The Johari−Goldstein β-Relaxation of Water

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There is a plethora of experimental data on the dynamics of water in mixtures with glycerol, ethylene glycol, ethylene glycol oligomers, poly(ethylene glycol) 400 and 600, propanol, poly(vinyl pyrro1idone), poly(vinyl methylether), and other substances. In spite of the differences in the water contents, the chemical compositions, and the glass transition temperatures T_g of these aqueous mixtures, a faster relaxation originating from the water (called the ν-process) is omnipresent, sharing the following common properties. The relaxation time τ_ν has Arrhenius temperature dependence at temperatures below T_g of the mixture. The activation energies of τ_ν all fall within a neighborhood of 50 kJ/mol. At the same temperature where mixtures are all in their glassy states, the values of τ_ν of several mixtures are comparable. The Arrhenius temperature dependence of τ_ν does not continue to higher temperatures and instead it crosses over to a stronger temperature dependence at temperatures above T_g. The dielectric relaxation strength of the ν-process, $\Delta\epsilon_\nu(T)$, has a stronger temperature dependence above T_g than below, mimicking the change of enthalpy, entropy, and volume when crossing T_g. These general property of the ν-process (except for the magnitude of the activation energy) had been found before in the secondary relaxation of the faster component in several binary nonaqueous mixtures. Other properties of the secondary relaxation in these nonaqueous mixtures have helped to identify it as the Johari-Goldstein (JG) secondary relaxation of the faster component. The similarities in properties lead us to conclude that the ν-processes in water mixtures are the JG secondary relaxations of water. The conclusion is reinforced by the processes behaving similarly to the ν-process found in 6 Å thick water layer (two molecular layers) in fully hydrated Na-vermiculite clay, and in water confined in molecular sieves, silica hydrogels, and poly-(2-hydroxyethyl methacrylate) hydrogels.

1. Introduction

Study of the molecular dynamics of glass-forming binary mixtures of water with other substances is interesting for fundamental understanding of glass transition as well as for practical purposes such as sugar/water mixtures in food science. The substances used to mix with water include ethylene glycol,[1] ethylene glycol oligomer (EGO) with various numbers of repeat units,[2−4] glycerol,[5,6] *n*-propylene glycol (*n*PG with *n* = 2, 3),[7] tripropylene glycol,[8] fructose,[9] poly(ethylene glycol) (PEG),[4,10] propanol,[11] poly(vinylpyrrolidone) (PVP),[10,12] and poly(vinyl methylether) (PVME).[13] Since pure water crystallizes on cooling, its relaxation dynamics in the supercooled state cannot be deduced from various experiments without uncertainty and controversy including the glass transition temperature, T_g. Therefore, the study of mixtures with water which do not crystallize, serves yet another purpose—that is, to infer, from the observed relaxation dynamics of water in the mixtures at various concentrations, the properties of supercooled pure water in its inaccessible temperature range below about 235 K. In many mixtures, a relaxation process attributed to water was observed by dielectric spectroscopy[14] in wide temperature ranges, and in some cases down to below 136 K, the putative onset of glass transition temperature of vitreous water.[15] We

follow ref 14 in referring these water-related relaxation processes categorically as the ν-process.

Due to its small size and preeminence of hydrogen bonding, water can be expected to behave differently than other glass-former molecular substances in the pure state or in mixtures. However, when interpreting the dynamics of water as a component in binary mixtures, it is beneficial to be aware of the general physics of component dynamics established for mixtures of other glass-formers including small molecules[16−19] and amorphous polymers.[20] This is precisely one of the purposes of this paper. We also have the occasion in this paper to discuss the dynamics of pure water in pores of hydrophilic polymers and in other matrices, in the form of ultrathin films, as well as in the bulk state. It is also beneficial to compare the observed dynamics of water under these conditions with the established general properties of other glass-forming substances. For the latter, the structural α-relaxation occupies most attention because it is responsible for the observed glass transition. In addition to the α-relaxation there is the universal Johari−Goldstein (JG) secondary relaxation that transpires at an earlier time.[21] The JG relaxation is local and not as prominent as the α-relaxation because of weaker relaxation strength. Nevertheless, it plays a fundamental role as the precursor of the α-relaxation and becomes the only type of motions observed at high temperatures. The fundamental role of the JG relaxation is best brought out

by its presence in totally rigid glass formers.[21] Since rigid molecules have no internal degree of freedom, the JG relaxation therein cannot be assigned to any trivial secondary relaxation (i.e., motion of an isolated part of the molecule). It must involve motion of the molecule as a whole, thereby acting naturally as the precursor of the cooperative many-molecule α-relaxation. Other indications of the fundamental nature of the JG relaxation are its having many properties mimicking that of the α-relaxation, albeit less spectacular.[22] These properties include, for its relaxation time τ_{JG}, the pressure dependence, sensitivity to aging and thermal history, non-Arrhenius temperature dependence above T_g, and merging of τ_{JG} with τ_α, the α-relaxation time.[22] At any fixed τ_α, the separation of the two relaxations, measured by $\log(\tau_\alpha/\tau_{JG})$, correlates with the width of the dispersion of the α-relaxation for many glass-formers.[22] Another correlation between JG relaxation and the α-relaxation was found recently by nuclear magnetic resonance techniques.[23] Its relaxation strength, $\Delta\epsilon_{JG}$, has stronger temperature dependence above T_g than below T_g,[24,25] similar to the temperature dependences of enthalpy, volume and entropy. All the above-mentioned properties can be used as criteria to distinguish the important JG secondary relaxations from other secondary relaxations as far as glass transition is concerned.[22] JG relaxation of a component in binary mixtures also bears the same relations to the α-relaxation of the same component, and have the same properties as JG relaxations of pure glass-formers.[16–19] Hence, it is proper to compare the properties of the ν-process observed in aqueous mixtures with those of JG relaxation.

In the following sections, the general properties of component dynamics found in other mixtures and blends are reviewed and compared with the data of the mixtures with water. The main thrust in making these comparisons is to show that the ν-process is actually the local secondary relaxation of water in the mixtures, which becomes the Johari-Goldstein (JG) secondary relaxation of pure water when the data of mixtures are extrapolated to that limit. Special attention is paid to propanol-water mixtures.[11,14] Because T_g of propanol is lower than that of pure water by any estimate, the ν-process appears at a frequency lower than that of the α-relaxation of the mixture and has properties resembling the JG secondary relaxation of pure water. We also consider the relaxation of water in silica hydrogels,[26,27,28] in fully hydrated Na-vermiculite clay,[29,30] and in poly(2-hydroxyethyl methacrylate) (PHEMA).[31–34] We compare the relaxations of water in these three cases with the relaxation of some other glass-formers that are confined in spaces with dimension less than a few nanometers. One observed common feature is that the relaxation time has Arrhenius temperature dependence. Also, the observed α-relaxation is faster than in the bulk and its τ_α is located not far from the JG relaxation time τ_{JG} of the bulk glass-former. Thus, the similarities of behavior in nanoconfinement suggest that the relaxation of nanoconfined water with Arrhenius temperature dependence is the JG relaxation of bulk water. This identification of this relaxation in nanoconfined water is further supported by the near coincidence of its relaxation time with that of the JG relaxation time of water inferred from the ν-process in some water mixtures. The paper ends with the conclusion that the JG relaxation of water has been found and located.

2. The Primary α-Relaxation and JG β-Relaxation of a Component: Mixtures of Molecular Liquids and Polymers

Experiments which probe selectively the relaxation dynamics of a component in a binary homogeneous mixture are most informative. This ideal situation was achieved in broadband dielectric relaxation measurements by choosing the probed component to have much larger dipole moment than the other component. Oligomers of styrene and polystyrene mix well with many glass-formers, and are ideal for being used as the unseen component because the dipole moment of the styrene repeat unit is very small and the response is close to the resolution limit of conventional dielectric spectrometers. Outstanding examples in the pioneering work by Blochowicz and Rössler[16,17] include mixtures of 2-picoline (a small molecule glass-former with comparatively large dipole moment ($\mu = 2.1$ D) and a glass transition temperature of $T_g = 133.6$ K, with tristyrene ($T_g = 234$ K), or with polystyrene having molecular weight $M_n = 1020$ and $T_g = 300$ K, or with polystyrene having molecular weight $M_n = 2140$ and $T_g = 331$ K. By weight, the concentrations of 2-picoline range from 5% to 100% in the 2-picoline/tristyrene mixtures. The dielectric spectra show two distinctly different relaxation processes all originating from motions of the polar molecule component (2-picoline) in the mixtures. The relaxation time, $\tau_{\alpha p}$, of the slow one has Vogel−Fulcher−Tammann−Hesse (VFTH) temperature dependence down to times as long as 10^2 or 10^4 s (for data from several mixtures, see Figure 1), just like the primary α-relaxation of neat 2-picoline and other glass-formers. The steepness index,[35] m, of τ_α of 2-picoline in the mixture is larger than that of neat 2-picoline. It increases with decreasing concentration of 2-picoline in the mixture, corresponding to a stronger T_g-scaled temperature dependence of $\tau_{\alpha p}$. For each mixture, a dielectric T_{gp} of the polar component (2-picoline) is defined as the temperature at which $\tau_{\alpha p}(T_{gp}) = 10^3$ s. At temperatures near and below T_{gp}, the temperature dependence of $\tau_{\alpha p}$ changes from the VFTH dependence above T_{gp} to the Arrhenius dependence. The other observed relaxation process, being faster, is by definition a secondary relaxation of 2-picoline in the mixture. This secondary relaxation has the characteristics of the Johari-Goldstein β-relaxation,[18,22,36] which include the increase of its relaxation time, $\tau_{JG,p}$, on elevating pressure[37,38] and the fact that 2-picoline is a rigid molecule. Secondary relaxations of rigid molecules must involve the entire molecule and hence they necessarily belong to the class of Johari-Goldstein β-relaxations. The T_g of 2-picoline is 100 K lower than tristyrene, and 197 K lower than polystyrene with $M_n = 2140$.

Independent measurements were made on the dynamics of two other polar rigid small molecules, *tert*-butylpyridine (TBP) ($T_g = 164$ K) and quinaldine (QN) ($T_g = 180$ K) in mixtures with tristyrene and oligomers of styrene with concentration ranging from 5 wt % to 100% of TBP and QN.[39,40] Again, two relaxation processes originating exclusively from the motions of the polar molecules are found (see Figure 2). The α- and JG β-relaxations of TBP or QN in mixtures have properties exactly analogous to that of 2-picoline in mixtures, including the pressure dependence of the JG β-relaxation time.[39,40] For mixtures with concentrations below 50% of 2-picoline, 60% of TBP, and 40% of QN, the JG relaxation appears as a well resolved peak in the dielectric loss spectrum. The JG loss peak frequency $\nu_{JG,p}$, and hence also $\tau_{JG,p} \equiv 1/2\pi\nu_{JG,p}$, is determined unequivocally without the need of using any assumed procedure to fit the spectrum. The so obtained $\tau_{JG,p}$ of 2-picoline, *tert*-butylpyridine, and quinaldine in the mixtures all have a peculiar temperature dependence across T_{gp}. Below T_{gp}, the temperature dependence of $\tau_{JG,p}$ is Arrhenius, but it changes to a much stronger temperature dependence at higher temperatures after crossing T_{gp}. Furthermore, the dielectric relaxation strength of the JG relaxation, $\Delta\epsilon_\beta(T)$, has a stronger temperature dependence above T_{gp} than below (see Figure 3), a feature found also for JG relaxation in neat glass-formers.[22] These general properties of the JG relaxation, demonstrated by examples taken from the three kinds of mixtures at some chosen concentrations of the polar molecules in Figures 1−3, are also found in the relaxation of the water component in aqueous mixtures, as we shall see.
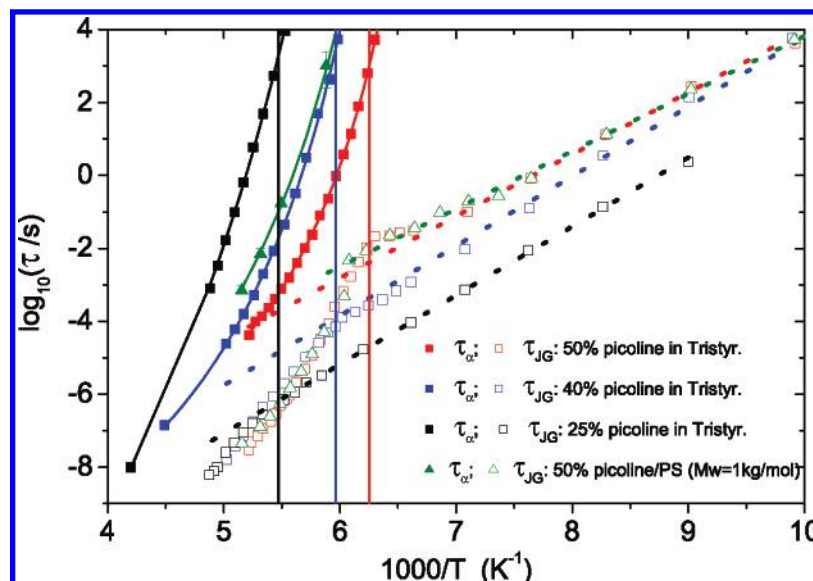
Figure 1. Relaxation map for mixtures of the polar molecule, picoline, in tristyrene. Full and open symbols represent the α- and JG β-relaxation times of the picoline component, respectively. Continuous lines are from VFTH equation fits. Dotted lines are Arrhenius fits. Each continuous vertical line indicates the location of T_g of a mixture near which τ_{JG} changes from its Arrhenius temperature dependence below T_g to a stronger dependence above T_g. Data are taken from refs 16 and 17 and re-plotted.
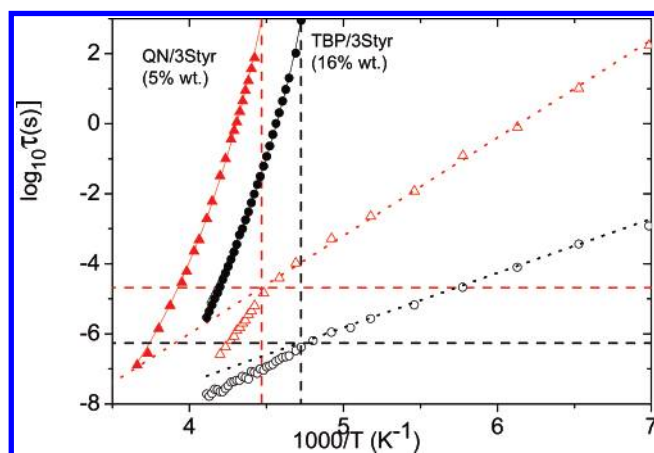

Figure 2. Relaxation map for mixtures of polar molecules 16 wt % tert-butyl-pyridine (black circles) and 5 wt % quinaldine (red triangles) in tristyrene. Full and open symbols represent the α- and JG β-relaxation times, respectively. Continuous lines are VFTH equation fits. Dotted lines are Arrhenius fits. Each broken vertical line indicates the location of T_g of a mixture near which τ_{JG} changes from its Arrhenius temperature dependence below T_g to a stronger dependence above T_g. Dashed vertical and horizontal dashed lines show the crossover of temperature dependence of τ_{JG} at T_g. Data are taken from ref 19 and re-plotted.
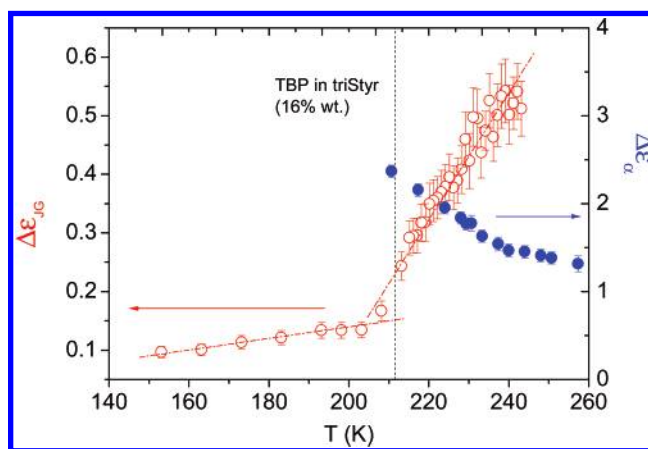

Figure 3. Dielectric strengths $\Delta\epsilon_\alpha$ and $\Delta\epsilon_\beta$ of the mixture of 16 wt % tert-butyl-pyridine (TBP) in tristyrene. Full symbols are for $\Delta\epsilon_\alpha$ of the α-relaxation (right axis) and open symbols for $\Delta\epsilon_\beta$ of the JG β-relaxation (left axis). Dotted lines are linear fits of $\Delta\epsilon_\beta$ below and above T_g. Dashed vertical line indicates $T = 211.5$ K [where $\log(\tau_\alpha/s)$ ∼ 3] and is near the temperature at which occurs the crossover of temperature dependence of $\Delta\epsilon_\beta$ with an elbow-shape. Data are from Kessairi, K. PhD dissertation, University of Pisa, Pisa, Italy, 2007.

Naturally, the results in Figures 1−3 have impact on the interpretation of the experimental data on relaxation of water in aqueous mixtures.

Another important fact that will have impact is the observation of both the α- and the JG β-relaxations contributed by the same component in the mixtures discussed above. This is found also in polymer blends. For example, both the α- and the JG β-relaxations of the poly(ethyl methacrylate) ($T_g = 334$ K) component in blends with 30 and 40 wt % of poly(4-vinylphenol) ($T_g = 441$ K) show up in the isothermal broadband dielectric spectra.[41] Runt and co-workers found a secondary relaxation which they called β' in the amorphous 20% PEO/80% PMMA blend.[42] It is remarkable that the frequency-temperature locations of the β'-relaxation are essentially the same as those they observed previously on the secondary relaxation of neat semicrystalline PEO they referred to as γ'.[43] The β'-relaxation in the blend and γ'-relaxation in neat PEO

have the same activation energy that is indicative they are one and the same local process. These properties had led these authors to suggest that the γ'-process is the primitive α-relaxation of the coupling model[18,44,45] or the JG relaxation in the amorphous region of semicrystalline PEO, and the β'-relaxation is the JG relaxation of PEO in the amorphous 20% PEO/80% PMMA blend. The α-relaxation of the PEO component in the blend cannot be resolved in the dielectric spectra because it overlaps with the much more intense JG β-relaxation of the PMMA component. However, its presence is ensured by the response observed in calorimetric measurements,[42] which signifies the glass transition of the PEO component facilitated by the α-relaxation of the PEO component at its glass transition temperature, T_{gPEO}. A final example is the poly(vinyl methylether) (PVME) component in PVME/PS blends.[20] The isochronal loss spectrum of the blend with 30 wt % PVME shows two broad peaks with maxima at about 237 and 285 K,
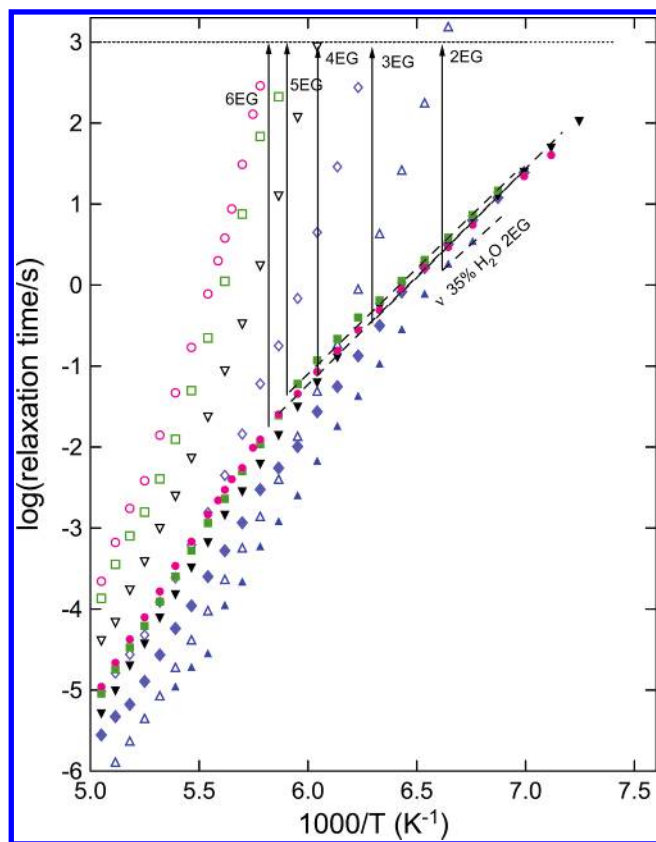
Figure 4. Temperature dependence of the dielectric relaxation time τ_α (open symbols) and τ_ν (corresponding closed symbols) of mixtures of 35 wt % of water with various ethylene glycol oligomers as indicated. Circles for 6EG. Squares for 5EG. Downward-pointing triangles for 4EG. Diamond for 3EG. Upward-pointing triangles for 2EG. Some of the data of τ_ν (closed symbols) overlap and cannot be easily resolved. For this reason, we use the dashed lines to indicate the Arrhenius temperature dependences assumed by τ_ν of the mixtures starting approximately at temperatures slightly below T_g of the mixtures defined by $\tau_\alpha(T_g) = 10^3$ s located by the vertical arrows drawn. The change of temperature dependence of τ_ν at T_g is similar to that seen of the JG β-relaxation of the faster component in nonaqueous mixtures (see Figures 1 and 2). The data are taken from refs 2, 3, and 4.

respectively, and they are indicators of the presence of both the α- and the JG β-relaxations of the PVME component in the blend.

3. The Primary α-Relaxation and JG β-Relaxation: Water−Alcohol and Water−Polymer Mixtures

As said in the Introduction, small in size and with strong affinity for hydrogen bonding, water may not behave in exactly the same ways as other glass-formers in mixtures. One has also to bear in mind that the other component of aqueous mixtures are hydrophilic, and susceptible to hydrogen bonding with water. These include 1-propanol,[11] ethylene glycol (EG),[1] ethylene glycol oligomers with two to six repeat units (EGO),[2−4] tri-propylene glycol,[7,8] glycerol, xylitol, sorbitol,[8] poly(ethylene glycol) 400 and 600,[4,10] fructose,[46] and poly(vinylpyrro1idone) (PVP).[12,47] In all aqueous solutions, a faster ν-relaxation is observed in addition to the slower relaxation by broadband dielectric relaxation. The slower relaxation has the VFTH temperature dependence of primary α-process which is due to the cooperative motion of water and solute molecules that give rise to the glass transition of the mixture, T_{gm}, observed also by calorimetry. In aqueous mixtures with PVME and PVP, the intervention of d.c. at low frequencies preempts the observation of the α-process.[10,12,13] From the increase of its dielectric
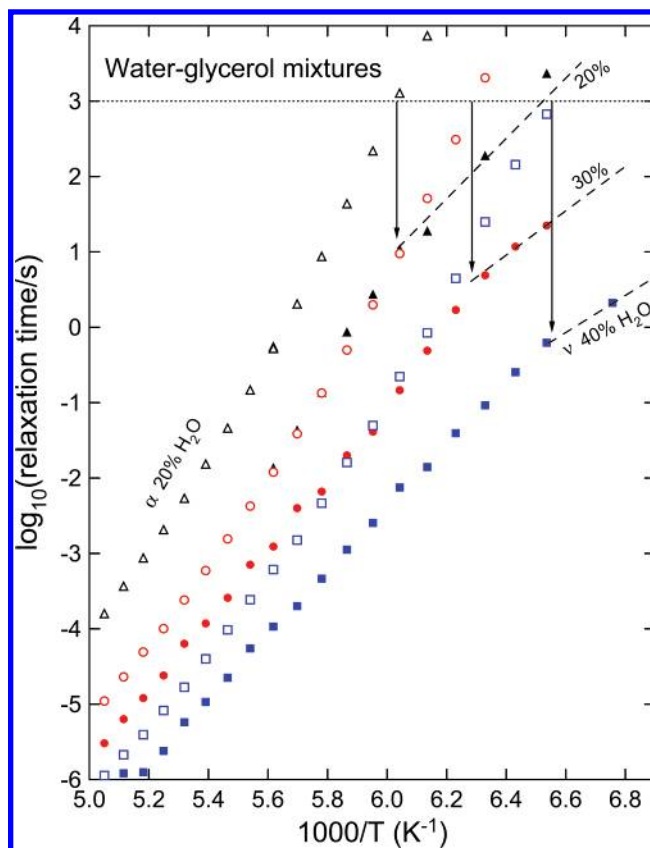

Figure 5. Temperature dependence of the dielectric relaxation time τ_α (open symbols) and τ_ν (corresponding closed symbols) of mixtures of various wt % of water with glycerol. Triangles for 20 wt % water. Circles for 30 wt % water. Squares for 40 wt % water. Each dashed line indicates the Arrhenius temperature dependences assumed by τ_ν of the labeled mixture starting approximately at T_g of the mixture defined by $\tau_\alpha(T_g) = 10^3$ s located by the vertical arrow drawn. The change of temperature dependence of τ_ν at T_g is similar to that seen of the JG β-relaxation of the faster component in nonaqueous mixtures (see Figures 1 and 2). Data are taken from refs 5 and 6.

strength with water content in the mixtures, as well as the increase of its relaxation time, τ_ν, on replacing the protonated water by deuterated water,[7] it is clear that the faster ν-relaxation originates from water, and has been called the ν-process.[14] The relaxation time, τ_α, of the structural α-relaxation of the mixture and τ_ν of the accompanying ν-process had been determined from isothermal dielectric relaxation spectra[1−9,14] for many different aqueous mixtures. The results of τ_α (open symbols) and τ_ν (closed symbols) for mixtures of 35 wt % water with five ethylene glycol oligomers, 2EG, 3EG, 4EG, 5EG and 6EG, are shown as a function of reciprocal temperature altogether in Figure 4. For ease of identification of the data of τ_α and τ_ν from the same mixture, the same shapes of the open and closed symbols are used. Similar plots of τ_α and τ_ν are given for 20, 30, and 40 wt % water mixtures with glycerol in Figure 5. In all cases, τ_α has VFTH-like temperature dependence down to the longest times measured or down to temperatures near the T_g of the mixture indicated by heat capacity measurements. On the other hand, the temperature dependence of τ_ν is Arrhenius at lower temperatures but it crosses over to a stronger temperature dependence when temperature is increased above T_g. In these two figures, the dielectric glass transition temperature T_g, defined by $\log[\tau_\alpha(T_g)] = 3$, is indicated by the location of the vertical arrow corresponding to $1000/T_g$ for each mixture. It can be seen by inspection of the figures that the change of the temperature dependence of τ_ν occurs near the dielectric T_g in
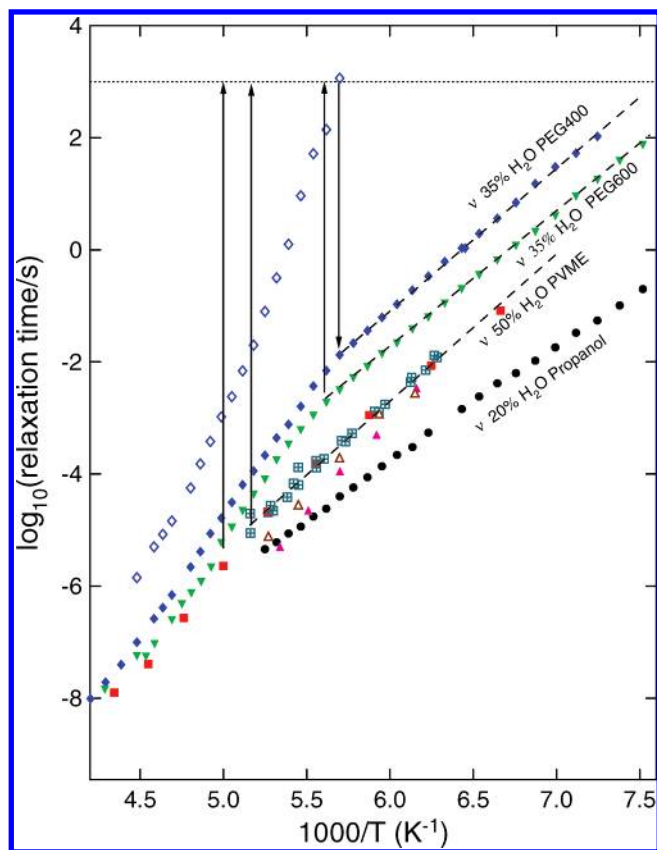
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Figure 6. Temperature dependence of the dielectric relaxation time τ_α (open diamond) and τ_ν (closed diamond) of mixtures of 35 wt % of water with PEG400 [data from refs 4 and 14]. The rest of the symbols are τ_ν of various aqueous mixtures. Closed downwardpointing triangles are τ_ν for mixtures of 35 wt % of water with PEG600 [data from refs 4 and 14]. Closed squares are for mixtures of 50 wt % of water with PVME. Closed circles are for 20 wt % water with propanol. Squares with cross inside are for 50 wt % of water with poly(vinylpyrro1idone) (PVP) of molecular weight 40000 [data from ref 12]. Open upward-pointing triangles for 38.6 wt % water containing poly(2-hydroxyethyl methacrylate) or PHEMA [data from ref 31]. Closed upward-pointing triangles for 48.4 wt % water containing PHEMA [data from ref 32]. Each dashed line indicates the Arrhenius temperature dependence assumed by τ_ν of the labeled mixture starting approximately at a temperature slightly below T_g of the mixture defined by $\tau_\alpha(T_g) = 10^3$ s for 35 wt % of water with PEG400, and the rest by their T_g obtained by calorimetry, all are indicated by locations of the vertical arrows drawn.

all cases. The same behavior is found in mixtures of 35 wt % water with PEG400, PEG600[4] and poly(vinyl methylether) (PVME)[13] as shown in Figure 6. For these mixtures, except for 35 wt % water in PEG400, τ_α cannot be determined from the dielectric spectra because the structural relaxation is masked by large conductivity contribution. Nevertheless, the calorimetric T_g has been determined and it is very close to the temperature above which we see the temperature dependence of τ_ν depart from the Arrhenius dependence at lower temperatures. This general crossover property of the temperature dependence of τ_ν is exactly the same as we found for the fast component in nonaqueous binary mixtures as discussed in the previous section (see Figures 1 and 2). Thus, we are led to conclude that the ν-process is the JG secondary relaxation of water in the mixtures.

In general, the dielectric strength, $\Delta\epsilon_\nu$, of the ν-process increases monotonically with temperature with an elbow shape that indicate a change of slope at T_g. The example of the temperature dependence of $\Delta\epsilon_\nu$ from three mixtures of 35 wt % of water in 3EG, 5EG, and PEG600 are shown in Figure 7.[4,14] This property is typical of secondary JG relaxation of a component in nonaqueous mixtures shown before in Figure 3, and also in neat glass-formers.[22,24,25] The dielectric frequency
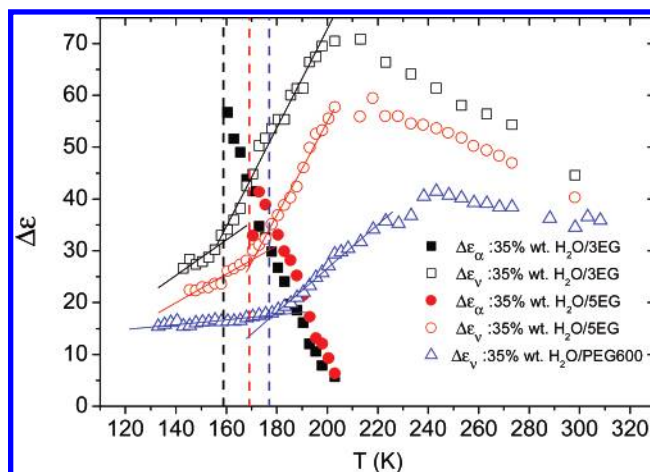

Figure 7. Dielectric strengths $\Delta\epsilon_\alpha$ and $\Delta\epsilon_\beta$ of the mixture of 35 wt % of water with 3EG, 5EG, and PEG600. Full symbols are for $\Delta\epsilon_\alpha$ of the α-relaxation and open symbols are for $\Delta\epsilon_\beta$ of the JG β-relaxation. Full lines are linear fits of $\Delta\epsilon_\beta$ below and above T_g. Each dashed vertical line indicates the temperature T_g near which the elbow-shape crossover of temperature dependence of $\Delta\epsilon_\beta$ occurs. Here T_g is defined as the temperature at which $\log[\tau_\alpha(T_g)/s] \sim 3$. The figure is constructed based on data published in refs 3 and 4.
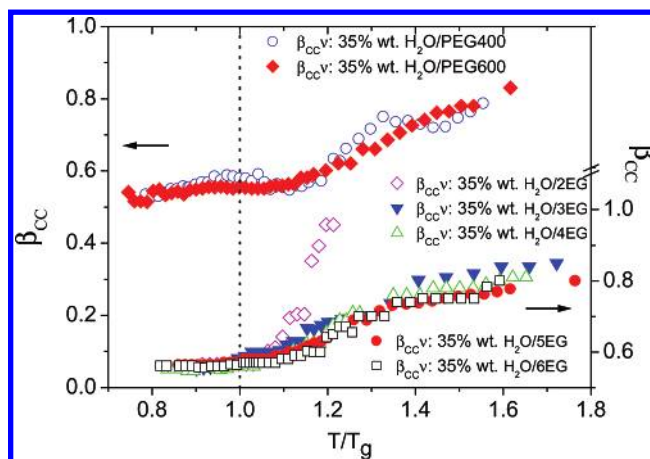

Figure 8. The Cole−Cole parameter, β_{CC}, of the ν-process in 35 wt % of water in 2EG, 3EG, 4EG, 5EG, 6EG, PEG400, and PEG600 shown altogether as a function T/T_g. Data are taken from refs 3 and 4.

dispersion of the ν-process was fitted by the Cole−Cole function in the manner as usually done for secondary relaxations in glass-formers. The Cole−Cole parameter, β_{CC}, was determined for each aqueous mixture as a function of temperature. The results for 35 wt % of water in 2EG, 3EG, 4EG, 5EG, 6EG, PEG400, and PEG600 are shown altogether as a function T/T_g in Figure 8. The increase of β_{CC} with temperature seen here for all mixtures is similar to that found in β_{CC} of the JG relaxation in other glass-formers and also in the JG relaxation of the 2-picoline component and the quinaldine component in tristy-rene. Hence, both the temperature dependences of $\Delta\epsilon_\nu$ and β_{CC} of the ν-process are strong indications that the ν-process is the secondary JG relaxation of the water component in the aqueous mixtures.

When compared with the dynamics of nonaqueous mixtures discussed in the previous section, the natural question is the secondary relaxation of the other component in the aqueous solutions. For example, in the PMMA/PEO blends, the JG relaxation of both the higher T_g and the lower T_g components are detected by dielectric spectroscopy.[42,43] However, in aqueous mixtures, it is more difficult to detect the JG relaxation of the usually higher T_g component by dielectric spectroscopy. This is due to the large dipole moment of water molecule, which makes the ν-process a dominant feature in the dielectric

spectrum in the frequency region where we expect to find the JG relaxation of the other component. Besides, most of the other components of the aqueous mixtures considered here have no resolved JG relaxation in their pure states, and thus is not expect to show one when mixed with water. Only in exceptional cases such as neat tri-ethylene glycol (3EG) is its JG relaxation resolved in dielectric spectra. In solution with 20 wt % and 35% water, the JG relaxation of 3EG is barely detectable to be located at the high-frequency flank of the more intense loss peak of the much more prominent ν-process[14]

Another case of interest is the mixture 20 wt % water/1-propanol.[11] Three relaxation processes, I, II, and III in order of increasing frequency, have been observed before in neat 1-propanol.[48] The most intense process I with narrow frequency dispersion of Debye originates from the relaxation of the hydrogen-bonded network. Process II is the structural α-relaxation,[48,44] and process III is the JG β-relaxation of 1-propanol.[44] The dielectric loss spectra of the 20 wt % water/1-propanol mixture have these three relaxation processes of neat 1-propanol at almost the same frequencies for the same temperature.[11] Therefore, the JG-β relaxation of the 1-propanol component is present in the mixture. An additional relaxation process is found at frequencies lower than process I. From this fact and the concentration dependence of the relaxation strength, the observed lowest frequency process is due to the molecular motion of water in the mixture. Such a ν-process coming from water in the 20 wt % water/1-propanol mixture has relaxation time τ_ν longer than τ_α of the structural α-process of the mixture. This relation between τ_α and τ_ν in the 20 wt % water/1-propanol mixture is opposite to that found in all the other aqueous solutions studied here. However, this is not unexpected, considering the fact that neat 1-propanol has $T_g = 95.9$K,[11] which is lower than that of pure water by any estimate. By contrast, in all other aqueous mixtures discussed so far, the T_g of the solutes in their neat form are higher than that of water. As shown in the relaxation map of Figure 6, the relaxation time of the ν-process in the 20 wt % water/1-propanol mixture has the Arrhenius temperature dependence, and it is the shorter than any of the τ_ν of the water-related ν-relaxations in other aqueous solutions at the same temperature. Its activation energy is only a bit smaller than those of the τ_ν of the ν-relaxations in other mixtures. These features of ν-process in the 20 wt % water/1-propanol mixture indicate that it is the JG relaxation of the water component. No crossover of τ_ν to a stronger temperature dependence is observed because in this case τ_ν is longer than τ_α of the 1-propanol in the mixture. One may ask if the α-relaxation of the water component can be observed at longer times (lower frequencies) than τ_ν in the isothermal dielectric spectra. Experimentally, the presence of conductivity contribution preempts observation even if the α-relaxation of the water component is present at lower frequencies. Theoretically, we expect that the relaxation time of α-relaxation of the water component may not be too different from τ_ν, to be explained as follows. For mixtures in general, the faster component enhances the mobility of the slower component, makes the temperature dependence of its α-relaxation time tending toward more Arrhenius-like, and decreases the steepness ("fragility") index m[36,49,50]. According to the coupling model (CM) for component dynamics in mixtures,[18,36,49,50] these come about from the reduction of the coupling parameter, n_s, of the slower component, a fact supported by molecular dynamics simulations.[51−53] Reduction of n_s also has the effect of diminishing the separation between the α-relaxation time, $\tau_{s\alpha}$, and the JG β-relaxation time, τ_{sJG}, of the slow component (s). This is a

consequence of the relation from the CM, $\log_{10}\tau_{s\alpha} - \log_{10}\tau_{sJG} = n_s(\log \tau_{s\alpha} + 11.7)$.[18,22,44,45] If n_s is reduced to zero or a small number, the α- and the JG relaxations merge together, and they practically become one and the same relaxation process. This scenario can happen in the 20 wt % water/1-propanol mixture, where the faster 1-propanol component severely reduces the coupling parameter of the water component. Such a scenario has support from the dielectric relaxation strength of the water relaxation to decrease with increasing temperature (not shown), opposite to that for the ν-relaxations in other mixtures.

In nonaqueous binary mixtures, each component has its own primary α-relaxation and glass transition temperature, which have been detected by dielectric, mechanical, and NMR spectroscopies as two separate α-loss peaks in some cases such as poly(vinylethylene)/polyisoprene blends,[54,55] or two different T_g's by calorimetry. In aqueous solutions discussed above, there is only one α-loss peak in the dielectric spectra, and a single T_{gm} found by calorimetry. The difference between the component α-dynamics of aqueous solutions and nonaqueous solutions is due to hydrogen bonding of the water with the other hydrophilic components. Consequently, neither the water nor the other component can be separately identified in the cooperative motion, and there is only one combined structural α-relaxation. The discussions given above rationalize the only difference between the component dynamics of aqueous solutions from nonaqueous mixtures.

The relaxation time of the ν-process, τ_ν, is dependent on the concentration and the molecular structure of the solute. Hydrogen bonding of water to the slower solute, with higher T_g, slows down even the local ν-process of water, and hence τ_ν increases with decreasing concentration of water. In fact, $\tau_\nu(T_{gm})$ systematically decreases with wt % of water in mixtures of water in 3EG, in glycerol, in ethylene glycol,[14] and in tri-propylene glycol.[7] However, the trend is reversed in 5, 13, 22, and 30 wt % of water in fructose,[14] where $\tau_\nu(T_{gm})$ increases from about 10^{-6} s at 5 wt % to 10^{-4} s at 30 wt % of water, where T_{gm} here is defined at the temperature at which $\tau_\alpha(T_{gm}) = 10^2$ s. Recently, the genuine JG β-relaxations of the family of sugars including fructose have been found to locate in between the α-relaxation and the faster but more prominent secondary γ-relaxation (whose relaxation time does not change with pressure).[56] Possibly the so-called ν-process observed in aqueous mixtures with fructose is a combination of these two secondary relaxations in fructose modified by water, and hence we have the exception to the rule found for ν-process in other solutes which are truly related to water. The data collected on the ν-process of mixtures of water with 1-propanol also show a reversal of the general trend. At T_{gm} defined by $\tau_\alpha(T_{gm}) = 100$ s, it was reported that $\tau_\nu(T_{gm}) = 2500$ s for 10 wt % of water, while $\tau_\nu(T_{gm}) = 28000$ for 20 wt % of water.[11] This reversal in trend is easy to explain because water becomes the slow component in its mixture with 1-propanol, but not the faster component in the other aqueous mixtures.

At temperatures below T_{gm} of the mixture, τ_ν of all mixtures have Arrhenius temperature dependence with activation energies of about 50 kJ/mol, which is not much larger than the energy of breaking two hydrogen bonds before translation or rotation of the molecule can occur (57 kJ/mol according to ref 31). These properties of τ_ν demonstrated in Figures 4−6 are also indications that the ν-process in all these aqueous mixtures are the local JG process of the water component. In Figure 6, we append also the relaxation time of the sub-T_g relaxation found in the mixture of 50 wt % of water with poly(vinylpyrro1idone) (PVP) of molecular weight 40000 by Jain and Johari (square with cross

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inside).[12] It has activation energy of 52.8 kJ/mol. Its values are nearly the same as that of τ_ν of the 35 wt % water in PVME. Also appended in the same Figure 6 are the data of τ_ν of 38.6 wt %[31] (open triangles) and 48.4 wt %[32] (closed triangles) water containing poly(HEMA), and they have activation energy of 60.8 and 66.8 kJ/mol respectively. Again the relaxation times of water in these hydrogels are about the same as that of water in PVME and PVP.

Although the ν-processes in various mixtures are of the same nature, their τ_ν's are not expected to have the same value because the concentration of water as well the mobility and chemical structure of the other component are different. Packing of the solute molecules is dependent on its molecular structure, and it also is a determining factor of τ_ν in the mixture. In spite of the differences in concentration and solute, τ_ν does not vary immensely. Measurements on aqueous mixtures at different concentrations with different solutes, including nEG where n ranges from 1 to 6, glycerol, PEG400, PEG600, PVP, PVME, and PHEMA, all show that the difference between their τ_νs are not large when considered over a common temperature range in their glassy states where the τ_νs have Arrhenius temperature dependence (see Figures 4−6). On the other hand, the primary α-relaxation time of these mixtures are immensely different because of their VFTH-like temperature dependence and widely different glass transition temperatures, as well as different steepness ('fragility') indices. Analogous changes of τ_{JG} of the faster component with concentration and the makeup of the other component are found in picoline/tri-styrene, picoline/polystyrene, picoline/ortho-terphenyl,[16,17] TBP/tri-styrene, and QN/tristyrene mixtures.[19]

We had emphasized before that a general property of the ν-process is the change of temperature dependence of τ_ν near T_{gm} from the Arrhenius dependence below T_{gm} to stronger temperature dependence above T_{gm}. This is demonstrated in Figures 4−6, where in each figure the vertical arrow indicates the location of $1000/T_{gm}$ of the aqueous mixtures with T_{gm} defined either as the temperature at which the α-relaxation time of the mixture, $\tau_{\alpha m}$, has attained the value of 10^3 s or the calorimetric glass transition temperature of the mixture. It can be seen from these figures that τ_ν changes its temperature dependence near $1000/T_{gm}$. We recall from Section 2 that such change of temperature dependence of τ_ν has been found for the JG relaxation time, $\tau_{JG,p}$ of the fast component in several nonaqueous mixtures at the glass transition temperature, T_{gp}, of the same component. Below T_{gp}, the temperature dependence of $\tau_{JG,p}$ is Arrhenius, but it changes to a much stronger temperature dependence at higher temperatures after crossing T_{gp}. This crossover of temperature dependence behavior of τ_ν analogous to that of JG relaxation in nonaqueous mixtures (see Figures 1 and 2) lends further support to identifying the ν-process as the JG β-relaxation of water component in aqueous mixtures.

There is another interpretation of the ν-process offered by others that is principally based on one property, i.e., the crossover of the temperature dependence of τ_ν at T_{gm}.[7,13] The interpretation was proposed before for the relaxation of the faster component in binary nonaqueous mixtures of two glass-formers[20] and is deemed to be generally applicable. For the ν-process of aqueous mixtures, it goes as follows. The ν-process in aqueous mixtures was interpreted[7,13] as the equivalent of the cooperative α-relaxation of glass-forming liquids, which is distinctly different from our interpretation here as JG β-relaxation of the water component. Above T_{gm}, it involves collective motions of the molecules over the cooperative length, ξ, which

increases with decreasing temperature, and its relaxation time τ_ν has VFTH-like temperature dependence. At T_{gm} and temperatures below it, the frozen glassy matrix "confines" the water molecules to move within a finite size, and this size limits the growth of ξ of water and forestalls the increase of τ_ν according to the VFTH-like dependence with decreasing temperature. A temperature independent ξ at temperature below T_{gm} means that the temperature dependence of τ_ν becomes Arrhenius, and the crossover of temperature dependence of τ_ν at T_{gm} is explained in this way. This "confinement" or "finite size effect" explanation is basically a general argument on the α-relaxation of the fast component in a mixture, and was applied to nonaqueous[20] and aqueous mixtures.[7,13] Unfortunately, this argument contradicts the dielectric relaxation data of the nonaqueous mixtures presented in Figures 1−3. In these mixtures, both the primary α-relaxation and the JG β-relaxation of the faster polar component p are observed. The component α-relaxation time, $\tau_{\alpha p}$, has VFTH dependence for temperatures down to T_{gp} where $\tau_{\alpha p}(T_{gp})$ attains a long time such as 10^3 s. There is no sign of $\tau_{\alpha p}$ crossing over to Arrhenius temperature dependence at times ranging from about 10^{-5} s to about $10^{0.5}$ s found for τ_ν in various aqueous mixtures at T_{gm}. Instead, the JG relaxation of the fast component shows such a crossover of temperature dependence at T_{gp} where $\tau_{JG,p}(T_{gp})$ can fall within a broad range of times depending on the composition of the mixture just like τ_ν. Another problem of the confinement or finite size effect explanation occurs when confronting the data of the ν-process in the 20 wt % water/1-propanol mixture. The ν-process turns out to be the slowest of all processes in the 20 wt % water/1-propanol mixture. In this case, certainly there is no "frozen matrix" to confine the motion of water, and yet τ_ν of the ν-process in the 20 wt % water/1-propanol mixture has activation energy (40 kJ/mol) not much different from the other aqueous mixtures (47 kJ/mol for 35 wt % water/PEG600 mixture, see Figure 6). Moreover, the difference between τ_ν in the 20 wt % water/1-propanol mixture and τ_ν in 50 wt % water/PVME mixture is not large, ranging from 0.6 decade to 1.6 decade over a wide range of temperature (see Figures 4−6). The data of temperature dependence of τ_ν in mixtures of 20, 30, 40, and 50 wt % of water with tri-propylene glycol (3PG) had been extrapolated to 100% water.[7] The extrapolated temperature dependence of water crosses over from VFTH-like dependence to Arrhenius dependence at a temperature where $\tau_\nu \approx 10^{-4}$ s. For α-relaxation times as short as 10^{-4} s, all glass-formers including pure water should be equilibrium liquids and no crossover from the VFTH dependence to the Arrhenius dependence can take place. Hence the crossover of the extrapolated data for pure water contradicts the assumption that the ν-process of aqueous mixtures is the primary α-relaxation of the water component.

4. Water Sequestered in Pores of Hydrophilic Polymers and in Other Matrices

The α-relaxation of glass-formers is a cooperative process involving many molecules, the extent of which is given by the experimentally determined length-scale of dynamic heterogeneity, L.[57] From the L determined for a few glass-formers, it correlates with the non-exponentiality parameter n ($0 < n < 1$), that appears in the stretch exponent of the Kohlrausch correlation function

$$\phi(t) = \exp[-(t/\tau_\alpha)^{1-n}] \tag{1}$$

of the α-relaxation of neat bulk glass-formers.[58] In the context

of the coupling model (CM), n is the coupling parameter, which governs the α-relaxation through the relation

$$\tau_{\alpha} = [t_c^{-n}\tau_0]^{1/(1-n)} \qquad (2)$$

Here t_c is about 2 ps for molecular glass-formers, and τ_0 is the primitive relaxation time, which has been shown to be approximately equal to the JG secondary relaxation time τ_{JG} for many molecular and polymeric glass-formers, i.e., $\tau_{JG} \approx \tau_0$.[18,19,22,36–39,44,45] When a glass-former is subjected to extreme nanoconfinement, the dimension of the sample becomes smaller than L, the spatial extent of the many-body relaxation is reduced and so is the coupling parameter n. The same happens for molecules located near free surface and interface in the absence of chemical or physical interaction. When n becomes small, it follows from eq 2, that τ_{α} becomes shorter and the difference between τ_{α} and τ_{JG} is less because of the relation, $\log(\tau_{\alpha}/\tau_{JG}) \approx n[11.7 + \log(\tau_{\alpha})]$. In the limit when $n \rightarrow 0$, the α-relaxation is transformed into a non-cooperative relaxation like the JG relaxation. This was found before in 1,2 diphenylbenzene (OTP) in 2 nm silanized glass pores,[59] in poly(methylphenyl siloxane) (PMPS) thin films confined in galleys nanocomposites with width less than 2 nm,[60] and by Schönhals and co-workers for poly(dimethyl siloxane) (PDMS) and poly(methylphenyl siloxane) (PMPS) with low molecular weight of 1000 g/mol confined in nanopores with size down to 2.5 nm.[61,62] Additional evidence of near extinction of many-body dynamics in the case of PMPS confined in 2.5 nm pores include the change from Vogel–Fulcher–Tammann-Hesse (VFTH) temperature dependence to Arrhenius temperature dependence of the relaxation time with activation energy characteristic of JG relaxation, the dielectric strength changes from decreasing with increasing temperature of α-relaxation to increasing with increasing temperature and vanishing specific heat jump, all typical of secondary relaxation.[61,62] The segmental relaxation time of PMPS thin films in intercalated nanocomposites, with PMPS confined within the 1.5–2.0 nm spacing between organically modified silicates, and OTP and polymers confined in 2.5 nm glass pores were found to be close to τ_0, of the bulk glass-formers calculated by the CM eq 2 from the known parameters n and τ_{α} of the bulk glass-formers.[63,64,65] Exact agreement is not expected because the 2.5 nm confined PMPS with vanishing specific heat jump is in a different thermodynamic state than the primitive relaxation or the JG relaxation of bulk PMPS, and bulk PMPS exhibits a jump of specific heat across T_g. Nevertheless, from the results we can infer the cooperative many-molecule dynamics of these glass-formers under extreme nanoconfinement are nearly suppressed, and the observed relaxation times are close to that of the primitive relaxation or the JG β-relaxation of the bulk substances.

The dynamics of 6 Å thick water layer (two molecular layers) in fully hydrated Na-vermiculite clay were measured by dielectric spectroscopy.[29] From the discussion of other glass-formers given in the previous paragraph, under this extreme confinement condition we can expect that the α-relaxation and the JG relaxation in the 6 Å thick layer of water can no longer be distinguishable from each other. Thus, the relaxation time of the α-relaxation of the thin layer of water could become much faster than that of bulk water, and its temperature dependence is changed to either approaching or assuming the Arrhenius dependence of the possibly JG β-relaxation instead of the VFTH dependence of the α-relaxation in bulk water. These changes seen in other glass-formers under extreme confinement were found by Bergman and Swenson in the two molecular layers of water confined in fully hydrated Na-vermiculite clay. The
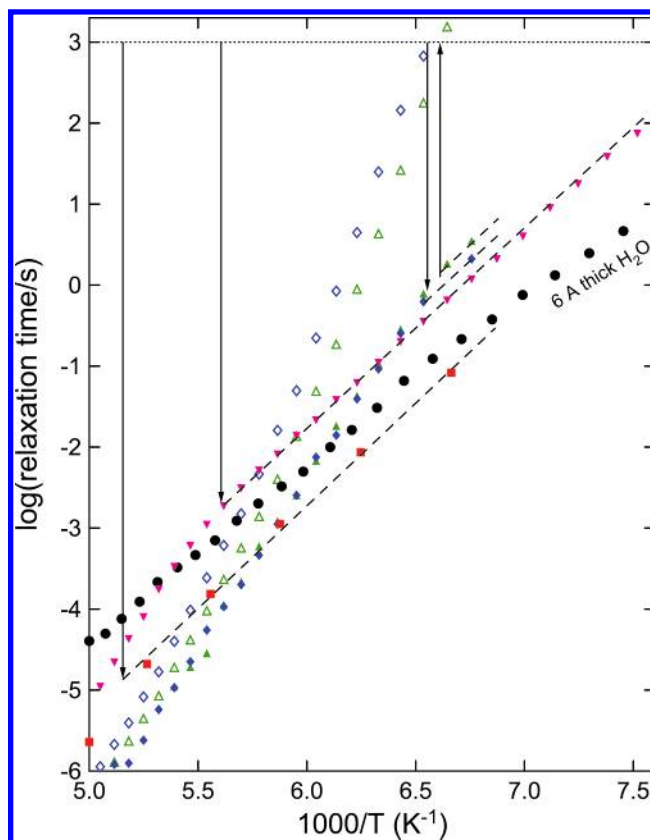

Figure 9. Temperature dependence of the dielectric relaxation time τ_ν (closed circles) of 6 Å thick layer of water in fully hydrated Na-vermiculite clay [data from refs 29 and 30]. These data are compared with τ_ν for mixture of 50 wt % of water with PVME (closed squares) [data from ref 13], mixtures of 40 wt % of water with 2EG (closed upward-pointing triangles), mixtures of 40 wt % water with glycerol (closed diamonds), and mixtures of 35 wt % of water with PEG600 (closed downward-pointing triangles) [data from refs 2, 3, 4, and 14]. Open triangles and open diamonds are τ_α of the mixtures of 40 wt % of water with 2EG and mixtures of 40 wt % water with glycerol respectively. The dashed lines and the vertical arrows have the same meaning as in Figures 4–6.

relaxation times of the only process found in 6 Å thick water layer, $\tau_{6Å}$, has approximately Arrhenius temperature dependence throughout and they are shown in Figure 9 together with the relaxation times, τ_ν, of the ν-process in some selected aqueous mixtures. It can be seen from the figure that $\tau_{6Å}$ has about the same activation energy but also the same order of magnitude as τ_ν of the mixtures. These coincidences mutually support the interpretation $\tau_{6Å}$ here and τ_ν in the previous section that they all are the relaxation times of JG β-relaxation of water in various circumstances. Although the processes are of the same nature, they are not expected to have the same value because the environments in which the processes transpire are not the same. For the 6 Å thick water layer, $\tau_{6Å}$ maintains the Arrhenius temperature dependence throughout the entire temperature range. The absence of crossover to stronger temperature dependence at a higher temperature here, but found for τ_ν of the mixtures, is understandable because of the higher T_g component is not present in the case of the 6 Å thick water layer. Experimentally this is clear from the absence of any α-relaxation in the 6 Å thick water layer.

Broadband dielectric data of pure water confined in silica hydrogels were reported by Schirò et al.[28] and earlier by Cammarata et al.[26,27] The relaxation time of one of the processes observed is found[28] to be the same as $\tau_{6Å}$ of the 6 Å thick water layer in vermiculite clay. Schirò et al. stated that the Arrhenius
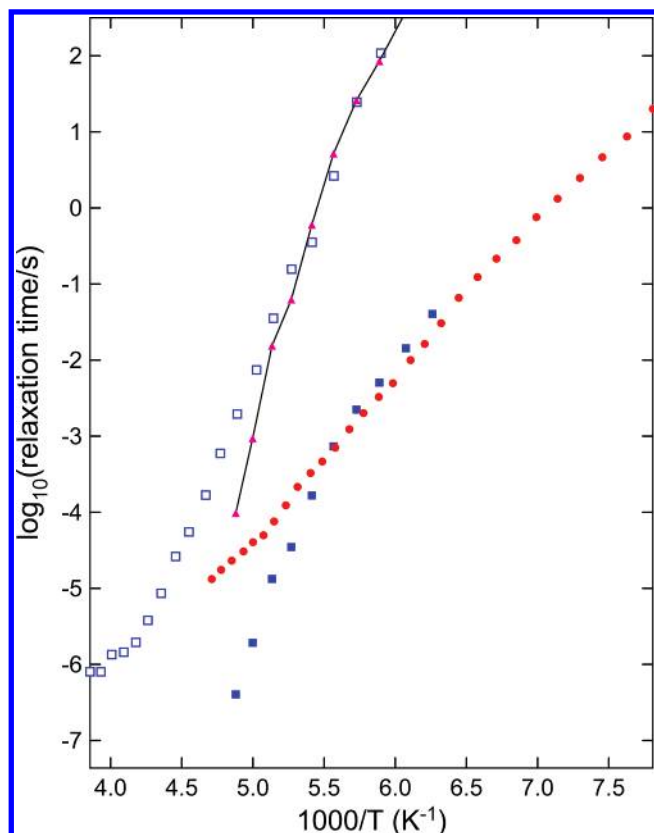
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Figure 10. The relaxation times, τ_{sMS} and τ_{fMS}, of a slower (open squares) and faster (closed squares) relaxation of water confined in molecular sieves of cylindrical pore with diameter of 10 Å [data from ref 69]. The Arrhenius temperature dependence of τ_{fMS} changes to stronger temperature dependence at temperatures above approximately 180 K, same behavior as τ_ν of the ν-process in various aqueous mixtures. The value of τ_{sMS} calculated by the coupling model eq 3 are shown by closed triangles connected by a line. For comparison, we plot also the dielectric relaxation time τ_ν (closed circles) of 6 Å thick layer of water in fully hydrated Na-vermiculite clay [data from refs 29 and 30].

Figure 11. The relaxation times, τ_{sC} (open diamonds, and open inverted triangles for dry samples) and τ_{fC} (closed diamonds, and closed inverted triangles for dry samples), of a slower and faster relaxation of water confined in aged silica hydrogels [data from ref 26]. The relaxation time, τ_{fC}, of the faster relaxation has Arrhenius temperature dependence in the lower temperature range with an activation enthalpy of about 50 kJ/mol. Shown for comparison are the τ_{sMS} (open squares) and τ_{fMS} (closed squares), of the slower and faster relaxations of water confined in molecular sieves of cylindrical pore with diameter of 10 Å [data from ref 66]; τ_ν (closed circles) of 6 Å thick layer of water in fully hydrated Na-vermiculite clay [29 and 30]; τ_α (open triangles) and τ_ν (dashed line) of mixtures of 38.6 wt % of water with PHEMA [data from ref 31]; τ_ν (plus signs) of mixtures of 50 wt % of water with PHEMA [data from ref 68].

relaxation process observed is due to confinement and not from specific interaction between water and the confining matrix, as proposed in the paper by Cammarata et al.

The dynamics of water confined in a molecular sieve had been studied by means of dielectric spectroscopy.[66] In a cylindrical pore with diameter of 10 Å, two major relaxation processes were observed (see Figure 2b in ref 66, and Figure 10 in the present paper). According to the authors of this paper, the much more intense slower process (open circles) is contributed by most of the water molecules in 10 Å pores, and is likely due to strong interactions with the hydrophilic inner surfaces of molecular sieves. Its relaxation time, τ_{sMS}, increases with decreasing temperature to attain 100 s at about 170 K. The relaxation time of the weak faster process, τ_{fMS}, has Arrhenius temperature dependence at low temperatures below about 175 K, and is nearly the same as $\tau_{6Å}$ in fully hydrated Na-vermiculite clay. However, the Arrhenius temperature dependence of τ_{fMS} does not persist at higher temperatures, changing to stronger temperature dependence at temperatures above 180 K. This crossover of temperature dependence of τ_{fMS} is the same as what we have seen in τ_ν, of the ν-process in various aqueous mixtures (see Figures 4−6 and 9), and is a general property of JG β-relaxation. The striking similarity of this feature of τ_{fMS} and that shown by τ_ν leads us to interpret the observed faster process in a molecular sieve as the JG β-relaxation associated with slower process, which is the
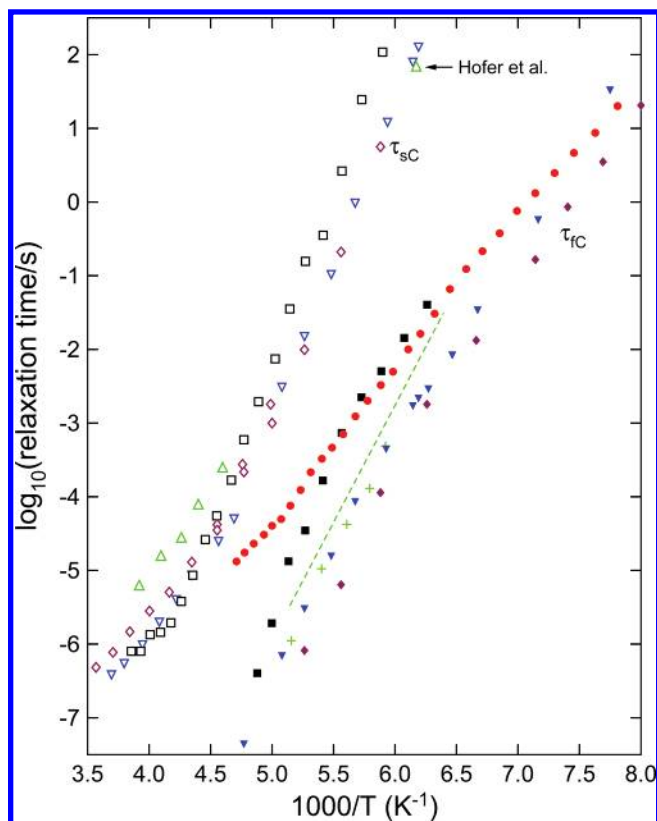
α-process of water but this water is strongly interacting with the hydrophilic inner surfaces of the molecular sieve. Such a relation between the two processes is further supported by applying the coupling model (CM) relation between τ_{JG} and τ_α given by combining $\tau_{JG} \approx \tau_0$ and eq 2 to the present case of τ_{fMS} and τ_{sMS} for water confined in 10 Å pores. Using the CM relation adapted for the present case:

$$\tau_{sMS}(T) = [t_c^{-n}\tau_{fMS}(T)]^{1/(1-n)} \qquad (3)$$

we calculate τ_{sMS} from the data of τ_{fMS} (closed squares in Figure 10) by assuming $t_c \approx 2$ ps as other molecular glass-formers and $(1 - n) \equiv \beta_K = 0.69$. With this choice of the Kohlrausch exponent, $\beta_K = 0.69$, the calculated τ_{sMS} (closed triangles) are in approximate agreement with the experimental values (open squares) as shown in Figure 10. The value of $\beta_K = 0.69$ chosen is not far from the value of 0.65 reported by Swenson et al.[67] as the Kohlrausch exponent obtained by means of quasi-elastic neutron scattering after averaging the result from various scattering vectors.

Two relaxations of pure water confined in aged silica hydrogels were observed also by Cammarata et al.[26] Their relaxation times are shown in Figure 11 as a function of reciprocal temperature. The relaxation time, τ_{fC}, of the faster

relaxation has Arrhenius temperature dependence in the lower temperature range with an activation enthalpy of about 50 kJ/mol. The resemblance of these properties of the faster relaxation to that of some of the ν-process in aqueous mixtures suggests that it is the JG β-relaxation of water confined in hydrogels. The slower relaxation has VFTH temperature dependence for its relaxation time, τ_{sC}, like that of typical α-process. Cammarata et al. suggested that this relaxation originates from water molecules within the pores that do not interact strongly with the matrix and behave collectively. Another possibility is interaction of water with silica and silica being modified by hydrolysis. Whichever is the ultimate interpretation of the slower relaxation, it is an α-relaxation, and the faster relaxation with Arrhenius temperature dependence may be its JG β-relaxation. Their relaxation times, τ_{sC} and τ_{fC}, may be related by the CM eq 3 just like the relation between τ_{sMS} and τ_{fMS} of water confined in a molecular sieve shown in the previous Figure 10. In fact, when we compare τ_{sC} with τ_{sMS}, and τ_{fC} with τ_{fMS} in Figure 11, the values of each pair are similar, indicating the origins of the fast process as well as the slow process are similar in the two cases.

We have considered before the relaxation of water confined in a hydrogel of PHEMA studied by Pathmanathan and Johari (PJ).[31,32] Within the experimental frequency range from 10 to 10^5 Hz, again there are two relaxation processes. The faster relaxation of the 38.6 wt % water has Arrhenius temperature dependence for it relaxation time, τ_{fPJ}, with activation energy of 60.8 kJ/mol as shown before in Figure 6. They are shown here again in Figure 11 by the Arrhenius fit to the data (dashed line) but without the data themselves to avoid crowding, together with the data, τ_{fX}, by Xu et al. on 50 wt % water (crosses).[68] It can be seen from this figure that the relaxation times, τ_{fPJ} and τ_{fX}, are near τ_{fC} of the faster process found by Cammarata et al. as well as τ_{fMS} confined in a molecular sieve. This coincidence suggests that τ_{fPJ} and τ_{fX} are the JG relaxation time of water in the PHEMA hydrogel. The slower process of water in PHEMA hydrogels can only be observed at higher temperatures dielectrically. At lower temperatures, the d.c. conductivity dominates and preempts the observation of the slow process. Its relaxation time, τ_{sPJ}, determined from the dielectric loss spectra at several temperatures are shown as open triangles in Figure 11. Again, at the same temperature, τ_{sPJ} is about the same as τ_{sC} or τ_{sMS}.

Calorimetric measurements of H_2O and D_2O in hydrogels of PHEMA by Hofer et al.[69] show water has a very weak endothermic step at 132 ± 4 K for H_2O and another endothermic step at 162 ± 2 K (H_2O) and 165 ± 2 K (D_2O), all for a heating rate of 30 K/min. The lower temperature, 132 ± 4 K, is nearly the same as T_g of hyperquenched glassy water.[70,72,73] The activation energy of the α-relaxation of hyperquenched glassy water is about 55 kJ/mol,[69,72] which is also close to 60.8 kJ/mol for τ_{fPJ}. Moreover, from the calorimetric data, PJ deduced that $\tau_{fPJ} = 53$ s at 135 K. Hence they interpreted the faster process as the α-relaxation of supercooled water in the hydrogel of PHEMA. The larger endothermic step at 162 K at the heating rate of 30 K/min indicates the relaxation time of the slower process, τ_{sPJ}, is also 53 s at 162 K. This result, shown by a lone open triangle located at $1000/T = 6.17$ in Figure 11 and indicated its origin from Hofer et al. [69,72] seems to be the continuation of τ_{sPJ} obtained by dielectric measurements at higher temperatures. Can be seen by inspection of Figure 11, τ_{sPJ}, τ_{sMS}, and τ_{sC} all have comparable values over the same temperature region where they increase toward long time-scale of vitrification. The activation enthalpy of τ_{sPJ} from calorimetric

relaxation near 162 K is about 120 kJ/mol, twice the activation energy of τ_{fPJ}. From the contrasting properties of τ_{sPJ} and τ_{fPJ} discussed above, we suggest in PHEMA hydrogels that the slower process is the relaxation of water interacting with PHEMA, like water interacting with the inner surface of molecular sieves[66] or with the silica in silica hydrogels.[26] The faster process could be considered as the JG β-relaxation of water in PHEMA hydrogels. Again τ_{sPJ} and τ_{fPJ} are related by an analogue of the CM eq 3.

New study of water confined in silica gel cylindrical pores with pore diameter of 2 nm by adiabatic calorimetry and dielectric relaxation by Oguni and co-workers[74] reported again the presence of a faster and a slower process. The authors interpreted the faster relaxation as due to 1 molecular layer of interfacial water, and the slower one the counterpart of the α-relaxation of bulk water. However, this interpretation is not unique. The temperatures at which the relaxation times of the two relaxations reaches an arbitrarily chosen long time are similar to those found by Cammarata et al. in silica hydrogels, and by Pathmanathan and Johari, and Hofer et al. in PHEMA hydrogels. An alternative interpretation of the origin of the two relaxations found by Oguni and co-workers can be similar to those we have given for the other cases.

Pathmanathan and Johari interpreted the fast process with relaxation time τ_{fPJ} as the α-relaxation of supercooled water in the hydrogel of PHEMA, no different from that in bulk glassy water. This interpretation is different from our interpretation of it as the JG β-relaxation of water. However, they can be reconciled if the coupling parameter n of the α-relaxation of bulk glassy water is nearly zero. In this scenario, the α-relaxation and JG relaxation times are equal in the framework of the coupling model, and the two relaxations are no longer be distinguishable from each other. However, this scenario may not be true because inelastic UV scattering[75] and optical Kerr effect[76] experiments on bulk water at higher temperatures give values of n equal to about 0.40 (from 260 to 340 K at momentum transfer ≈ 0.1 nm^{-1})) and 0.44−0.40 (254 K− 314 K) respectively. On the other hand, dielectric relaxation measurements gave narrower dispersions[77−85] and smaller n values. In view of the uncertainty of the actual coupling parameter of bulk water, we refrain from making any judgment at this time.

5. Summary and Conclusion

Various experimental data, including increase of the dielectric relaxation strength with concentration of water, have confirmed that the ν-process in aqueous mixtures originates from motion of water. Slower than the ν-process is the α-relaxation process with VFTH-like temperature dependence for it relaxation time, τ_α. This is the α-relaxation of the aqueous mixture in which water molecules participates in cooperative motion with the solute molecules, and it is responsible for vitrification of the mixture at T_{gm} where $\tau_\alpha(T_{gm})$ attains a long time such as 10^3 s. Some properties of the relaxation time, τ_ν, are found common to all ν-processes in various aqueous mixtures. The same properties are found in the JG relaxation of a component in nonaqueous mixtures as well as in neat glass-formers, and thus supporting our identification of the ν-process as the JG relaxation of water component in the aqueous mixtures. The following properties have been considered in this paper.
(i) The relaxation strength, $\Delta\epsilon_\nu$, of the ν-process change near T_{gm} from a weaker dependence below T_{gm} to a stronger one above T_{gm}, on heating through the glass transition temperature. This change is similar to $\Delta\epsilon_{JG}$ seen before in JG relaxation of

a component in nonaqueous mixtures and in neat glass-formers, and is a mimicry of the changes observed in the enthalpy *H*, entropy *S*, and volume *V* of neat glass-formers when crossing the glass transition temperature.

(ii) The relaxation time, τ_ν, at the glass transition temperature T_{gm} is much shorter than $\tau_\alpha(T_{gm}) = 10^3$ s, and its magnitude depends on the other component of the aqueous mixture and its concentration. However, in the glassy states and for the same temperature, τ_ν of various mixtures at comparable water concentration differs by at most a few decades.

(iii) The activation energies of τ_ν at temperatures below T_{gm} of all aqueous mixtures considered here have values that are not too different from each other and near 50 kJ/mol, which is about the energy required to break two hydrogen bonds before the water molecule can translate or rotate.

(iv) τ_ν has Arrhenius dependence at temperature below T_{gm} of the mixture, but a stronger and VFTH-like temperature dependence above T_{gm}. It is important to emphasize that this crossover of temperature dependence of τ_ν has been observed for the Johari-Goldstein (JG) relaxation time of the faster component in several nonaqueous mixtures. There is no mistake in identifying the process in these nonaqueous mixtures as the JG process because the faster component is a rigid molecule and its relaxation time increases on applying pressure. Besides, a slower α-relaxation of the faster component with VFTH-like temperature dependence and dynamics distinctly different from the faster JG relaxation has been observed. From the similarity in properties of the ν-process in the aqueous mixtures and the JG relaxation of a component in nonaqueous mixtures, we can conclude that the ν-process is the JG process originating from the faster water component for all temperatures above and below T_{gm}.

(v) The ν-process is found to be the slowest of all relaxations in 10 and 20 wt % of water in 1-propanol, including the α-relaxation of the 1-propanol in the mixtures. Its relaxation time τ_ν has Arrhenius temperature dependence with activation energy slightly smaller than that of τ_ν for other mixtures at temperatures below T_{gm}. At the same temperature, τ_ν of 10 and 20 wt % of water in 1-propanol is in order of magnitude agreement with that of τ_ν of some other aqueous mixtures in the glassy state. The faster 1-propanol molecules can only enhance the mobility of water but certainly cannot confine the water molecules. Thus, the observation of a ν-process in the water/1-propanol mixtures with similar characteristics as the ν-process in the other aqueous mixtures indicates that the interpretation of the latter at temperatures below T_{gm} as relaxation of water confined by the frozen matrix is untenable.

(vi) In 6 Å thick water layers confined in clay, the only relaxation process observed is Arrhenius throughout the temperature range investigated. At the same temperature, its relaxation time is about the same as the ν-process of several aqueous mixtures in their glassy states, particularly those at higher levels of concentration of water. If there is any cooperativity (i.e., many-molecule relaxation dynamics) in bulk water, it is substantially or entirely removed in two layers of water due to the small size that preempts cooperative motion. Thus, the α-relaxation collapses to become effectively the same as the JG relaxation of water, and its relaxation time should not be too different from the ν-processes in aqueous mixtures because they have been interpreted also as the JG relaxation. This is indeed found, and the finding reinforces the conclusion that the ν-process is the JG relaxation of water in aqueous mixtures. If there is no cooperativity in bulk water, then one can regard the observation of the process in the 6 Å thick water

layers confined in clay as the direct observation of the α-relaxation of bulk water. In fact, its relaxation time assumes the value of approximately 5 s at 135 K, which is supposedly the glass transition of hyperquenched water.[15,69−72] However, more work is needed before this scenario can be confirmed.

(vii) Water confined in molecular sieves shows the presence of two relaxations. The slower one has the characteristics of α-relaxation and is due to water interacting with the hydrophilic inner surface of the pores. The relaxation time of the faster relaxation is in every respect similar to τ_ν of aqueous mixtures. These include the crossover of its temperature dependence from VFTH-like to Arrhenius near the temperature at which we expect vitrification of the slow process, similar relaxation times and comparable activation energies. Thus, the faster process can be interpreted as JG relaxation like the ν-process in aqueous mixtures. Water in silica hydrogels and PHEMA hydrogels also has one faster and a slower relaxation, and their relaxation times are remarkably similar to those of water confined in molecular sieves. Hence, they are interpreted in the same manner. Also are the two processes found by Oguni and co-workers[74] in water confined inside 2 nm diameter cylindrical silica gel pores. The adiabatic calorimetry and dielectric data of Oguni and co-workers of the two processes in 2 nm pores are similar to the differential calorimetry data of Hofer et al.[69] and the dielectric data of Pathmanathan and Johari of water in PHEMA hydrogels.[31] The endotherms of the fast process in both Oguni et al. and Hofer et al. are weak. Hyperquenched water also has weak endotherm at about 136 K[70−72] consistent with the interpretation that it is the JG relaxation of water. The fast process with Arrhenius temperature dependence has relaxation time reaching 53 s at 135 K, the glass transition temperature of hyperquenched water.[71−73] From this, Pathmanathan and Johari however had suggested that the faster relaxation is the α-relaxation of water. If so, then the Arrhenius temperature dependence of its relaxation time suggests that the α-relaxation is non-cooperative and cannot be distinguished from the JG relaxation. This explains why the relaxation times of the faster process are nearly the same and have about the same activation energy as those of the ν-process of many aqueous mixtures including the 10 and 20 wt % of water in 1-propanol, and the ν-process of the 6 Å thick water layers confined in clay (all identified as the JG β-relaxation by us).

In conclusion, from the plethora of experimental data of water in mixtures and in confinement, we have found a fast relaxation originating from the water component (called the ν-process) with properties that are general and similar in many respects to those of the Johari-Goldstein secondary relaxation of the faster component in nonaqueous mixtures and in neat glass-formers. These evidence lead us to conclude that the Johari-Goldstein secondary relaxation of water exists, and is identified by the ν-process. The result should have an impact on understanding relaxation and glass transition of bulk water and dynamics of water/protein mixtures,[86] but further investigation is needed before any definitive conclusion can be made.

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