

## Proton NMR relaxation times allow to study molecular correlations within water/methanol solutions

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**Summary.** — The dynamic behavior of water/methanol solutions has been studied by means of NMR spectroscopy as a function of concentration and temperature, including the supercooling regime. In particular, the thermal evolution of the longitudinal or spin-lattice and of the transverse or spin-spin relaxation times,  $T_1$  and  $T_2$ , respectively, has been investigated at three methanol molar fractions. In such a way, the reciprocal influences of hydrophobic effects on the water properties as well as that of the hydrophilicity on the solute (through hydrogen bond interactions) have been pointed out by means of a single characteristic correlation time  $\tau_c$ . This is interesting taking into account that this correlation time reflects all local structural configurations and characterizes the corresponding dynamics. One of the main result of this NMR investigation shows how the different molecular correlations are energetically favored by temperature variations.

### 1. – Introduction

Water is a chemically simple compound consisting of two hydrogen and one oxygen ( $\text{H}_2\text{O}$ ) atoms and is very important since it is the means in which most of the biochemical processes take place [1, 2]. Its particular chemical-physical characteristics including its anomalies have been studied for a long time to fully understand its behavior [3-10]. They are a consequence of the hydrogen bonds that are established between each water molecule and the other neighboring molecules. The anomalies, that include its polymorphism presenting two liquid local structures of water called Low-Density Liquid (LDL) and High-Density Liquid (HDL), are enhanced in the supercooled regime [11-13]. The hydrogen bonding network is important as it enters many biological mechanisms such

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as the folding/unfolding process of proteins [14-18]. Water is the most common solvent in nature. The compounds or functional groups that show affinity for water are called hydrophilic, many of them are also lipophobic. On the contrary, the compounds or functional groups that do not have affinity for water are called hydrophobic, many of them are also lipophilic [19]. Hydrophobic molecules are apolar molecules that often have a long chain of carbon atoms and are not very soluble in water which is a polar molecule [20]. A molecule is called amphiphilic (or amphipathic) when it contains both a hydrophilic and a hydrophobic group. These molecular characteristics mean that amphipathic molecules, immersed in an aqueous liquid, tend to spontaneously form a double layer, in which the hydrophilic heads are facing outwards and hydrophobic tails inward. Methanol is the smallest amphiphilic molecule, hence the investigation of water/methanol solutions allows a simpler investigation of the competition between hydrophobic and hydrophilic interactions [21]. Hydrophobic interactions describe the relationships between water and hydrophobic molecules; an example of hydrophobic interaction is the water-oil mixture. The American chemist Walter Kauzmann, in the context of his studies on the thermodynamic stability of proteins, discovered that non-polar substances, in water, tend to aggregate rather than distribute themselves in it, so as to have minimal contact with water. When a non-polar species comes into contact with water, the hydrogen bonds break and, around the apolar species, a sort of cage is formed with an ordered structure called clathrate, an inclusion compound in which the guest molecules are found inside a cage made up of host molecules. This orientation is disadvantaged by the second law of thermodynamics whereby spontaneous phenomena occur with an increase in the degree of disorder or with an increase in entropy, while in this case a decrease in entropy occurs ( $\Delta S < 0$ ) [22]. Hydrophobic interaction is of fundamental importance in many research fields including life sciences. Today it appears to be still an open question in contrast to the hydrophilicity that instead turns out to be well described. In fact, despite the numerous Molecular Dynamics (MD) simulation studies [23-26], there are only a few experimental reference points [27] (for example, we do not have an analytical description of the hydrophobic intermolecular potential).

Water/methanol solutions are highly non-ideal, that is, they show non-linear behaviours of dynamic and thermodynamic variables as a function of the composition [28]. The reason seems to be ascribed just to the occurrence of hydrophobic and hydrophilic interactions. As early as 1935, Gibson noticed the non-ideality of such solutions from studies on excluded volume, assuming that methanol favored the association between water molecules [29]. Frank and Evans later supported the still-debated hypothesis that methanol favors "iceberg-like" structures for water [30]. Then, Schott made fluidity measurements and argued that the water/methanol association is favored by an increase in temperature [31]. However, other experimental works provided contrasting evidence [32-36].

In this work, using NMR spectroscopy, molecular correlations and their activation energies have been described in order to detail the competition between hydrophilicity and hydrophobicity in water/methanol solutions as a function of temperature at fixed methanol molar fraction. NMR allows to measure both system structure and dynamics. In particular, it allows to obtain relaxation times of the individual molecular groups present in the system. In 1964 Hertz and Zeidler understood that the NMR relaxation times ( $T_1$  and  $T_2$ ) indicated that the reorientation times of the water molecules, close to the solute with the alkyl groups, are double compared to those of the pure water and that the activation energy about the reorientation in the presence of the solute is greater than that in pure water [37]. But how can the temperature and concentration

variations of  $T_1$  and  $T_2$  be used to explain hydrogen bonding (HB) interactions? This can be done in terms of Bloembergen, Purcell and Pound (BPP) theory [38-40] for which both relaxation times can be expressed in terms of a single correlation time  $\tau_c$  [41]. The individual evolution of  $\tau_c$  with temperature and of  $T_1$  and  $T_2$  as a function of  $\tau_c$  can be used to explain how the HB interactions, which create the characteristic transient tetrahedral network of water, affect methyl methanol and the way in which methanol influences the structure of water [42].

## 2. – Methods

As mentioned above,  $^1\text{H}$  NMR is a unique probe able to follow simultaneously but individually the dynamics of the different chemical groups present within the system [43, 44]. In particular, by means of  $^1\text{H}$  NMR experiments we analyzed the relaxation times at methanol molar fractions  $X_{\text{MeOH}} = 0.24, 0.5$  and  $0.7$  in the range  $310\text{ K} > T > 205\text{ K}$  and measure both the proton spin-lattice relaxation time (longitudinal,  $T_1$ ) and the proton spin-spin relaxation time (transverse,  $T_2$ ). We considered temperatures below  $315\text{ K}$  because this is associated with the “end” of the preponderance of the hydrophilic effect [45]. In fact, above it, water begins to behave as a simple liquid [12]. For the NMR experiments we used a Bruker Avance spectrometer operating at  $700\text{ MHz}$ . The spin-spin relaxation time,  $T_2$ , *i.e.*, the time in which the transverse component of the magnetization is canceled due to the interaction between the spins of the same species has been measured through the spin-echo pulse sequence (Carr-Purcell-Meiboom-Gill [46, 47]). Here a  $\pi/2$  pulse is first applied to the spin system, then, after a variable delay, a  $\pi$  pulse is applied and produces a signal called echo. By varying the so-called echo time, it is possible to evaluate the spin-spin relaxation time  $T_2$ . The spin-lattice relaxation time,  $T_1$ , *i.e.*, the time in which the longitudinal component of the magnetization returns to its equilibrium value is a measure of the dipolar interactions of the studied spins with the surrounding environment [48, 49]. Its value varies to tens of thousands of milliseconds for protons of hydrogenated compounds, and usually becomes smaller at lower temperatures. The  $T_1$  relaxation times have been obtained through the inversion recovery pulse sequence. In this sequence a  $\pi$  pulse is applied in order to project the macroscopic magnetization along the negative direction of the  $Z$ -axis; then a  $\pi/2$  pulse is applied at changing time to sample the recovery of the longitudinal equilibrium connected with the relaxation time  $T_1$ . More details about the experiments can be found elsewhere [35, 36]. Through the Bloembergen-Purcell-Pound (BPP) theory, it is possible to express  $T_1$  and  $T_2$  in terms of a single correlation time  $\tau_c$ ,

$$(1) \quad T_1 = \left\{ \frac{\Delta}{5r^6} \left[ \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right] \right\}^{-1},$$

$$(2) \quad T_2 = \left\{ \frac{\Delta}{10r^6} \left[ 3\tau_c + \frac{5\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{2\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right] \right\}^{-1}.$$

which means that it can be obtained by solving the corresponding biquadratic equation

$$(3) \quad 12B(\omega_0 \tau_c)^4 + (37B - 8)(\omega_0 \tau_c)^2 + 10B - 5 = 0,$$

where  $B = T_2/2T_1$ ,  $r$  is the interatomic distance (angstrom),  $\Delta$  is a constant determined by the proton gyromagnetic ratio ( $\gamma$ ) and the Planck constant ( $2\pi\hbar$ ) as  $\Delta = 3/2(\gamma^4 \hbar^2)$

and  $\omega_0$  is the Larmor precession frequency. Thus, by measuring both  $T_1$  and  $T_2$  one can calculate  $\tau_c$  and achieve important insight into the molecular correlations of the molecule. Indeed by following separately the relaxations of the three functional groups we have information on both hydrophilic and hydrophobic correlations.

### 3. – Results and discussion

We investigate the dynamics of the hydroxyl and the methyl groups by measuring their relaxation times as a function of temperature at the following methanol molar fractions,  $X_{\text{MeOH}} = 0.24$  (squares), 0.5 (circles) and 0.7 (triangles). This allows determining the correlations between the hydrophobic and hydrophilic moieties in the mixture. Figure 1 shows the trend of  $T_1$  at the mentioned molar fractions in the range  $310 \text{ K} > T > 205 \text{ K}$ . We use gray open symbols for water hydroxyl ( $\text{OH}_w$ ), open black symbols for methanol hydroxyl ( $\text{OH}_m$ ) and full gray symbols for the methyl group ( $\text{CH}_3$ ) of methanol.

At high temperature the  $T_1$  values of water and methanol hydroxyls (left panel) are essentially the same, whereas they become progressively different on cooling showing a minimum at about 225 K.  $T_1$  of methyl groups (right panel) shows a monotonic decrease with temperature characterised by a smaller total variation, with respect to that of hydroxyls, showing a round off at about 225 K.

Figure 2, analogously to fig. 1, shows the behaviour of  $T_2$ . For easier reading we use the same symbols as the previous one. It is important to mention that it was already noted that the  $T_2$  of the hydroxyls in the solution is two orders of magnitude lower than that in pure liquids, indicating the presence of strong interactions between the hydrophilic groups of water and methanol [36, 44]. The most salient feature is the presence of a maximum (left panel) at about the same temperature of the minimum in  $T_1$ .

Similarly, the  $T_2$  of methyls (right panel) shows a maximum about 225 K but differently it shows a minimum at about 265 K, which can be ascribed to the onset of the hydrophobic effect that indeed progressively increases with temperature. Another important temperature to mention is about 290 K, where experiments of proton chemical shift illustrated that this is a hydrophilic/hydrophobic competition threshold above which the

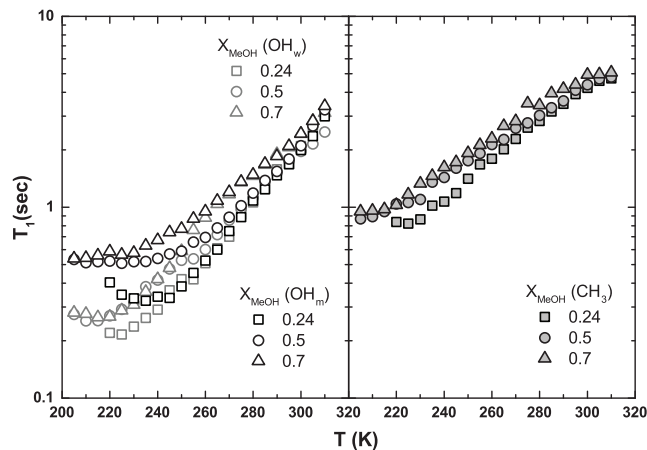


Fig. 1. – The figure shows the thermal trends of  $T_1$  at molar fractions  $X_{\text{MeOH}} = 0.24, 0.5$  and  $0.7$  in the range  $310 \text{ K} > T > 205 \text{ K}$  of the hydrophilic groups  $\text{OH}_w$  and  $\text{OH}_m$  (left) and hydrophobic groups  $\text{CH}_3$  (right).

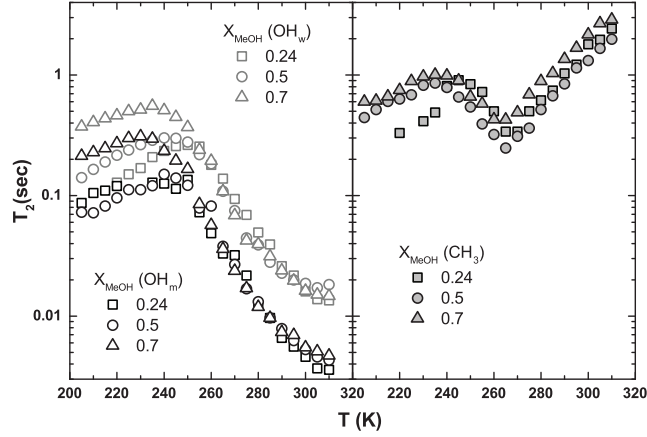


Fig. 2. – The figure shows the trends of  $T_2$  at molar fractions  $X_{\text{MeOH}} = 0.24, 0.5, 0.7$  of the hydrophilic groups  $\text{OH}_w$  and  $\text{OH}_m$  on the left and hydrophobic group  $\text{CH}_3$  on the right.

hydrophobic force dominates the hydrophilic interaction. This value depends slightly on the concentration, because it is influenced by the quantity of hydrophobic molecular groups present in the solution [35].

Figure 3 shows the thermal trend for the same molar fraction of  $\tau_c$ , evaluated by means of eq. (3). Note that the  $\tau_c$  behaviour depends only on the temperature, whereas its amplitude is also a function of concentration. The evolution of the temperature trend of  $\text{OH}_w$  and  $\text{OH}_m$  shows a similar behavior decreasing down to 225 K ( $1000/T \simeq 4.4 \text{ K}^{-1}$ ) and then increasing up to 205 K ( $1000/T \simeq 4.9 \text{ K}^{-1}$ ) (left panel). Contrariwise, the  $\tau_c$  of the methyl groups increases with temperature up to 265 K ( $1000/T \simeq 3.78 \text{ K}^{-1}$ ) where it shows a maximum, then decreases down to 225 K after which it grows slowly (right panel). From these  $\tau_c$  data and for all intervals and molar fractions, we calculated the

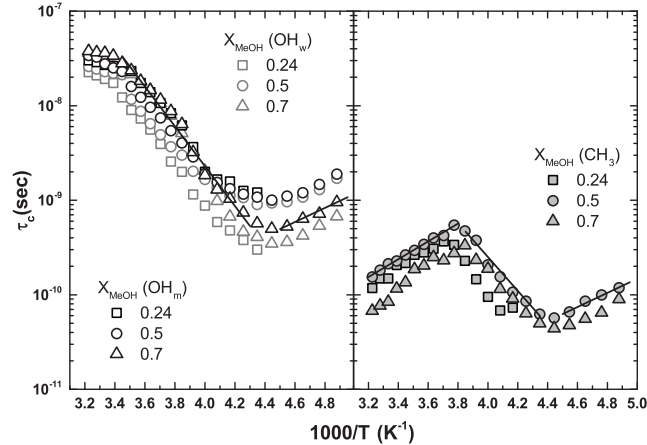


Fig. 3. – The figure shows the trends of  $\tau_c$  at different molar fractions  $X_{\text{MeOH}} = 0.24, 0.5$  and  $0.7$  of the hydrophilic group  $\text{OH}_w$  and  $\text{OH}_m$  on the left and  $\text{CH}_3$  on the right. The solid lines correspond to the Arrhenius fits for  $X_{\text{MeOH}} = 0.7$  ( $\text{OH}_m$ , left panel) and for  $X_{\text{MeOH}} = 0.5$  ( $\text{CH}_3$ , right panel). All the calculated activation energies are reported in table I.

corresponding activation energy, by using the Arrhenius equation. The activation energy, being the minimum energy necessary to trigger a reaction or a thermally activated process, was in fact defined by Arrhenius in 1899. According to this relation, as the temperature increases, the fraction of molecules that has an energy higher than the value of the activation energy increases. However, under certain conditions this fraction reduces with temperature providing a negative activation energy [50-52]. Figure 3 reports as examples the Arrhenius fits for  $X_{\text{MeOH}} = 0.7$  ( $\text{OH}_m$ , left panel) and for  $X_{\text{MeOH}} = 0.5$  ( $\text{CH}_3$ , right panel) as solid lines. Table I lists the activation energies for different concentrations for the different chemical groups present in the water/methanol solutions for the indicated temperature ranges and the studied molar fractions. In the range  $310 \text{ K} > T > 265 \text{ K}$  the Arrhenius activation energies for the  $\text{CH}_3$  groups have negative values at all molar fractions, indicating that their molecular rearrangement is not favored by a temperature decrease. For  $290 \text{ K} > T > 230 \text{ K}$ , the value of activation energies is positive for the  $\text{OH}_w$  and  $\text{OH}_m$  indicating that their molecular rearrangement is favored by a temperature decrease down to about 225 K. We recall that this temperature corresponds to the maximum of the local correlation for water molecules as reported in another study [36]. In the range  $260 \text{ K} > T > 230 \text{ K}$  the value of activation energies for  $\text{CH}_3$  is positive, thus their molecular rearrangement is favored on cooling.

Finally For  $220 \text{ K} > T > 205 \text{ K}$  the values of activation energies are negative for all groups indicating that their molecular rearrangements are not favored below 225 K. Thus, the correlations between the hydrophilic hydroxyl groups of water and methanol within the solutions are maxima at this temperature. This scenario illustrates how the reorganization of HBs depends on the temperature and influences the dynamics of the different functional groups in solution. In particular, our data confirm that the formation of hydrogen bonded structures is enhanced at low temperatures whereas the methyl groups are more structured at high temperatures. Note that the activation energies of  $X_{\text{MeOH}} = 0.5$  show extremal values, within experimental errors, in all the considered thermal ranges. This situation confirms the peculiar characteristics shown by the equimo-

TABLE I. – *Activation energies in kcal/mol of the molecular correlations for the different chemical groups present in water/methanol solutions for the indicated temperature intervals and methanol molar fractions.*

	$X_{\text{MeOH}}$	310–265 K	290–230 K	260–230 K	220–205 K
$\text{OH}_w$	0.24	–	$3.93 \pm 0.11$	–	–
	0.5	–	$3.12 \pm 0.16$	–	$-1.47 \pm 0.13$
	0.7	–	$4.51 \pm 0.16$	–	$-1.63 \pm 0.11$
$\text{OH}_m$	0.24	–	$3.58 \pm 0.16$	–	–
	0.5	–	$3.32 \pm 0.13$	–	$-1.39 \pm 0.13$
	0.7	–	$4.19 \pm 0.17$	–	$-1.49 \pm 0.14$
$\text{CH}_3$	0.24	$-1.97 \pm 0.15$	–	$3.24 \pm 0.52$	–
	0.5	$-1.87 \pm 0.07$	–	$3.56 \pm 0.21$	$-1.49 \pm 0.13$
	0.7	$-2.36 \pm 0.14$	–	$3.32 \pm 0.14$	$-1.61 \pm 0.16$

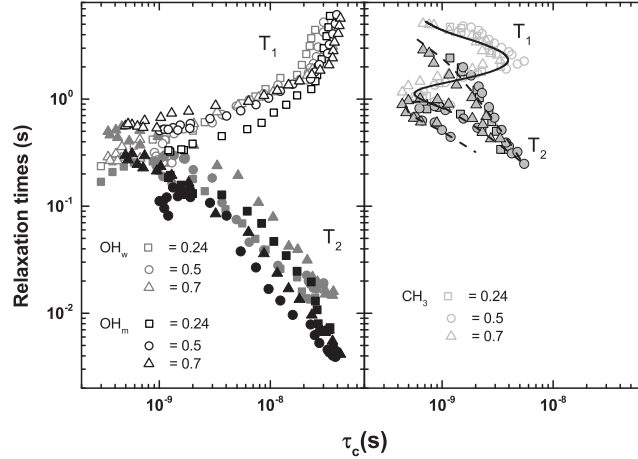


Fig. 4. – The figure shows the values of  $T_1$  and  $T_2$  at different molar fractions  $X_{\text{MeOH}} = 0.24, 0.5$  and  $0.7$  of the hydrophilic groups  $\text{OH}_w$  and  $\text{OH}_m$  on the left and hydrophobic group  $\text{CH}_3$  on the right as a function of  $\tau_c$ .

lar solution [53]. Regarding the increase of hydrophobic interactions with temperature, Wang *et al.* in 2008 illustrated a hydrophobic-hydrophilic transition of water confined in hydrophobic nanotubes. A significant slowdown in the molecular reorientation of this adsorbed water has also been noted. The observed transition demonstrates that the structure of the interfacial water could depend significantly on temperature, which could lead to intriguing temperature dependencies involving interfacial water on hydrophobic surfaces [54].

Finally fig. 4 reports  $T_1$  and  $T_2$  as a function of  $\tau_c$ . It is noteworthy that at low temperatures the data relating to water hydroxyl ( $\text{OH}_w$ ) better reproduce the hyperbolic behavior predicted by the BPP theory compared to methanol hydroxyl ( $\text{OH}_m$ ). At high temperature the data show a sharp change in  $T_1$  at about 265 K, that is the onset temperature of the hydrophobic effect. This occurs because the lower lifetime of HBs favours the predominance of hydrophobicity also reflected in the inflection point for the values of  $T_2$ .

In detail, at around 265 K the methanol OH shows a maximum in the spin-spin relaxation time  $T_2$  and a variation in the growth rate of the longitudinal  $T_1$  whose values cross those of the  $T_1$  of the methyl group.

Finally, the relaxation times of the methanol methyl group (right panel of fig. 4) show a cuspid behavior both at 265 K and at 225 K. As already mentioned, this is the temperature of water dynamical crossover, which is particularly important for hydrated biological systems [55, 56]. These two temperatures have a fundamental role in systems with simultaneous hydrophilic and hydrophobic interactions. The overall scenario highlights how the competition between the hydrophobic and hydrophilic effect determines the molecular correlations within water/methanol solutions.

#### 4. – Conclusions

In this work we report the study of molecular correlations within water/methanol solutions. Our results indicate that when HB interactions that facilitate clustering in

water solutions compete with interactions with opposite behaviors, *e.g.*, hydrophobicity, the effects of these latter interactions become relevant for temperatures where the water tetrahedral network is no longer stable. We show how the temperature-concentration evolutions of  $T_1$  and  $T_2$  as far as the measured  $\tau_c$  can be used to explain how the HB interactions, that create the characteristic water tetrahedral transient network, affect the methanol, and how methanol influences the water structure. For  $\tau_c$  for all intervals and molar fractions we calculated the corresponding activation energy. This gives us information on the different molecular correlations and on their temperature dependence that influence the dynamics of the different functional groups in solution. The analysis in terms of  $\tau_c$  which encompasses all local structural configurations allowed the investigation of the dynamical behavior and of the properties of the solutions at the considered conditions, pointing out the temperatures able to describe the competition between hydrophobicity and hydrophilicity. Overall, our data show that the temperature increase progressively reduces the lifetime of the hydrogen bond interactions. Finally we identify two temperatures that play an important role in this contest between hydrophobicity and hydrophilicity. 225 K is the temperature for which the correlations between water molecules are maxima and the hydrogen bonded network is completely developed. Finally, above about 265 K, hydrophobicity becomes progressively stronger and governs the physical properties of the solutions.

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