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Dynamics of water clusters in solution with LiCl

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HIGHLIGHTS

- We observe three different water clusters in a solution with LiCl at eutectic point.
- Two important dynamical changes occur at two relevant temperatures for water.
- The driving force is the tendency of water to develop its characteristic HB network.

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ABSTRACT

In this work we study by means of Nuclear Magnetic Resonance spectroscopy the dynamics of the different water clusters that form within a solution with LiCl at eutectic concentration in the temperature range 320–205 K. This solution is considered a model system allowing the investigation of water properties in the deep supercooled regime in its bulk phase. Our data reveal two important dynamical changes occurring at two relevant temperatures for water: the highest temperature coincides with that of the water density maximum (277 K) and the lowest with that of the so-called dynamical crossover (≃225 K). We interpret our data in terms of the different influence that the ions exert on water by lowering the temperature and of the tendency that water displays to develop its characteristic hydrogen bond network.

1. Introduction

The dynamics of supercooled glass forming materials can be highly nonlinear, especially for those glass-formers that are defined fragile because their structure changes rapidly when temperature changes [1]. In fact, Angell in 1995 has classified glass-forming liquids into two different classes by using the concepts of fragility and glass transition [1].

In the last years, some authors suggested a different and universal scenario by invoking the concept related to the so-called dynamical crossover or fragile-to-strong transition [2–5]. It was observed that all supercooled glass-forming materials show a dynamical transition, that can be more or less evident depending on the system, before intervening the dynamical arrest or glass transition [2,4,6]. The higher is the temperature the higher is the number of degrees of freedom that the system can explore. Therefore, the corresponding dynamics of the system is characterized by multiple relaxations that

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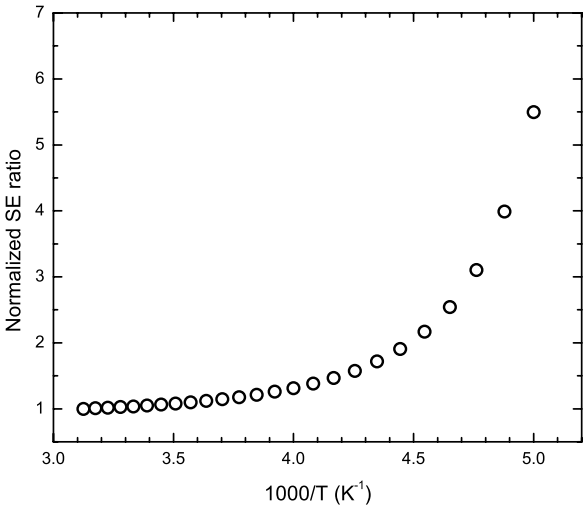

Fig. 1. The thermal evolution of normalized SE ratio. It is noteworthy the sharp increase below 240 K.

involve the exploration of the local minima of the energy landscape [7]. By lowering the temperature, and thus the number of allowed energy states, the system can only experience a dynamics characterized by hopping processes between minima of uniform height [8]. This scenario is consistent with the theoretical predictions of the extended version of the Mode Coupling Theory (MCT) for which the critical temperature of the ideal version of the theory corresponds to the temperature of a dynamical crossover [3,9,10]. In other words, the fluids dynamics is characterized by two different behaviors above and below a precise temperature. Theory agrees with experiments that the dynamics of the system can be considered as the sum of two contributions: that of the ideal MCT i.e., the cage dynamics and that of the EMCT i.e., the hopping process. The cage dynamics shows a temperature dependence that can be represented by a power law function diverging at the MCT critical temperature. Below it the hopping process is the only possible dynamics that shows an Arrhenius dependence with temperature [9,10].

The detailed analysis of the dynamical behavior of water is relevant for pure science and technological applications. In particular water dynamics is more intriguing in the supercooled regime and there is a big and actual debate on the existence and on the significance of the dynamical crossover [11–19]. This liquid–liquid transition was observed experimentally for water in particular environments and in MD simulations. However, it is hard to supercool bulk water below the homogeneous nucleation temperature.

It is well known that an eutectic solution of water in LiCl can be cooled to 200 K without the occurrence of any crystallization process [20,21]. For that reason, aqueous solutions of LiCl were used to investigate the occurrence of the dynamical crossover and contrasting scenarios have emerged [5,22–27]. The existence of different results seems, at least in part, due to the usage of different techniques that cover (and probe) different dynamical regimes [4,22,24,27].

The coexistence of different local structures and of the associated relaxations does not allow a simple data interpretation.

For example NMR and OKE experiments did not observe any abrupt change in the water dynamics by means of the self-diffusion and time constant, respectively. However, by considering the stretching exponent of the time constant distribution, a dramatic change at the temperature of about 240 K was observed [28]. Moreover, by taking into account the Stokes–Einstein (SE) relation, it breaks just about that temperature signaling the decoupling between transport properties [29]. In Fig. 1 we report the Stokes–Einstein ratio, $D\eta/T$, obtained by the data reported in Ref. [29], as a function of T and normalized with respect to its value at the highest temperature. As one can see, for $T \gtrsim 240$ K this quantity is nearly constant reflecting the validity of the SE relation that instead breaks below 240 K where the reported quantity shows a sharp increase. The related decoupling between translational and rotational dynamics has been explained by invoking the existence of dynamic heterogeneities, which refers to the presence of transient spatially separated regions with vastly different relaxation times [30].

Optical and dielectric spectroscopies have detected the presence of extra signals such as an excess wing for temperatures below 225 K but the interpretations are somehow contradictory [27,31]. Furthermore, Molecular Dynamics (MD) simulations showed that the water tendency to develop its characteristic tetrahedral network provokes a segregation of the system. The ions are not included in the network of water molecules and contribute to the formation of solute rich regions within the system [32,33].

Previous studies have shown that water properties are not too altered by the presence of ions suggesting that it can be considered a model system for studying deeply supercooled water in its bulk phase [21,23–26,28,34,35]. At the same time, it was shown that the local tetrahedral structure of water is partially distorted by the presence of ions [36]. In particular, according to the Collins scenario, Li cation is an enhancer of the water tetrahedral structure (structure maker) whereas the