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Quasielastic neutron scattering study of acidic solutions

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Abstract. The aim of the present work is to characterize by quasielastic neutron scattering (QNS) not only the usual transport processes occurring in aqueous solution but also something specific to the high proton conductivity in acidic solutions. The addition of a strong acid such as H_2SO_4 or HNO_3 to water provokes a marked slowing down of the mean translational diffusive motions and, to a lesser extent, of the rotational ones. Furthermore, we have evidenced a weak and broad additional QNS component which is not present in pure water. However, the presence of this component also in concentrated salt solutions eliminates the hypothesis of a fast proton transport process and indicates that some kind of relaxation process of the ionic environment could be involved.

1. Introduction

It is now well established that valuable information on the structure and dynamics of aqueous solutions can be obtained from neutron scattering experiments [1].

In a previous paper [2] we have started an investigation of aqueous acidic solutions in order to characterize by quasielastic neutron scattering (QNS) not only the usual transport processes occurring in aqueous solution but also the eventual contribution of fast proton kinetics in highly conducting solutions.

The first objective has been reached since mean translational and rotational diffusion constants have been determined for sulphuric acid solutions. The conclusion concerning the second objective was less clear. An additional component was detected in the acidic solutions and tentatively assigned to abnormally fast proton diffusivity but the corresponding diffusion constant D^+ was very high (about $2.2 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ at 263 K). Furthermore, this additional component was observed only at small momentum transfers ($Q < 0.5 \text{ \AA}^{-1}$).

To confirm and extend these first results we have performed new QNS experiments with better-adapted experimental conditions.

(i) The solutions were contained between two thin PTFE sheets instead of the previous copper cells [2] to decrease the background contribution and to avoid any problem of corrosion.

(ii) Concentrations corresponding to a eutectic composition in the phase diagram and to the maximum in specific conductivity have been selected; solutions can then be studied at low temperatures.

(iii) A wide range of instrumental resolutions (from about 1 to 70 μeV) has been covered at the Institut Laue–Langevin, Grenoble.

(iv) In addition to the H_2SO_4 and Cs_2SO_4 solutions, HNO_3 and NH_4NO_3 solutions have been studied for comparison.

2. Results

In a QNS experiment on aqueous solutions, the $S(Q, \omega)$ incoherent scattering law reflects essentially the proton motions occurring in the 10^{-9} – 10^{-12} s time scale. The momentum transfer dependence of the scattering law allows fortunately the various contributions to be separated provided that the hypothesis of uncoupled translational, rotational and vibrational motions is valid in the QNS region.

We consider first the proton translational diffusion averaged over all kinds of water molecule in the solution:

$$S^t(Q, \omega) = \Gamma_t / \pi(\omega^2 + \Gamma_t^2). \quad (1)$$

Γ_t (the half-width at half-height (HWHH)) is given, according to the random-jump diffusion model [2–4], by

$$\Gamma_t = \hbar Q^2 l_0^2 / \tau_0 (1 + Q^2 l_0^2) \quad (2)$$

where τ_0 is the residence time of a water molecule in a quasi-equilibrium state and $l_0 = \sqrt{D_t \tau_0}$ a characteristic jump length.

When $Q \rightarrow 0$ in equation (2), $\Gamma_t \rightarrow D_t Q^2$. D_t is thus a mean translational diffusion constant which can be determined from the limiting slope of $\Gamma_t = f(Q^2)$ plots as shown in figure 1. Numerical values are given in table 1. Their accuracy (less than 10%) is reasonably good as shown by the perfect agreement with values for pure water obtained by other methods and given in the literature.

Once D_t is known, the QNS spectra obtained at higher Q -values can be treated in terms of a convolution product of equation (1) by the rotational contribution $S^r(Q, \omega)$. To a first approximation, the latter has been simulated by an isotropic rotational diffusion model on a sphere of O—H radius 0.98 Å [2, 4].

Finally, the whole experimental $S(Q, \omega)$ profile is fitted with the two main parameters τ_0 and D_t . Some values are given in table 1.

As already pointed out [2], the previous model reproduces satisfactorily the pure water data (figure 2(a)), but careful examination of the QNS wings for acidic solutions confirms the presence of an additional component. Good agreement with the experimental data is achieved by convoluting the previous model by a single Lorentzian which involves about 10% of the total intensity and has a width (HWHH) of about 0.2–0.3 meV (figures 2(b) and 2(c)).

A parallel study of the salt solutions under the new experimental conditions indicates that the additional component is also present (figure 2(d)) and therefore not specific of the acidic solutions.

3. Discussion

Knowledge of the water diffusive motions constitutes an essential starting point for the understanding of proton kinetics in acidic solutions.

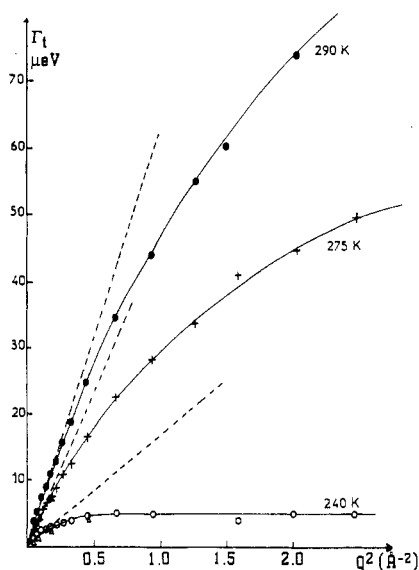


Figure 1. HWHH Γ_t versus Q^2 of the translational Lorentzian, equation (1), once the rotational contribution is taken into account. The broken curves correspond to the limiting slope at small Q -values. The open triangles for $Q^2 < 0.5 \text{ \AA}^{-2}$ correspond to data obtained with the IN10 spectrometer and the open circles to data obtained with the IN6 spectrometer.

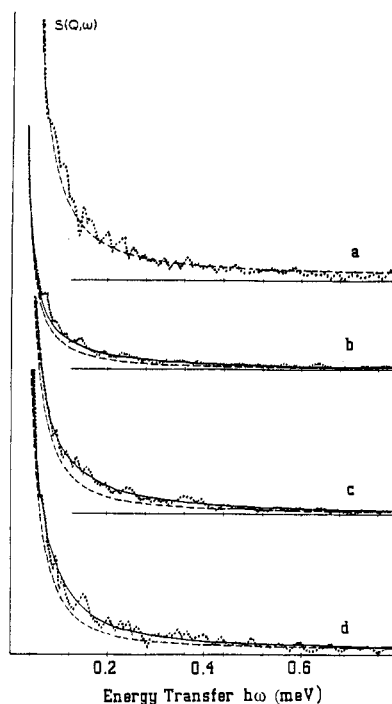


Figure 2. Experimental profiles (points) obtained with the IN5 spectrometer and fitted by a convolution of the translational and rotational scattering laws (see text) with (broken curves) and without (full curves) an additional Lorentzian component: a, pure water; b, 5 M H_2SO_4 ; c, 6.1 M HNO_3 ; d, 6.1 M NH_4NO_3 . For all these spectra, the momentum transfer at $h\omega = 0$ is $Q = 0.426 \text{ \AA}^{-1}$ and the intensity is cut at 1/10 of the maximum. The temperature is 275 K for pure water and 270 K for the solutions.

The mean translational diffusion characterized by D_t and τ_0 (table 1) is slower in acidic solutions than in pure water because of a more pronounced structure. In the series H_2O , 6 M HNO_3 , 3.2 M H_2SO_4 and 5 M H_2SO_4 , D_t decreases linearly with increasing viscosity which is, at 290 K, 1 cP, 1.35 cP, 1.81 cP and 2.53 cP respectively.

Table 1 indicates also that the residence time τ_0 increases in the same series in such a way that the square root of the mean quadratic jump length $L = \sqrt{6D_t\tau_0}$ remain of the same order of magnitude. Typically, the L -value of about 1.6 \AA at 290 K is similar to the distance between the two protons of H_2O . However, L increases strongly when the temperature is lowered. For 5 M H_2SO_4 at 240 K, the L -value of about 4.2 \AA is rather related to a cluster of several water molecules solvating an ion.

The rotational dynamics of a given water molecule in such clusters are comparatively less affected by the nature of the acid, its concentration and the temperature (table 1). However, the D_r -values have to be taken only as indicative in the comparison of various solutions. Indeed, if the isotropic rotational diffusion model is generally considered as an acceptable approximation for pure water [2], it is certainly much less adapted to

Table 1. Values of the mean proton self-diffusion constant D_t , of the residence term τ_0 and of the rotational diffusion constant D_r deduced from the $S(Q, \omega)$ spectra recorded on various spectrometers of the Institut Laue–Langevin, Grenoble. IN10 is a back-scattering spectrometer, IN6 a time-focusing spectrometer and IN5 a time-of-flight spectrometer. E_a refers to the activation energy of the translational diffusion.

Sample	T (K)	$D_t \times 10^9$ ($\text{m}^2 \text{s}^{-1}$)	$\tau_0 \times 10^{12}$ (s)	$D_r \times 10^{-10}$ (s^{-1})	E_a (kJ mol^{-1})	Spectrometer	λ_0 (\AA)
5 M H_2SO_4 - H_2O	215	0.100	≈ 526		17.2	IN10	6.28
5 M H_2SO_4 - H_2O	240	0.230	131	3.8	17.2	IN10, IN6	6.28, 5.9
5 M H_2SO_4 - H_2O	270	0.562	10.2	7.6	17.2	IN5	9
5 M H_2SO_4 - H_2O	275	0.655	7.8	9.4	17.2	IN10, IN6	6.28, 5.9
5 M H_2SO_4 - H_2O	290	0.912	4.6	12.1	17.2	IN6	5.9
6.1 M HNO_3 - H_2O	250	0.456	11.2	4.4	18.6	IN5	9
6.1 M HNO_3 - H_2O	270	0.889	3.3	6.1	18.6	IN5	9
6.1 M NH_4NO_3 - H_2O	270	0.912	3.3	6.8	18.6	IN5	9
6.1 M NH_4NO_3 - H_2O	285	1.50	1.6	9.1	18.6	IN5	9
6.1 M NH_4NO_3 - H_2O	298	1.97			18.6	IN5	9
H_2O	275	1.22	3.0	11.2	18.6	IN6	5.9
H_2O	277.5	1.30	1.8	11.5	18.6	IN5	9
H_2O	290	1.88	1.3	14.6	18.6	IN6, IN5	5.9, 9

concentrated solutions where nearly all the water molecules are involved in the first solvation shell of the ions. There, another limiting model, the uniaxial rotational diffusion of H_2O around its symmetry axis, is physically more likely [5]. Actually, a careful measurement of the incoherent structure factor for the rotation allows this problem to be treated independently of any hypothesis of motion. This analysis, not given here for lack of space, will be presented in a forthcoming paper [6].

The more intriguing problem remains the absence of presence of an additional component related to a fast proton transport process in the acidic solutions. Several Raman line-broadening studies on aqueous solutions of CF_3COOH [7], H_2SO_4 [8], HNO_3 and NaNO_3 [9] invoke fast chemical exchange between ion pairs and free ions. The involved lifetimes are in the 10^{-11} s range.

Hertz and co-workers [10] have concluded that fast H^+ motion is absent in HCl - H_2O solutions. We confirm here our first observation [2] of an additional component in a momentum transfer range where the incoherent structure factor for the rotation is close to unity and anyhow nearly the same for any rotational model.

A new finding is, however, the presence of this component in both acid and salt solutions (figure 2). This rules out our previous suggestion [2] of an abnormally fast proton diffusivity and orientates the interpretation towards dynamical processes related to the relaxation of 'water cages' around the ionic species.

It must be recalled that in our analysis of the QNS profiles the vibrational contribution was restricted to a Debye–Waller factor $\exp(-\langle u^2 \rangle Q^2)$. It is not excluded that an overdamped density of states centred at zero energy transfer appears in the ionic solutions especially when the temperature is lowered and L is increased. Many propositions have been put forward in the literature of a coupling between acoustic phonons with either optical or relaxation modes to interpret central peaks in light scattering experiments [11–13].

It would be very important to follow the momentum transfer dependence of the QNS additional component to assess its interpretation. We have seen that this is very dependent on good evaluation of the rotational contribution. If some kind of collective excitation is effectively involved, its contribution would be enhanced in the QNS spectra of deuterated samples.

4. Conclusion

Important parameters of the mean proton translational and rotational motions in aqueous solutions can be directly measured by QNS. This is a compulsory step before looking at an eventual contribution related to fast proton kinetics in acidic solutions.

Actually, we have evidenced such an additional component in both salt and acid solutions. Although its shape and Q -dependence are not still determined with sufficient accuracy for clear interpretation, we think that the involved dynamical process is related to a relaxation mode of the water molecules in the ionic solvation shells. Further experiments, including $H-D$ substitution, are planned to see whether this relaxation mode is driven by simple chemical exchange or by some kind of collective excitation.

Acknowledgment

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References

- [1] Bellissent-Funel M C and Neilson G W (ed) 1987 *The Physics and Chemistry of Aqueous Ionic Solutions* (Dordrecht: Reidel)
- [2] Lassègues J C and Cavagnat D 1989 *Mol. Phys.* **68** 803
- [3] Egelstaff P A 1967 *An Introduction to the Liquid State* (New York: Academic)
- [4] Bellissent-Funel M C, Kahn R, Dianoux A J, Fontana M P, Maisano G, Migliardo P and Wanderlingh F 1984 *Mol. Phys.* **52** 1479
- [5] Bellissent-Funel M C, Dianoux A J, Fontana M P, Maisano G and Migliardo P 1989 *Physica B* **156-7** 132
- [6] Lassègues J C and Cavagnat D 1990 *Solid State Ion.* at press
- [7] Kreevoy M M and Mead M C 1965 *Discuss. Faraday Soc.* **39** 166
- [8] Irish D E and Chen H 1970 *J. Phys. Chem.* **74** 3796
- [9] Strehlow H, Wagner I and Hildebrand P 1983 *Ber. Bunsenges. Phys. Chem.* **87** 516
- [10] Bertagnolli H, Chieux P and Hertz H G 1987 *J. Chem. Soc. Faraday Trans.* **83** 687
- [11] James D W and Irmer R 1982 *Chem. Phys. Lett.* **85** 518
- [12] Aliotta F, Vasi C, Maisano G, Majolino D, Mammace F and Migliardo P 1986 *J. Chem. Phys.* **84** 4731
- [13] Tao N J and Lindsay S M 1988 *J. Phys. Chem.* **92** 5855