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DYNAMICS OF PROTONS IN WATER AND AQUEOUS ZnCl₂ SOLUTIONS


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Abstract - We studied the diffusive motions of the protons in pure water and ZnCl₂ aqueous solutions, using incoherent quasi-elastic neutron scattering. We showed that it is essential to take into account the rotational motion of the water molecules; the associated characteristic relaxation time varies from 0.8 ps for H₂O to 20 ps for the saturated solution which is interpreted in terms of hindered rotations for the concentrated solutions. The translational linewidth is conveniently fitted over the whole Q-range, using the Random Jump Diffusion model for which the jump length turns out to be roughly the same for pure H₂O and the saturated solution, fairly close to the distance between protons in the water molecule.

The experiments have been performed on the IN6 time of flight spectrometer at the Laboratoire commun CEA, CNRS.
ILL, Grenoble. At a wavelength $\lambda = 5.9$ Å (incident energy = 2.35 meV), 16 spectra were taken, simultaneously, for an angular range varying from 12.80 up to 110.30 degrees. The energy resolution (FWHM = 50-70 µeV) was determined using a vanadium standard sample. The solutions were placed in teflon-coated aluminium planar cells with 0.15 mm thick walls, and 0.65 mm thickness. Since the transmission varied between 0.74 and 0.793 for H2O and the saturated ZnCl2 solution, we have applied multiple scattering corrections using the Monte Carlo program DISCUS /5/.

Our experiments have been performed at (T = 298 K), on pure water and ZnCl2 solutions in H2O for the following concentrations : 3M, 6M and 12.6M (saturated solution). In figure la and lb, we present the corrected intensity spectra of water and of the saturated solution corresponding to a scattering angle of 64.20 degrees.

The main contribution to the scattering cross section is the incoherent scattering by protons. In the Born approximation for N identical nuclei /6/, the cross section is proportional to the incoherent scattering function $S_{\text{inc}}(Q,\omega)$ where $Q$ and $\omega$ denote the momentum and energy transfers. $S_{\text{inc}}(Q,\omega)$ is the Fourier transform of the Van Hove /7/ self correlation function $G_S(q,\tau)$. The incoherent intermediate scattering function can be written as:

$$ I_{\text{inc}}(Q,\tau) = \exp[-iQ \cdot r(0)] \exp[iQ \cdot r(t)] $$

(1)

where $r$ is the position vector of one proton, so that $r = R + a + u$ with $R$ : molecular mass centre position vector, $a$ : mean position vector of the proton relative to the mass centre. Finally, $u$ represents all the small amplitude displacements (vibrations). Assuming no time correlation between these motions, and as in the quasi-elastic region, the vibrations only contribute to the intensity through a Debye-Waller factor, the incoherent scattering law will thus be a convolution of the translational and rotational parts. We assume that the proton translational motion is characterized by a translational diffusion broadening $\Delta E_T$, and consequently

$$ S_{\text{trans}}(Q,\omega) = \frac{1}{\pi} \frac{\Delta E_T}{(\Delta E_T)^2 + \omega^2} = \frac{1}{\pi} \frac{DQ^2}{(DQ^2)^2 + \omega^2} $$

(2)

where $\Delta E_T$ is the half width at half maximum of the quasi-elastic line (HWHM) and $D$ the self diffusion coefficient.

For simplicity, we assume that the proton has an isotropic rotational diffusion motion around the centre of mass of the molecule characterized by a rotational diffusion coefficient $D_\alpha$, this motion being described by the Sears model /8/.

Using the expression (2) and the Sears model, the theoretical scattering function /9/ is given by:

$$ S_{\text{inc}}(Q,\omega) = \exp(-Q^2 u^2) \left\{ j_0(Qa) \frac{1}{\pi} \frac{\Delta E_T}{(\Delta E_T)^2 + \omega^2} + \sum_{l=1}^{\infty} j_2(Qa) \frac{\delta(2l+1)}{(l+1)D_\alpha + \Delta E_T} \right\} $$

(3)

where $j_l$ are the spherical Bessel functions and $a$ is comparable to the O-H bond length ($a = 0.98$ Å). This scattering law is then convoluted with the instrumental resolution function to fit the experimental data.

As a first step in the analysis we have tried to fit the data with the single Lorentzian (SL) form which corresponds to $D_\alpha = 0$ in equation (3). In figure 2, we
Fig. 1a - Quasi-elastic spectra of H₂O (T=298K, θ=64.20°, Q=1.13 Å⁻¹).

- Experimental points, --- SL fit, —— Fit with D_r = 0.13 meV, (insert x 10), —— Vanadium data (FWHM = 48.8 μeV).

Fig. 1b - Quasi-elastic spectra of aqueous ZnCl₂ saturated solution (T=298K, θ=64.20°, Q=1.13 Å⁻¹), o Experimental points, --- Fit with D_r = 0.005 meV.
Fig. 2 - $\Delta E_T$ versus $Q^2$ for $H_2O$ at $T=298K$. $\bullet$ From a SL fit, $\circ$ From a fit with $D_r=0.13$ meV, $x$ Sakamoto et al's data (SL) at $T=296K$, $\delta$ White's data (SL) at $T=296K$, $- -$ Random jump diffusion model (SL), $-- -$ Random jump diffusion model ($D_r=0.13$ meV), Typical error bar.

present the $\Delta E_T$ variation with $Q^2$ obtained by this fit. The results are in good agreement with those of Sakamoto et al /10/ and also with those of White /11/. However, it is apparent from a close examination of the variation of $(I^{inc.-I^{inc.}})^{exp.-calc.}$ versus $\omega$, especially in the tail region, that the fit with a single lorentzian is poor (Fig.1a).

Using the expression (3), we have fitted the quasi-elastic part of the measured spectrum for a given angle by the following relation: $F(Q,\omega)=A S_{inc}(Q,\omega)+B$ where $A$ represents an amplitude factor and $B$ the experimental background which can contain some inelastic contribution. Only three rotational lorentzians have been considered (i.e. $l \leq 3$) and the experimental spectra have been fitted by using 4 parameters, $\Delta E_T$, $D_r$, $A$ and $B$. We have evaluated, in each case, the translational diffusion contribution and the term including the rotational diffusion contribution.

We obtained the value of $D_r=0.13$ meV for pure $H_2O$. $D_r$ decreases down to 0.005 meV as solute concentration is raised up to saturation. Correspondingly, the characteristic relaxation time $\tau_r=W/6D_r$ varies from $\tau_r=0.8$ ps for $H_2O$ to 20 ps for the saturated solution. At low salt concentrations, the symmetry of the octahedral coordination in the first hydration shell $\left(6H_2O\right)/3,12/$ allows the water molecules to rotate very easily, giving rise to a value of $D_r$ similar to that of water. When the salt concentration becomes equal to 12.6M, the water molecules/zinc ions ratio is about 2 and so the binding forces between the elementary units, which allow the structure to be extended over medium range distance are very strong. Thus the water molecule rotations become very hard, giving rise to a very low value of the $D_r$ coefficient.
In figure 3, we present the HWHM variation $\Delta E_T$ versus $Q^2$ obtained by fitting the expression (3) for pure $H_2O$ ($D_r=0.13$ meV) and the saturated solution ($D_r=0.005$ meV) at 298K. The corresponding results for 6M and 3M solutions are also presented. According to the Random Jump Diffusion model for translational diffusion /13/ the quasi-elastic half width should be given by:

$$\Delta E_T = \frac{M Q^2 \xi^2_o}{\tau_0 (1+Q^2 \xi^2_o)}$$  \hspace{1cm} (4)

$\xi_o$ is a characteristic length in a random distribution of jump lengths given by:

$$a(\xi) = \xi e^{-\xi/\xi_o}$$  \hspace{1cm} (5)

and $\tau_0$ is the residence time of a molecule in a quasi-equilibrium position.

We found that eq.(4) could fit conveniently the $\Delta E_T$ vs $Q$ behaviour. For the saturated solution of ZnCl$_2$ in $H_2O$, the fit yields the following values for the parameters: $\xi_0=0.58\pm0.05$ Å, $\tau_0=8.1\pm0.5$ ps (and thus the hydrodynamic diffusion coefficient $D=\xi^2_0/\tau_0$ turns out to be $D=0.41.10^{-5}$ cm$^2$ sec$^{-1}$/14/). For pure $H_2O$, we obtained $\xi_0=0.64\pm0.05$ Å in agreement with the results of Chen et al /15/, and $\tau_0=1.7\pm0.1$...
ps, so that $D = 2.40 \times 10^{-5}$ cm$^2$ sec$^{-1}$, which is the correct value of the macroscopic diffusion coefficient at room temperature. From (5), we may deduce the mean quadratic jump length $L^2 = 2\sigma^2 = \frac{6D}{\pi\eta}$. We obtained for the saturated solution and for pure water the values $L = 1.43$ Å and $L = 1.58$ Å respectively which are close to the distance between protons in the H$_2$O molecule ($d_H = 1.55$ Å).

It is interesting to note that for the case of pure H$_2$O the random diffusion model of eq.(4) does not seem to fit the higher Q data. This discrepancy might be due to technical problems in the fitting, caused by the comparable half-widths that the rotational and translational components have in the high Q range. However, it might also imply a definite tendency of the AE to bend over at high Q's. In this case, a more appropriate model for the translational diffusion of water molecules could be that proposed by Chudley and Elliott /16/.

Clearly in order to distinguish between these two models further measurements at higher Q values are needed. At this time we prefer to interpret our data on the basis of the random jump model since it is more "liquid-like" and involves less radical assumptions about the microscopic diffusional motion of the H$_2$O molecules.

In this paper, we showed that there exist, at least, two components in the quasi-elastic neutron spectrum from water and highly concentrated ZnCl$_2$ solutions. The broad one is associated with the rotational motion of the H$_2$O molecules.

The translational part is described in the whole Q-range investigated by a random jump diffusion model for both the pure H$_2$O and the saturated ZnCl$_2$ solution.

Let us note that even in pure H$_2$O the residence time $\tau_0$ turns out to have the relatively large value of 1.7 ps and increases up to 8 ps for water in the saturated solution. Such times are obviously long enough to sustain collective vibrational excitations in the locally ordered regions and thus confirm the assignment of low frequency Raman spectra in these systems as vibrational density of states /2/. Another result concerns the value of the mean jump length L which turns out to be roughly the same for pure H$_2$O and saturated solution and close to the value of the distance between protons in the H$_2$O molecule. For the intermediate case of the more dilute solutions, the analysis is more complex and shall be reported in a further publication.

From the present data, on ZnCl$_2$ aqueous solutions, we have not been able to separate a contribution from different species of water as it has been reported by Enderby et al /17/ in a recent work on NiCl$_2$ solutions. However, we feel that, at least at high concentrations, the concept of hydration shells may lose its usefulness. In fact our data confirm that such systems are best described by intermediate range ordered patches inside which essentially all the H$_2$O molecules are more or less equivalent.

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These results are relative to a NMR relaxation study of water molecules in concentrated ZnCl₂ solutions. There is some discrepancy with our results for the measured values of the self diffusion coefficient of the saturated solution. Furthermore, it seems to us that the separation between intermolecular and intramolecular contributions to the relaxation is quite arbitrary for a molecular liquid, since the intermolecular contribution is influenced by the rotational motion of the molecule. Thus, it is difficult to compare the rotational correlation times obtained by the two methods.