

Ice Nanocrystals in Glycerol–Water Mixtures

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We discuss the minimum size of ice nanoparticles in water-rich glycerol–water mixtures, as studied by broadband dielectric spectroscopy (BDS) in the frequency range from 1 Hz to 250 MHz and differential scanning calorimetry (DSC) at the temperature interval from 138 to 313 K. It is known that the extra water which is free from the glycerol hydrogen bond network forms the water cooperative domain. This cooperative domain leads to a freezing of water. With the formation of the frozen water state, another distinct water structure forms on the interface between the ice nanocrystal and mesoscopic glycerol–water domain. The mole fractions of different stages of water (i.e., water molecules in the mesoscopic domain, ice nanocrystals, and the interface between the two) were determined, and the minimum number of water molecules that can gain the bulk ice properties was estimated as ~ 300 water molecules.

Introduction

Determination of the minimum number of molecules that can provide the bulk properties of the liquid or solid states is one of the fundamental questions of modern soft condensed matter physics. Using broadband dielectric spectroscopy (BDS),^{1,2} Kremer et al. have studied this problem with hydrogen-bonded (H-bond) liquids which are confined to zeolites and nanoporous glasses.³ They found, for example, that six ethylene glycol molecules are “sufficient for performing a liquidlike dynamic”,^{3,4} although it is still difficult to generalize such a number for different systems.³ In the case of crystals, it is probable that many more molecules are necessary to gain bulk properties. In fact, the study of infrared spectra combined with FT-IR and computer simulation for ice nanoparticles, which are prepared by rapid expansion of water vapor at 100 K within a vacuum container, indicates that a “...‘crystalline’ subsurface region exists down to a cluster size of ~ 3 nm or ~ 500 molecules”.⁵ On the other hand, it is known that rapid cooling of micrometer-sized water below the glass transition temperature of water (~ 130 K) under atmospheric pressure can lead to a glassy state of water (or amorphous ice) instead of ice I_h.⁶ Moreover, the effects of the low pressure on the ice nanocrystal are not fully clarified. Therefore, a study of ice nanocrystals prepared with relatively slow freezing rates at room pressure is important.

The consideration of glycerol–water mixtures below 40 mol % of glycerol at low temperatures gives a unique opportunity to study the so-called “water cooperative domains”⁷ that will lead to the formation of ice nanocrystals. It was shown that these water pools can be frozen at high water concentrations.⁸ The critical (minimum) size of the water pool which can be frozen would somehow be related to the minimum size of the ice nanocrystal.

It was found in our previous study that the freezing of the extra water (i.e., the water pools) in 20 mol % or lower concentration of glycerol–water mixtures causes an increase of the glycerol concentration of the mesoscopic domains up to 40 mol %.⁸ This critical mole fraction (x_g) would relate to the

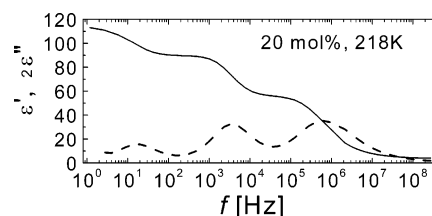


Figure 1. Typical dielectric spectrum of 20 mol % of the glycerol–water mixture at 218 K in the water-frozen state, where solid and dashed curves show the real and imaginary part of complex dielectric permittivity, respectively. Note that contribution caused by dc conductivity has already been subtracted from the imaginary part of the shown spectrum.

numbers of H-bonds of glycerol ($n_g \approx 6$; reported in ref 9) and water molecules ($n_w = 4$); thus, $x_g = 100\% \cdot n_w / (n_w + n_g) = 40\%$.^{8,10} The existence of the critical mole fraction of 40 mol % is also confirmed by differential scanning calorimetry (DSC) data and even by simple dc conductivity data.⁸ Figure 1 shows a typical dielectric spectrum of a glycerol–water mixture in the water frozen state. Three relaxation processes are observed: those that result from the mesoscopic glycerol–water domains (high-frequency process), ice particles (low-frequency process), and interfacial water between the two (middle-frequency process).⁸ The activation energy of ~ 33 kJ/mol corresponding to the interfacial water is similar to the reported values ~ 28 kJ/mol for bound water on protein surfaces in aqueous solutions.¹¹ The properties of the interfacial water and the size of the ice nanocrystals will be discussed in the current paper based on the BDS and DSC data.

Materials and Methods

The glycerol–water mixtures with alcohol content between 5 and 95 mol % and with steps of 5 mol % were prepared from anhydrous glycerol (product number 49767, Fluka, Buchs, Switzerland) and double-distilled water (resistivity 18 M Ω ·cm). BDS measurements were performed in the frequency range from 1 Hz to 250 MHz at temperatures from 173 to 323 K in steps of 3 K by using a Novocontrol BDS-80. All the measurements were performed after temperature stabilization starting from the

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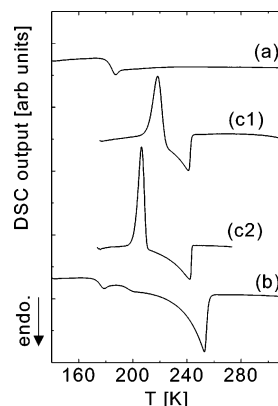


Figure 2. DSC curves of (a) 60, (b) 15, and (c) 20 mol % of glycerol–water mixtures. The heating rate is 10 K/min for all, except 2 K/min for (c2).

lowest temperatures to the higher temperatures, consecutively. DSC measurements of glycerol–water mixtures (80, 60, 40, 30, 20, 15, 10, and 2.5 mol % of glycerol) were performed by use of a DSC 2920 calorimeter (TA Instruments) in the temperature interval from 138 to 313 K (173–313 K for 20 mol %) with a heating rate of 10 K/min (additionally 2 K/min for 20 mol %). Both BDS and DSC data are partly reported in our previous papers.^{8,10} In the present paper, new DSC measurements of 20 mol % of glycerol–water mixtures were carried out, and further data analysis of BDS and DSC results was performed for the water-rich mixtures in order to determine the size of the ice nanocrystals.

Results and Discussion

The glass transition temperature (T_g) of glycerol is known as ~ 190 K.¹² In glycerol–water mixtures, the T_g decreases with increase of water content while the extra–water is not frozen.⁸ Figure 2a shows the typical DSC data of the 60 mol % glycerol–water mixture, where the glass transition was observed at around 181 K. In the water-rich mixtures, the extra water can be frozen during the cooling to the starting (lowest) temperature of DSC measurements. The T_g does not depend on concentration anymore and within measurement accuracy is equal to the T_g of the 40 mol % mixture (~ 170 – 172 K).⁸ In addition to the glass transition phenomenon, the broad melting behavior was observed by DSC measurements for water-rich mixtures, as shown in Figure 2b. Previously, the broad melting behavior was discussed in terms of the exchange rates in the kinetic description of three stages of water, such as ice, interfacial water, and water in the mesoscopic glycerol–water domain.⁸ In the particular case of the 20 mol % of glycerol–water mixture, the extra water was not frozen at the starting temperature of the DSC measurements. However, it was frozen during the measurements, and then the broad melting behavior was also continuously observed as shown in curves c1 and c2 of Figure 2. We note that the glass transition should also exist in the 20 mol % mixture; however, the T_g was beyond the temperature range of the DSC measurements for the 20 mol %. The shape and temperature of the crystallization peak were greatly dependent on the heating rate. Moreover, in the case of a faster heating rate of 10 K/min, this peak partly overlapped the temperature range of the broad melting behavior, as shown in Figure 2c1. In contrast, the shape and temperature of the broad melting behavior were not dependent on the heating rate. This result indicates that the broad melting is an equilibrium or quasi-equilibrium behavior where the amount of the ice is balanced by the water exchange rates.⁸

TABLE 1: Mole Fractions and Estimated Size of Ice Nanocrystals

χ	χ_{ice}	χ_{gw}	χ_s	r (Å)	N
0.025	0.72	0.04	0.21	37.2	6600
0.05	0.64	0.08	0.24	30.3	3600
0.10	0.44	0.15	0.31	17.5	690
0.15	0.32	0.23	0.30	13.6	320
0.20	0.25 ^a	0.30	0.25	13.1	290

^a The integration presented in eq 1 was carried out for the peak of the crystallization in DSC data in which the heating rate was 2 K/min.

The amount of ice in the glycerol–water mixtures can be estimated from the total melting enthalpy (ΔH) that can be obtained by integration of the transition heat capacity (ΔC_p) over the broad melting (or crystallization) temperature interval in the DSC data:

$$\Delta H = \int_{T_1}^{T_2} \Delta C_p dT = \int_{T_1}^{T_2} (C_p - C_{p(\text{baseline})}) dT \quad (1)$$

where T_1 is the starting temperature of the broad melting (or crystallization), T_2 is the end temperature of the phase transition, and $C_{p(\text{baseline})}$ is the extrapolated heat capacitance baseline in the same temperature interval.¹³ The weight fraction of ice at below the starting temperature of the broad melting can be estimated by the ratio $\Delta H/\Delta H_0$, where ΔH_0 is the melting enthalpy of bulk ice.¹⁴ Thus, the mole fraction of the ice in the glycerol–water mixture is

$$\chi_{\text{ice}} = \frac{\Delta H}{\Delta H_0} \frac{1 - \chi}{c_w} = \frac{\Delta H}{\Delta H_0} \frac{(1 - \chi)M_w + \chi M_g}{M_w} \quad (2)$$

where χ is the glycerol mole fraction, c_w is the total weight fraction of water, and M_g (92 g mol^{−1}) and M_w (18 g mol^{−1}) are the molecular weight of glycerol and water, respectively. On the other hand, the mole fraction of water in the mesoscopic glycerol–water domain would be $\chi_{\text{gw}} = 1.5\chi$, since the concentration of the mesoscopic glycerol–water domain is close to the critical concentration of 40 mol %. This critical concentration can be also confirmed by glycerol concentration dependence of the dielectric relaxation strength ($\Delta\epsilon$). In the water-frozen state, $\Delta\epsilon$ was monotonically increased with glycerol concentration, and it can be extrapolated to the value of 40 mol % glycerol. Thus, finally we can obtain the mole fraction of the interfacial water: $\chi_s = 1 - \chi - \chi_{\text{ice}} - \chi_{\text{gw}}$. Table 1 shows estimated mole fractions of the three stages of water for various concentrations of the glycerol–water mixtures in the water-rich region.

Let us now estimate the size of ice nanocrystals in the glycerol–water mixtures under an assumption of a spherical shape of the nanocrystals. The ratio of the volume fraction of the interfacial water (V_s) and the ice (V_{ice}) in the glycerol–water mixtures can be described by

$$\frac{V_s}{V_{\text{ice}}} = \frac{\chi_s/\rho_s}{\chi_{\text{ice}}/\rho_{\text{ice}}} = \frac{(r + d)^3 - r^3}{r^3} \quad (3)$$

where ρ_{ice} and ρ_s are density of the ice and the interfacial water, r is the radius of the ice nanocrystals, and d is the thickness of the interfacial water layer, respectively. For a rough estimation, we can substitute the density of bulk ice (0.917 g cm^{−3} at 273 K) and that of bulk water (1.000 g cm^{−3} at 273 K) for ρ_{ice} and ρ_s , respectively.¹⁵ To solve eq 3 for r , we have to estimate d considering the BDS data. The dielectric relaxation process due to the interfacial water was well described by the Cole–Cole

equation,⁸ and the Cole–Cole parameter α ($0 < \alpha \leq 1$) was close to unity (e.g., $\alpha = 0.96$ for 20 mol % at 218 K). This fact indicates that the dynamical structure of the interfacial water is well uniform.¹⁶ A model where a single layer of water surrounds the ice nanocrystal can satisfy this condition. Therefore, it would be reasonable to assume d as the corresponding distance of the single water layer (3.1 Å, estimated from the density of water). Under this consideration, we estimated the mean size and number of water molecules (N) of the ice nanocrystals and presented them in Table 1. Note that the most critical assumption in this evaluation is $\rho_s = 1.000 \text{ g cm}^{-3}$ because the density of the interfacial water is experimentally unknown. However, our simple estimations with the known value of low-density amorphous ice^{6,15} (0.94 g cm^{-3}) show that using this value the maximum error in radius evaluation should be $\sim 3\%$.

The smallest number of water molecules presented in Table 1 is $N = 290$ for the 20 mol % glycerol–water mixture. This number is quite reasonable, as a computer simulation study of ice nanocrystals is well performed in the 293–water system.¹⁷ We note that the estimated number of water molecules in the ice nanocrystals was dramatically increased for 5 and 2.5 mol % of glycerol–water mixtures. In contrast, the increase of glycerol concentration, especially for 15 and 20 mol % of glycerol, leads the size of the ice nanocrystal to converge to $\sim 1.3 \text{ nm}$ in its radius. With further increase of glycerol concentration (25 mol %), it became very difficult to obtain stable ice nanocrystals. Thus, we suppose that the minimum size of the ice nanocrystal in glycerol–water mixtures consists of ~ 300 water molecules. This size of ice nanocrystal is enough to gain the same values of the macroscopic parameters of bulk ice such as the dielectric relaxation time and the activation energy.^{8,18}

References and Notes

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