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Dynamical properties of water-methanol solutions studied by depolarized Rayleigh scattering

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The dynamics of water in water-methanol solutions is studied by depolarized Rayleigh light scattering as a function of concentration and temperature. The obtained data give evidence of a well-defined maximum in the hydrogen bonding relaxation time at equimolar concentration. This phenomenon is consistent with the presence of well-defined shells of water around the methanol molecules as observed recently by means of a neutron diffraction experiment. In addition, our data show that the water rotational relaxation time increases with increasing solute concentration. This suggests that the water structure in these shells is more stable than bulk water structure at the same temperature. [S1063-651X(96)05207-5]

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I. INTRODUCTION

In the physics of complex fluids there are still many open questions related to the properties of water around amphiphiles or alcohol molecules [1]. In particular, several studies have been devoted to clarify the role of the hydrophobic headgroups of alcohol (or amphiphile) molecules in determining physical properties of water [2,3], or vice versa. Pure water can be considered (on the basis of the various models proposed in order to explain its behavior) as an extensive three-dimensional (polymericlike) network of hydrogen bonded molecules [4]. In this structure, neighboring water molecules assume specific tetrahedral orientational correlations.

Pure alcohols present similar bonds (but alkyl groups cause association in chains or rings) so that all molecular interactions in water-alcohol mixtures are ruled by hydrogen bonding. It is well established that mixtures of these two fluids exhibit anomalous behavior compared with the properties of their pure components; this phenomenon may be ascribed to the hydrophobic groups. The negative excess of entropy observed [5] on mixing water with hydrophobic species, and the large nonideal changes in other thermodynamical quantities, need to be completely understood and represent challenging problems in the physics of aqueous solutions.

Starting from the pioneering work of Frank and Evans [6], who proposed the idea that the hydrophobic entities enhance the water structure towards a more ordered one near the alcohol headgroups, many investigations, in particular, molecular dynamics (MD) computer simulation, were performed on this subject and give controversial results. Indeed, some MD studies [7] seem to indicate that hydrophobic solutes, at lower concentrations, have only a weak effect on water-water correlations, implying that there is no need to invoke an enhanced water ordering and that most of the changes into the thermodynamic quantities can be estimated by only considering solute-water correlations. Others, however, have obtained opposite results, i.e., a hydration sphere exists around hydrophobic entities in an aqueous solution [8,9].

Water-methanol (CH_3OH) mixtures have been studied with the aim of obtaining definitive answers to these questions. For this system, the hydrophobic group CH_3 makes a substantial contribution to the thermodynamic properties of the mixture; a particularly typical result of this being the presence of a minimum in the partial molar volume of methanol [1]. Many different theoretical models have been proposed in order to explain the water properties in this complex system. However, MD computer simulation [10–12] was used extensively because it is very difficult to obtain direct and detailed structural information from experiments (for x-ray and neutron scattering experiments, the system presents a very low scattering cross section).

By means of MD, it was possible to obtain some insight into the effect of hydrophobic entities on the water structure. Applying this technique to the water-methanol solutions considered here, it was observed that the water pair correlation functions sharpened slightly compared to those of the pure liquid. In addition, it is for this system that recent MD results [11] predicted that a shell of water should form around a methanol molecule.

An experimental confirmation of such a prediction has been obtained very recently by a careful neutron diffraction study, performed at a low methanol concentration (1:9 molar ratio methanol water) [13]. The corresponding data analysis shows the existence of a definite hydration shell of water molecules at a certain distance from the carbon atom of the methanol molecule. For this methanol concentration, it was suggested additionally, that this shell is formed without a significant modification of the water structure (orientational order between water molecules). More precisely, neutron data showed that water molecules in this shell form a disordered cage but retain the tetrahedral local coordination found in pure water.

These experimental studies of the water structure in

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methanol-water solutions, as well as recent MD studies on the same system [11] and on other hydrophobic entities in aqueous solutions [8,9], seem to confirm that hydration effects do not lead to significant changes in the water structural order. Motivated by these findings, our aim has been to characterize these systems by means of dynamic light scattering. As is well known, this technique is a powerful tool for the study of condensed matter; depending on the frequency range used and the scattering geometry it can furnish information both on local (microscopic) and collective properties of the scatterers [14]. Because asymmetric molecules (in particular, water molecules) give a strong contribution to the depolarized intensity, the depolarized Rayleigh light scattering technique (DRLS) has been used widely to obtain information on the rotational dynamics of the scatterers (together with the corresponding relaxation times) or to the bonding energy for assembled molecules [14].

DRLS has been used in the past for studing the dynamical properties of pure bulk water in the normal and supercooled state, obtaining significant results on the physics of the system. The characteristic times (lifetimes) of the hydrogen bonds in pure water, in particular, are well determined by means of depolarized light scattering [15,16]. In addition it was observed that DRLS can give accurate information on the water configuration around amphiphiles or alcohol molecules even at a very large solute concentration [17].

Taking into account the results of neutron diffraction measurements [14] and MD computer simulation experiments on water-methanol mixtures [10–12], we have performed an experimental study of the same system by using DRLS. The aim of the present investigation was to obtain additional information on the physical properties of water in such mixtures, particularly for water close to dissolved alcohol molecules. In this way we were able to address a very important issue, i.e., to clarify if the thermodynamical anomalies (e.g., negative excess of entropy) observed on mixing water with hydrophobic species is dynamic rather than structural in origin. In order to obtain more detailed information on this we performed DRLS measurements on the methanol-water system as a function of concentration and temperature, and we compared the results obtained for mixtures with those obtained for the pure components, in particular, water.

II. EXPERIMENTAL DETAILS

DRLS is originated by fluctuations of the off-diagonal part of the polarizability tensor α_{ij}. The corresponding time correlation function $G^{anis}(t)$, together with its Fourier transform $I_{VH}(\omega)$, can be characterized by various contributions depending on the different mechanisms involved in the scattering process [12]. The scattered intensity is written in the form

$$I_{VH}=\int_{-\infty}^{+\infty} dt\, e^{-i\omega t}\{\langle \delta\alpha^{*}_{xy}(k,0)\,\delta\alpha_{xy}(k,t)\rangle \sin^{2}(\theta/2) + \langle \delta\alpha^{*}_{yz}(k,0)\,\delta\alpha_{yz}(k,t)\cos(\theta/2)\rangle\}, \tag{1}$$

where brackets denote a thermodynamic average and θ is the scattering angle. The $I_{VH}(\omega)$ spectrum also takes into account contributions due to the coupling between rotational motion and collective hydrodynamic transport modes [14].

DRLS measurements were performed using a fully computerized double pass double monochromator (SOPRA, model DMDP 2000) with a half-width at half-maximum resolution (HWHM) of 700 MHz. All the spectra were measured in the frequency range -100–$100\ \mathrm{cm}^{-1}$. The scattering geometry was the usual 90° setup with the incident beam (5145 Å line of an Ar^{+} laser, operating at an average power of 1 W) vertically polarized with respect to the scattering plane. The scattered light was collected through a Glan-Thompson polarizer (extinction coefficient $>10^{-7}$). The scattering cell was thermostated (within ± 10 mK) using a refractive index matching bath.

Water of liquid chromatographic quality and methanol of high purity grade (>99.9%) were employed in this work. Methanol was used without further purification. The solutions were prepared by weight at the following concentrations (molar fractions of methanol in water): $X=0.03$, 0.0769, 0.09, 0.1, 0.111, 0.1665, 0.25, 0.5. These values correspond to molar ratios of 1:32, 1:12, 1:11, 1:9, 1:8, 1:6, 1:3, and 1:1, respectively. In the temperature range covered, 10 °C–40 °C, we also studied pure water and pure methanol. The concentration $X=0.1$ corresponds to that of neutron experiments (1:9 molar ratio) [13]; it is thus possible to compare the results of the different measurements. It may be noticed, that, extending the concentration range of MD computer simulations and neutron experiments (in which only diluted methanol solutions were studied), we also investigated solutions of high methanol concentrations, with attention on the temperature dependence. This was important to achieve a detailed description of the hydration phenomenon around the methanol molecule. In Fig. 1 a typical DRLS spectrum is reported.

The measured spectra display two contributions: a wide ($\omega \geqslant 30\ \mathrm{cm}^{-1}$) component and a narrow one ($\omega \leqslant 7\ \mathrm{cm}^{-1}$), this latter one caused by molecular rotational motion. These contributions are modeled by Lorentzian lines related to the exponential time decay of the local order. Both contributions were also observed in the pure water spectrum [16]. On this basis, our data were fitted with a double Lorentzian convoluted with the instrumental response function (dotted lines in Fig. 1). The HWHM, $\Gamma(\omega)$ of each Lorentzian (and the relative intensity) is obtained directly by the data fitting; the continuous line in Fig. 1 is the result of the fitting procedure.

III. RESULTS AND DISCUSSION

The two contributions observed here can be related to the properties of bulk water in the normal and supercooled regions. Bulk water, in fact, is known to give two Lorentzian lines; a *fast* one, with a half width of $40\ \mathrm{cm}^{-1}$ (nearly temperature independent), and a *slow* one ranging from about $1.7\ \mathrm{cm}^{-1}$ ($T=-20\ ^{\circ}\mathrm{C}$) to about $8\ \mathrm{cm}^{-1}$ ($T=50\ ^{\circ}\mathrm{C}$). The *slow* contribution $\Delta\omega \simeq 1.7$–$8\ \mathrm{cm}^{-1}$ is known to be related to the rotational motion of water molecules, and more precisely to the hydrogen bond lifetime [15–17]. The corresponding relaxation time follows an Arrhenius temperature dependence with an activation energy that corresponds to the hydrogen bond energy [18].

The physical origin of the *fast* contribution ($\Delta\omega \simeq 40$

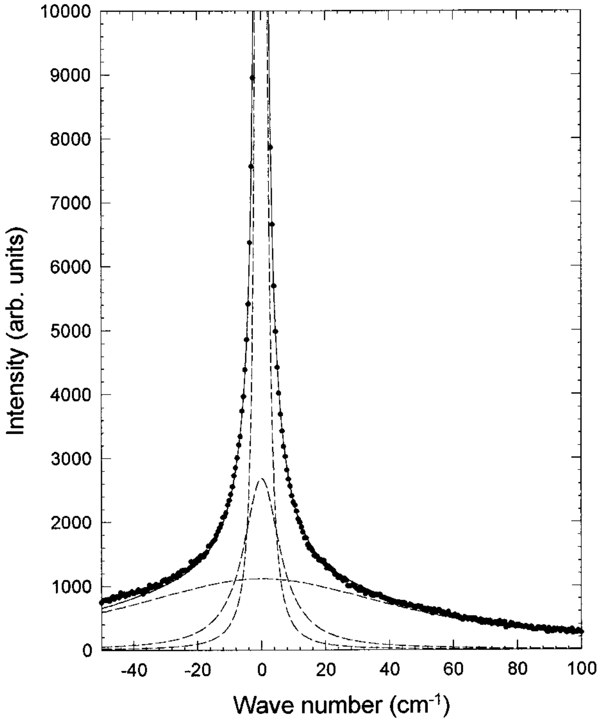

FIG. 1. Typical DRLS spectrum of a water-methanol mixture. The continuous line represents the best fit with the instrumental resolution and the two significative physical Lorentzian contributions (dotted lines).

cm^{-1}), first reported very recently [16], is not clear yet; however, it may be related to the correlations of reorientational modes of water molecules [19] or to collision induced light scattering generated by dipole-induced dipole mechanisms [16]. Our results for pure water are in complete agreement with literature data [16]. From our measured spectra we conclude that the *slow* contribution depends strongly on T, whereas the *fast* contribution is nearly independent of temperature. In addition, the experimental error of the *slow* contribution is quite small (± 0.2 cm^{-1}), thus allowing precise data analysis, while the error corresponding to the *fast* contribution is very large (± 10 cm^{-1}) and strongly depends on background subtraction. Being the microscopic bases and the phenomenon that originates the *fast* dynamical contribution far to be completely understood, a very careful analysis of the pure water spectrum as well as the aqueous solution spectra is required. However, bearing in mind the large uncertainty in the values obtained it is difficult to consider speculative interpretations of this high frequency band. This suggests that great care has to be exercised in the data analysis of the present DRLS experiment. We may isolate with confidence from the data obtained only the behavior of the *slow* contribution. In particular, following what can be deduced from DRLS data for pure water, we will try to discuss the actual data in terms of the hydrogen bond relaxation time τ_s (obtained from the corresponding linewidth).

Figure 2 reports the values of τ_s obtained as a function of the methanol molar fraction X for the different temperatures studied. As can be seen, there is a strong dependence on X and T of τ_s. The main findings are the following:

(a) A maximum is present for all temperatures at the same methanol molar fraction ($X \cong 0,4$), i.e., at about the same concentration where thermodynamic quantities of the mixture show unusual behavior, ascribed to hydrogen bonding [1,5,10–12] that governs all interactions in the system. In particular, we obtain a marked slowing down of this relaxation time in the same concentration range where minima of the excess of volume, diffusion coefficient, and excess of enthalpy have been observed.

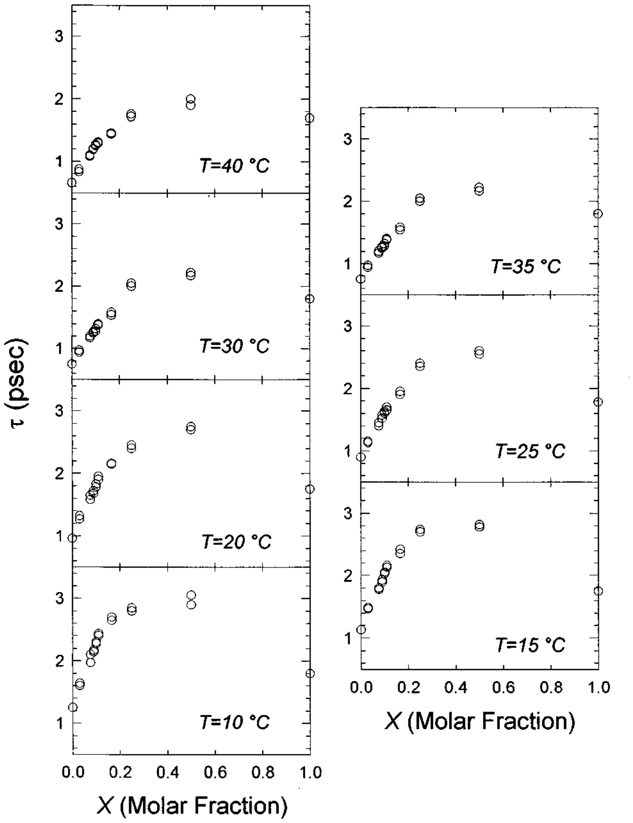

FIG. 2. Hydrogen bond (HB) relaxation time τ_s versus methanol molar fraction for the different studied temperatures.

(b) A strong temperature dependence which, within experimental error, is present for all the concentrations studied, whereas the behavior of pure methanol is nearly temperature independent.

Overall, the data behavior suggests that we observe a dynamics that can be directly related to hydrogen bonding. Both these results, in fact, are in complete agreement with MD simulations [11,12] and do not contradict the neutron experiment [13]. More precisely, looking at the dependence of τ_s on X, we observe that the maxima in this relaxation time have the same behavior and give about the same values (within experimental errors) as the hydrogen bond lifetime corresponding to water-water interactions calculated from MD [11]. In particular, this MD computer simulation showed clearly that among the four hydrogen bond lifetimes (water-methanol, methanol-water, methanol-methanol, and water-water) only the water-water lifetime displays a marked maximum in the equimolar mixture, whereas the other ones increase with X.

In addition, also for solutions with a large content of water molecules ($X \cong 0.1$) there is a significant freezing of the measured relaxation time compared with the one corresponding to the ideal solution (represented roughly by a straight line connecting the water and the methanol values). If we

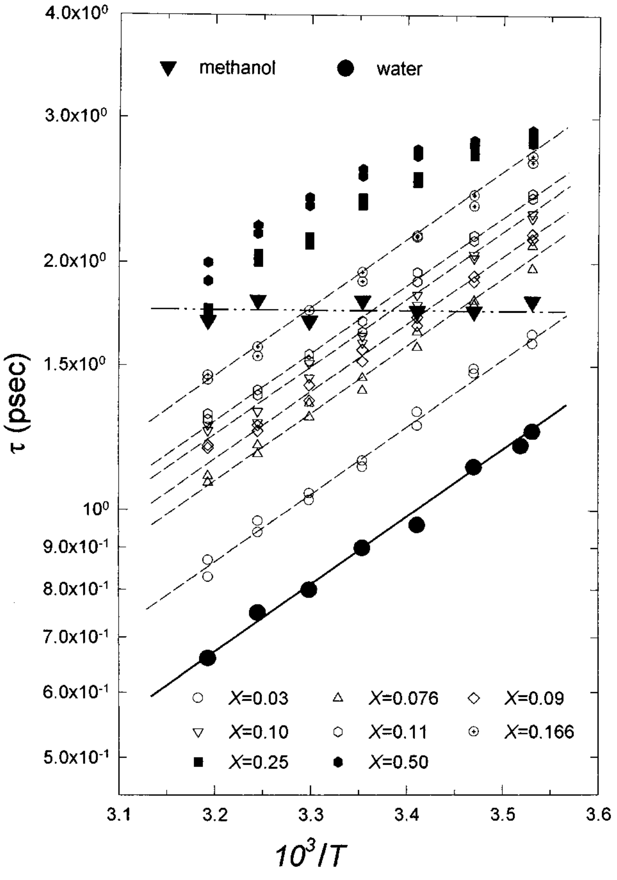

FIG. 3. Logarithmic plot (for the different studied concentrations X) of the τ_s values versus $1/T$.

regard as correct the mean result of the MD simulation [11], i.e., that the dynamical slowing down is entirely due to the hydrogen bond lifetime involving water interactions, our experimental result proves the existence around the methanol molecules of a hydration shell comprising a finite number of water molecules. However, a direct confirmation that τ_s represents the hydrogen bond lifetime of the water-water interaction can be obtained by comparing the temperature dependence for different concentrations, with that obtained for pure water and pure methanol.

In Fig. 3, for each measured X, the τ_s values versus $1/T$ are reported in a logarithmic plot. It is seen that all solutions with concentrations $X \leqslant 0.1669$, i.e., solutions in which there are at least five water molecules around a methanol molecule, show the same Arrhenius temperature behavior as pure bulk water. For solutions of greater methanol concentration, and, in particular, the equimolecular mixture, the temperature dependence measured for τ_s is quite different. Since for these concentrations the number of molecules of the different compounds is comparable, we can assume that in this case the observed dynamics is strongly influenced by the water-methanol hydrogen bond interaction. Also, in this latter case, we find an agreement with the findings of the cited MD computer simulation cited above, which show that for low methanol concentrations, $X \leqslant 0.2$, the number of hydrogen bonds per molecule is entirely due to the water-water configurations, whereas around the equimolecular concentration the effects of the water-methanol and methanol-methanol interactions are more relevant; in addition the calculated water-methanol hydrogen bond has the longest lifetime.

As is well known, the behavior of bulk water is dominated by a tetrahedral arrangement of molecules, i.e., by molecules that form four hydrogen bonds (at $T = 25\ ^\circ\mathrm{C}$ the percentage of four-bonded molecules is about 55%). With decreasing temperature, the fraction of tetra-bonded molecules increases. All theoretical models (continuous or discrete) developed for water [4] refer to this tetrahedral coordination of molecules. For example, percolation concepts have been used successfully to explain the anomalies observed in the supercooled state. In particular, this increase in the fraction of tetra-bonded molecules is due to a clustering of four-bonded molecules that give rise to correlated percolating *patches* whose size increases with decreasing temperature [4]; the structure of such clusters of four-bonded molecules is less dense than the remaining aggregates composed of the other four species (free, one-, two-, and three-bonded molecules). For pure water, this increase in tetra-bonding, as the temperature is lowered corresponds to a slowing down of the hydrogen bond dynamics (i.e., an increase in the hydrogen bond lifetime τ_s [15,16]).

In our case, the addition of methanol seems give rise to analogous effects (Figs. 2 and 3); the hydrogen bond lifetime strongly increases especially in the concentration range 0 to 0.2. This overall behavior is related to the water-methanol interactions via the hydrogen bond and, in particular, agrees with the MD results concerning the number of hydrogen bonds per molecule in solution and with the acceptor character of the two different molecules in solution. It can be considered as a significant goal of the MD simulation the observed dependence of these two latter quantities with the composition.

At low methanol concentration, the acceptor character of the solute is enhanced; this is attributed to the way in which water molecules distribute around methanol molecules, such that the number of four-coordinated water molecules stays nearly constant but the number of three- and two-coordinated ones increases. The net result of this is a less dense water structure (i.e., a more *open* structure similar to the supercooled one [4]). This can also explain the results of neutron diffraction experiments performed at $X = 0.1$ where a well-defined tetrahedral local coordination in the water structure is observed.

Further increase of methanol concentration (with its consequent increasing number of hydrophobic methyl groups) up to $X = 0.5$ leads to a decrease of the number of four-coordinated water molecules but increases the number of hydrogen bonds related to changes in the water-methanol coordination. The result is an overall increase in the number of different bonds and consequently in a slight increase in τ_s. However, the change in coordination numbers around the equimolecular composition, and therefore in the type of hydrogen bond interaction, is reflected in the temperature dependence of the measured lifetime. At larger concentrations, in addition, the donor character of water is dominant whereas in pure methanol the two-coordinated molecular association is prevalent. The addition of water to methanol causes a gradual decrease in the number of two-coordinated molecules and a simultaneous increase in three-coordinated species. This explains the observed decrease of τ_s. The picture proposed here agrees with the results of the self-diffusion experiments in which a well-defined minimum is observed [20]. For water, the diffusion process is described in terms of jump diffusion with a resident time that is just related to the hydrogen bond lifetime [21].

IV. CONCLUSIONS

In summary, we have performed depolarized light scattering experiments in methanol-water mixtures and we have obtained information on the water dynamics around the alcohol molecule. Specifically, we conclude that water, for water rich solutions, is arranged in shells around methanol molecules (a finding in accordance with recent neutron diffraction results at lower methanol contents). In addition we have observed that inside the shell, the dynamical properties of the system are related to the water-water hydrogen bond lifetime. At the concentrations investigated, the donor character of water implies hydrogen bond lifetimes larger than those in pure water at the same temperature, indicating a more stable water structure. For higher methanol concentrations the mixture properties can be related to the water-methanol correlation, in agreement with MD experiments performed on the same system.

In conclusion we should emphasize that all the phenomena observed are entirely related to the hydrogen bond dynamics and that they occur on a picosecond time scale (water and water-methanol structures persist only for these times). The DRLS results presented suggest that the thermodynamic anomalies observed by mixing water with hydrophobic species are dynamical rather than structural in origin.

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