# Hydrogen Bond Induced Nonmonotonic Composition Behavior of the Glass Transition in Aqueous Binary Mixtures

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ABSTRACT: The glass transition temperature, T_g, of a binary mixture commonly varies monotonically between the T_gs of its two components. However, mixtures of strongly associating liquids can instead exhibit a nonmonotonic T_g variation. The origins of such nonideal mixing behavior have often been correlated with composition dependent structural variations. For binary mixtures between a hydrogen- (H−) bonded liquid and water, however, such behavior is generally not well understood. The ubiquity and importance of aqueous mixtures both in nature and in man-made applications stresses the needed for a better understanding. We here demonstrate nonmonotonic T_g variations in binary mixtures of n-propylene glycol monomethyl ethers (nPGMEs) and water, where the composition dependent T_g show maxima within an intermediate composition range. We show that these T_g maxima correspond to crossovers in the composition dependence of the step amplitude in the isobaric heat capacity at T_g. We further demonstrate that the observed effects are caused by H-bond interactions involving the nPGME hydroxyl group. We can account for our obervations using a simple model based on two effects due to the added water: (i) an H-bond induced formation of effective relaxing entities and (ii) a plasticizing effect at high water contents.
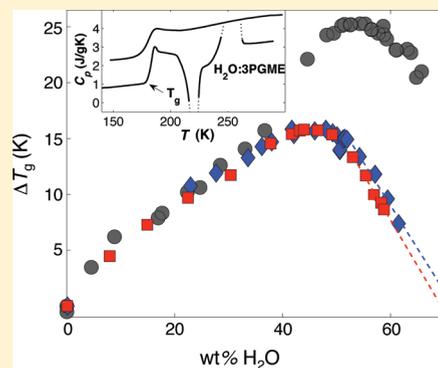
The macroscopic properties of a liquid are closely linked to its structural α relaxation. As a liquid is cooled into its supercooled regime, its α relaxation undergoes a dramatic slowing down, which remains poorly understood. As the characteristic time scale of the α relaxation exceeds the longest probed experimental time scale, ∼100 s, the sample falls out of thermal equilibrium and effectively forms a disordered solid—a glass. The temperature where the liquid leaves equilibrium is called the glass transition temperature, T_g, and is an important characteristic of any glass-forming material. For binary mixtures of glass-forming liquids, the T_g values normally vary monotonically between the component T_gs and are often described using the so-called Gordon−Taylor (G−T) equation,[1] which assumes ideal mixing and can be derived using free-volume arguments.[2] Also nonideal mixtures often show monotonic T_g variations and the G−T equation can sometimes still qualitatively describe the composition behavior.

In contrast, there are several examples of binary mixtures that show a nonmonotonic behavior. First, these include a few covalently bonded binary structural glasses,[3−5] such as the binary mixture $As_x−Se_{1-x}$. This binary glass has a T_g maximum at the composition $x = 0.4$, for which a maximum number of As−Se bonds are formed; since As−Se bonds are stronger than either As−As or Se−Se bonds the result is a T_g maximum.[4] Second, nonmonotonic behaviors are observed for H-bonded mixtures of amines (R-NH$_2$) and alcohols, where a T_g maximum is observed for nearly equal molar concentrations;[6−9] this behavior can be accounted for by the improved H-bonding ability of the mixed

state.[8,10] A third example is the nonmonotonic composition dependence observed for mixtures of deoxycholic acid and tri-O-methyl-$β$-cyclodextrin that are mixed and vitrified by mechanical milling.[11] These observations were also suggested to result from composition dependent structural changes since both components are known to form inclusion compounds. Thus, a common theme for systems where nonmonotonic T_g behaviors occur is the existence of significant composition dependent structural variations.

An important class of binary mixtures consists of an H-bonding liquid and water. Aqueous liquid mixtures are ubiquitous both in nature and in technology, and important examples include the sugar solutions in plants, the cytoplasm of our cells and the cryoprotectants used for protein storage.[12] Examples of nonmonotonic T_g variations for completely amorphous aqueous systems have to our knowledge only been observed for aqueous butyltripropylammonium chloride (BTPC),[13] which shows a T_g maximum for intermediate water concentrations.[13,14] The effect was suggested to be related to the formation of clathrate type water structures induced by the polar end-groups of BTPC, but significant phase separation and thus multiple T_gs complicate the analysis. To our knowledge, all other reports for single-phase aqueous mixtures show monotonic T_g variations within the composition range where no crystallization is observed.

For water that is mixed with an alcohol, the mixing entropy is often clearly lower than that expected for an ideal mixture. This has traditionally been interpreted as due to solute induced structuring of water.[15] However, neutron diffraction studies together with empirical potential structure refinement techniques have revealed that the low mixing entropy can instead be rationalized as due to nanoscopic phase segregation.[16,17] For water–methanol mixtures, support was found for a scenario where water, at low concentrations, form clusters that are strongly coordinated to the hydroxyl groups of the surrounding methanol molecules.[16,18] The methanol hydroxyl groups act as links between the hydrophobic methyl groups and the water clusters and it was also found that the methyl groups themselves display clustering. The room temperature viscosity of the mixture displays a nonmonotonic concentration dependence with a maximum observed for a water–methanol molar ratio of ∼3:1 and it has been found that at this composition both the water molecules and the methyl groups form percolating networks.[18] The "local" water structure in such mixtures was observed to be remarkably similar to that of pure water. Because of interference from crystallization, however, systematic investigations of mixtures of water and monoalcohols have rarely been carried out in the supercooled temperature range.[19,20]

We here address the present lack of understanding of mixed aqueous systems by performing a systematic investigation of the glass transition behavior of mixtures of water and a series of model H-bonded liquids, n-propylene glycol monomethyl ethers, nPGMEs, with the structure $CH_3-[OCH_2CH(CH_3)]_n-OH$ where $n = 1, 2, 3$ for the monomer, dimer and trimer, respectively. In aqueous mixtures, all three liquids show nonmonotonic T_g behaviors with maxima at intermediate water fractions; this behavior contrasts the commonly observed monotonic variation between the components T_gs. We demonstrate that the observed behavior is directly related to the presence of hydroxyl endgroups on the nPGME molecules and show that the effect disappears if these are exchanged for non-H-bonding groups. We further find that nonmonotonic T_g behaviors are observed also for mixtures of nPGMEs and several other H-bonded liquids. We are able to account for our observations using a simple model based on the H-bond mediated building up of larger effective structural units upon addition of water, and a water-induced plasticizing effect at high water concentrations.

■ EXPERIMENTAL SECTION

All liquids were purchased from Sigma-Aldrich and freeze-dried before measurements.[21] We characterize the glass transitions by measuring the calorimetric heat capacity, C_p, for cooling/heating rates of $-30/+10$ K min^{-1} using a differential scanning calorimeter (TA Instruments, Q1000). The experimental procedure is described in more detail in ref.[22] C_p exhibits a step at T_g as the structural relaxation time crosses the time-scale set by the cooling/heating rate. Both the T_g values, determined as the onsets of the heat capacity steps upon heating, see the inset of Figure 1, and the heights of the steps in C_p at T_g, ΔC_p, were determined.

■ RESULTS

The results of the calorimetric measurements of water–nPGME mixtures, are shown in Figure 1. On cooling, no sign of crystallization is found for any sample, see inset of Figure 1. On heating, all samples reveal one distinct glass transition. At high water
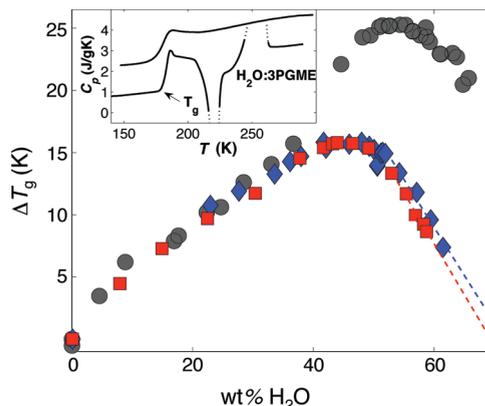
Figure 1. Difference in glass transition temperatures from that of the pure materials, $\Delta T_g = T_g - T_g^{pure}$, as a function of water weight fraction for water-nPGME mixtures, $n = 1$ (○), 2 (◇), and 3 (□). The dashed lines are linear extrapolations for the concentration range above ∼50 wt %. The inset shows the isobaric heat capacity, C_p, for a water-3PGME mixture with 55 wt % water. The cooling data (upper data set) exhibit one distinct glass transition and no crystallization. The heating data (lower data set) display one glass transition, one crystallization and one melting event. For clarity, the cooling curve is shifted by +1.5 J g^{-1} K^{-1}.

contents (>51, 40, and 38 wt % for $n = 1, 2, 3$) one crystallization and one melting event supersedes the glass transition upon heating. We find no indications of phase separation for any of the samples. ΔT_g, the difference in T_g between the mixture and the corresponding pure nPGME (T_g^{pure}=143.6, 162.3, 168.7 K for $n = 1, 2, 3$) are shown in Figure 1. An initial growth of ΔT_g with increasing water content is observed for all three systems, but for intermediate water fractions a maximum in ΔT_g is reached above which ΔT_g decreases monotonically. The results for $n = 2$ and 3 are essentially identical throughout the whole concentration range, with a maximum $\Delta T_g = 16$ K observed at 45 wt % water (corresponding to 6.7 and 9.2 water molecules per nPGME molecule, respectively). The monomeric system shows the same qualitative behavior, but here ΔT_g shows an abrupt increase at ∼37 wt % (∼75 mol %) water and the maximum $\Delta T_g = 25.5$ K takes place for 55 wt % water.

For binary aqueous mixtures it is not possible to cover the full concentration range, ranging from one pure material to the other, due to crystallization at high water contents. Thus, to better understand the variation over the full concentration range, we also measure the calorimetric T_g in mixtures of PGME ($n = 1$) and a 33 mol % aqueous hydrogen peroxide (H_2O_2) solution. Aqueous H_2O_2 is a good glass-former and shows strong similarities to pure water regarding boiling and melting points, permittivity, viscosity and T_g dependence upon addition of salts.[23,24] We find a nonmonotonic variation of T_g with a maximum in ΔT_g of ∼10 K around 30 wt % solvent, as shown in Figure 2. This nonmonotonic behavior is consistent with that observed for the mixtures of water and nPGMEs. Note that we are here able to measure T_g over the full range from pure PGME to pure 33 mol % H_2O_2/water solution. To further investigate the generality of these results, we also investigate mixtures of 3PGME and propylene glycol (PG). The latter is a H-bonded liquid with glass-transition related dynamics that have been suggested to resemble that of water.[25] As shown in Figure 2, mixtures of 3PGME and PG also show nonmonotonic T_g behavior very similar to that observed for PGME and the
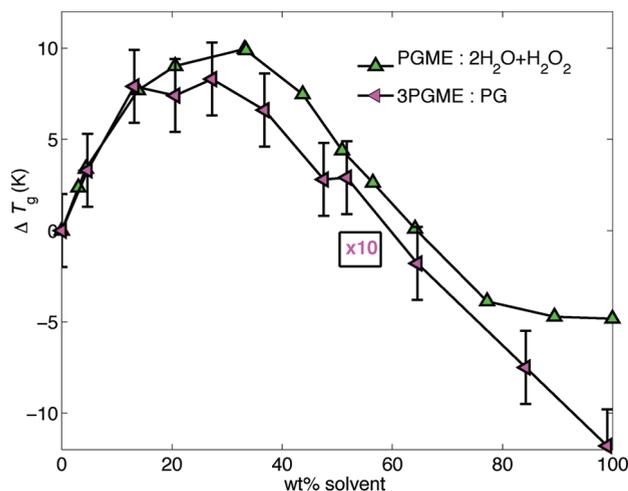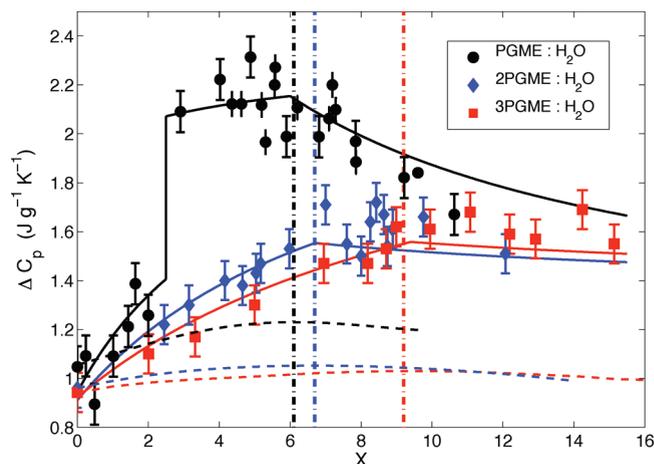
Figure 2. Difference in glass transition temperatures from that of the pure materials, $\Delta T_g = T_g - T_g^{pure}$, as a function of solvent weight fraction for mixtures of PGME and 33 mol % aqueous H_2O_2 (Δ) and 3PGME and PG (triangle pointing left), respectively. For the latter system the ΔT_g have been multiplied by a factor of 10 to facilitate an easy comparison between the two data sets.

Figure 3. Heat capacity step, ΔC_p, at T_g for nPGME-water mixtures for $n = 1$ (circles), 2 (diamonds), and 3 (squares) as a function of the water/nPGME molar ratio, X. The dashed lines represent the increase in ΔC_p only taking the increased T_g into account (see the text for details). The vertical dash-dotted lines indicate the concentrations where T_g reaches maximum values, as shown in Figure 1. The solid lines are explained in the text.

aqueous H_2O_2 solution; the effects are, however, considerably less pronounced. Thus, we conclude that the nonmonotonic concentration variation of T_g for nPGME is observed both in aqueous mixtures and in mixtures of similar nature.

Returning to the aqueous nPGME system, we find that for low water contents, all three nPGMEs show a systematic increase of ΔC_p as the statistical number of water molecules per nPGME molecule, X, increases, as shown in Figure 3. A small increase in ΔC_p is expected for increasing X only due to the increase in T_g, since $\Delta C_p = T_g \left[(\partial S^{liquid}/\partial T)_p - (\partial S^{glass}/\partial T)_p \right]$, where S is the entropy. The effects on ΔC_p arising solely from this composition dependent T_g are shown in Figure 3 as dashed lines; these effects clearly give only a small contribution to ΔC_p. Thus, the main contribution to the increase in ΔC_p results from a change in the T-dependence of the entropy at T_g. For all mixtures, ΔC_p increases with water content up to the concentration where T_g has a maximum. These concentrations are marked by the vertical dash-dotted lines in Figure 3. A crossover in the ΔC_p behavior at a composition corresponding to the maximum in ΔT_g is common to all three systems. The monomer shows a behavior qualitatively similar to that of the dimer and trimer, but consistent with its ΔT_g behavior, a sudden increase in ΔC_p is observed at the corresponding concentration. For large water concentrations, ΔC_p level out or even decrease slightly for all three systems.

■ DISCUSSION

Several studies have demonstrated the important role of H-bonding via the hydroxyl end-groups for the dynamics of pure oligomeric propylene glycols; both light scattering and dielectric relaxation studies have demonstrated polymer-like dynamics already for chains of seven repeat units, suggesting the formation of H-bond mediated effective chains.[25,26] Moreover, the glass-transition dynamics of nPGMEs were compared to those of n-propylene glycol dimethyl ethers, nPGDEs, which share the same monomeric unit but lack the hydroxyl end-groups and thus H-bonding. The results indicate that the molecular entities characteristic of the structural relaxation are larger than the individual

molecules meaning that effective relaxing units (ERU) are formed. The size of these ERUs were estimated and it was suggested that pure nPGMEs effectively form ERUs of two molecules through an H-bond mediated coordination of hydroxyl end-groups.[25]

As water is added to the nPGMEs, we expect the water molecules to preferentially coordinate to the strongly H-bonding hydroxyl end-groups, thus increasing the size of the ERUs and in turn leading to an increase in both ΔT_g and ΔC_p. It is interesting to note the analogous behavior for mixtures of methanol and water, where the added water form clusters that are strongly coordinated to the hydroxyl groups of the surrounding methanol molecules.[16] Because of the dynamic nature of H-bonds, we expect that an ERU saturates at some effective size, corresponding to a characteristic number of water molecules per hydroxyl group. Such a saturation should be directly manifested as a crossover in the composition dependence of both ΔT_g and ΔC_p. Referring to the behavior shown in Figure 1 and 2, the simplest interpretation of the maximum observed in ΔT_g and the corresponding crossover in the temperature dependence of ΔC_p is thus that these are manifestations of this behavior.

To test the hypothesis that the hydroxyl (OH−) end-groups play a key role in the observed mixture behavior, we also study mixtures of water and tripropylene glycol dimethyl ether, 3PGDE, which has the same structure as 3PGME except that its OH-end group has been exchanged for a methoxy group (O−CH$_3$). For aqueous 3PGDE mixtures, single T_g solutions are formed up to concentrations ∼20 mol % water. As shown in Figure 4, we find that T_g decreases monotonically within this concentration interval, in contrast to the behavior observed for 3PGME; this suggests a T_g < 150 K for pure water. For pure water, the supercooled temperature range, 150 < T < 235 K,[27,28] is largely inaccessible due to crystallization and there is thus still no concensus regarding its T_g value. The traditional interpretation of the available data is that water has a $T_g \sim 130-140$ K, but widely different values including $T_g \sim 165$ K[29,30] or $T_g \sim 228$ K[31] have also been suggested. Taking into account the limited data
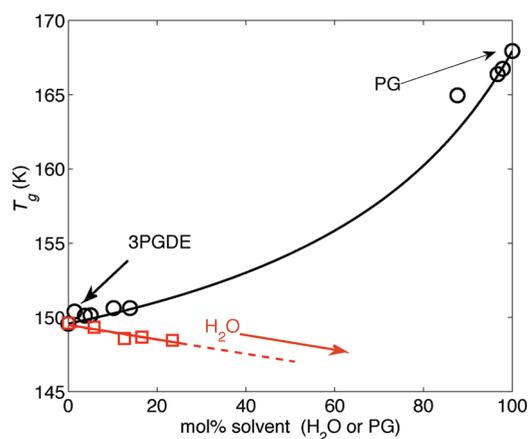
Figure 4. Composition dependent T_g for mixtures of 3PGDE and PG (circles) as well as 3PGDE and H_2O (squares). The upper solid (black) line represents the volume weighted average between the two pure components. The red line is a guide to the eye.

range for this system, the results suggest a monotonic composition behavior with a T_g for water ~140 K; we note that this value is in agreement with results from extrapolations of T_g for dilute salt solutions.[32,33] It is also interesting to note that simple linear extrapolations of the ΔT_g data, as shown in dashed lines in Figure 1, suggest that $T_g = 141$ and 144 K at 100% water for the 2- and 3PGME mixtures, respectively. Moreover, a similar result with $T_g \sim 136$ K has been obtained from extrapolations of data for aqueous butyltripropylammonium chloride.[14] However, it is important to keep in mind that the relation between the extrapolated T_g behavior for dilute solutions and that of pure bulk water is far from clear.[31,34]

To investigate the behavior for 3PGDE mixtures over a wider concentration range we study mixtures of 3PGDE and PG, as these liquids are miscible for concentrations <15 or >90 mol % PG. Consistent with the aqueous mixture results, we find support for a monotonic T_g variation, which over the measured composition range is well described by the prediction for a volume weighted average of the two components. We thus conclude that the nonmonotonic effects observed for the nPGME:s are directly related to the presence of the nPGME OH-group. It is interesting to compare these results with recent studies[22,34] on aqueous mixtures of n-propylene glycols, nPG, which share its monomeric molecular structure with nPGME, but have hydroxyl groups in both ends. The chain-ends of pure nPGs readily hydrogen bond, which already for the pure materials leads to the formation of extended hydrogen bonded structures.[25,26] The two hydroxyl groups of nPG thus leads to different hydrogen bond induced structures compared with those found in nPGME, for which the ERUs were estimated to be composed of 2 molecular units instead of the ~8 estimated for nPG.[25] Also, due to the hydrophilic nature of both its ends, nPG is expected to coordinate differently compared with nPGME in aqueous mixtures. In agreement with this, and as demonstrated in refs 22 and 34, addition of water to nPG leads to a monotonic decrease of T_g, which strongly contrasts the nonmonotonic concentration dependence of the nPGME mixtures. We can thus conclude that the behavior observed for nPGMEs is a direct result of its single hydroxyl end-group.

To quantify the role played by OH-groups, we calculate the contribution to the heat capacity step per mole of nPGME
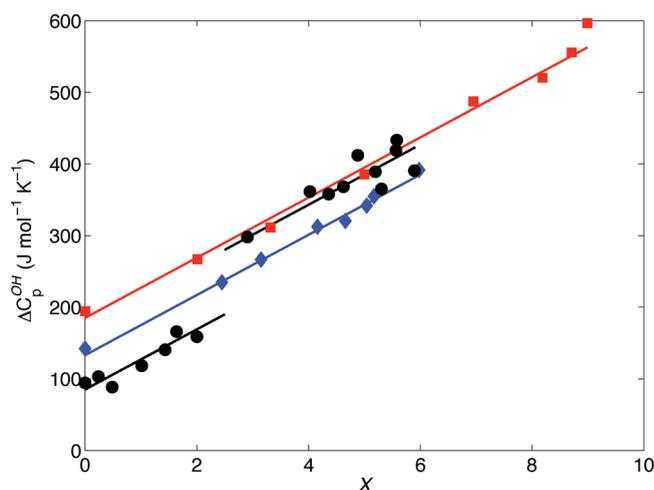
Figure 5. Amplitude of the step in the heat capacity at T_g per mole of hydroxyl groups ΔC_p^{OH} as a function of the number of water molecules per nPGME molecules for $n = 1$ (circles), $n = 2$ (diamonds) and $n = 3$ (squares). The solid lines represent a contribution to ΔC_p of 41 J mol^{-1} K^{-1} for each water molecule statistically added per hydroxyl group.

OH-groups, ΔC_p^{OH}:

$$\Delta C_p^{OH} \ [\text{J} \ mol^{-1} \ \text{K}^{-1}] = \Delta C_p \ [\text{J} \ g^{-1} \ \text{K}^{-1}]$$

$$\times w_{n,PGME}^{-1} \ [g/g]$$
$$\times M_{n,PGME} \ [g \ mol^{-1}]$$

where ΔC_p is the heat capacity per unit mass of sample, $w_{n\text{PGME}}$ is the mass fraction and $M_{n\text{PGME}}$ is the molar mass of nPGME, respectively. ΔC_p^{OH} is shown as a function of X, the statistical number of added water molecules per OH-group, in Figure 5, for concentrations below saturation. For the 2- and 3PGME mixtures, we find identical linear increases of ΔC_p^{OH} with increasing X, corresponding to a contribution of ~41 J mol^{-1} K^{-1} to ΔC_p^{OH} per added mole of water. Thus, below the saturation concentration, each water molecule statistically added per OH-group brings a well-defined contribution to the heat capacity step. This contribution of ~41 J mol^{-1} K^{-1} together with the ΔC_p values for the pure 2- and 3-PGME, respectively, predict the behavior of ΔC_p vs water weight fraction in the composition range below the maximum in ΔC_p, as shown with solid lines in Figure 3. It is interesting to compare the value 41 J mol^{-1} K^{-1} to $\Delta C_p = 22 \pm 3$ J mol^{-1} K^{-1}, which is estimated for pure water from extrapolation of calorimetry results for dilute aqueous salt solutions.[32,33]

As demonstrated in Figure 1 and 2, the behavior of the PGME monomer differs from that of the dimer and trimer by the change in both ΔT_g and ΔC_p occurring for a water mole fraction ~3; this behavior is a strong indication of a structural change. Interestingly, as shown in Figure 5, we find that the slope of ΔC_p^{OH} vs X is the same before and after this change. Thus, except for the structural change observed for the monomeric system, all three systems behave in a highly similar manner, each with the same contribution to ΔC_p^{OH} per added mole of water.

For water contents above the maximum in ΔC_p, ΔC_p levels out or even decreases slightly, as shown in Figure 3. On the basis of the hypothesis that ERUs grow until the maximum value of ΔC_p is reached, we speculate that for higher water contents the excess water coexists with the saturated ERUs, acting as a plasticizer and thus resulting in a T_g decrease. As discussed above, it is here

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interesting to note that for water concentrations above those corresponding to the viscosity maximum in methanol—water mixtures, neutron diffraction studies demonstrate a percolating water phase with a local structure similar to that of pure water,[16] Therefore, to describe the ΔC_p behavior at high water concentrations, we use a molar weighting between the literature value for pure water, $\Delta C_p = 22$ J mol^{-1} K^{-1},[32,33] used as characteristic of the excess water, and the maximum ΔC_p value. The results are shown as solid lines in Figure 3, and we find that this simple approach can describe the data well.

The effects observed in this work, both for ΔT_g and ΔC_p, correspond to dynamics and thermodynamics acting on timescales ~100s. If higher temperatures, or correspondingly shorter time-scales are investigated, one expects to observe less pronounced effects since it is well-known that H-bond interactions are less effective at high temperatures.[35] Consistent with this, using quasielastic neutron scattering, QENS,[36] which probes time-scales of the order of 10—100 ps, a nonmonotonic variation of ~5 K was observed for 2PGME-water mixtures[37] instead of the 15 K observed in this work. This result is in agreement with the observed degree of nonmonotonic concentration dependence of the room temperature viscosity of water—methanol and water—ethanol mixtures[38] as well as the observation that the nanoscopic segregation in water—methanol mixtures is enhanced by cooling.[39]

■ CONCLUDING REMARKS

In conclusion, we here present nonmonotonic composition variations of the glass transition temperature in binary mixtures of n-propylene glycol monomethyl ethers (nPGMEs) and water. We demonstrate that the observed effects are directly related to the presence of nPGME hydroxyl groups and show that the T_g maxima correspond to crossovers in the composition dependence of the step amplitude in the isobaric heat capacity at T_g. Using a simple model based on (i) the formation of H-bond induced effective relaxing entities and (ii) a plasticizing effect at high water contents where the relaxing entities have reached a maximum size, we account for our observations. Our results stress the importance of future work aimed at reaching a better quantitative understanding of the effects of hydrogen bond induced structure formation in binary glass forming liquids.

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■ ACKNOWLEDGMENT

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