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Multiple glass transitions and two step crystallization for the binary system of water and glycerol[☆]

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Abstract

Glass formation/crystallization phenomena were studied in water and glycerol mixtures using adiabatic calorimetry. The sample was cooled rapidly from room temperature and its thermal response was followed on heating from 80 to 300 K. The binary mixtures with the glycerol contents more than 55% (w/w) (19 mol%) yielded the homogeneous glassy states, consisting of randomly mixed water and glycerol molecules. Their glass transition temperatures showed the composition dependence of the Gordon–Taylor equation, and extrapolated exactly to that of pure water (135 K). The mixtures in the 0–55% (w/w) glycerol range crystallized partly on cooling and exhibited three anomalies in the temperature drift rate on heating. The first of these three is associated with the onset of reorientational motions of water molecules in the hexagonal ice which increases from 107 to 120 K on increasing the glycerol composition. The second is the composition independent temperature of 164 K that corresponds to the mixture with 76% (w/w) glycerol (38 mol%, known as the maximally freeze-concentrated solution), which is the mixture with the maximum composition of water that can be cooled without crystallization. The third is associated with the ice crystallization followed by ice dissolution in the range 185–202 K. In addition, the sample with 60% (w/w) glycerol composition (23 mol%) exhibited two distinguishable exothermic peaks on heating. The initial one is large and is attributed to crystallization into a novel two-dimensionally ordered structure of ice, and the second is due to the transformation of the layered structures into the hexagonal ice.

Keywords: Adiabatic calorimetry; Glycerol; Water; Glass transitions; Crystallization

1. Introduction

The supercooled states of glycerol and water are among the most important for both fundamental science and practical applications. The former is often used for fundamental studies of the glassy and supercooled states because of its good glass forming ability, which makes it very suitable for long time studies of the supercooled liquid state. Glycerol is also very useful for the pharmaceutical and food industry as well as the cosmetic industry. This is mainly because of its demulcent, antifreeze and emollient properties. The crystallization kinetics of water is in striking contrast to that of glycerol. In a bulky sample, one must add antifreezing agents to avoid crystallization and historically glycerol was used for that purpose in e.g. radiators of cars. Even if this is normally not the case now, mixtures of water and glycerol occur much more frequently nowadays than in the past because of the various improvement of properties obtained by adding glycerol in water containing products.

Without the use of antifreezing agents, it is virtually impossible to cool bulky water rapidly enough to avoid crystallization. In order to obtain the glassy state by cooling, one must either use vapour condensation onto a substrate which is kept near liquid nitrogen temperatures or quench micron-sized droplets of water. This difficulty to obtain and study the supercooled state of liquid water has resulted in substantial differences in reported properties of the supercooled state and has lead to speculations of water's behaviour in its supercooled state. For example, the during long time accepted glass transition temperature T_g for water has become disputed. Using differential thermal analysis with a heating rate of 20 K min^{-1}, McMillan and Los [1] found $T_g = 139$ K for amorphous solid water (ASW) formed by vapour deposition onto a cold surface. A few years later, Sugisaki et al. [2] obtained $T_g = 135$ K for ASW using adiabatic calorimetry. (The heating rate was not given but it is typically ~0.1 K min^{-1}

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in adiabatic calorimetry.) Subsequently, results close to these were also found in other studies, e.g. the study of Hallbrucker et al. [3] using differential scanning calorimetry (DSC). Moreover, it has been shown that after heating of ASW from 77 to 113 K in vacuum (annealed ASW), the resulting state is indistinguishable from hyperquenched water droplets HQW [3,4] and, consequently, that annealed ASW and HQW are most likely identical states. For example, HQW and ASW have the same T_g, and both states will here be refereed to simply as ASW. (DSC yields $T_g = 136$ K for HQW using a heating rate of 10 K min^{-1} [5].) However, the value for T_g of ASW has been questioned and the significantly higher value of $T_g = 165$ K was recently suggested [6–8]. It was argued [6,7] that glasses which form only by extreme rapid quenching normally exhibit crystallization on reheating before the relaxation rate is low enough to see the heat capacity jump associated with the glass transition. The result of $T_g = 135$ K obtained by extrapolations of T_g of homogenous mixtures of water and other substances has been dismissed on the basis that these substances have not had water-like hydrogen bonding capacity [8]. Using water mixed with 50 vol.% or more propylene glycol, which was considered as having such property, yielded values for T_g of about 165 K by long extrapolation [8]. This result provides one of few experimental evidences that T_g could be significantly higher than 135 K.

Here we report a study of the fundamentally important binary state diagram using adiabatic calorimetry and, in particular, the glass transition behaviour for glycerol/water mixtures. Using the same model for water mixed with glycerol as that used for water and propylene glycol mixtures [8], yields T_g values for the homogeneous mixtures that extrapolates exactly to the experimentally determined value for T_g of ASW [1–3,5], i.e. 135 K as observed in many other investigations. Moreover, we find that the T_g associated with the reorientational motion of H_2O-molecules in hexagonal ice is affected by even small amount of glycerol. We also discuss our results in terms of the different suggestions for explaining the many glass-like anomalies observed for glycerol/water mixtures which crystallize on cooling.

2. Experimental

The sample of glycerol obtained from Aldrich (99.5% purity) was mixed with water purified by using Milli-Q® Ultrapure Water Systems, which was degassed and loaded in a calorimetric cell with an internal volume of about 2.8 cm^3. It was sealed with helium gas to aid thermal equilibrium. The cell was transferred to an adiabatic calorimeter, which has been described before [9], employing a mechanical switch to cool the sample without using heat exchange gas in the cryostat. The temperature was measured using a rhodium–iron resistance thermometer calibrated on the ITS-90, an internationally accepted temperature scale. At each composition, the mixture was quenched at the fastest possible rate, which varied with temperature. The cooling rate was ∼10 K min^{-1} at 250 K and it decreased to ∼2 K min^{-1} near 100 K. The glass transition temperatures for the observed anomalies were taken as the temperatures where the drift rate changed from positive to negative values.

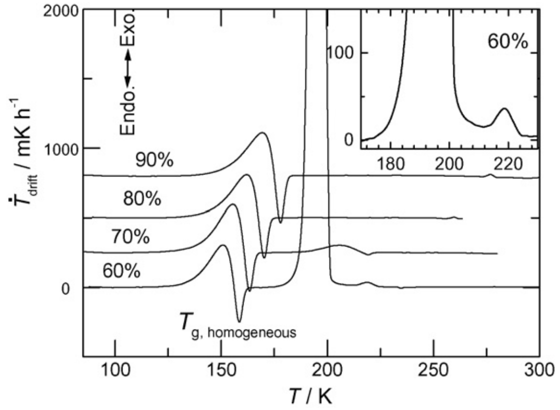

Fig. 1. Temperature drift rate as a function of temperature on heating with an average rate of ∼0.08 K min^{-1} for samples with increasing mass fraction glycerol in the range 60–90% (w/w). The large exothermic peak for the sample with 60% (w/w) glycerol is due to crystallization. (The curves have been shifted vertically for clarity.) The inset shows the double peak in the drift rate for a sample of 60% (w/w) glycerol, which agree well with previous results of an initial crystallization into a two-dimensionally ordered structure and a subsequent further transformation into hexagonal ice.

3. Results and discussion

Fig. 1 shows typical results for the temperature drift rate on heating the samples with glycerol fractions larger than 60% (w/w) (23 mol%). The samples had been cooled with an average rate of ∼5 K min^{-1} and the temperature of the sample, which was monitored, showed no signs of crystallization during cooling. For samples with glycerol fractions larger than 60% (w/w), the cooling and heating rates were sufficient to avoid crystallization. For a sample with 60% (w/w) glycerol, the cooling rate was sufficient to avoid crystallization on cooling but the sample crystallized on heating, yielding the large peak in the drift rate with at about 190 K.

As can be seen in Fig. 1, only one glass transition occurred on heating, labelled $T_{g,homogeneous}$. Consequently, the quenched sample was homogeneous in this composition range, and the glass transition pertains to a random mixture of glycerol and water. The glass transition temperature T_g extrapolate, at decreasing water content, to that obtained for pure glycerol using adiabatic calorimetry $T_g = 184$ K [10]. Moreover, the values for T_g approach that for pure water ($T_g = 135$ K [2]) with increasing water content. The behaviour agrees with the finding by Harran [11] using DSC, but our values for T_g are about 10 K lower, which is due to the use of different heating rates of 20 K min^{-1} in the work of Harran [11] and 0.08 K min^{-1} in this work. We cannot, of course, rule out the possibility that T_g versus composition drastically changes behaviour and increases significantly on further increase of the water content, but there are no indications of that up to a water fraction of 80% (w/w) [11]. Instead the values extrapolate well to the temperature where the heat capacity anomaly is observed for pure water. A fit of the Gordon–Taylor equation [12]: $T_g(x) = [T_{g,glycerol}x + T_{g,water}k(1-x)]/[x + k(1-x)]$, where x is the glycerol mass fraction, $T_{g,glycerol} = 184$ K [10], and k is a fitting parameter, yields $T_{g,water} = 135.5$ K with a standard error of 0.9 K. That is, the result is in excellent agreement with the glass transition anomaly observed for pure water but differ significantly from the result obtained using the same approach on water mixed with propylene glycol [8]. We can conclude that it would be an odd coincidence if the heat capacity anomaly observed for ASW at 135 K would not be due to T_g despite that most binary aqueous mixtures yield a T_g that extrapolate well to this anomaly within the observable composition range, and that also other experimental work yield the same result for T_g.

In the present work we cannot determine the nature of the crystals formed at crystallization, which normally occurred for samples with glycerol content less than 60% (w/w). However, a neutron scattering study of a water solution with 55% (w/w) glycerol (19 mol%), has revealed that the crystallization proceeds in two well-distinguished steps and that the initial crystallization yields a novel two-dimensionally ordered ice structure [13,14]. This structure forms at about 188 K after heating of the quenched liquid from below the glass transition temperature. The structure is stable until the temperature is raised further to 208 K, where hexagonal ice is formed. The results obtained here for a sample of 60% (w/w) glycerol shows a discontinuity in the heat capacity data and the temperature drift rate shows a large increase at about 185 K (see inset in Fig. 1). This temperature agrees reasonably well with that where the formation of the two-dimensionally ordered structure was observed in the neutron scattering study. As shown in the inset in Fig. 1, a small peak in the temperature drift rate can also be observed just above the large peak. The onset temperature is ∼215 K, i.e. somewhat higher than the temperature where a change could be observed in neutron scattering spectra. However, since the crystallization occurs for a metastable state, the discrepancies in temperatures are likely caused by differences in heating rates, sample sizes and compositions. Consequently, the two peaks are presumably due to an initial crystallization into a two-dimensionally ordered structure and, subsequently, further transformation into hexagonal ice. Thus, the formation of a two-dimensional ordered structure is associated with large enthalpy and entropy changes, whereas those of the further ordering process into the ice Ih structure are significantly smaller.

In the present study, it was difficult to cool rapidly enough to avoid crystallization for a 55% (w/w) glycerol sample. However, in one run, the temperature drift rate data exhibited only one glass transition anomaly on heating, which corresponds to the homogeneous glass transition, indicating that the sample did not crystallize on cooling (not shown in a figure). On further heating, the sample crystallized at about 171 K and there was no second peak in the temperature drift rate above this temperature. This significant difference in the crystallization behaviour as compared to the 60% (w/w) glycerol sample and that reported previously [13] can be attributed to the formation of hexagonal ice nuclei on cooling. This would explain the lower crystallization temperature as well as the lack of a second peak. That is, in this case the sample crystallized directly into ice Ih, and it occurred at a lower temperature than the 60% (w/w) glycerol sample due to the presence of hexagonal ice nuclei.

Fig. 2 shows results for the mixtures with glycerol content less than 55% (w/w). For these mixtures, the increasing tendency for crystallization brought about by the larger water content prevented supercooling of the homogeneous liquid to below the glass transition temperature. That is, the cooling rate set by the combined heat capacity of our sample and the sample cell and the limited thermal diffusivity was insufficient to avoid crystallization. The temperature of the sample during cooling showed a significant change in the cooling rate at about 20 K below the melting temperature. With the cooling rate used here, samples in the range 55–60% (w/w) glycerol could be supercooled to yield the homogeneous glass, but could also crystallize partly on cooling or the subsequent heating. For the partly crystallized samples, which crystallized either directly on cooling (i.e. samples with 55% (w/w) or less glycerol content) or after heating up to about 200 K, a subsequent heating from about 80 K yielded three anomalies in the temperature drift rate at about: 115, 164 and 200 K, with a slight variation with composition. These anomalies all have drift rate characteristics typical for glass transitions.

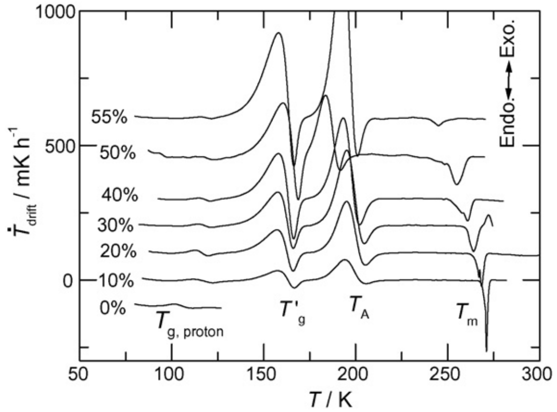

Fig. 2. Temperature drift rate as a function of temperature on heating with an average rate of ∼0.08 K min^{-1} for samples with increasing mass fraction glycerol in the range 0–55% (w/w). At least two glass transitions can be observed, which are associated with the protons of H_2O ($T_{g,proton}$) and the maximally freeze-concentrated solution (T'_g), respectively. The drift rate anomaly at high temperatures (T_A) is presumably associated with ice crystallization followed by ice dissolution.

The low-temperature anomaly (∼115 K) occurs also for pure water, and since it occurs only for glycerol/water mixtures that have crystallized, these results show that it must be associated with a motion present in the tetrahedrally co-ordinated hydrogen-bonded structure of ice Ih. On each of the four hydrogen bonds there are two proton sites, and these are occupied according to the rules that there are two protons adjacent to each oxygen and that only one proton is located on each bond, which are referred to as the “ice rules” [15]. This preserves the water molecule but allows also for disorder in the orientation of the molecules or, equivalently, proton disorder. The anomaly is therefore confidently ascribed to the onset of the reorientational motion of H_2O or proton jumps in hexagonal ice on the time-scale of the adiabatic measurements. It is labelled $T_{g,proton}$ in Fig. 2, and it occurs at about 106 K for a sample that has not been annealed [16]. The results here show that $T_{g,proton}$ increases from 107 to 114 K by adding 5% (w/w) glycerol (1 mol%), which corresponds to only 1 glycerol molecule in 100 water molecules.

On further increase of glycerol content, $T_{g,proton}$ is less strongly affected but increases slightly and is about 120 K for a sample of 55% (w/w) glycerol. Since $T_{g,proton}$ is somewhat dependent on the thermal history near $T_{g,proton}$, the change of T_g with composition could be due to different cooling rates caused by different crystallization behaviour and therefore indirectly caused by changing glycerol content. However, the cooling rate did not change with glycerol content in the important range 90–115 K, where annealing affects the transition behaviour. Moreover, the change of $T_{g,proton}$ with composition is too large to be explained by the small differences in thermal history. Therefore, it must be due to a direct effect of glycerol. It is well known that the reorientational relaxation time for the H_2O-molecules can be changed by doping. Small amount of KOH ($\sim 10^{-4}$ mole fraction) increases the relaxation rate by introducing lattice defects that relaxes the ice rules [17]. In this case, glycerol has apparently the opposite effect and decreases the reorientational rate and, as a consequence, $T_{g,proton}$ increases. A hypothesis is that the interaction between glycerol- and H_2O-molecules decreases the possibility for reorientational motions of the latter, which could reside at the ice crystal surface. Reorientational restrictions of surface molecules, which normally have a higher mobility than bulk molecules, will decrease the reorientational rate also of the H_2O-molecules in the bulk as the reorientations of these are restricted by the ice rules. As a consequence, $T_{g,proton}$ increases significantly until the mobility of most of the surface molecules are restricted by the interactions with glycerol molecules.

On further heating, two more glass-like anomalies are observed above 150 K in the range 0–55% (w/w) glycerol content (Fig. 2). These are likely due to T_g of the maximally freeze-concentrated solution at ∼164 K, i.e. the concentration with the maximum amount of water that can be cooled slowly without crystallization, and ice crystallization followed by ice dissolution in the range 185–202 K [11,18,19], respectively. These interpretations are, however, disputed and we shall discuss also the proposal of yet another glass transition in the range 185–202 K.

The C_p step at the transition at 164 K increases as the concentration of glycerol increases (Fig. 3(b)) and T_g agrees with $T_{g,homogeneous}$ for compositions slightly above the eutectic mixture. The former result shows that an increasing amount of the sample is involved in the glass transition, and this correlates well with that an increasing amount of the sample can form a glassy state of the maximally freeze-concentrated solution, yielding a T_g in this vicinity. As the crystallization into ice Ih cannot be prevented for low glycerol concentrations, the composition of the liquid part should follow the melting curve and finally reach that for the eutectic mixture as more and more ice crystals precipitates from the solution. The eutectic composition is 66.7% (w/w) glycerol (28% mole fraction) and the eutectic temperature is 226.5 K [20]. On further cooling, the ice crystallization will proceed and the liquid part becomes supercooled. Ultimately the liquid part will vitrify and the glycerol concentration of the vitrified liquid will exceed that of the eutectic mixture. If the process follows the extrapolated liquidus (or melting) curve, then the vitrified liquid will have the composition of the maximally freeze-concentrated solution C'_g, which consequently is the concentration at the intersection of the melting curve and the $T_{g,homogeneous}$ curve. A glass transition temperature of 164 K corresponds to a composition of ∼76% (w/w) (38 mol%) according to the results for $T_{g,homogeneous}$ (see Fig. 4), whereas an extrapolation of the melting line using a second-order polynomial fitted to the melting temperatures yield as high value as 89% (w/w) (61 mol%). Using the same procedure, Ablett et al. [18] obtained 80% (w/w) (44 mol%). The latter extrapolation procedure is uncertain and even if it is unlikely that the sample would exactly follow the extrapolated melting curve down to the glass transition temperature, it seems as a better procedure to use the former data to establish C'_g and T'_g, which yield $T'_g = 164$ K and $C'_g = 76\%$ (w/w). The maximally freeze-concentrated solution of 76% (w/w) corresponds to a glycerol molar concentration of 38%. It follows that 1.6 water molecules are, in average, associated with each glycerol molecule. Padró et al. [21] have used molecular dynamics calculations to calculate the hydrogen bonding statistics and found 3.3 and 5.7 hydrogen bonds per molecule in average for H_2O and glycerol, respectively. Consequently, a composition of 1.7 H_2O-molecules per glycerol molecule (5.7/3.3) would be the optimum concentration if each hydrogen bond on the glycerol molecules should be associated with a hydrogen bond on a water molecule. This yields a concentration of ∼75% (w/w) (37 mol%), which is in excellent agreement with the compo-

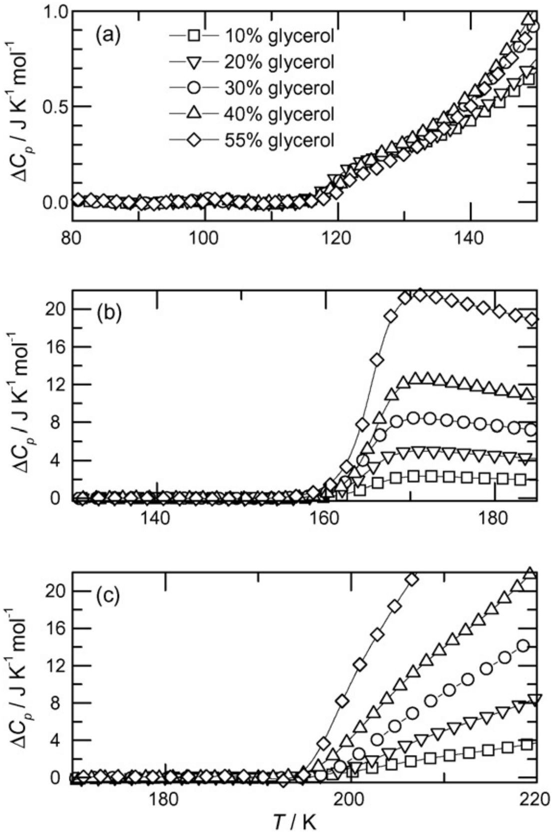

Fig. 3. The step in the heat capacity at the three drift rate anomalies for samples with glycerol content in the range 10–55% (w/w). A second-order polynomial was fitted to the data below T_g and subtracted from the data to show the step in C_p at T_g more clearly.

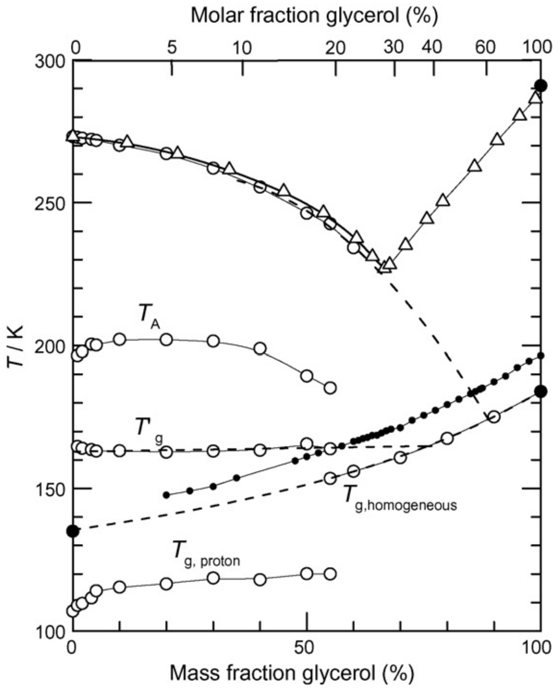

Fig. 4. The glass and melting transition temperatures as a function of glycerol content. The solid lines represent spline fits and the dashed lines represent tentative extrapolations using the Gordon–Taylor equation [12] for the glass transition curve, a second-order polynomial for the melting curve and a linear fit of the data for T_g''. The dots are data of Harran [11] for T_g on heating at rate 20 K min^{-1}using DSC. The filled symbols show the glass transition and melting temperatures for the pure components [2,10]. Open triangles are data of Lane [20].

sition of the maximally freeze-concentrated solution. Thus this seems to be the energetically most favourable glassy complex of water and glycerol. An even more glycerol rich state than 76% (w/w) might be formed using slow cooling, which is indicated by the extrapolation of the liquidus curve to higher concentrations of glycerol as $T_{g,\mathrm{homogeneous}}$ decreases with decreasing cooling rate.

It remains to establish the nature of the high temperature anomaly in the range 185–202 K, which is here labelled T_A. Since it occurs above T_g of pure glycerol, it cannot be due to T_g of the maximally freeze-concentrated solution. The similar anomalies that occurs in ethylene glycol [22], sucrose [23] and trehalose [24] have been attributed to a second glass transition due to a non-homogeneous glass formation upon rapid cooling. That is, in those cases the sample must become inhomogeneous on a mesoscopic scale during cooling. This possibility explains well the experimental data of aqueous sucrose solutions and has been suggested also for glycerol aqueous solutions [25]. The results for aqueous sucrose solutions, which are observed after various thermal treatments, have been discussed in detail by Goff et al. [23]. Briefly, two glass transitions arise if the (ultra viscous) liquid part of the sample becomes inhomogeneous on cooling just above the vitrification temperature. This results in a sucrose rich part, in the form of inclusions in the ice crystals, which will have a higher T_g than the bulk glass, which has somewhat higher water concentration. (The occurrence of the T_g in the sucrose rich part has also been associated with a concomitant onset of ice dissolution.) However, this explanation is unlikely correct for the glycerol/water system as the high temperature anomaly can be 17 K above T_g for pure glycerol, and not below as in the water/sucrose system. Consequently, for the glycerol/water system, this explanation presumably requires that micron-sized inclusions of pure glycerol are formed and that the interaction with the surrounding ice crystals can significantly increase the T_g of the domains, which seems unrealistic.

Recently, both DSC and dielectric spectroscopy have been used to study the phase and glass transitions as well as the relaxation behaviour above 150 K for glycerol/water mixtures [26–29]. The behaviour was studied from “water rich” [26] to “glycerol rich” [27] mixtures. In the glycerol rich range, which contain more than ∼77% (w/w) glycerol (40 mol%), only one main relaxation process was observed [27]. This is in correspondence with previous DSC results [11] and the results obtained here, which yield a single glass transition anomaly. That is, in this range, the mixtures become easily supercooled homogeneous liquids. For water rich mixtures, which yields partial crystallization on cooling, the spectrum in the range 1 Hz–250 MHz shows three dielectric relaxation processes at 218 K [26,28]. These were associated with the mesoscopic glycerol–water domains of maximum freeze-concentrated composition, pure water, and interfacial water, respectively [26]. The dielectric results thus indicate that three glass transitions, as observed here, could be visible in calorimetric data. As described above, two of these are confidently identified in the calorimetric data, and only the one associated with interfacial water remains. However, the relaxation time for the process is shorter than 10 ms at 180 K [26], which precludes that it could cause a glass transition at ∼200 K. In fact, extrapolation to low temperatures indicates that its glass transition should occur below the temperature range studied here.

On the basis of the available data for the glycerol/water system only, we can conclude that the origin of the high temperature anomaly described by Ablett et al. [18], seems most probable. It has been shown that cold crystallization occurs near this temperature for a quenched amorphous sample [13], and therefore that a supplementary crystallization is likely to occur upon heating of a rapidly cooled, and partly crystallized, sample. This also shows that the mobility of the water molecules is large so that ice dissolution, following the (extrapolated) equilibrium melting line should become feasible upon further heating. This picture requires that the equilibrium melting line is not followed down to the vitrification temperature on cooling, but it does not require a non-homogeneous glass. After a supplementary crystallization on heating, the sample would adopt the energetically favoured state on the extrapolated equilibrium melting line, and dissolution would be energetically favoured on further heating. (It should be noted that the most stable state requires that glycerol crystallizes, but it does not occur due to the vanishingly small nucleation rate.) This explanation seems most reasonable for the glycerol/water system, and in a recent detailed study of the sucrose/water system, Schawe [30] has concluded the same on the basis of convincing thermodynamic arguments.

4. Conclusions

Water–glycerol mixtures show a complex glass transition behaviour for compositions in the range 0–55% (w/w) fraction glycerol that crystallizes partly on cooling. In this composition range, three glass transition-like anomalies occur on heating from 80 K. A low-temperature anomaly at about 115 K is due to the reorientational motion of the H_2O-molecules in hexagonal ice. The associated glass transition temperature increases 7 K by adding 5% (w/w) glycerol (1 mol%), indicating that the glycerol molecules *decreases* the reorientational rate of the nearest neighbour H_2O-molecules. Due to the ice rules this has a strong effect also on ice molecules in the bulk. On further heating, the vitrified liquid of maximally freeze-concentrated solution exhibits a glass transition at about 164 K. Its composition ($C_3H_8O_3$:H_2O = 1:1.6) indicates that each hydrogen bond on the glycerol molecules is associated with one on a water molecule. A third anomaly in the temperature drift rate and a step increase the heat capacity occurs at ∼200 K, and it is most likely due to cold crystallization followed by ice dissolution, but a third glass transition cannot be completely ruled out.

The crystallization kinetics for a sample that could be cooled rapidly enough to avoid crystallization on cooling but crystallized on heating (samples with compositions ∼60% (w/w) glycerol) agrees with that found in previous studies of the structure [13,14]. The results show that the crystallization proceeds in two clearly distinguished steps, where the first step is associated with a large enthalpy change, and is attributable to crystallization into a two-dimensionally ordered structure. On further heating this structure transforms gradually into hexagonal ice, with only a small associated enthalpy of transformation.

The results for the glass transition temperature of the homogeneous glass of randomly mixed glycerol and water molecules extrapolates exactly to the experimentally determined glass transition temperature of 135 K for amorphous solid water (hyperquenched liquid water or water vapour) using the Gordon–Taylor equation [12]. This finding corroborates results of most experimental studies of the glass transition for amorphous solid water [4] but is in disagreement with a recent deduction [6–8].

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