



Why is there no clear glass transition of confined water?



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ABSTRACT

To overcome the problem of crystallization of supercooled bulk water and water rich solutions we have studied water–glycerol mixtures confined in 21 Å pores of the silica matrix MCM-41 C10. The results from the differential scanning calorimetry (DSC) measurements shows an almost concentration independent glass transition temperature, T_g , at about 176 K for water concentrations up to 80 wt%, suggesting that the confined water has no influence on T_g in this concentration range. Rather, the findings indicate that the water molecules in the solutions have a stronger preference to coordinate to the hydroxyl surface groups than the glycerol molecules, which results in a micro-phase separation of the two liquids. The water phase does not give any sign of a T_g and therefore the observed T_g should be associated with the glass transition of the glycerol phase. Finally, we discuss why the confined water does not exhibit any clear calorimetric T_g .

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1. Introduction

Water is clearly the most important substance on earth, without which life, as we know it, would not be possible. The special and important properties of water in biology are caused by the intermolecular hydrogen bonds. These hydrogen bonds give also rise to a large number of other anomalous properties of liquid water, such as unusually high surface tension and heat capacity, and a density maximum at a temperature of 4 K above its melting temperature.

The many peculiar properties of water and its related biological importance have naturally made water to our most studied substance. However, despite all these research efforts central knowledge and understanding of its structural and dynamical properties are still partly lacking. The fact is that not even the glass transition temperature, T_g , and the glass transition related dynamics can be considered as established. The main reason for this is the difficulty to supercool bulk water. Ultrapure water can be supercooled down to its homogenous nucleation temperature at about 235 K, but in the temperature range from 235 K down to 150 K it will inevitably crystallize. However, it has been shown that for extremely fast cooling rates ($>10^5$ K/s) this temperature range can be passed sufficiently fast to avoid the nucleation process to occur [1,2]. By such rapid quenching to temperatures below 150 K it has been possible to study the behavior of glassy or amorphous solid water [1–4]. With differential scanning calorimetry (DSC) mea-

surements a possible glass transition has been detected at about 136 K for small droplets of hyperquenched water [1,2], which therefore is considered to be the most widely accepted T_g of water. However, this T_g -like feature is extremely weak, since the change in heat capacity is only about 2% of what is typically observed for aqueous solutions at T_g [5]. Therefore, it has been questioned [6–12] whether this weak calorimetric feature should be considered as a true T_g of bulk water. For instance, according to a fast scanning calorimetry study by Bhattacharya et al. [12] the true T_g of bulk water should be located above 150 K [12], i.e., in the temperature range where the glassy water immediately crystallizes [1,2]. Although bulk water is not studied in the present paper, also our results indicate that T_g of bulk water should be located far above 136 K.

Since the temperature of the glass transition should, by definition, be approximately the same as the temperature where the glass transition related structural (α) relaxation time reaches 100 s, it should, in theory, also be possible to determine the dynamic T_g by studies of the α -relaxation in the deeply supercooled regime. In reality such relaxation studies are, however, almost impossible to perform on bulk water due to its almost instantaneous crystallization in the temperature range 150–235 K. To avoid this problem of crystallization and hopefully be able to find some answers about the dynamical properties of supercooled bulk water it has become popular to study supercooled water in geometrical confinements or mixed with another chemical component. Of course, if such constraints on the hydrogen bonded network of water can prevent crystallization at any temperature, it is also likely that the general structural and dynamical properties of bulk

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water are substantially altered in such systems. Nevertheless, it seems likely that some knowledge and understanding of the properties of supercooled bulk water should be gained also from studies of confined water and aqueous solutions in the supercooled regime. Moreover, studies of confined water and aqueous solutions are highly relevant for understanding the role of water in biology, where almost all water can be considered as confined water and/or mixed with ions and other molecules to aqueous solutions [13]. Thus, confined water and aqueous solutions are essential to study both for understanding the role of water for life and vegetation as well as for gaining more fundamental understanding of supercooled water. In this paper we have combined the two different approaches, and performed DSC studies of mixtures of water and glycerol confined in 21 Å pores of the silica matrix MCM-41 C10. From previous studies it is known that this is basically the largest possible pore size for which crystallization of water is avoided at any temperature [14–17]. Thus, in contrast to the bulk water–glycerol system, which is fully amorphous over long times only at water contents up to about 25 wt%, it is possible to study the same system confined in MCM-41 C10 over the whole concentration range without having problem of crystallization. The results show that the concentration dependence of T_g is completely different for the confined solutions, compared to the bulk solutions. The findings are very interesting and suggest that the two liquids become micro-phase separated in the confinement. Hence, no plasticization (or anti-plasticization) effect of water can be observed for water contents up to about 80 wt%, and the results also support previous indications that confined water does not exhibit any clearly observable calorimetric glass transition [14,15,18,19]. This latter finding is in stark contrast to most other liquids in the same or similar confinements (see e.g. Refs. [20,21]). Possible explanations for the anomalous behavior of confined water are discussed.

2. Sample preparations and experimental details

The silica matrix MCM-41 C10 was prepared by the modified Beck method, as described in more detail in Ref. [22]. Long chain alkyltrimethylammonium bromide $C_{10}H_{21}(CH_3)_3N^+Br$ was used as the template organic reagent. The number of carbon atoms in the long alkyl group determines the pore diameter of the silica matrix, and with 10 carbon atoms a pore diameter of 21 Å is obtained. The size of the pores was determined by N₂ adsorption at the temperature of liquid nitrogen, in which an analysis program developed by Dollimore-Heale was employed [15]. High resolution electron microscopy was also employed to confirm the pore size, as described in Ref. [15]. The dimension of the pore diameter corresponds to about six water molecules along the diagonal of the pores. The different pores are ordered in a hexagonal structure, but the pore walls are amorphous and covered with hydroxyl groups. The properties of water confined in the MCM-41 C10 matrix has been extensively studied by, for instance, neutron diffraction [17], quasielastic neutron scattering (QENS) [14,23], X-ray diffraction [24], dielectric spectroscopy [16,25] and DSC, Fourier transformed infrared (FTIR) spectroscopy and gravimetric adsorption measurements [15].

Glycerol of $\geq 99\%$ purity, purchased from Sigma, C.A.S number (56-81-5), was mixed with double distilled water (Milli-Q water) to obtain aqueous solutions containing 5–95 wt% water. The solutions were put in ultrasonic baths for 30 min to ensure that homogenous mixtures were produced. Thereafter, samples (5–20 mg) of the bulk solutions were directly placed in hermetically sealed aluminum pans immediately before the DSC measurements were performed. Samples of water–glycerol solutions confined in the 21 Å pores of MCM-41 C10 were obtained by soaking the powder of MCM-41 C10 directly into the corresponding bulk solutions

under vacuum. After the pores of MCM-41 C10 had been filled with the bulk solutions the powder was removed from bulk solutions and gently dried by a tissue before the samples (5–20 mg) were placed in hermetically sealed aluminum pans prior to the DSC measurements.

The DSC measurements were performed on the TA Instruments DSC Q1000. The glass-transition was measured at a rate of 10 K min⁻¹ after the samples were cooled rapidly from 313 to 123 K at a rate of -30 K min⁻¹. The glass transition temperature of each sample was determined as the inflection point of the step in heat capacity. Four samples of each concentration were measured in order to determine the sample-to-sample variability, which was used for the estimation of the experimental uncertainty of the measured T_g -values.

3. Results and discussion

In Fig. 1(a) DSC data are shown for bulk samples of glycerol and water–glycerol mixtures. For pure glycerol a T_g at 190 K is observed, in good agreement with previous findings [21,26–29]. The T_g -value decreases rapidly with increasing water content until the water content is sufficiently high (≥ 45 wt%) to cause ice formation already during the cooling procedure (not shown) of the samples. For the sample with 35 wt% water, where ice formation was avoided during the cooling procedure, a lowest T_g of 166 K is obtained, as also seen in Fig. 2 showing the concentration dependence of T_g . At higher water concentrations (≥ 45 wt%) T_g is stabilized to approximately 174 K, suggesting that the effective water concentrations of these freeze-concentrated solutions are about the same. By comparing with the T_g -values for the water concentrations 15 wt% ($T_g \approx 179$ K) and 25 wt% ($T_g \approx 172$ K) we can conclude that the maximally freeze-concentrated solution, as obtained for the samples with ≥ 45 wt% water, contains about 22 wt% water. Thus, for all these water-rich samples the unfrozen solution contains approximately 22 wt% water, and the remaining water is located in ice particles. The average size of these ice particles grows with increasing water content from nm sized clusters to bulk-like ice clusters, as evident from the increase of their melting temperature from 240 K for the sample with 45 wt% water to 270 K for the sample with 95 wt% water.

For the samples in the concentration range 45–85 wt% water there is another glass-transition-like feature around 200 K, which increases somewhat in temperature with increasing water content. However, since this feature occurs at a higher temperature than T_g of pure glycerol it seems unlikely that it should be related to a true glass transition. More probable is the explanation that this feature is caused by ice dissolution, as proposed by Inaba and Andersson in Ref. [30]. The ice dissolution, or pre-melting, occurs because some of the ice particles that have been formed, in particular during the heating scan, will no longer be stable due to that dissolution is energetically more favorable at higher temperatures [30].

Fig. 1(b) shows corresponding DSC data of glycerol, water, and their mixtures confined in the 21 Å pores of MCM-41 C10. From these data it is evident that no crystallization or melting events can be observed for any of the confined liquids, in agreement with previous studies of water confined in the same silica matrix [14–17]. It can also be seen that T_g of confined glycerol is more than 10 K lower than for bulk glycerol, suggesting that a confinement induced speeding up of the glass transition related structural relaxation of glycerol dominates over a possible slowing down of the dynamics due to interactions with the hydroxyl groups of the inner silica surfaces [31]. The finding is consistent with a molecular dynamics simulation study by Buzzelez et al. [32], where they find that the temperature dependence of the diffusion constant of glycerol in a 24 Å pore of silica is much weaker than for bulk glycerol.

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