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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, $6H_2O$ and LiCl, $4H_2O$ 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, $6H_2O$ (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, $6H_2O$ and LiCl, $4H_2O$ 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 H_2O (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) .
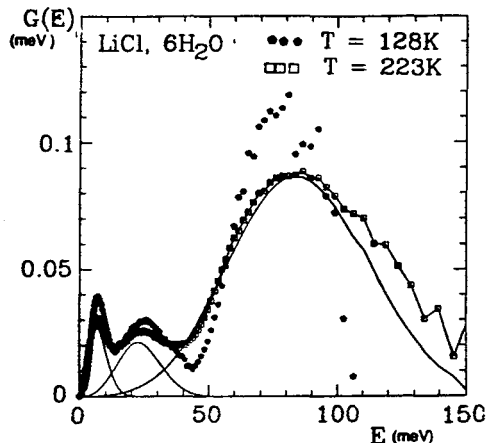

Fig. 1. Generalized density of states obtained for LiCl, $6H_2O$ in the glassy and liquid states and assignements of the principal bands for the liquid state (see 2).

The **influence of temperature** on the different modes has been followed in this desordered systemdown to the **non ergodic situation** (T < 142 K for LiCl, $6H_2O$).(Fig. 2)
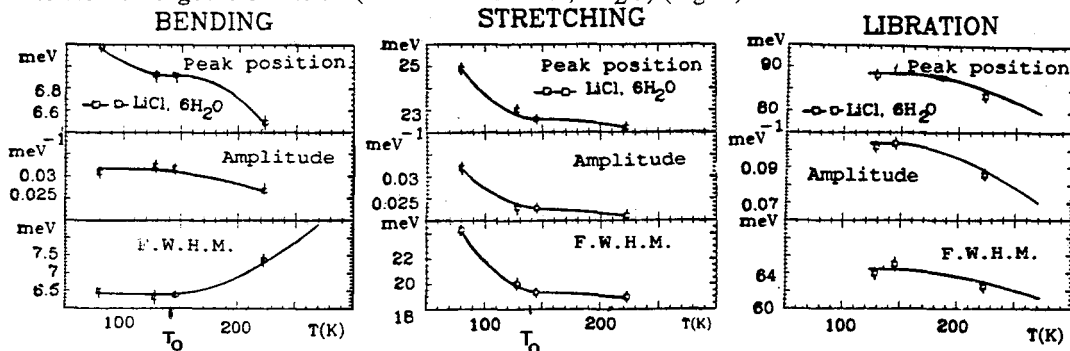

Fig 2. Evolution of the three fundamental bands characterizing the bending, stretching, librational motions assigned to H bonded H_2O in LiCl, $6H_2O$ versus temperature.

- 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 To 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 $T_o < T < T_p$. 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°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, $4H_2O$.
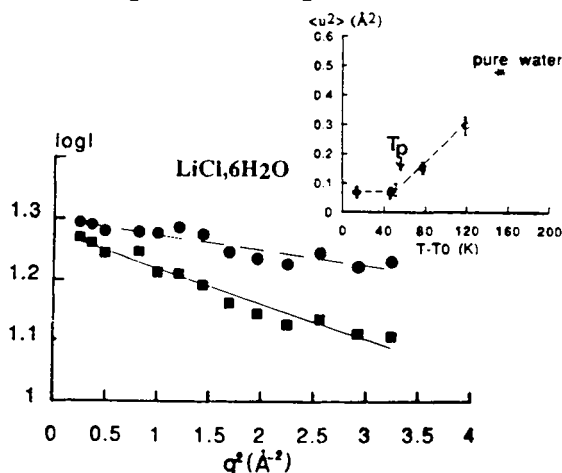

Fig. 3 a. Debye-Waller factor measured by QENS for LiCl, $6H_2O$ in the liquid (■)223 K and in the super-cooled liquid : (●) 192 K
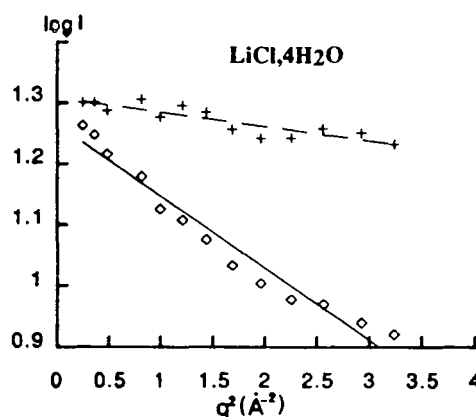
Fig. 3b. Debye-Waller factor measured by QENS for LiCl, $4H_2O$ in the liquid state (◊) 275 Kand in the supercooled liquid state (+) 210K
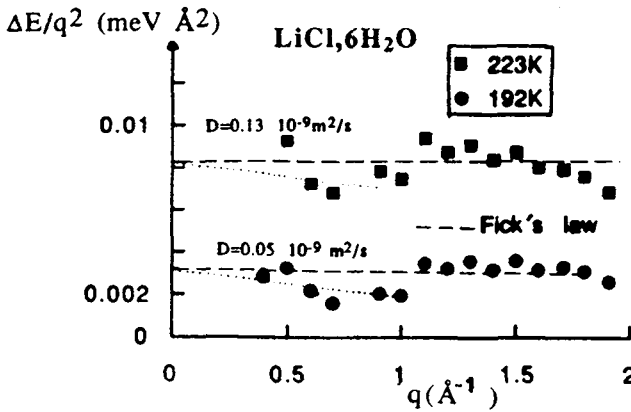
Insert : Mean square displacement of H_2O in LiCl, $6H_2O$ and in LiCl, $4H_2O$ in liquid and super- cooled liquid versus (T - To), To being the lowest temperature limit of the liquid metastability.

* Proton delocalization in pure water (11)

The mean square displacement obtained for H_2O in LiCl, $6H_2O$ and LiCl, $4H_2O$ and refeared 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 LiCl, $6H_2O$ permits to obtain diffusion coefficient in agreement with litterature (4).

Fig. 4. FWHM of $S(q, \omega)$ divided by q^2 for LiCl, $6H_2O$ at different temperatures above and below T_p.

The narrowing of the central mode for all q values inferior to $q_{max} (\approx 1.9 \text{ Å}^{-1})$ confirms the coupling of this mode with hydrodynamics (6).
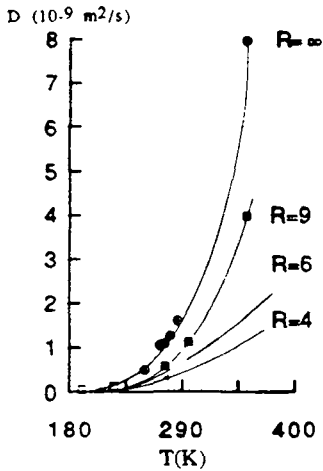
Fig. 5. H_2O diffusion coefficient evolution with temperature in LiCl, RH_2O for various R.

• 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 $q = q_{max} = 1.9$ Å^{-1}, q_{max} beeingthe momentum transfer of the main peak of the strcture 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_O and crystallisation temperature for the first hydrate formed : R = 5
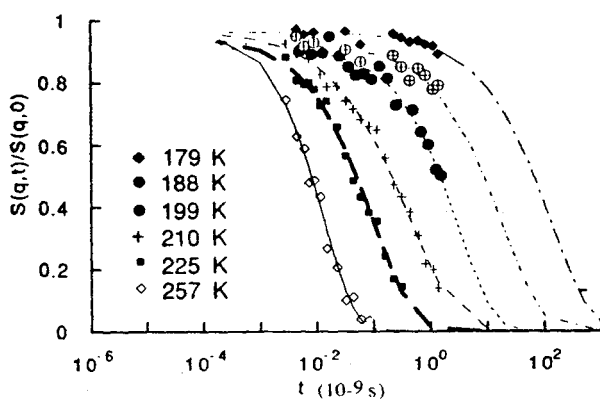

Fig. 6a. Neutron spin echo response at $q = q_{max} = 1,9$ Å for LiCl, $6D_2O$ measured and analyzed according to ref. (7).
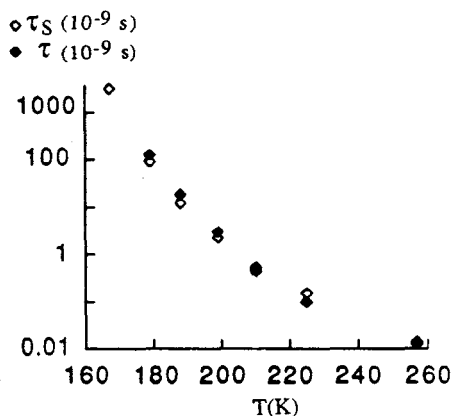
Fig 6b. Relaxational time deduced from NSE (♦) for LiCl, $6D_2O$ compared to τ_s obtained from kinematic viscosity (◊) according to ref. (8) for LiCl, $5.75\ H_2O$.

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_O of the metastability.and the non ergodic character appears down to T_O (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_O 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.

References :

[1]   FORNAZERO J., El HACHADI A, DUPUY J, Molecular Structure (1991) 250, 421
       A. El HACHADI - Thesis Lyon July 1991

[2]   DUPUY J., JAL J.F., CHIEUX P., DIANOUX A.J., J. Molecular Structure (1991) 250, 315.

[3]   DIANOUX A.J., Phil. Mag. B.1989, 59, 17.

(4)   MILLS R., V.M.M. LOBO in Self diffusion in electrolyte solutions, Physical Sciences data 36
       (1989) Elsevier.

[5]   BOON J.P. ,YIP S., Molecular hydrodynamics, Mac-Graw-Hill Inc (1980)
       MORKEL C, GRONEMEYER C., Z. Phys. B. Condensed Matter, 72, 433 (1988)

[6]   de SCHEPPER I.M, ERNST R.H, Physica 98 A (1979) 189

[7]   PREVEL B,JAL J.F, LEGRAND J.F, CHIEUX P,DUPUY J, to be published in Euro phys..

[8]   MOYNIHAN C.T, BALITACTAC N,BOONE L, LITOVITZ J.A, J of Chem. Phys,   (1971),
55, 3013.

[9]   MEZEI, F, ED.Neutron Spin Echo in lecture Note in Physics 128 Springer-Verlag Berlin-
       Heidelberg   New-York (1980)

[10]   DUPUY J, JAL J.F., CARMONA P, AOUIZERAT-ELARBY A., CHIEUX P, in Relaxation
       Complex Systems and related topics Ed by I.A. Campbell, C. Giovannello, Plenum Press N.Y.
       (1990) p. 175.

[11]   LILLEY T.H., in Water. A comprehensive treatise F. Franks Ed (1973) 3, 265.

[12]   International symposium "hydrogen bond physics" Il Ciocco Italie septembre 1990.
       " H-Bond characteristic in supercooled and vitreous aqueous solutions"
       " Ice nucleation and growth in Electrolytes : role of ionic forces"