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The evaluation of the hydrophilic–hydrophobic interactions and their effect in water–methanol solutions: A study in terms of the thermodynamic state functions in the frame of the transition state theory

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ABSTRACT

Aqueous solutions of amphiphilic molecules are characterized by the competition between hydrophilic and hydrophobic interactions. These interactions have a different energetic dependence with the temperature. Whereas hydrophilic interactions have been well characterized, a complete theory for the hydrophobic ones is still lacking as well as the comprehension of the effect that the solvent exerts on the solute and vice versa. In this paper from the measured relaxation time, we evaluated the thermodynamic state functions of water–methanol solutions in the frame of the transition state theory. In particular we study the behavior of the Gibbs free energy, enthalpy and entropy of water, methanol and some of their solutions as a function of both temperature and water molar fraction. Our results indicate that the temperature of about 280 K represents a crossover between two regions dominated by hydrophobicity (high T) and hydrophilicity (low T).

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1. Introduction

Understanding the unusual properties of water and water systems is of great interest in both science – including the fields of physics, chemistry and biology – and technology. Water exhibits properties that are counterintuitive when compared with those of normal liquids; as it is well known some of its thermodynamic and transport properties, especially in the supercooled regime [1], are anomalous. Examples are the divergent-like behaviors in its thermodynamic response functions observed below its melting point T_m^W , explained in terms of a liquid polymorphism [2].

It is now clear that intermolecular hydrogen bond (HB) interactions determine the chemical physics of water in both bulk and solution configurations. Each water molecule has two positively charged lobes containing the protons and two lone pairs of electrons. The HB is a non-covalent interaction between an elec-

tropositive hydrogen atom on one molecule and an electronegative oxygen atom on a second molecule. The HB is also the result of an important property of water in solutions: molecular hydrophilicity.

The hydrophilicity (i.e. HB interaction) also governs the open local tetrahedral order of water molecules giving rise to a clustering process. As water is cooled the HB orders the nearest neighbor molecules, which gradually assume the characteristic four-coordinated geometry. In ordinary ice, each water molecule has four nearest neighbors, a hydrogen donor to two of them and a hydrogen receptor from the other two. The network emerges because the oxygen atom in a water molecule has two hydrogen-donating sites, and the two hydrogens are single acceptors.

The water liquid phase is governed by tetrahedrality, but in contrast to the solid crystalline phase with a permanent network held together by HB, it is local and transient. Regions of local tetrahedral order can possess a larger specific volume than the overall average. The entropy, on the other hand, always decreases upon cooling because the specific heat is, of necessity, positive. At higher temperatures the behavior of water is the same as in simple liquids [3] and as T decreases below 277 K, the local specific volume increases due to the progressive increase in tetrahedral order. Water stud-

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ies of the thermodynamical response functions suggest that when the temperature is decreased the onset of the tetrahedral water patches occurs at $T^* \approx 320$ K. This local structure continues down to the amorphous region of the phase diagram where two glassy phases, characterized by different densities, have been observed [4].

The water glassy polyamorphism (two amorphous phases of different densities) is one of the most intriguing properties observed in the system [4,5]. In the very low temperatures regime, there are a high-density amorphous ice (HDA) and a low-density amorphous ice (LDA) and a first-order transition between HDA and LDA occurs when the pressure and temperature are changed. This suggests that liquid water may also be polymorphous [2], i.e., a mixture of a low-density liquid (LDL) and a high-density liquid (HDL). The HDL predominates in the high T regime when the local tetrahedrally-coordinated structure is not fully developed; whereas in the LDL an open “ice-like” HB network is present. The anomalous behavior of water is thus caused by the “competition” between these two local liquid forms, and the HB clustering that occurs when the temperature is lowered into the supercooled state is behind the diverging behavior of the various liquid water thermal response and transport functions. The liquid water polymorphism has been confirmed experimentally in confined water [6–11].

The water P - T phase diagram includes the liquid, these amorphous phases, many ice structural forms and also an intriguing metastable supercooled liquid region below the melting and the homogeneous nucleation lines. Such a rich thermodynamics in the supercooled liquid regime, essentially due to the hydrophilicity, proposes water as a prototype of glass-forming material. Water, in fact shows at $T_L \approx 225$ K a crossover from a fragile to strong glass forming behavior (FSDC) where both LDL and HDL are observed and the violation of the Stokes-Einstein relation (SER) occurs accompanied by an extreme in the thermal expansion coefficient and specific heat [6,7,12–14].

The hydrophobicity – opposite property to hydrophilicity – is equally important in science and technology. It occurs in aqueous solutions when nonpolar substances aggregate by excluding water. Amphiphilic molecules (or surfactants) are examples of moieties with these properties. They are usually organic compounds with a head (polar if ionic or HB if non-ionic) in close contact with water molecules and an apolar aliphatic chain, their tail, that avoids water molecules (hydrophobic groups) [15]. Thus, these opposite conditions define an amphiphile, and although in solutions (water or oil) a single molecule cannot satisfy both of them, a cluster of molecules can, and building blocks of mesoscopic structures can originate under stable thermodynamical conditions [16]. These systems meet all the “soft condensed matter” research field that focuses on long helical rods (e.g., polypeptides, DNA, RNA, and proteins), discoid organic molecules, polymers, colloids, and many different multimolecular-associated structures (membranes and bilayers) and mesoscopic structures that, despite their complexity, can be described in terms of current statistical physics by means of scaling laws and the concept of universality [17,18].

The hydrophobic effect is as important as the hydrophilic, but its properties have not yet adequately understood. Although past studies addressed the effect solutes have on the structure and energetics of the solvent [19,20], unlike hydrophilicity, which can be fully described in terms of the HB interactions, despite many attempts there are not any analytical forms for quantitatively treating hydrophobicity. For example, a complete experimental measurement of the pair distribution function $g_{AA}(r)$ between hydrophobic molecules (A) lacks, as well as the corresponding potential of mean force $W(r) = -k_B T \ln g_{AA}(r)$ between the two A molecules, i.e., it is necessary to understand the forces underlying hydrophobic interactions, and to evaluate all their implications [21].

In this paper written on the occasion of 65th birthday celebration of Piero Baglioni who has made significant contribution to the understanding of soft-condensed matter chemical–physics, we propose some experimental findings useful to clarify the hydrophobic effect and its competition with the hydrophilicity in a quantitative way and to give a basis for a proper theory.

In principle, hydration forces on the conformation of the shells about a hydrophobic solute can affect the structure of the solute itself. This is scientifically relevant because solute molecules can assume dipole moments that significantly change the solution by changing the thermodynamical variables, i.e., the changes in the solute structure in a solution can strongly affect the hydration thermodynamical functions (entropy and energy) of a hydrophobic solute. Until now these functions have been ascribed to the effect of the solute on the structure of the neighboring water, ignoring the change in the structure of the solute itself. At the same time the vice versa holds, the solvent changes the solute properties in a new configuration that can affect itself.

Recently by studying, with the nuclear magnetic resonance (NMR) technique, the thermal denaturation of hydrated lysozyme we find that its hydrophilic (the amide NH) and hydrophobic (methyl CH_3 and methine CH) peptide groups show different energetic behaviors. This, from a side clarifies the role of hydrophilicity in the stabilization of protein configurations, but at the same time reveals as hydrophobicity contributes in this important protein folding and unfolding process [22].

Subsequently, we have considered that water and methanol solutions can be useful to understand the mutual hydrophobicity–hydrophilicity effects. Being methanol the smallest amphiphilic molecule with a mass comparable with that of water, the relative inter- and intra-molecular effects are indeed comparable.

The solution was studied at different concentrations and across a wide temperature range from 330 K (near the methanol boiling point) to 200 K. An important property of NMR is that it allows a simultaneous study of the separate hydrophilic groups of the two molecules (the hydroxyls of water OH_W and methanol OH_M) and the only hydrophobic moiety present in solution (the methanol methyl group CH_3). In particular we have studied the thermal behavior of the longitudinal spin-lattice, T_1 , and the transverse spin-spin, T_2 , relaxation times of the macroscopic magnetization, corresponding separately to the two hydroxyls and the methyl groups. After, by means of the classical Bloembergen, Purcell, and Pound (BPP) model [23–25], we obtain, for each hydrophilic and hydrophobic groups, a correlation time τ_c reflecting the relaxations of all the local structural configurations and characterizing the thermal motion effects of the magnetic nuclei on the spin-spin interaction. A data comparison reveals the existence of a crossover temperature, $T^{HH} \approx 270$ K, representing the hydrophobic–hydrophilic competition effects in the sense that it is directly connected to the solute hydrophobicity and to its effect on the solvent, and viceversa to the effect of hydrophilicity on the hydrophobic solute (the CH_3 metabolite). The main results are the following: in the supercooled regime the solute–solvent correlations are stronger because the HB interactions have a lifetime long enough to sustain a stable water network; but increasing T the HB interaction lifetime progressively decreases and destroys the water clusters with a consequent decoupling in the dynamic modes of the system. At the higher temperatures there is a crossover ($T^{HH} \approx 270$ K) in which hydrophobicity becomes stronger and governs the properties of the solutions. This finding is consonant with results obtained for water confined in hydrophobic nanotubes that show how hydrophobicity becomes effective in the high T regime, $T > 281$ K [26].

Starting from these results, here we consider the idea to study the same methanol–water mixtures and the corresponding local structures due to the hydrophilic–hydrophobic competition on

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