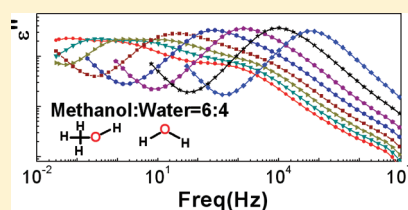


## Component Dynamics in Miscible Mixtures of Water and Methanol

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**ABSTRACT:** In binary mixtures with hydrophilic substances, water is usually the more mobile component and its relaxation time is shorter than those of the other components. An exception is the case of the mixture of 1-propanol with 45 mol % water, where the  $\alpha$ -relaxation of water is slower than the  $\alpha$ -relaxation of 1-propanol and even slower than the local relaxation of water confined in various spaces of nanometer size. This unusual result, so far obtained in a mixture of 1-propanol with water at a single composition, deserves confirmation by experiments in another mixture at more than one composition. Toward this goal, we have chosen mixtures of methanol with water at concentrations of water ranging from 10 to 40 mol % and investigated the dynamics of the slower water and the faster methanol components by broadband dielectric relaxation measurements. The  $\alpha$ -relaxation time of the water component becomes shorter with increasing content of the faster methanol component in the mixture as expected and is much shorter than in the mixture of 1-propanol with 45 mol % water. In mixtures with lower water contents of 10–20 mol %, the  $\alpha$ -relaxation of the methanol component has a narrow frequency dispersion and no resolved Johari–Goldstein  $\beta$ -relaxation, indicating a low degree of intermolecular coupling or cooperativity of methanol. An increase of the content of the slower water component effectively enhances intermolecular coupling of the methanol component. Consequently, the  $\alpha$ -relaxation of the methanol component becomes more cooperative, as evidenced by broadening of its frequency dispersion and the appearance of a resolved Johari–Goldstein  $\beta$ -relaxation of methanol when the water concentration is higher than 30 mol %. The observations are rationalized by application of the coupling model.



## I. INTRODUCTION

The dynamics of water is interesting for study because of the prevalence of water in many different systems of importance. Study of the dynamics of bulk water in the supercooled liquid state at lower temperatures and frequencies is impossible because of crystallization.<sup>1,2</sup> Thus, information is deduced by either relaxation of water in aqueous mixtures of hydrophilic solutes<sup>3–5</sup> or confined in structures of nanometer size.<sup>6–12</sup> Most hydrophilic solutes are less mobile than water, and the dynamics of the solute is slowest in the aqueous mixture, showing up as a structural  $\alpha$ -relaxation of the mixture. It is detectable by calorimetry and dielectric relaxation spectroscopy, with its relaxation time,  $\tau_\omega$ , having non-Arrhenius  $T$  dependence usually described by the Vogel–Fulcher–Tammann law. The relaxation of the water component is faster and usually observed to have the characteristics of a secondary relaxation.<sup>3–5</sup> One such characteristic is that its relaxation time,  $\tau_W$ , changes temperature dependence at the glass transition temperature,  $T_g$ , of the aqueous mixture. The change is from Arrhenius  $T$  dependence in the glassy state of the aqueous mixture for  $T < T_g$  to a stronger  $T$  dependence for  $T > T_g$ .<sup>3–5</sup> Increasing water content in the mixtures before water crystallizes invariably leads to shorter  $\tau_\alpha$  and  $\tau_W$ . Confinement of water in various structures of nanometer size to avert crystallization has found relaxation of water with properties similar to those of the secondary relaxation of water in mixtures but with

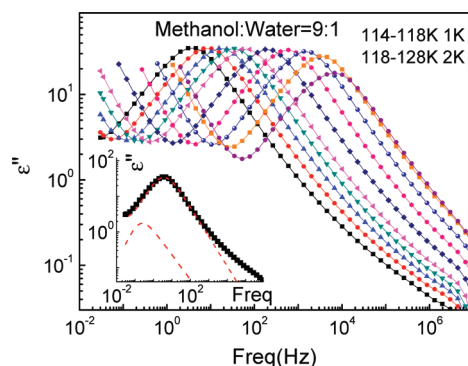
relaxation times,  $\tau_{\text{conf}}$  faster than  $\tau_W$  in all mixtures studied,<sup>3–5</sup> except that in the case of 20 wt % water in 1-propanol.<sup>3,5,13</sup> So far,  $\tau_W$  in 20 wt % (or 45 mol %) water in 1-propanol is the shortest of all  $\tau_W$  values in other mixtures and slightly shorter than the shortest  $\tau_{\text{conf}}$  ever observed. Comparisons of  $\tau_W$  of various mixtures and  $\tau_{\text{conf}}$  can be found in ref 5.

The exceptionally fast  $\tau_W$  of water in a mixture with 1-propanol ( $\text{C}_3\text{H}_7\text{OH}$ ) has been attributed to 1-propanol having the lowest  $T_g$  of all hydrophilic solutes published so far.<sup>1,5,13</sup> The slowest of all observed relaxations in 20 wt % water in 1-propanol is from the water component, and it is slower than the  $\alpha$ - and  $\beta$ -relaxations of 1-propanol in the mixture. This is perhaps unsurprising because the glass transition temperature of 1-propanol,  $T_g = 96$  K from calorimetry<sup>14</sup> and 99 K from dielectric relaxation measurements,<sup>15</sup> is lower than any suggested  $T_g$  of uncrystallized water.<sup>1</sup> Although the dielectric relaxation data are reliable, and the rationalization of the observation is reasonable, it is desirable to have additional support from observation of  $\tau_W$  of similar nature in other aqueous mixtures with the hydrophilic solute as mobile or even more mobile (or lower  $T_g$ ) than 1-propanol.

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**Figure 1.** Dielectric loss of a mixture of 90 mol % methanol–10% water from 114 to 128 K. A broadening of the relaxation peak at the low-frequency side is evidenced, and the fitting of the HN equation indicates the presence of slower relaxation shown in the inset.

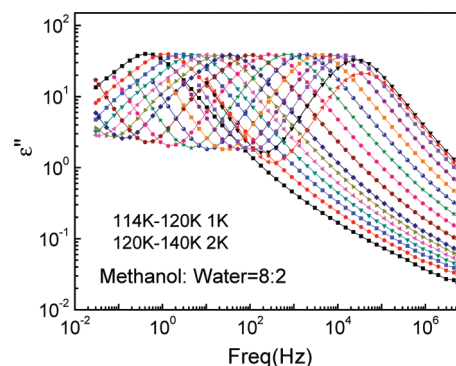
For this purpose we studied mixtures of water with methanol ( $\text{CH}_3\text{OH}$ ). From the phase diagram of water and methanol mixtures,<sup>16,17</sup> the mixtures are miscible within the range of composition from 10 to 40 mol % water and crystallization can be avoided at lower temperatures. By making broad-band dielectric relaxation measurements of mixtures within this composition range, we have studied not only the dynamics of water but also that of methanol in the mixtures and the dependence on the composition. The observed effects of the presence of methanol on the dynamics of water and vice versa are elucidated and interpreted theoretically. The results are beneficial for the study of the dynamics of both water and methanol, the smallest of the primary alcohols.

## II. EXPERIMENTAL SECTION

The dynamics of the binary mixtures of methanol and water was studied by dielectric relaxation measurements over a broad frequency range from 0.01 Hz to 10 MHz. To achieve a high cooling rate to avoid the crystallization of the mixtures, the sample chamber (cryostat) was precooled to  $\sim 110$  K and then the sample cell holding the liquid mixtures was plunged into the cryostat. Frequency-dependent impedance measurements were performed in a Novocontrol broad-band dielectric spectrometer (Concept 80) with a liquid nitrogen cooling system. The dielectric relaxations of the samples were isothermally measured at each temperature by holding the liquid between two brass electrodes, which are separated by Teflon strips of 25  $\mu\text{m}$  thickness. The measurements started from a temperature of 114 K for each measurement, and the temperature was controlled by a Novocontrol Quatro controller with a temperature accuracy within 0.1 K.<sup>18</sup>

## III. RESULTS

**a. Water (10 mol %) in Methanol.** Isothermal dielectric loss spectra of the mixture of 10 mol % water in methanol (90M–10W) are shown in Figure 1. At such a low mole fraction of water, the loss comes mainly from the motion of the methanol component. The loss peak is narrow with a full width at half-maximum of less than 1.5 decades of frequency. However, it is asymmetrically broadened on the low-frequency side, unlike the shapes of the loss peaks of most if not all neat glass formers, which are usually broader on the high-frequency side and well fitted by



**Figure 2.** Dielectric loss of a mixture of 80 mol % methanol–20% water from 114 to 140 K. A slower relaxation is visible.

either the Cole–Davidson (CD) function<sup>19</sup> or the Fourier transform of the Kohlrausch–Williams–Watts (KWW) function:<sup>20,21</sup>

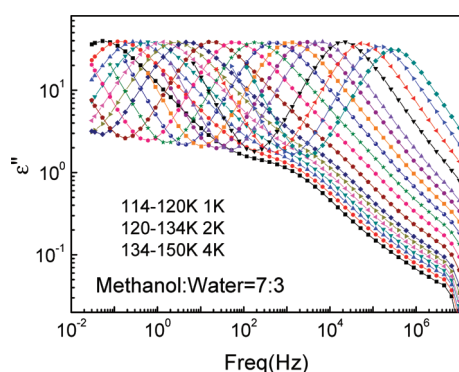
$$\varphi = \exp[-(t/\tau)^{\beta_{\text{KWW}}}] \quad (1)$$

where  $\tau$  is the relaxation time and  $\beta_{\text{KWW}}$  is the stretching exponent.

This abnormal broadening on the low-frequency side of the loss peak can be considered an indication of the contribution from the slower water component. To fit the dielectric data showing more than one relaxation process from the two components of the mixtures, a number of Havriliak–Negami (HN)<sup>22</sup> equations are used:<sup>23</sup>

$$\varepsilon^*(\omega) = \varepsilon_\infty + \sum_{j=1} \frac{\Delta\varepsilon_j}{[1 + (i\omega\tau_j)^{\alpha_j}]^{\gamma_j}} + \frac{\sigma_{\text{dc}}}{i\omega\varepsilon_0\omega} \quad (2)$$

where  $\varepsilon_\infty$  is the high-frequency dielectric constant and  $\Delta\varepsilon_j$  is the dielectric strength,  $\tau_j$  is the dielectric relaxation time, and  $\alpha_j$  and  $\gamma_j$  are the dispersion parameters of the  $j$ th relaxation process. Since multiple processes appear in the isothermal spectra and the fitting procedure used involves several HN functions, there are substantial uncertainties in the parameters determined. Estimates of error have been made. For the relaxation times of both components, water and methanol, the error estimates are shown by error bars in the relaxation map (to be shown later in Figures 6 and 7) for 90M–10W presently discussed as well as other compositions to be discussed later. For the  $\alpha$ -relaxation of each component, the HN parameters,  $\alpha_j$  and  $\gamma_j$ , so obtained are used for conversion into the exponent  $\beta_{\text{KWW}}$  of the KWW function. More support for the interpretation that the low-frequency part of the loss peak comes from the slower water component will be given later from the trend shown by the spectra of mixtures on increasing the mole fraction of water. No resolved secondary relaxation appears on the high-frequency flank of the loss peak, but there is an excess of loss over the power law  $\varepsilon''(f) \propto f^{-m}$  of any fit by the CD or KWW function, where  $m$  is a fraction of unity. In many glass formers, this excess loss turns out to be the contribution from an unresolved secondary  $\beta$ -relaxation.<sup>24</sup> The  $\beta$ -relaxation is not resolved because its relaxation time,  $\tau_\beta$ , is not sufficiently short compared to the  $\alpha$ -relaxation time,  $\tau_\alpha$ , and its relaxation strength is much smaller than that of the  $\alpha$ -relaxation, as found, for example, in glycerol, propylene glycol, and propylene carbonate.<sup>24–26</sup> The observation of an  $\alpha$ -loss peak in 90M–10W with a width as narrow as that of the  $\alpha$ -loss peak of the aforementioned glass formers supports the identification

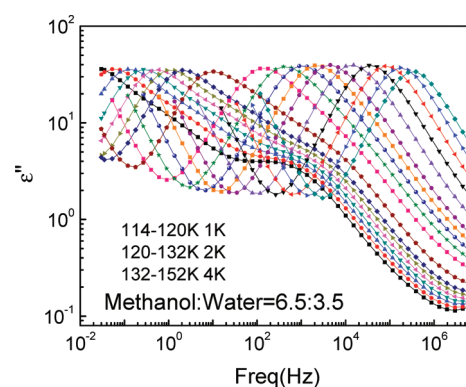


**Figure 3.** Dielectric loss of a mixture of 70 mol % methanol–30% water from 114 to 150 K. A fast relaxation is visible. A broadening of the main relaxation peak is detected, indicating the presence of two relaxations.

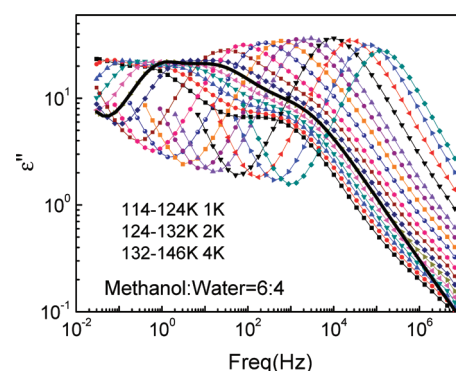
of the excess wing as an unresolved  $\beta$ -relaxation of the Johari–Goldstein (JG) kind of the methanol component caused by the small separation between  $\tau_\alpha$  and  $\tau_\beta$ .<sup>24–26</sup> Further support comes from either the empirical correlation that  $\log[\tau_\alpha/\tau_\beta]$  increases monotonically with the full width at half-maximum normalized by that of the Debye relaxation,  $w$ , of the  $\alpha$ -loss peak<sup>25,26</sup> or the same prediction of the coupling model, which will be presented separately in section V.

**b. Water (20 mol %) in Methanol.** The isothermal spectra obtained in a mixture with the water content increased to 20 mol % (80M–20W) are presented in Figure 2. The change of the spectra by increasing the water content helps to further interpret the dynamics of the water and the methanol components in the mixture with 10 mol % water. First, on increasing the concentration of water from 10 to 20 mol %, the  $\alpha$ -loss peak is shifted to lower frequencies while the temperature is held constant. At 114 K, the shift is about 1 decade. Second, there is extra broadening on the low-frequency side of the loss peak, which indicates that it is due to the presence of more water acting as the slower component, and thus, the methanol component is further slowed. Third, there is also a substantial increase in the full width at half-maximum normalized by that of the Debye relaxation,  $w_{M0}$ , of the  $\alpha$ -loss peak of the methanol component. Fourth, there is the appearance at higher frequencies of a wider and stronger excess wing, suggesting the start of an increased separation between the  $\alpha$ -relaxation and the  $\beta$ -relaxation times of the methanol component. The nature of the slower relaxation of the water component can be inferred from the temperature dependence of broadening on the low-frequency side of the loss peak. By inspection of Figure 2, it is clear that the broadening increases with decreasing temperature, suggesting an increase of the dielectric strength of the relaxation of the water component with decreasing temperature. This property is confirmed in mixtures with higher concentrations of water to be discussed below. From this we can conclude that the observed relaxation of the water component is the  $\alpha$ -relaxation. The relaxation strength of the water component in 45 mol % water in 1-propanol also increases with decreasing temperature, and hence, it is the  $\alpha$ -relaxation as in the present case.

**c. Water (30 and 35 mol %) in Methanol.** The trend of changes in the dielectric spectra with increasing water mole fraction elucidated in the above becomes more evident in the mixture with 30 mol % water (70M–30W). For the first time, the  $\beta$ -relaxation is resolved as a shoulder in the loss spectra at lower temperatures (see Figure 3). The increase of the water content is responsible for the rise of the low-frequency flank of the loss peak, making it more



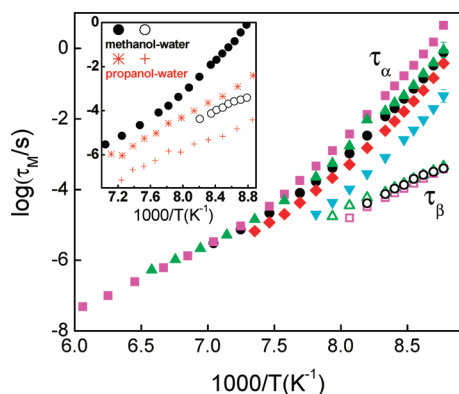
**Figure 4.** Dielectric loss of a mixture of 65 mol % methanol–35% water from 114 to 152 K. Three relaxations can be observed at low-temperature measurements.



**Figure 5.** Dielectric loss of a mixture of 60 mol % methanol–40% water from 114 to 146 K. The thick line is the fitting curve with three HN equations.

symmetric but broader. Continued increase of the water mole fraction in the mixture to 35% (65M–35W) changes the shoulder to a peak, making absolutely clear that it is the resolved  $\beta$ -relaxation of the methanol component (see Figure 4). Concurrently, one can observe an alteration of the shape of the loss peak from being broader at lower frequencies at 10 or 20 mol % water to being broader on the high-frequency side at 35 mol % water. This observed alteration with increasing water content originates from more than one factor given as follows: (1) the relaxation of the water component becoming slower and having a larger dielectric strength, leading to separation and resolution of the  $\alpha$ -relaxation of the water component from the  $\alpha$ -relaxation of the methanol component, (2) the attendant reduction of the dielectric strength of the methanol  $\alpha$ -relaxation, making it to appear as a broad contribution on the high-frequency side of the loss peak. The losses contributed by the  $\alpha$ -relaxations of water and methanol are shifted to lower frequencies at constant temperature. The slowing of the  $\alpha$ -relaxation of water and methanol together is due to the increasing mole fraction of the slower water component, which is intuitively easy to understand. On the other hand, there is no noticeable shift of the  $\beta$ -relaxation of the methanol component by comparing the loss constituting the shoulder. Thus, the separation between the  $\alpha$ -relaxation and  $\beta$ -relaxation of methanol has increased. Since the slower (faster)  $\alpha$ -relaxation increases (decreases) in strength with increasing water content, the slower relaxation is definitely coming from the water component.





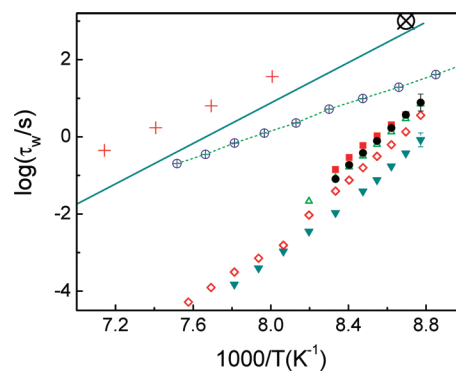
**Figure 6.** Arrhenius plot of  $\tau_{M\alpha}$  (closed symbols) and  $\tau_{M\beta}$  (open symbols) for the methanol component in mixtures with water at several molar fractions: 10% (inverted triangles), 20% (tilted squares), 30% (squares), 35% (triangles), and 40% (circles). Note that the data for  $\tau_{M\beta}$  are shown for compositions with 30%, 35%, and 40% water and not lower because the  $\beta$ -relaxation is not resolved at lower water contents. In the inset,  $\tau_{M\alpha}$  (closed circles) and  $\tau_{M\beta}$  (open circles) of the methanol component in a methanol–water mixture with 40 mol % water are compared with the  $\alpha$ -relaxation time,  $\tau_{P\alpha}$  (\*), and  $\beta$ -relaxation time,  $\tau_{P\beta}$  (+), of 1-propanol in a mixture with water containing 45 mol % water taken from refs 3 and 13.

**d. Water (40 mol %) in Methanol.** The trends of all the relaxations found in the mixture on increasing the water content to 35 mol % water continues to be observed in the same direction in the mixture with 40 mol % water (60M–40W), the highest concentration of water studied without running into problems of crystallization. The  $\alpha$ -relaxations of water and methanol both become slower as shown in Figure 5 by their shifts to lower frequencies at the same temperature, and they become more separated from each other. The observed changes of dynamics of the methanol component on increasing the mole fraction of water are no different from those found in the more mobile (lower  $T_g$ ) component on increasing the concentration of the less mobile (higher  $T_g$ ) component in binary mixtures of van der Waals liquids.<sup>27–30</sup> These similar changes observed include the monotonic increases of the following three quantities of the faster methanol component: (1) the width of the frequency dispersion of the  $\alpha$ -relaxation, (2) the  $\alpha$ -relaxation time  $\tau_{M\alpha}$  and (3) the separation of the  $\beta$ -relaxation from the  $\alpha$ -relaxation measured by the difference [ $\log \tau_{M\alpha} - \log \tau_{M\beta}$ ] at a predetermined value of  $\tau_{M\alpha}$ . For binary mixtures of van der Waals liquids, all three effects have been attributed to the monotonic increase of intermolecular coupling of the faster component by increased presence of the slower component.<sup>27–30</sup>

#### IV. DISCUSSION

We have fitted the isothermal loss spectra in Figures 1–5 to determine the frequency dispersion and the  $\alpha$ -relaxation times  $\tau_{W\alpha}$  of water and  $\tau_{M\alpha}$  of methanol and the  $\beta$ -relaxation time  $\tau_{M\beta}$  of methanol. Two HN functions are used for the dielectric spectra of the mixture with 10 and 20 mol % water and three (one extra to account for the  $\beta$ -relaxation of methanol) for those of the mixtures with 30, 35 and 40 mol % water. An example of the fits to the dielectric loss of the 40 mol % water mixture at 119 K is shown in Figure 5 by the thick line.

Due to overlapping of the relaxation processes, some uncertainties are unavoidable in the obtained values of their relaxation times,  $\tau_{M\alpha}$ ,  $\tau_{M\beta}$ , and  $\tau_{W\alpha}$  and the frequency dispersions. The



**Figure 7.** Relaxation times,  $\tau_{W\alpha}$ , of the water component in mixtures with methanol of several compositions. Water mole fractions: 10% (closed inverted triangles), 20% (open tilted squares), 30% (closed squares), 35% (open triangles), and 40% (closed circles). For comparison, shown are the relaxation times of water in other systems: mixture of 1-propanol with 45 mol % water (open circles with “+” inside, linked together by dashed line, from refs 3 and 13), dielectric data (ref 8) of the  $\tau_W$  of water confined in MCM-41 with a pore diameter of 2.14 nm at a hydration level of 0.55 (red “+”), relaxation time of the fast process of water confined within 1.2, 1.6, and 1.8 nm nanopores of MCM-41 obtained by adiabatic calorimetry with  $\tau_W = 10^3$  s at  $T = 115$  °C (circle with black “x”, from ref 9), Arrhenius fit to  $\tau_W$  of 20% water nanoconfined in graphite oxide obtained by dielectric relaxation measurements (solid straight line, from ref 12), actual data not shown.

reciprocal temperature dependences of  $\tau_{M\alpha}$  in mixtures of all compositions and  $\tau_{M\beta}$  for water mole fractions of 30% and higher are presented in the main part of Figure 6. Uncertainties of the values are indicated by error bars in the figure. The super-Arrhenius  $T$  dependence of  $\tau_{M\alpha}$  and the much weaker  $T$  dependence of  $\tau_{M\beta}$  are typical for a pair of  $\alpha$ - and  $\beta$ -relaxations. It is worthwhile to point out in Figure 6 that  $\tau_{M\alpha}$  in a mixture with 30 mol % water is slightly longer than in mixtures with 35 and 40 mol % water. This unexpected result is likely an artifact caused by the large uncertainty in deducing the  $\tau_{M\alpha}$  in a mixture with 30 mol % water from the fits to the spectra in Figure 3, where the contributions from the water and the methanol components merge together to form the loss peak.

In the inset of Figure 6, comparison is made of these characteristics of methanol in mixtures with 40 mol % water with the corresponding  $\alpha$ - and  $\beta$ -relaxation times,  $\tau_{P\alpha}$  and  $\tau_{P\beta}$ , of the 1-propanol component in a mixture with 45 mol % (equivalent to 20 wt %) water published in refs 3 and 13. Mixtures with 45 mol % water cannot be studied because of intervention by crystallization. It can be seen by inspection, despite the lower water content, that the  $\alpha$ -relaxation of the methanol component is slowed by water much more than the 1-propanol component. The larger effect of water on methanol than 1-propanol can be rationalized by the significant increase of intermolecular coupling in the mixture with 40 mol % water compared with the mixture with 10 mol % water, as evidenced by the large increase in the separation between  $\tau_{M\alpha}$  and  $\tau_{M\beta}$  at fixed  $\tau_{M\alpha}$  or by the fact that neat methanol shows nearly exponential relaxation.<sup>31</sup> On the other hand, only a small change in the separation between  $\tau_{P\alpha}$  and  $\tau_{P\beta}$  at fixed  $\tau_{P\alpha}$  was observed for 1-propanol when mixed with 45 mol % water.<sup>3,13</sup>

The  $T$  dependences of the  $\alpha$ -relaxation times,  $\tau_{W\alpha}$ , of the slower water component in all the mixtures are shown by the Arrhenius plot in Figure 7. The trend of decreasing  $\tau_{W\alpha}$  with increasing concentration of methanol (the more mobile component) is evident. Again,

the exception is  $\tau_{W\alpha}$  of water in the mixture with 30 mol % water, but the exception is likely an artifact of the large uncertainty in deducing  $\tau_{W\alpha}$  and  $\tau_{M\alpha}$  from fits to the loss peaks that do not allow the contributions from the two components to be unequivocally determined. In Figure 7, we compare  $\tau_{W\alpha}$  of the water component in mixtures with methanol with that in the mixture of 1-propanol containing 45 mol % water. It is clear from the comparison that methanol is much more effective than 1-propanol in accelerating the relaxation of the water component upon mixing, and this is reasonable since methanol having only one carbon atom should be more mobile than 1-propanol having three carbon atoms. Of interest is the comparison with the fast relaxation of water confined in nanometer size spaces,  $\tau_{\text{conf}}$  without suffering from crystallization at lower temperatures. Shown in Figure 7 are relaxation times of water confined in the nanoporous matrix MCM-41 with a pore diameter of 2.14 nm at a hydration level of  $h = 0.55$  obtained by dielectric spectroscopy.<sup>8</sup> Also shown is the relaxation time of  $10^3$  s at  $T = 115$  K obtained by adiabatic calorimetry measurements of the enthalpy relaxation of water confined within 1.2 nm MCM-41 nanopores,<sup>9</sup> which seems to be in accord with the dielectric data when extrapolated to lower temperatures. The magnitudes of the relaxation time of the 6 Å ultrathin water layer (two molecular layers) confined in fully hydrated Na-vermiculite clay measured by dielectric spectroscopy (not shown) are slightly longer.<sup>7</sup> Included in Figure 7 is the Arrhenius temperature dependence of the dielectric relaxation times of uncrystallized water intercalated in graphite oxide with a water concentration of 25 wt % (data points not shown).<sup>12</sup>

The relaxation times  $\tau_{W\alpha}$  of the water component in mixtures with methanol are shorter than the relaxation time of nanoconfined water  $\tau_{\text{conf}}$  by about 2 orders of magnitude at 115 K, which increases with temperature to about 4 orders of magnitude at about 132 K. This observation, that  $\tau_{W\alpha}$  of the water component in mixtures with methanol can be orders of magnitude faster than  $\tau_{\text{conf}}$  of nanoconfined water, is noteworthy because of the following consideration. The  $\tau_{\text{conf}}$  has been interpreted as the relaxation time of noncooperative relaxation or  $\beta$ -relaxation of water,<sup>5,8,12</sup> while  $\tau_{W\alpha}$  in mixtures with methanol or with 1-propanol<sup>3,5</sup> is the  $\alpha$ -relaxation time of the water component, a conclusion arrived from the observed increase of its relaxation strength with decreasing temperature.

The temperature dependence of the relaxation times  $\tau_{W\alpha}$  of water in methanol over an extended temperature range is not Arrhenius as can be seen from the data of 90M–10W and 80M–10W in Figure 7. This is not surprising because  $\tau_{W\alpha}$  is the  $\alpha$ -relaxation time of the water component in the mixture with methanol. If the long time portion of the  $\tau_{W\alpha}$  data of 90M–10W is forced into fitting to an Arrhenius law, its activation energy of 80 kJ/mol is much higher than the activation energy of 55 kJ/mol of confined water in MCM-41 with a pore diameter of 2.14 nm at a hydration level of 0.55.<sup>8</sup> The fact that  $\tau_{W\alpha}$  has a stronger  $T$  dependence (or higher activation energy) and yet is shorter than  $\tau_{\text{conf}}$  seems peculiar at first sight. However, this is perfectly reasonable after considering the drastic difference in nature of the two relaxation times. While  $\tau_{\text{conf}}$  is the JG  $\beta$ -relaxation time of confined water, which is local and noncooperative,  $\tau_{W\alpha}$  is the  $\alpha$ -relaxation time of water in methanol and its  $T$  dependence is controlled by the volume and entropy change of the mixture with temperature.

Molecular segregation in methanol–water mixtures has been reported on the basis of neutron diffraction,<sup>32</sup> proton nuclear magnetic resonance,<sup>33</sup> and molecular dynamics simulation<sup>32</sup> on cooling and compression. The microscopically hydrophilic/

hydrophobic segregation might create a special confinement effect, directly leading to the formation of reverse micelles or water-in-oil-type microemulsions in the mixtures of high methanol concentration. Our previous study on liquid dynamics in confinements of water-in-oil microemulsions found that the dynamics of “water” would be changed greatly by that of “oil” and a considerable acceleration in the former is likely provided the latter is much faster.<sup>34</sup> This might partly explain the experimental observation of the faster dynamics of water in the methanol–water mixtures than that in confined water.

It is worthwhile to reemphasize the interesting findings of this paper. First, by mixing with methanol, relaxation of water has been made faster than the JG  $\beta$ -relaxation of water when confined in nanometer spaces. Second, pure methanol has a low degree of cooperativity, fragility, and nonexponentiality, and it has no resolved JG  $\beta$ -relaxation, but by mixing with a sufficient mole fraction of water, its cooperativity, fragility, and nonexponentiality are all enhanced and its JG  $\beta$ -relaxation is resolved.

## V. COUPLING MODEL EXPLANATION

From the results presented in section III and the discussions given above, we have seen experimental evidence of the trends in the changes of the dynamics of the two components in water–methanol mixtures on varying the composition. Starting from the 90M–10W mixture with a low concentration of the slower water component in section III, subsection c, the observed  $\alpha$ -loss peak contributed mainly by methanol is narrow, and on its high-frequency flank appears an excess wing. This property of the methanol component is like that found in some neat glass formers<sup>24–26</sup> also having a narrow  $\alpha$ -loss peak, where the excess wing has been identified as an unresolved  $\beta$ -relaxation of the Johari–Goldstein kind caused by the small separation between  $\tau_\alpha$  and  $\tau_\beta$ .<sup>35,36</sup> Naturally, the same interpretation applies to the methanol component in the 90M–10W mixture. Further support comes from the empirical fact that  $\log[\tau_\alpha/\tau_\beta]$  increases monotonically with the full width at half-maximum normalized by that of the Debye relaxation,  $w$ , of the  $\alpha$ -loss peak.<sup>25,26</sup> This empirical fact is consistent with the prediction of the coupling model,<sup>26</sup> rewritten in the following form:

$$\log \tau_\alpha - \log \tau_\beta = n[\log \tau_\alpha - \log t_c] \quad (3)$$

Here  $n$  is the fractional exponent in the KWW function,  $n = 1 - \beta_{\text{KWW}}$ , and  $t_c$  is on the order of 1–2 ps for molecular glass formers. The empirical fact readily follows from eqs 1 and 3 because  $w$  increases with  $n$  according to the relation<sup>37</sup>

$$n = 1.047(1 - w^{-1}) \quad (4)$$

It should be mentioned that eqs 3 and 4 hold only for neat glass formers where the fractional exponent  $n$  of the KWW function in eq 1 is the true coupling parameter in the context of the coupling model.<sup>26</sup> Mixtures are different because of the presence of concentration fluctuations and possible overlapping contributions from both components, both of which additionally broaden the frequency dispersion of the  $\alpha$ -relaxation of each component, as in the present case.<sup>38</sup> Not only will the KWW function not give a satisfactory fit to the  $\alpha$ -relaxation of each component, but also eqs 3 and 4 cannot be used to deduce quantitatively its true coupling parameter. Nevertheless, following the established results from binary mixtures of glass-forming van der Waals liquids,<sup>5,27–30</sup> there is an increase of the coupling parameter of the faster component ( $n_M$  of methanol in the present study) due

to enhanced intermolecular coupling/constraints by the presence of the slower component (water here), and the coupling parameter  $n$  ( $n_M$  of methanol in here) increases with the concentration of the slower (water) component. In the opposite direction, the coupling parameter of the slower component ( $n_W$  of water here) is reduced by the faster component (methanol here), and the reduction increases with the concentration of the faster component (methanol).

Returning to the spectra of the 90M–10W mixture in Figure 1, the narrow  $\alpha$ -loss peak of the methanol component with  $w < 1.5$  and the absence of a resolved  $\beta$ -relaxation both indicate that the methanol component has a small coupling parameter,  $n_M$ . This is unsurprising because of the smaller amount of water present and the fact that the water component is only slightly slower than the methanol component at this composition (see the inset in Figure 1). It is also consistent with the molecular dynamics simulation results on the correlation functions of neat methanol having values of the KWW exponent,  $\beta_{KWW} \equiv 1 - n$ , close to unity.<sup>31</sup>

On slightly increasing the water content in the mixture to 20 mol % water, the isothermal spectra of 80M–20W presented in section III, subsection b still show a single loss peak contributed substantially by the methanol component. However, there is now a substantial increase in the full width at half-maximum of the loss peak, and hence also  $w_M$ , the normalized full width at half-maximum of the  $\alpha$ -loss peak contributed by the methanol component. This increase of  $w_M$  is taken as evidence for the increase of the coupling parameter,  $n_M$ , of the methanol component by the increased mole fraction of the slower water component. Collaborative evidence can be drawn from the concomitant appearance at higher frequencies of a wider and stronger excess wing, suggesting an increased separation between the  $\alpha$ -relaxation and the  $\beta$ -relaxation times of the methanol component. From this, an increase of  $n_M$  can be deduced by the application of eq 3.

Significant changes in the dielectric spectra become apparent in Figures 3 and 4 on increasing the water mole fraction in the mixtures further to 30 and 35 mol % water. As described before in section III, subsection c, the  $\beta$ -relaxation of the methanol component is resolved as a shoulder and a peak in mixtures with 30 and 35 mol % water, respectively. Thus, the separation between the  $\alpha$ -relaxation and  $\beta$ -relaxation of the methanol component clearly increases with the concentration of water. Moreover, the shape of the  $\alpha$ -loss peak of the 65M–35W sample becomes broader on the high-frequency side, in contrast to being broader at lower frequencies observed in mixtures with 10 or 20 mol % water. This and other changes of the spectra given before in section III, subsection c, all indicate slowing of the  $\alpha$ -relaxation of water, as well as methanol, due to the increasing mole fraction of the slower water component. These observed changes can be explained by the coupling model applied to component dynamics in mixtures.<sup>39,40</sup> A increase of the concentration of the slower water component has the consequence of increasing the intermolecular couplings and constraints and hence an attendant increase of the coupling parameters  $n_W$  of water and  $n_M$  of methanol. It follows from eq 3 that the increase in  $n_M$  of methanol explains the larger difference between  $\log \tau_{M\alpha}$  and  $\log \tau_{M\beta}$  and hence the resolution of the Johari–Goldstein  $\beta$ -relaxation of the methanol component when the mole fraction of water is increased to 30% and beyond.

At the highest content of water, 40 mol %, in the 60M–40W mixture, the  $\alpha$ -relaxations of water and methanol both become slower and broader in frequency dispersion than those of the other mixtures. Furthermore, the two  $\alpha$ -relaxations become

more separated in time from each other. There is also a further increase in the separation of the  $\beta$ -relaxation from the  $\alpha$ -relaxation of the methanol component when compared by the difference  $[\log \tau_{M\alpha} - \log \tau_{M\beta}]$  at a predetermined value of  $\tau_{M\alpha}$ . All these effects shown in Figure 5 originate from the largest increase of intermolecular coupling and the associated coupling parameter  $n_{M\alpha}$  of the faster methanol component by the slower water component in the 60M–40W mixture with the highest content of water and can be explained by eqs 1, 3, and 4.

## VI. SUMMARY AND CONCLUSION

The purpose of the study of mixtures of water with methanol reported here is two-fold. One is to reinforce the previous and remarkable finding in a mixture with 1-propanol that water becomes the slower component and its  $\alpha$ -relaxation is rendered even faster than relaxation of water confined in a space of nanometer size. The relaxation of nanoconfined water is a noncooperative and local process identifiable as the  $\beta$ -relaxation of water. Methanol, having fewer carbon atoms than 1-propanol, should be more effective in accelerating the  $\alpha$ -relaxation of water in mixtures with methanol. This expectation is confirmed by the dielectric relaxation measurements of mixtures of methanol with the water concentration ranging from 10 to 40 mol %, which show the relaxation time of the  $\alpha$ -relaxation of water in mixtures with methanol is even shorter than in mixtures with 1-propanol. Remarkably, the  $\alpha$ -relaxation time of water in mixtures with methanol can become so short in some temperature ranges that it is several orders of magnitude shorter than even the local relaxation time of nanoconfined water.

Molecular dynamics simulations have indicated that methanol is a strong liquid with a low degree of cooperativity or intermolecular coupling. However, pure methanol is not amenable to study at low frequencies in the glass transition range due to crystallization. The other purpose of the present study of mixtures of methanol with water is to investigate the change of dynamics of methanol by the slower water component. The dielectric relaxation measurements of a mixture at a low concentration of water of 10 mol % show that the  $\alpha$ -relaxation of methanol has a narrow dispersion and no resolved secondary  $\beta$ -relaxation. These characteristics of the dynamics of methanol in a mixture with 10 mol % water should be reinforced in pure methanol, had measurement been possible, because the presence of the slower water can only enhance the cooperativity of methanol. On increasing the water content in the mixture to 30 mol % and higher, enhancement of cooperativity in the  $\alpha$ -relaxation of the methanol component by water becomes evident. The evidence comes from the appearance of a resolved Johari–Goldstein  $\beta$ -relaxation well separated from the  $\alpha$ -relaxation, both coming from the methanol component. Although this change of the dynamics of a more mobile (lower  $T_g$ ) component by the other component has been reported before in binary mixtures of van der Waals glass formers,<sup>27–30</sup> it is the first such case for binary mixtures of hydrogen-bonded liquids involving water, as far as we know.

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