0 and crystallisation temperature for the first hydrate formed : $R = 5$

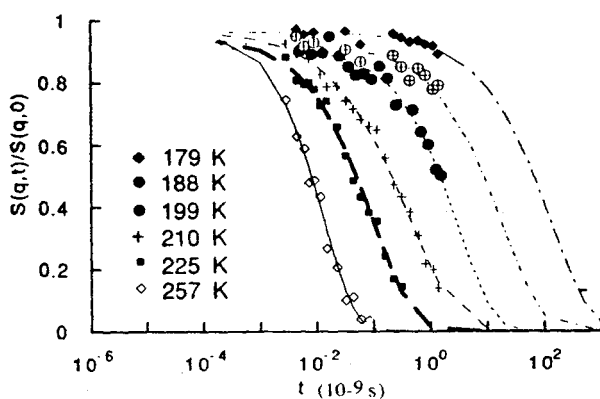


Fig. 6a. Neutron spin echo response at $q = q_{\max} = 1.9 \text{ \AA}^{-1}$ for LiCl, $6D_2O$ measured and analyzed according to ref. (7).

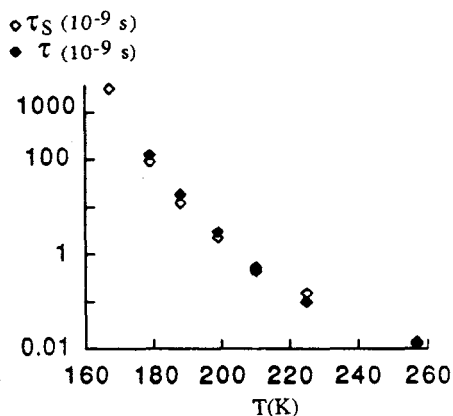


Fig 6b. Relaxational time deduced from NSE ($\blacklozenge$) for LiCl, $6D_2O$ compared to τ_s obtained from kinematic viscosity ($\diamond$) according to ref. (8) for LiCl, $5.75 \text{ H}_2\text{O}$.

This result confirms the connexion between the relaxational process and the third order phase transition, at T_p . Slowing down is observed in the supercooled liquid scaled to the lowest limit T_0 of the metastability, and the non ergodic character appears down to T_0 (7).

In conclusion, in these molecular aqueous solutions, collective vibrational motion of H_2O such as stretching, mean square displacement and relaxational response in the hydrodynamic regime and at finite momentum transfer are sensible to the approach of some characteristic temperatures of the system such as T_0 and T_p an apparent third order transition in the vicinity of the equilibrium melting point. The existence of diffusive motion confirms the coupling with the hydrodynamics. The extension of these studies to the more concentrated domain, offers the opportunity to study the coupling between ionic conduction and relaxational slowing down.

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