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Low-temperature heat capacity of a two-dimensionally ordered structure of ice crystallized from glycerol aqueous solutions[☆]

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ABSTRACT

A two-dimensionally ordered structure of ice crystallized from a glycerol 55% (w/w) aqueous matrix has been studied by adiabatic calorimetry. Its heat capacity was measured between $T = 5$ K and $T = 15$ K and found to be consistently larger than that of hexagonal ice (ice Ih) by an average of 1.3%. The composition and the heat capacity of the maximally freeze-concentrated solution, i.e. the non-crystallizing glycerol-rich phase that remains after water's partial crystallization, were also investigated.

1. Introduction

In terms of the vitrification/crystallization response to cooling, water and glycerol are on diametrically opposite ends. Glycerol's normal response to cooling, even at slow rates, is to form non-equilibrium glasses instead of the equilibrium crystals [1]. As for crystallization-prone water, it only vitrifies if subjected to very special conditions (see e.g. Ref. [2]). However, when water is mixed with glycerol, the glass-former impinges on the mixture a tendency to vitrify in response to cooling, the extent depending on the glycerol/water relative proportions. Thus, relatively water-rich glasses can be prepared, provided a fast enough cooling rate is given. With differential scanning calorimetry at a cooling rate of 20 K min^{-1}, for example, the maximum water content reported for a mixture to avoid crystallization is a water mass fraction of about 80% [3]. With adiabatic calorimetry at an average cooling rate of 5 K min^{-1}, it is about 45% [4]. Having prepared such glass, it is possible to force the solution to partially crystallize on heating. We can therefore investigate the phenomenon of crystallization of water from supercooled matrices, i.e. water's partial crystallization occurring at temperatures substantially lower than the equilibrium freezing temperature.

A neutron-diffraction study [5,6] found that water's crystallization from a supercooled matrix results in the initial formation not of ordinary hexagonal ice (ice Ih), but instead, of a distinct "*two-dimensionally ordered structure of ice*" [5]. Fig. 1 shows one of the typical results obtained at $T = 190$ K for a glycerol aqueous solution, 55% (w/w) partially deuterated glycerol $-C_3H_5(OD)_3-$ dissolved in D_2O. Although we cannot determine the structure in detail, this particular ice must have some ordered structure in a two-dimensional manner. We therefore refer to it as "2D-Ice" for short. It was also found that further heating of the mixture leads to the transformation of the metastable 2D-Ice into hexagonal ice as evidenced by the change in the neutron-diffraction patterns. In particular, at about $T = 208$ K the shapes and number of peaks evolve from a two-peak pattern to a three-peak pattern clearly identified with the reflections of the ice Ih structure (see Fig. 1 in Ref. [5] and Fig. 14 in Ref. [6] for details). It is interesting to note here that the formation of 2D-Ice and ice amorphous in a hydrophobic slit pore was predicted in an MD simulation [7].

In addition to neutron-diffraction data, a recent study by adiabatic calorimetry [4] has provided further evidence to support the observation that water's crystallization proceeds in two well-distinguished steps. A measurement on heating of a 60% (w/w) glycerol aqueous solution initially in a vitreous state showed a large increase in the temperature drift at about $T = 185$ K, and a subsequent small peak at approximately $T = 215$ K (see Fig. 1 in Ref. [4]). In the light of the above-mentioned neutron-diffraction results, these two thermal events were interpreted to be, respectively, the formation of the two-dimensionally ordered structure of ice and its ensuing transformation into hexagonal ice [4].

In this paper, we present the low-temperature heat capacity measurements to gain insights into the crystallization of water

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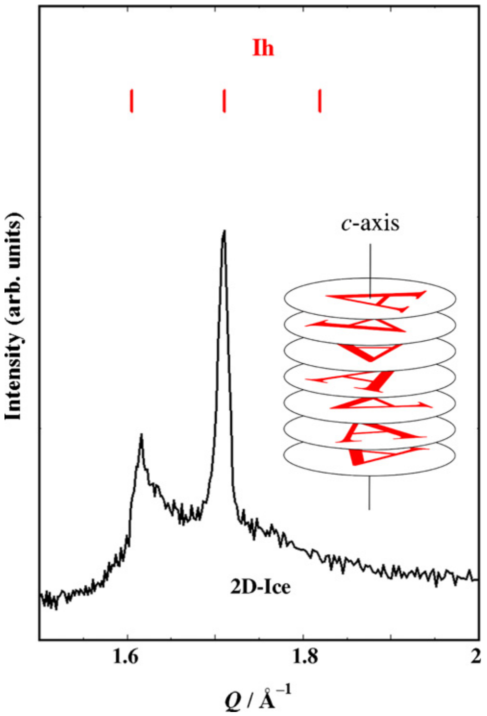

Fig. 1. Neutron-diffraction pattern obtained at 190 K from a glycerol 55% (w/w) aqueous solution after initial vitrification. The inset illustrates a model structure to explain the pattern [5]. The entity, what we call "2D-Ice" here, is completely different from hexagonal ice (Ih), whose peak positions are indicated as tick marks.

from glycerol aqueous solutions. The measurements were made before and after a 55% (w/w) glycerol aqueous solution was made to partially crystallize at temperatures so as to form 2D-Ice and, afterwards, ice Ih; $T = 190$ K and $T = 220$ K, respectively. We also investigated the composition and the heat capacity of the so-called "*maximally freeze-concentrated solution*", i.e. the non-crystallizing, glycerol-rich phase that remains after the partial crystallization has proceeded to its end.

2. Experimental

The samples were prepared using 99.5% (w/w) pure glycerol from Sigma–Aldrich and water from a Milli-Q Ultrapure Water System. Heat capacity measurements were performed from $T = 5$–15 K upon aqueous solutions of four different concentrations, namely glycerol 55.02%, 71.90%, 74.29% and 76.00% (w/w), by means of an adiabatic calorimeter. The typical mass of a sample was 2.5 g. The apparatus specifications [8] and sampling procedure [4] have already been described elsewhere. The overall accuracy for the present heat capacity measurement is better than 0.3% at 5 K, 0.2% at 7 K, and 0.1% above 10 K.

Initially, vitreous states of all four samples were attained through cooling at the fastest possible rate for our calorimeter, 10 K min^{-1}. The low-temperature heat capacities of the glasses thus produced were measured. In addition to this, the glycerol 55% (w/w) sample was subsequently heated up to and annealed at temperatures so as to make a part of its water contents crystallize into "2D-Ice" at first and, afterwards, transform into ice Ih; $T = 190$ K and $T = 220$ K, respectively. We made sure that both crystallization and transformation into ice Ih proceeded to completion as signaled by the end of the exothermicity or self-heating under adiabatic conditions. This three-step experimental cycle was repeated several times to ascertain the reproducibility of our measurements. Rather surprisingly, the reproducibility was excellent. All the heat capacity data fall within the experimental accuracy described above.

Since the low-temperature operative limit of our adiabatic calorimeter [4,8] is about $T = 5$ K, we also employed a Quantum Design PPMS 6000 calorimeter to explore the lower temperatures. The results obtained agree qualitatively with the adiabatic calorimetry data shown in Fig. 2, but are not presented here since the accuracy is not sufficient to resolve the small heat capacity difference between 2D-Ice and ice Ih. This can only be done reliably using a high-accuracy adiabatic calorimeter.

As for temperatures higher than $T = 15$ K, some measurements were carried out using our adiabatic calorimeter. In this range, however, the heat capacity difference between 2D-Ice and Ih diminishes with increasing temperature and finally becomes indiscernible. Therefore, we will only refer to them in Section 3.3 in connection with the nature of the maximally freeze-concentrated solution.

3. Results and discussion

In Fig. 2 we show heat capacity results, plotted as c_pT^{-3} against T, for the glycerol 55% sample after each of the three steps of the cycle: (1) vitrification; (2) annealing at $T = 190$ K and (3) annealing at $T = 220$ K. We see that the heat capacity of the homogeneous glass, the uppermost set of points, is much larger (10% at 5 K) than that of either of the two non-homogeneous, partially crystallized states of the mixture showed below in the figure. Moreover, we observe that the heat capacity of the sample annealed at $T = 190$ K is larger, by a small yet significant difference, than that of the same sample annealed at $T = 220$ K. The difference amounts to 1% at 5 K, 0.7% at 7 K, and 0.5% at 10 K, which exceeds the measurement accuracy as described above.

As we want to quantify the actual difference between the two of them; that is, not as mixtures in the manner of Fig. 2 but as independent entities, we need to segregate the two contributions: (a) the contribution from the pertinent form of ice and (b) the contribution from the maximally freeze-concentrated solution of glycerol, MFCS for short. If we would know, say, the heat capacity c_p of any of our two-phase separated mixtures together with the c_p of one of its constituting phases, we could easily calculate the c_p of the other constituting phase. That is, to calculate the ice phases' heat capacities from our data of Fig. 2 we have to establish first the maximally freeze-concentrated solution's heat capacity. To accomplish this we used an experimental trial and error procedure, as explained below. However, before proceeding to this explanation, it is necessary to make explicit the premises on which we base the interpretation of

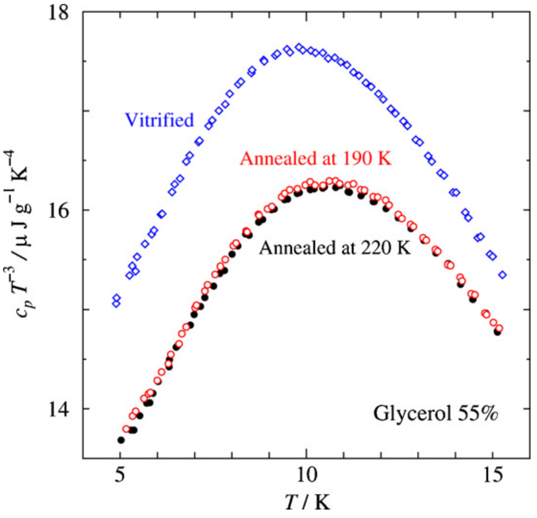

Fig. 2. Heat capacity, plotted as c_pT^{-3} against T, of a sample of glycerol 55% (w/w) after initial vitrification and subsequent annealing at $T = 190$ K and $T = 220$ K.

our heat capacity data. The premises, that we summarize as follows, will be revisited shortly in the light of our experimental results.

(i) When a glycerol–water mixture partially crystallizes, two phases are generated. One of them is pure water in crystalline form (ice) and the other phase (the maximally freeze-concentrated solution) is a non-crystalline glycerol-rich homogeneous mixture, the residue of the initial homogeneous matrix. The phases are supposed to be fully separated, each one contributing linearly to the mixture's heat capacity according to their relative amounts (set by the mass balance—lever rule). Note that we assume that glycerol does not crystallize at all.

(ii) The crystallization temperature (the annealing temperature) does not affect the amount of ice formed for a given sample (although for samples with different concentrations slightly different ice/glycerol-rich phase relative amounts are likely). That is, crystal structure differences notwithstanding, the amount of ice released from the matrix through annealing at 190 K or 220 K (2D-Ice and Ih, respectively) is supposed to be the same.

3.1. Characterization of the maximally freeze-concentrated solution (MFCS)

The existence of the maximally freeze-concentrated solution (MFCS) in the glycerol–water binary system is a consequence of the fact that glycerol does not easily crystallize. Because of that, when the homogeneity of the system breaks, only crystals of water and none of glycerol grow out of the matrix so the remaining phase grows increasingly rich in glycerol. Intuitively, we could think that this process continues until all water initially in the matrix forms ice so as to have two pure-component phases—pure ice and pure glycerol. But in fact, as we explain below, there is experimental evidence showing that water's crystallization ceases before full component-separation, stopping when the matrix attains a certain concentration of glycerol; hence the name of this solution that remains at the end: "*maximally freeze-concentrated solution*". This view has been used to explain the behavior of aqueous mixtures of sucrose and other carbohydrates [9]. The validity for our system in question has been assured by two studies on the glycerol–water phase diagram (see Refs. [3,4]). The MFCS was identified as the origin of a glass transition that takes place at almost the same temperature for all mixtures that have been subjected to crystallization, no matter their initial concentration. An extrapolation of this T-constant line to the plot of the glass transitions of homogeneous glasses in the phase diagram suggested a MFCS's glycerol concentration of 73.5% and 76% (w/w) for differential scanning [3] and adiabatic calorimetry [4], respectively.

In this work our interest in the maximally freeze-concentrated solution (MFCS) lies in the fact that it is a by-product of the crystallization of water that we need to characterize in order to, based on premise (i) above, calculate the heat capacities of the ices that arise during crystallization. We obtained the concentration and the heat capacity of the MFCS for the glycerol 55% sample by an experimental trial and error procedure in which we (1) assume a concentration of the MFCS and measure its heat capacity; (2) use the mass balance (lever rule) for a glycerol 55% mixture to calculate the proportions of each of the two phases – ice and MFCS – if the MFCS has the assumed concentration; (3) subtract the heat capacity of the MFCS from the heat capacity of the phase-separated glycerol 55% annealed at $T = 220$ K (see Fig. 2) to obtain a calculated heat capacity of hexagonal ice; (4) compare the calculated c_p of ice Ih with reference values [10] and repeat the procedure until calculated and reference values agree. The concentration of the MFCS for which this condition is attained is the result we were searching for. It is important to mention that in order to perform mathematical operations on our experimental heat capacity data such as the subtraction involved in step (3), we generated suitable polynomial fits for all data we used in our calculations.

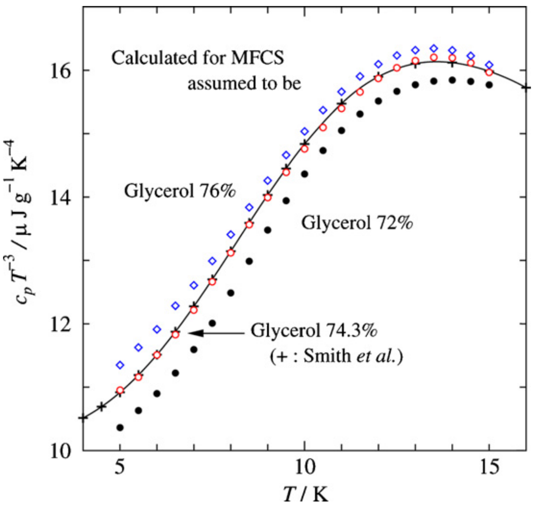

Fig. 3. Heat capacities, plotted as c_pT^{-3} against T, of 'hexagonal ices' calculated from a glycerol 55% (w/w) sample annealed at $T = 220$ K assuming that the maximally freeze-concentrated solution has a glycerol concentration of 72%, 74.3% or 76% (w/w). The heat capacity of hexagonal ice (Ih) as calculated for glycerol 74.3% agrees well with reference data as given by Smith et al. [10].

In Fig. 3 we show graphically the results for three different concentrations of the MFCS, namely glycerol 72%, 74.3% and 76% (w/w), for which calculated ice Ih's heat capacities were obtained following this trial and error procedure from (1) to (4). It can be observed that calculated and reference values [10] agree very well (within 0.1%) for the MFCS with a concentration of glycerol 74.3%. As a result, with this procedure we characterized the maximally freeze-concentrated solution in terms of its concentration – glycerol (74.3 ± 0.1)% – and its heat capacity (not presented here but used in the making of Fig. 3). The difference in experimental specific heat capacities between the two homogeneous glasses with a glycerol concentration of 72% and 76% (w/w), for example, amounts to 1%, which is directly reflected in the estimate of the concentration.

3.2. Characterization of the two-dimensionally ordered structure of ice (2D-Ice)

Having characterized the maximally freeze-concentrated solution for glycerol 55%, and evoking premise (ii), the calculations involved in establishing the heat capacity of the two-dimensionally ordered structure of ice are straightforward. We subtracted, weighting according to the mass balance, the heat capacity of the MFCS (homogeneous glycerol 74.3%) from the experimental heat capacity of the partially crystallized mixture where we recognize 2D-Ice to have arisen (glycerol 55% annealed at $T = 190$ K, see Fig. 2). The results of this calculation are shown in Fig. 4 where we see that between $T = 5$ K and $T = 15$ K the heat capacity of 2D-Ice is consistently larger than that of hexagonal ice by a significant difference. It is of 1.3% on average when compared to reference data for Ih [10]. This is the thermal fingerprint of 2D-Ice and it complements the neutron-diffraction-based characterization of 2D-Ice we have had so far. Thus, we can conclude that 2D-Ice has the following characteristics: (i) it is metastable with respect to ice Ih; (ii) it shows a neutron-diffraction pattern typical of two-dimensional layers (Fig. 1 in Ref. [5]) and (iii) it has a heat capacity larger than that of ice Ih.

Interestingly, this description brings to mind another structure of ice, the still controversial ice Ic (cubic ice) – see e.g. Hansen et al. [12,13] – that is also metastable with respect to ice Ih and counted as 1 of the 15 crystalline solid phases of water known to exist to date

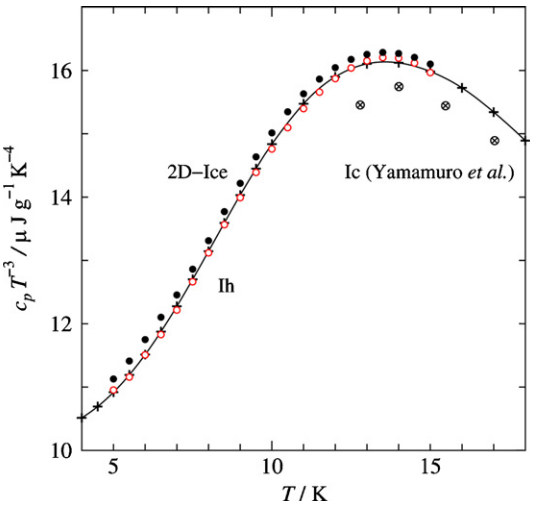

Fig. 4. Heat capacities, plotted as c_pT^{-3} against T, of the two-dimensionally ordered structure of ice (2D-Ice), hexagonal ice (Ih) – ours, circles; reference data [10], crosses – and cubic ice, as given by Yamamuro et al. [11].

[14]. In particular, the neutron-diffraction pattern for 2D-Ice [6] agrees reasonably well with diffraction patterns (see Fig. 2 in [15]) taken for cubic ice formed via high pressure ices. The patterns' resolution, however, is very different between Refs. [5,15]. We interpret that what looks like a kink on the left side of the (1 1 1) peak in [15] is resolved into an independent (1 0 0) peak in [5]. Although further studies are required to establish the nature of 2D-Ice and its relation to cubic ice, the findings here may offer a new way to prepare cubic ice and, thus, to study its properties. Previously, cubic ice has been prepared by several different methods including vapor deposition (see e.g. Ref. [16]), via water's high pressure polymorphs [17,18], from nucleation in a porous silica network [19] and through rapid quenching of aqueous aerosol droplets in a micro-sized cryoplate [20]. The characterization of the cubic ice obtained through any of these methods has mostly been done by diffraction techniques such as electron diffraction, X-rays, or neutron-diffraction.

We found in the literature only one measurement of cubic ice's thermal properties by Yamamuro et al. [11] that we reproduce in Fig. 4. In their study they report that cubic ice was prepared in bulk from water at high pressure through ices III and IX following a route first proposed by Bertie et al. [17]. They claim that the precision of their heat capacity data was 0.1%. As we see in Fig. 4, their results for cubic ice's heat capacity clearly do not agree with ours for 2D-Ice and this complicates the question whether our 2D-Ice and cubic ice are one and the same. Because of the metastable nature of both 2D-Ice and cubic ice, it is conceivable that a disagreement due to their different preparation methods may occur even if they were the same entity. However, it is unlikely that it could be as big as to imply that the heat capacity of ice Ic shifts upwards from smaller to larger values than those of ice Ih, as we should have to accept to reconcile the two sets of data in Fig. 4. The possibilities are rather that either (i) 2D-Ice is an entity distinct from ice Ic with similar "cubic" structure but different heat capacity; or (ii) 2D-Ice is actually ice Ic and the heat capacity measurements of ice Ic need to be re-examined. If it is the case (i), we should consider an interfacial effect in 2D-Ice, which is dispersed randomly in a matrix. In fact, small-angle neutron scattering [6] demonstrates that the crystallites of 2D-Ice appear to develop their surface area significantly. However, as proposed by Hansen et al. [12,13], the same is true also for the bulk Ic, in which a lot of stacking faults may exist. To confirm any of the two hypotheses further experiments as well as considerations are necessary and we cannot settle this matter at the moment.

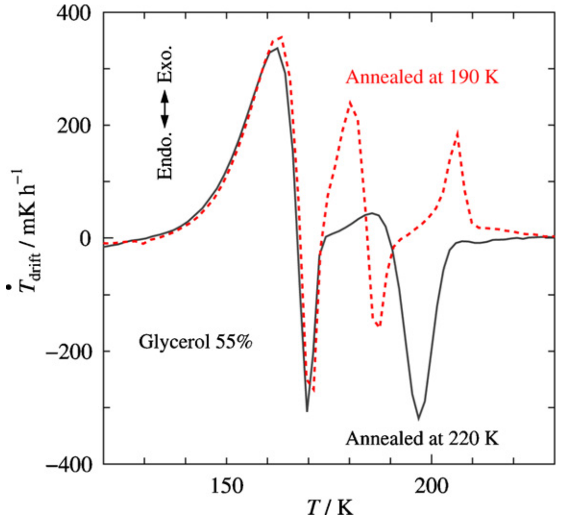

Fig. 5. Temperature drift rate as a function of temperature observed during adiabatic calorimetry on heating with an average rate of about 5 K h^{-1} for samples annealed at 190 K (2D-Ice) and annealed at 220 K (Ih).

3.3. *Revisiting the premises*

Although the premises stated above are mostly based on experimental facts on the glycerol–water binary system as summarized in the phase diagram (refer to Fig. 4 of Ref. [4]), premise (ii) needed additional experimental proof. Fig. 5 shows the temperature drift rates as a function of temperature for glycerol 55% after annealing at T = 190 K and T = 220 K, where 2D-Ice and ice Ih are present, respectively. To ensure that the cooling rates for both measurements were similar enough so that the vitrification of their maximally freeze-concentrated solution takes place equivalently, the sample containing ice Ih was also annealed at T = 190 K and only then cooled further. A careful interpretation of this kind of temperature drift rate figures has previously been given elsewhere (see Fig. 2 in Ref. [4]) and therefore we will not attempt here to describe at length all their features. We simply note that in Fig. 5 both sets of data show the glass transition of the maximally freeze-concentrated solution (MFCS) at the same temperature of 167 K. It is safe to say, therefore, that the concentration of the MFCS, i.e. the amount of ice formed, is not appreciably affected by the crystallization (annealing) temperature. In this way we prove the validity of premise (ii). As for premise (i), the fact that our calculations based on it gave coherent, non-contradictory results is new evidence of its validity.

4. Conclusions

In this paper we presented heat capacity results for a novel two-dimensionally ordered structure of ice (2D-Ice) obtained from a 55% (w/w) glycerol aqueous solution that was made to partially crystallize at T = 190 K and T = 220 K so as to produce two distinct forms of ice: the two-dimensionally ordered structure and ice Ih, respectively. The heat capacity of 2D-Ice was measured to be larger than ice Ih's by 1.3% on average. There are arguments that favor the view that 2D-Ice is actually cubic ice (ice Ic) but the evidence is inconclusive as yet because previous measurements of the heat capacity of cubic ice [11] disagree with our results for 2D-Ice. Thus, 2D-Ice may as well be a new metastable form of ice for which we provide heat capacity data for the first time. Further experiments are necessary to elucidate this matter. We also investigated the maximally freeze-concentrated solution for this sample and established that its concentration is virtually independent of the temperature of crystallization of the mixture.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2010.01.008.

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