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Pressure effect on water dynamics in tert-butyl alcohol/water solutions

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Abstract

We report here a quasi-elastic neutron scattering (QENS) investigation of the effect of pressure on the diffusivity properties of water in a dilute aqueous solution of hydrophobic molecules (tert-butyl alcohol, TBA). The experiment was performed at fixed TBA concentration (0.02 molar fraction) by varying pressure from 1 to 2000 bar at two different temperatures (268 and 278 K). The quasi-elastic line-shapes have been analysed in terms of a model based on the memory function formalism. Our data indicate that, on increasing pressure up to 2000 bar, the diffusion coefficient of water in the TBA/water mixture exhibits a relative increase larger than that of pure water under the same thermodynamic conditions. The extent of this effect increases with decreasing temperature. The observed behaviour is described in terms of pressure-induced distortions of the H-bonded random network of liquid water.

1. Introduction

The hydrophobic effect has attracted considerable interest owing to its important role in a wide range of biochemical processes taking place in aqueous solutions such as protein folding, micelle formation and conformational changes in biological membranes [1]. The hydrophobic effect arises from two related processes: at first, the introduction of a-polar solutes in water perturbs the H-bond network, inducing a reorganization of water around the solute molecules (hydrophobic hydration); secondly, the water mediated interactions among a-polar groups (hydrophobic interactions) lead to clustering phenomena involving water and a-polar molecules [2].

Detailed information on the hydrophobic effect may be obtained from the study of aqueous solutions of simple alkyl derivatives such as alcohols, amines and ethers, where the

hydrophobic effect is the dominant intermolecular interaction. These molecules possess a large hydrophobic group and one polar site, capable of participating in hydrogen bonding with water, which makes it possible to dissolve the solute molecules in water. In dilute aqueous solutions, these molecules behave as essentially hydrophobic species, their polar group providing only a minor contribution [2–4]. Among these systems, the series of monohydric alcohols is one of the most commonly investigated. Within this series, the tert-butyl alcohol (TBA) has the largest hydrophobic group (three methyl groups, CH_3) and can be used as model system to investigate structural and dynamical properties of water near a-polar solutes.

Several properties of the TBA/water mixtures have already been studied in great detail as a function of the solute concentration, x , in units of molar fraction. We recall the minimum in the apparent molar volume [5], the maximum in the excess heat capacity [6], the change in slope of the apparent molar compressibility [3], etc. All these anomalies occur in the same concentration range, 0.03–0.05 molar fraction (mf), and have been interpreted in terms of an evolution in the aggregation state of the solute molecules. The emerging picture is that, below this ‘threshold concentration’ the alcohol molecules are dispersed as monomers, while at higher concentration they start to aggregate (see [5] for a review). The association of hydrophobic groups is driven by the hydrophobic interactions up to $x \sim 0.13$, while at higher concentrations the hydrophobic effects become negligible and further association processes are mostly controlled by direct solute–solute interactions. In agreement with this description, molecular dynamics simulations (MD) [7] and neutron diffraction studies [8, 9] on TBA/water solutions indicate a small degree of association in dilute solutions ($x = 0.02$ – 0.03), while small aggregates, with bulky hydrophobic groups in contact, are observed at higher concentrations ($x = 0.06$ – 0.08) [9].

Most of the studies on the TBA/water mixtures, dealing with water-rich solutions (low solute concentration), investigate the structural changes of the aqueous solvent caused by the introduction of a-polar groups. MD and Monte Carlo simulations on TBA/water mixtures have been interpreted in terms of an increased water structuring with respect to pure water [7, 10, 11]; however this interpretation is still controversial [8, 12].

Concerning the dynamic properties, MD simulations [13, 14], dielectric [15] and nuclear magnetic resonance (NMR) [16] measurements have all shown a slowing down of water dynamics in the presence of TBA molecules, but the extent of this effect with respect to the hydrophobic group concentration has not been quantified so far. On more general grounds, the relation between the unusual properties of aqueous solutions of a-polar molecules and those of the hydrogen-bond network of pure water is far from being understood at a microscopic level. For this reason, we have recently carried out a QENS investigation [17] on TBA/water mixtures at room pressure, varying solute concentration in the water-rich region of composition (from 0 to 0.04 mf) in order to compare the changes in the microscopic diffusivity properties of water in the mixtures with those of pure water upon decreasing temperature, T . In this concentration range, the alcohol molecules are dispersed as monomers and the hydrophobic groups are preferentially hydrated (hydrophobic hydration). Our results show that

- (1) the introduction of the alcohol molecules leads to a decrease in the diffusion coefficient, D , of water in TBA/water mixtures analogous to that observed in pure water upon decreasing temperature;
- (2) the T -dependence of D in pure water and the x -dependence of D in the solutions can be rescaled to a common curve if one assigns to each solution a concentration-dependent ‘structural temperature’ T_S lower than the actual thermodynamic one according to the scaling law $T_S(x) = T_0 - ax$ (from our data, at $T_0 = 293$ K, we obtain $a = 540 \pm 40$ K/mf). In other words, the effect of TBA addition on water dynamics

is equivalent to that obtained by lowering the temperature of pure water by an amount proportional to the solute concentration.

Our data suggest that, in the concentration range where hydrophobic hydration effects dominate, the micro-diffusivity properties in the TBA aqueous solutions are mostly determined by the properties of the water random network. Since both the pressure and the temperature affect these properties, we have undertaken a QENS investigation on the pressure dependence of water diffusivity in TBA/water mixtures in order to check the validity limits of the scaling law. The QENS measurements were carried out on a TBA/water mixture at fixed TBA concentration, $x = 0.02$, at two different temperatures, $T = 268$ and 278 K, with varying pressure from 1 to 2000 bar. The data are discussed in comparison with those of pure water [18, 19] in the same thermodynamic conditions. In this pressure range, the diffusion coefficient of pure water shows a maximum, which represents one of the well-known anomalies of water. This phenomenon has been explained [20, 21] in terms of a competition between compression, which generally slows down the translational motions, and the effect of pressure on the random transient hydrogen-bonded network of liquid water, which increases water mobility by breaking the H-bonds. Hence, a comparison between the effects of pressure on the dynamics of water in the TBA/water mixtures and in pure water can provide indirect information on the properties of the hydrogen-bonded network and on the occurrence and the extent of water structuring induced by a-polar molecules.

2. Experimental details

Using the IRIS spectrometer at the ISIS pulsed neutron facility (Rutherford-Appleton Laboratory, UK) we have performed QENS measurements on a TBA/water solutions at fixed TBA concentration, 0.02 mf, at two temperatures (268 and 278 K), by varying pressure in the range 1–2000 bar. To this aim, we built a special cell, made from stainless-steel capillaries (inner diameter 0.4 mm), capable of withstanding pressures up to ~ 4 kbar. The solution was made up by weight, using distilled water and perdeuterated solute in order to minimize the incoherent scattering from TBA molecules. Because of the low scattering cross section of deuterium (7.64 b) with respect to hydrogen (82.02 b), the scattering contribution from perdeuterated TBA is negligible for all the investigated solutions. The spectra are therefore essentially proportional to the self-dynamic structure factor of water hydrogens. The spectrometer was operated in the 002 pyrolytic graphite configuration which provides a Q -range from 0.44 to 1.83 \AA^{-1} with an energy window from -0.25 to 1.2 meV and a resolution of $\Delta E = 15 \text{ \mu eV}$ (full-width at half maximum, FWHM). Empty cell and vanadium runs were performed in order to carry out the standard corrections (cell subtraction and self-shielding) and normalization, including a first-order multiple scattering correction.

3. Theoretical model for the dynamic structure factor

For the analysis of the present experiment, we applied a model based on the memory function formalism. Starting from the pioneering works by Zwanzig and Mori [22, 23], this formalism has been applied extensively to describe the dynamics of simple liquids [24–26]. Recently, it has also been applied to associated liquids like water [27–29, 17].

In the framework of the memory function formalism, the time evolution of the self-intermediate scattering function $F(Q, t)$ of water hydrogens can be described in terms of a

second-order memory function, $M_s(Q, t)$ [24], through a generalized Langevin equation:

$$\ddot{F}(Q, t) + \int_0^t \dot{F}(Q, t - \tau) M_s(Q, \tau) d\tau + \langle \omega_Q^2 \rangle F(Q, t) = 0 \quad (1)$$

where the second frequency moment, $\langle \omega_Q^2 \rangle$, is given by

$$\langle \omega_Q^2 \rangle = \left(\frac{k_B T}{m} \right) Q^2 \quad (2)$$

m being the molecular mass.

Due to the high incoherent cross section of hydrogen nuclei, neutrons are sensitive to water hydrogens. Therefore the use in the model of the molecular mass, in place of some effective hydrogen mass, implies that we consider hydrogens as markers describing mostly the centre-of-mass dynamics. Actually, in recent years molecular dynamics simulation studies [30, 31] proved that the time evolution of the intermediate scattering function related to the hydrogen motion is very similar to that of the oxygen atoms (or of the centre of mass) over the whole Q -range below the main structure peak, except for the early times ($t \lesssim 0.3$ ps). Hence, in the QENS timescale ~ 0.5 – 50 ps, the hydrogen intermediate scattering function reflects, to a large extent, the dynamics of the molecule centre of mass.

In equation (1), the memory function appears in the generalized friction term, which relates the value of intermediate scattering function at a given time t to its past history. In agreement with the developments of kinetic and mode coupling theories [32, 33, 25], and following previous works on the application of the memory function formalism to the dynamics of supercooled water [28, 29] and of water in TBA/water mixtures [17], we describe the second-order memory function of the self-intermediate scattering function as the superposition of two exponential relaxation processes.

The first process, characterized by a short decay time τ_1 , can be ascribed to localized interactions, both in space and time. They can be identified with the hindered motions of the water molecules inside the nearest-neighbour cage. The time-scale of these processes is of the order of $1/20$ ps and it accounts for about 95% of the total intensity of the memory function. The second relaxation process occurs over a longer time-scale τ_2 , and it may be associated with the structural relaxations of water clusters. These are related to the reorganization of the H-bonded network, following the diffusion of water molecules outside the nearest-neighbour cage. The typical time-scale of this process is of the order of 1–20 ps, and its presence suggests that a water molecule can migrate out the nearest-neighbour cage only through rearrangement of a large number of molecules surrounding it. This slow process contributes only a relatively small amount to the total intensity of the memory function ($\leq 5\%$), nevertheless it must be taken into account in order to obtain a satisfactory reproduction of the QENS spectra.

We would like to point out that the characteristic times τ_1 and τ_2 , describing the time evolution of the memory function, cannot be directly related to the characteristic times of the intermediate scattering function. Through the time convolution between the self-intermediate scattering function and the memory function (see equation (1)) both of them contribute to the time evolution of the self-intermediate scattering function in the time window probed by the experiment.

We therefore write the second-order memory function as

$$M_s(Q, t) = M_{so}(Q) [\alpha_Q e^{-t/\tau_1(Q)} + (1 - \alpha_Q) e^{-t/\tau_2(Q)}]. \quad (3)$$

The pre-factor $M_{so}(Q) = \Omega_0^2 + 2(k_B T/m) Q^2$ is related to the static properties of the solvent, since the Einstein frequency Ω_0 can be written as [24]

$$\Omega_0^2 = \frac{4\pi n}{3m} \int_0^\infty g_{OO}(r) \frac{d}{dr} [r^2 \phi'_{OO}(r)] dr \quad (4)$$

where m is the molecular mass, n is the particle number density, and $g_{OO}(r)$ and ϕ'_{OO} stand respectively for the oxygen–oxygen pair distribution function and the first derivative of the corresponding interatomic potential.

In the framework of this approach, the self-dynamical structure factor is written as

$$S(Q, \omega) = \frac{A_0 M_{so} A_2}{A_3 \left[\left(\frac{A_0 M_{so} A_2}{A_3} \right)^2 + \left(\omega - \frac{A_0 A_1}{A_3} \right)^2 \right]} \quad (5)$$

where

$$\begin{aligned} A_0 &= (k_B T / m) Q^2 \\ A_1 &= \omega - M_{so}(Q) \left[\frac{\alpha_Q \omega}{\omega^2 + \tau_1^{-2}} + \frac{(1 - \alpha_Q) \omega}{\omega^2 + \tau_2^{-2}} \right] \\ A_2 &= \frac{\alpha_Q \tau_1^{-1}}{\omega^2 + \tau_1^{-2}} + \frac{(1 - \alpha_Q) \tau_2^{-1}}{\omega^2 + \tau_2^{-2}}; \\ A_3 &= M_{so}^2 A_2^2 + A_1^2. \end{aligned}$$

The free parameters of the model are therefore α_Q , τ_1 , τ_2 , and Ω_0^2 . The transport coefficients can be expressed in terms of suitable integrals of the memory functions [34]. In particular, the self-diffusion coefficient, D_m , is given by

$$D_m = \lim_{Q \rightarrow 0} \frac{1}{Q^2} \left[\int_0^\infty K_s(t) dt \right]^{-1} \quad (6)$$

where $K_s(t)$ is the first-order memory function which is related to the second-order memory function by

$$\dot{K}_s(t) = - \int_0^t M_s(t - \tau) K_s(\tau) d\tau. \quad (7)$$

With the assumption that we made for $M_s(t)$ (equation (3)), the integral in equation (6) can be evaluated, leading to a relatively simple form for the diffusion coefficient:

$$D_m = \frac{k_B T}{m \Omega_0^2} \frac{1}{\alpha \tau_1 + (1 - \alpha) \tau_2}. \quad (8)$$

4. Results

Figure 1 shows as example of the QENS spectra from the TBA/water solution at 0.02 mf concentration, $T = 268$ K and momentum transfer $Q = 1.46 \text{ \AA}^{-1}$, for $p = 1$ bar and 2 kbar respectively. For both spectra, the result of the fit to the model is displayed.

The pressure increase gives rise to a broadening of the quasi-elastic width at both temperatures investigated. This indicates an increase in mobility with increasing pressure in the range 1–2000 bar that is qualitatively similar to that observed in pure H_2O , where a maximum in the diffusion coefficient is observed at around 1.5–2 kbar [18, 19]. This maximum becomes more and more pronounced upon decreasing temperature below room temperature. In water, this behaviour has been explained in terms of a competition between compression, which generally slows down the translational motions, and pressure-induced distortions of the random H-bond network, with the subsequent break-up of the cages made up from neighbouring molecules which leads to an increase in water mobility [20, 21]. This picture is supported by the pressure dependence of the relaxation times τ_1 and τ_2 in our data. Actually, for both

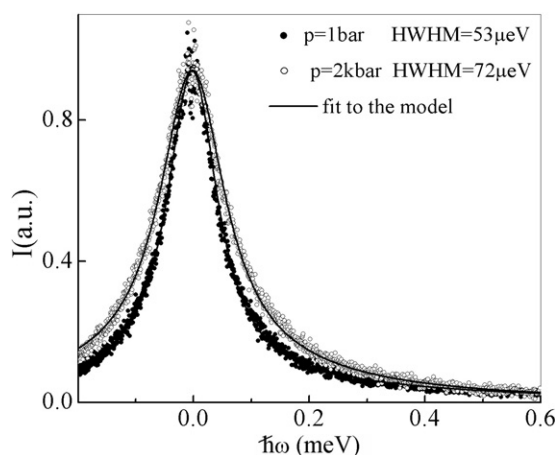


Figure 1. QENS spectra from the water/TBA solution at $x = 0.02$ mf, $T = 268$ K and $Q = 1.46 \text{ \AA}^{-1}$, for $p = 1$ bar (●) and $p = 2$ kbar (○). Continuous lines represent the fit to the model (equation (5)).

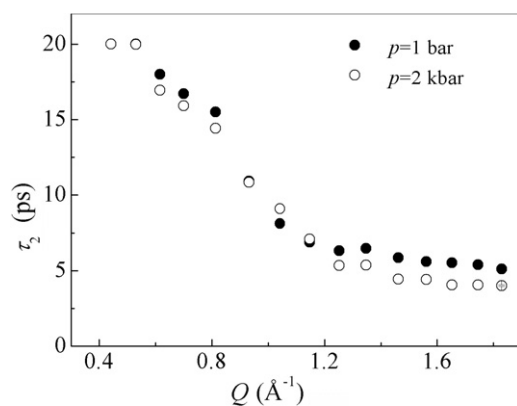


Figure 2. Q -dependence of the relaxation time τ_2 at $T = 268$ K for $p = 1$ bar (●) and $p = 2$ kbar (○).

temperatures considered, τ_1 is almost Q - and pressure-independent. The only thermodynamic parameter to which τ_1 is sensitive is temperature: on decreasing temperature from 278 down to 268 K, τ_1 increases from 0.05 to 0.09 ps. Unlike τ_1 , the relaxation time τ_2 is sensitive to pressure variations (figure 2). At each Q -value, a decrease in τ_2 is observed with increasing pressure, this indicates that pressure essentially affects the dynamical processes, involving deformation and relaxation of water cages. In particular, a pressure increase reduces the persistence time of the memory effects due to the relaxation of water structures.

We remark that, in all the τ_2 -curves versus momentum transfer, a rapid increase in τ_2 is observed with decreasing Q , from 1 to 0.4 \AA^{-1} (figure 2). At the same time, the α_Q weighting factor tends to 1 for $Q \lesssim 0.7$ (data not shown). This evolution of the parameters can be interpreted as an indication that memory effects arising from structural relaxation persist for longer times when observed over larger space lengths ($\gtrsim 6 \text{ \AA}$), but at the same time their effect on the dynamics of the system becomes progressively less relevant, since the effect of intermolecular interactions decreases when probed over a larger space scale.

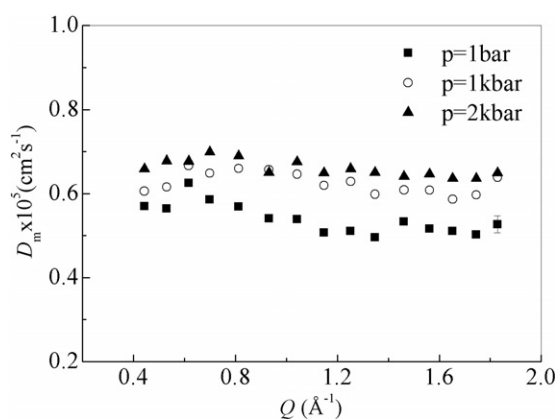


Figure 3. Q -dependence of the diffusion coefficient, D_m , obtained from equation (8) in the frame of the memory function model at different pressures and at $T = 268$ K.

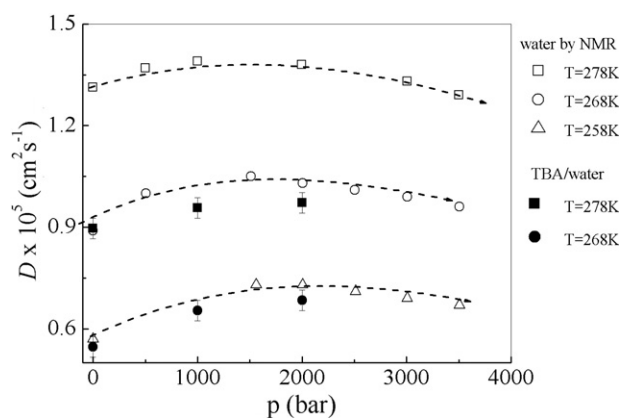


Figure 4. Diffusion coefficient of water, D , in TBA/water mixture (filled symbols) and in pure water (open symbols) versus pressure at different temperatures. The D -values relative to pure water are literature data from NMR measurements [18, 19].

In the framework of the memory function approach, equation (8) provides the centre-of-mass diffusion coefficient, D_m , at each Q value. Figure 3 shows, as an example, the values obtained at 268 K for the two pressures investigated. Within the experimental uncertainty, there is no significant Q -dependence, and Q -averaged values, D , can therefore be considered.

For both temperatures, D increases with increasing pressure, and this effect is more relevant at the lowest temperature (see figure 4). In figure 4, the pressure dependence of the diffusion coefficient for the water/TBA solution at the two temperatures investigated is compared to that of pure water at 258, 268 and 278 K (data obtained from NMR measurements [18, 19]). From figure 4, it clearly appears that, in the range 1–2000 kbar, the translational mobility of water molecules in the mixture increases on increasing pressure, in a way that is qualitatively similar to that of pure water. In particular, we remark that the D versus p curves of the water/TBA mixture at 278 and 268 K superimpose on those of pure water obtained at two thermodynamic temperatures 10 K lower, i.e. 268 and 258 K respectively. In other words, it turns out that the datasets relative to the mixture coincide with those of

pure water if one assigns them a ‘structural temperature’, T_S , 10 K lower than their actual thermodynamic temperature.

In agreement with our previous results on the TBA/water solutions, the effect of TBA molecules on water dynamics is therefore equivalent to a temperature decrease; in both cases water dynamics slow down. In [17], we described this behaviour in terms of a scaling law for the microdiffusivity parameters, introducing a ‘structural temperature’ T_S given by:

$$T_S = T - ax, \quad a = 540 \pm 40 \text{ K/mf}, \quad (9)$$

which allows us to quantify the effective temperature decrease as a function of solute concentration.

In particular, for the diffusion coefficient, D , we showed that

$$D(x, T, p = 1 \text{ bar}) = D(0, T - ax, p = 1 \text{ bar}), \quad 0 \leq x \leq 0.04, \\ T = 293 \text{ K}, \quad a = 540 \pm 40 \text{ K/mf} \quad (10)$$

where the parameters x , T and p denote solute concentration, thermodynamic temperature and pressure, respectively. Our present data (see figure 4) indicate that the above scaling law (equation (10)) holds not only at ambient pressure and room temperature but also over a wider pressure and temperature range, namely at least from 1 to 2000 bar and from 293 K down to 260 K. Indeed, the scaling factor a , within the experimental accuracy, is constant over the above temperature and pressure intervals.

5. Conclusions

The most direct way to get structural information on such a complex mixture is by using neutron diffraction coupled to isotopic substitution. However the evolution of the micro-diffusivity parameters with pressure that we derive from QENS experiments supports the picture that water is more structured in the TBA solution than in pure water. What is particularly remarkable in our data is that the scaling law that we derive, equation (10), holds in a relatively wide range of concentrations, temperatures and pressures.

The results of this experiment are compatible with Stillinger’s hypothesis [35] on the relation between anomalies of supercooled water and the hydrophobic effect phenomenon. Stillinger suggests that, in pure water, there is a distribution of cavities of various shapes and sizes, fluctuating about its mean. The introduction of a-polar molecules stabilizes those configurations that provide a sufficient number of cavities to accommodate them. The cavities are associated with the formation of unstrained hydrogen-bond polyhedral structures similar to those spontaneously formed in pure water on decreasing the temperature in the sub-zero region. Within the hydrogen bond network, the a-polar solute molecule acts as a marker for the locations at which ideal convex polyhedra are most likely to occur. In this sense, the inert solute ‘enhances’ the structure of water.

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