

# Ideal Mixing Behavior of the Debye Process in Supercooled Monohydroxy Alcohols

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Glass-forming monohydroxy alcohols exhibit two dielectric relaxation signals with super-Arrhenius temperature dependence: a Debye peak and an asymmetrically broadened  $\alpha$ -process. We explore the behavior of these distinct relaxation features in mixtures of such liquids by dielectric measurements. The study focuses on the viscous regime of two binary systems: 2-methyl-1-butanol with 2-ethyl-1-hexanol and 1-propanol with 3,7-dimethyl-1-octanol. We find that the logarithmic relaxation time,  $\log(\tau)$ , of the Debye peak follows an ideal mixing law (linear change with mole fraction), even in the case of mixing structurally dissimilar components. By contrast, the  $\log(\tau)$  versus mole fraction curve for the  $\alpha$ -process is nonlinear, indicative of slower structural relaxation relative to the expectation on the basis of ideal mixing behavior. The latter observation is analogous to the effect of composition on viscosity, heat of mixing, and glass-transition temperature, whereas the ideal mixing of  $\log(\tau)$  seen for the Debye peak is the exception. We conclude that the unusual ideal mixing behavior of dielectric relaxation in monohydroxy alcohols is not a result of structural similarity, but rather yet more evidence of the Debye process being decoupled from other dynamic and thermodynamic properties.

## 1. Introduction

Dielectric relaxation techniques have become an actively used method in the investigation of structure and dynamics for a wide variety of samples.<sup>1–3</sup> The most powerful feature of this method is the extremely wide frequency range across which effects such as conduction and polarization can be detected, microhertz to terahertz. In dielectric materials, relaxation associated with permanent dipoles, induced or transient dipoles, and space charges are the main sources of dielectric dispersion or absorption at not too high frequencies.<sup>4–6</sup> For molecular liquids which are free of charge carriers, the dielectric polarization is usually thought to originate from the orientational degree of freedom of permanent dipoles. Because sufficient dipole density is available in the majority of liquids, dielectric relaxation measurements yield very direct information about the molecular motion across a wide range of materials and time scales.

For the study of molecular motion or structural relaxation in liquids, a large variety of experimental methods is available, for example, mechanical, enthalpic, or volume relaxation, acoustic attenuation, light scattering, and nuclear magnetic resonance.<sup>7–9</sup> The different approaches to relaxation dynamics probe different time correlation functions of the system.<sup>10</sup> However, common to all these experiments on relaxation processes of liquids and glasses is the observation of a stretched exponential or Kohlrausch–Williams–Watts (KWW) decay behavior

$$\phi(t) = \phi_0 \exp[-(t/\tau)^\beta] \quad (1)$$

where  $\phi(t)$  is the time-dependent relaxing property,  $\tau$  the characteristic relaxation time, and  $\beta$  the stretching exponent with  $0 < \beta \leq 1$ . The exponent  $\beta$  is used to characterize the degree of broadening of the relaxation time dispersion in liquids and glasses, where  $\beta = 1$  corresponds to the purely exponential or Debye type case. For a given sample, various correlation functions display slightly different  $\beta$  values, so that it is a key parameter used to correlate and compare the different relaxation

processes.<sup>11,12</sup> On the basis of its small value of the stretching exponent, Angell and co-workers have concluded that enthalpy relaxation is a more fundamental quantity than others.<sup>11,12</sup> Irrespective of the relaxation process under study, it is now generally accepted that nonexponential (i.e., non-Debye,  $\beta < 1$ ) behavior is one of the universal features of the dynamics in supercooled liquids and glasses.<sup>13–15</sup>

For the majority of liquids, also the dielectric relaxation results exhibit non-Debye (or dispersive) dynamics, the effect being particularly pronounced in the supercooled or viscous regime near the glass-transition temperature  $T_g$ . Some liquids, however, especially monohydroxy alcohols, have been observed to show a dominant dielectric relaxation of the Debye type in their supercooled state, as initially reported by Mizushima.<sup>16</sup> At high temperatures/frequencies, Debye modes are not uncommon because molecular motion is not affected by strong intermolecular interactions or cooperativity. Because of its rare occurrence in the supercooled state, however, the Debye-type dielectric mode of monohydroxy alcohols has been subject to intense scrutiny.<sup>17–19</sup> Also, dielectric Debye relaxation peaks in primary alcohols are often accompanied by other loss peaks, which are positioned at higher frequencies and thus are indicative of additional faster dynamics.<sup>20–22</sup> Structural studies show that hydrogen-bonded liquids are more complex than those in which van der Waals interaction dominate. For instance, cyclic multimers have been suggested to prevail in some pure alcohols.<sup>23–25</sup> In recent years, evidence is being compiled that there is no simple relation between the dielectric Debye mode and structural relaxation in several associating liquids.<sup>26–29</sup>

In this paper, we explore a further property of the dielectric Debye relaxation in monohydroxy alcohols which is distinct from the typical behavior of structural relaxation. In some alcohols,<sup>29</sup> the Debye peak and the dielectric signature of structural relaxation ( $\alpha$ -process) are strongly separated on the frequency scale and both processes can be analyzed in sufficient detail. Here, we compare the relaxation times of the Debye and  $\alpha$ -process as a function of composition in binary mixtures of

glass-forming monohydroxy alcohols. Although numerous studies of the dynamics of alcohols and their mixtures exist,<sup>30,31</sup> less is known about the mixing behavior of two monohydroxy alcohols.<sup>32–35</sup> Because it has been common practice to associate the Debye relaxation with structural relaxation, the more subtle  $\alpha$ -relaxation remained disregarded in many cases. Additionally, most of the experiments on the dynamics of mixtures are performed at high temperature or high frequency (GHz), where the interference with fast relaxation processes<sup>36,37</sup> complicates the identification of the true  $\alpha$ -relaxation. In the present work, we exploit the large spectral separation of the two dielectric peaks of interest in the viscous state of some monohydroxy alcohols and study the effect of mixing on the respective dynamics. We find that the dielectric  $\alpha$ -process exhibits nonideal mixing behavior, analogous to what has been observed for other quantities which are related to structural relaxation. The Debye peak, however, follows an ideal mixing law regarding the logarithmic relaxation time, that is, its  $\log(\tau)$  varies linearly with the mole fraction  $x$ .

## 2. Experimental Section

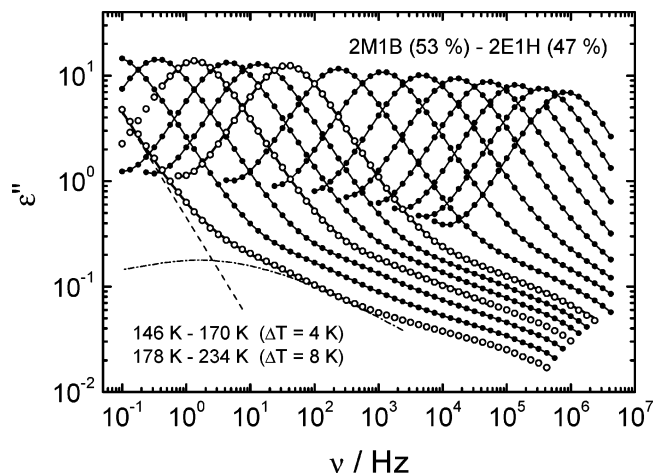
For the composition dependent studies, we chose the glass-forming alcohols 2-methyl-1-butanol (2M1B, 99+%), 2-ethyl-1-hexanol (2E1H, 99+%), 1-propanol (1POH, anhydrous 99+%), and 3,7-dimethyl-1-octanol (DM1O, 99+%). The alcohols are purchased from Aldrich and used as received. Binary mixtures of 2M1B with 2E1H and 1POH with DM1O have been prepared, with the composition being reported in terms of the mole fraction  $x$  of the lower  $T_g$  liquid. An important guide in choosing a pair of alcohols for a detailed mixture study is that the Debye and structural relaxation times show substantial separation. The 2M1B/2E1H mixture shows a ratio of  $\tau_D/\tau_\alpha$  as high as 3.3 decades.<sup>29</sup> The choice of the 1POH/DM1O mixture is based on the pronounced structural difference between the two compounds.

The dielectric measurements are conducted by holding liquids between two brass electrodes which are separated by thin Teflon stripes arranged in a radial geometry. All samples are measured inside a nitrogen-gas cryostat where the temperature is stabilized and measured by a Novocontrol Quatro temperature controller. Frequency dependent impedance measurements were performed using a Solartron 1260 gain-phase analyzer equipped with a Mestec DM-1360 transimpedance amplifier. Empty sample capacitors are used as the references to calibrate the frequency dependent transimpedance  $Z(\omega)$  of the DM-1360.<sup>38</sup>

In what follows, we will not discuss Goldstein–Johari type  $\beta$ -relaxations, although such secondary relaxations have been observed in some of the samples. Generally, three distinct features are detected in all the mixtures: dc-conductivity, a Debye-type relaxation, and a primary or  $\alpha$ -relaxation peak. We employ empirical fitting functions to quantify the characteristics of these processes:

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon_D}{1 + (i\omega\tau_D)^\alpha} + \frac{\Delta\epsilon_\alpha}{1 + (i\omega\tau_\alpha)^\alpha} + \frac{\sigma_{dc}}{\epsilon_0 i\omega} \quad (2)$$

where  $\epsilon_\infty$  is the dielectric constant in the high-frequency limit.  $\Delta\epsilon_D$  and  $\Delta\epsilon_\alpha$  are the relaxation strengths for the Debye (D) and primary ( $\alpha$ ) relaxation, while  $\tau_D$  and  $\tau_\alpha$  denote the respective relaxation times. The second and the third terms of this equation represent Cole–Cole (CC) functions with the symmetric broadening of the loss profiles quantified by the exponents  $\alpha'$  and  $\alpha$ . A CC function is also used for the Debye peak to be sensitive to a subtle broadening of the Debye relaxation.



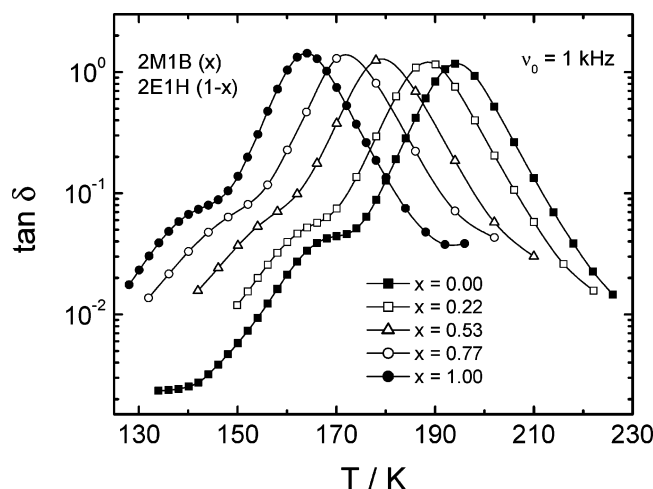
**Figure 1.** Frequency dependent dielectric loss of a 2-methyl-1-butanol (2M1B) 53 mol % – 2-ethyl-1-hexanol (2E1H) 47 mol % mixture for temperatures in the ranges 146–170 K (4 K step) and 170–234 K (8 K step). The dominant peaks are of Debye character, while the higher frequency shoulders reflect the  $\alpha$ - and  $\beta$ -relaxations. Fits to the Debye and  $\alpha$ -peaks on the basis of eq 2 are shown as lines for the temperatures  $T = 146, 158$ , and  $170$  K (identified by open symbol data points). The dashed line represents the Debye component of the fit while the dashed–dotted line shows the  $\alpha$  contribution for  $T = 146$  K.

Although Havriliak–Negami (HN) type fit functions are commonly used to reflect the asymmetrically broadened profiles of structural relaxation, our series of analyses found that CC functions yield better results for the present purposes. The dc-conductivity is quantified by the parameter  $\sigma_{dc}$ , but its magnitude is disregarded in what follows.

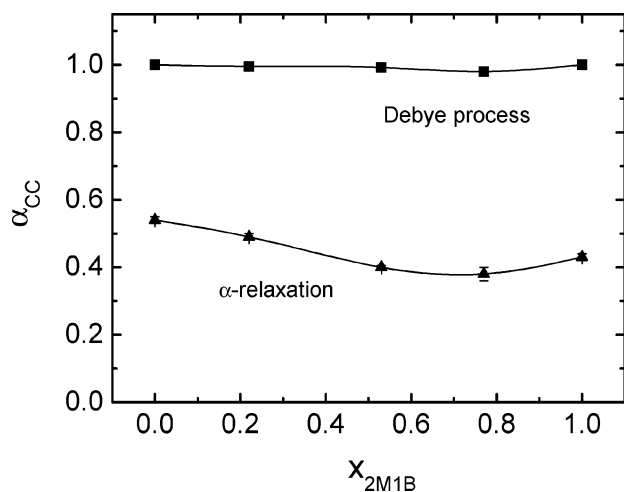
## 3. Results

As an example for dielectric loss profiles of alcohol mixtures, Figure 1 displays dielectric loss results of the 2E1H/2M1B solution with  $x = 53$  mol % 2M1B versus frequency for various temperatures. The curves include narrow and symmetric dominant relaxation peaks accompanied by shoulders indicative of further processes at higher frequencies, similar to the relaxation behavior in the pure liquids.<sup>29</sup> Accordingly, the dominant relaxation corresponds to a Debye relaxation, the more pronounced shoulder to the  $\alpha$ - or structural relaxation, and the smaller shoulder at even higher frequencies to the  $\beta$ - or secondary relaxation. Our main concern is how mixing changes the dynamics of the Debye and primary relaxation, that is, we compare  $\tau_D(x)$  and  $\tau_\alpha(x)$ . To this end, we plot  $\tan \delta = \epsilon''/\epsilon'$  versus temperature in Figure 2, where the dynamics is seen to shift along the temperature scale with concentration. Compared with the two pure alcohols, it is observed that the Debye and  $\alpha$ -relaxation peaks also exist in the mixtures, but with a smaller separation of their relaxation times relative to the pure components.

A data analysis based upon eq 2 is needed to quantify the mixing behavior in more detail. Although an asymmetrically broadened (Cole–Davidson or Havriliak–Negami type) profile is expected for the  $\alpha$ -peak, the overlap with the much stronger Debye signal and interference with the secondary peak forces us to reduce the number of parameters. The CC functions of eq 2 turned out to yield the most robust results across the entire composition range, largely because the primary relaxation peak becomes more symmetric at intermediate mole fractions. Typical fit curves are included in Figure 1 for several temperatures, showing that the two peaks of interest are well represented by eq 2, while the secondary peak remains disregarded. As an



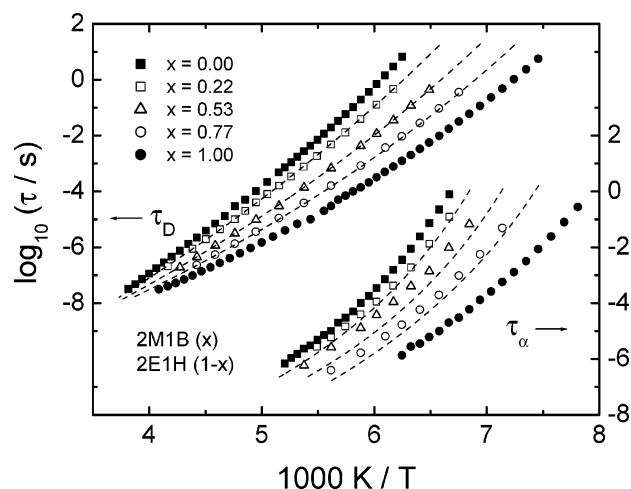
**Figure 2.** The loss tangent,  $\tan \delta$ , recorded at a fixed frequency of  $\nu_0 = 1$  kHz for pure 2-methyl-1-butanol (2M1B), pure 2-ethyl-1-hexanol (2E1H), and their mixtures at various compositions as indicated. The separation of Debye and  $\alpha$ -relaxation in the mixtures is smaller than that of pure alcohols.



**Figure 3.** Widths of the dielectric loss profiles in terms of the fitting parameters  $\alpha$  of eq 2 for mixtures of 2-methyl-1-butanol (2M1B) with 2-ethyl-1-hexanol (2E1H). The mixing leads to additional broadening of the dielectric relaxation peaks, an effect that remains very small for the Debye peak. The value of  $x$  represents the mole fraction of 2M1B.

example, the parameters and their errors for the  $T = 158$  K case in Figure 1 are  $\Delta\epsilon_D = 27.89 \pm 0.01$ ,  $\log(\tau_D/s) = -0.930 \pm 0.001$ ,  $\alpha' = 0.991 \pm 0.001$ ,  $\Delta\epsilon_\alpha = 0.964 \pm 0.03$ ,  $\log(\tau_\alpha/s) = -3.40 \pm 0.06$ , and  $\alpha = 0.37 \pm 0.02$ . The fit curves in Figure 1 are shown only within the frequency range in which the two larger peaks dominate over the secondary relaxation. The dashed and dashed-dotted line separation of the Debye and  $\alpha$ -peak contributions to the  $T = 146$  K curve in Figure 1 clearly shows that the Debye peak alone is insufficient to describe the experimental data.

Fitting the data using the Cole–Cole expressions in eq 2 to the dominant and the main shoulder relaxations reveals the broadening of the two peaks upon mixing in the 2M1B/2E1H systems. Within the experimental temperature range, the broadening parameters  $\alpha'$  and  $\alpha$  for the two peaks in eq 2 show only a marginal temperature dependence, and we thus consider these temperature invariant. The composition dependence of  $\alpha'$  and  $\alpha$  for the two processes is plotted in Figure 3. Slight broadening of the Debye relaxation is exhibited for intermediate values of the mole fraction. For the shoulder peaks or  $\alpha$ -relaxation, larger



**Figure 4.** Activation plots of the Debye and  $\alpha$ -relaxation peaks for pure 2-methyl-1-butanol (2M1B), pure 2-ethyl-1-hexanol (2E1H), and their mixtures at the indicated mole fractions. The dashed lines represent ideal mixing behavior for  $\log(\tau)$  according to eq 4. For 2M1B, the VFT parameters are  $A = -12.8$ ,  $B = 937.3$  K, and  $T_0 = 64.7$  K for the Debye peak and  $A = -14.0$ ,  $B = 661.9$  K, and  $T_0 = 78.6$  K for the  $\alpha$ -relaxation. For 2E1H, the values are  $A = -15.9$ ,  $B = 1752$  K, and  $T_0 = 55.0$  K for the Debye peak and  $A = -11.9$ ,  $B = 476.8$  K, and  $T_0 = 109.8$  K for the  $\alpha$ -relaxation.

broadening effects are obvious with decreasing  $\alpha$  value upon mixing, and the biggest broadening is observed around 50 mol % 2M1B.

Figure 4 shows the activation plots of the Debye and  $\alpha$ -relaxation dynamics of the pure alcohols and their mixtures. The curves can be fitted well by the Vogel–Fulcher–Tammann (VFT) equation:<sup>39</sup>

$$\log_{10}(\tau/s) = A + \frac{B}{T - T_0} \quad (3)$$

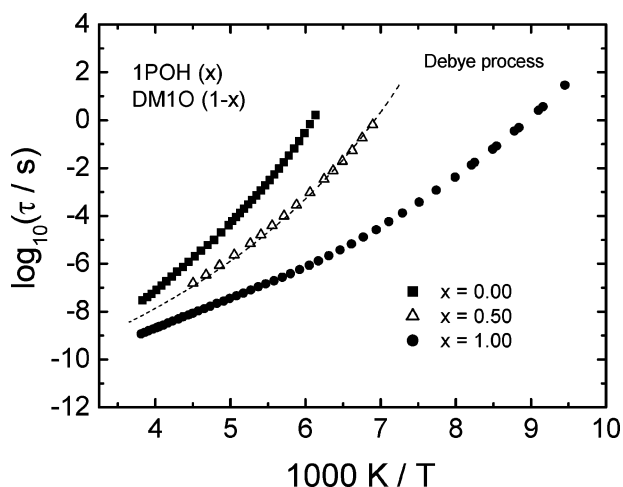
where  $A$ ,  $B$ , and  $T_0$  are constants. Early studies on the Debye dynamics of mixtures of methanol with ethanol and 1-propanol reported an ideal mixing behavior at higher temperatures (room temperature), that is, a linear variation of  $\log(\tau)$  with the mole fraction.<sup>34</sup> In an analogous fashion, we check the mixing behaviors of both the Debye and the  $\alpha$ -relaxation dynamics, in this case in the supercooled liquid region near  $T_g$ . On the basis of the fit results for pure compounds “1” and “2” ( $\tau_1$  and  $\tau_2$ ), a linear combination (ideal mixing) along the mole fraction scale  $x$  is established:

$$\log(\tau_{\text{mix}}) = (x) \times \log(\tau_1) + (1 - x) \times \log(\tau_2) \quad (4)$$

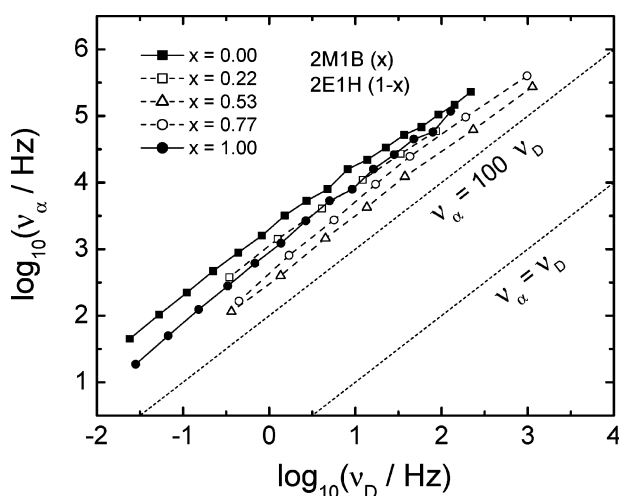
where  $x$  stands for the mole fraction of component 1 with  $\tau_1$  being the relaxation time of component  $i$ . This analysis is then applied separately to the Debye and the  $\alpha$ -relaxation. For the experimentally realized compositions, the calculated results based upon eq 4 are included in Figure 4 as dashed lines. One can see that the experimental results of the Debye dynamics are well represented by eq 4, suggesting that the Debye relaxation dynamics follows ideal mixing in the supercooled regime. By contrast, the experimental data of the  $\alpha$ -relaxation does not match the dashed lines derived from assuming ideal mixing.

In the dielectric measurements of alcohol mixtures by Mashimo et al.,<sup>34</sup> the ideal mixing behavior is attributed to the structural similarity of alcohols. To check this argument and to confirm this ideal mixing behavior, the dielectric relaxation of the 50 mol % mixture of 1-propanol and 3,7-dimethyl-1-octanol





**Figure 5.** Activation plot of the Debye relaxation of pure 1-propanol (IPOH), of pure 3,7-dimethyl-1-octanol (DM1O), and their 50 mol % mixture. The dash line is calculated according to ideal mixing for  $\log(\tau)$  following eq 4. The VFT fit parameters of eq 3 are  $A = -11.9$ ,  $B = 622.1$  K, and  $T_0 = 59.4$  K for IPOH and  $A = -13.3$ ,  $B = 1007$  K, and  $T_0 = 88.2$  K for DM1O. The 1-propanol data is taken from ref 26.



**Figure 6.** Peak frequency  $\nu$  of the  $\alpha$ -relaxation ( $\nu_\alpha$ ) versus that of the Debye relaxation ( $\nu_D$ ) for pure 2-methyl-1-butanol (2M1B), pure 2-ethyl-1-hexanol (2E1H), and their mixtures at various compositions as indicated. The graph shows that mixing leads to a smaller separation between Debye and  $\alpha$ -relaxation relative to the pure materials.

is demonstrated in Figure 5. It turns out that the Debye dynamics again follows the ideal mixing behavior of eq 4. However, because of the proximity of Debye and  $\alpha$ -peaks in these mixtures, we were not able to characterize the  $\alpha$ -relaxation dynamics.

A comparison of the peak frequencies  $\nu = 1/2\pi\tau$  for the Debye and  $\alpha$ -relaxation is provided in Figure 6, including data for the mixtures and their pure components. This graph reveals that the separation of the two relaxations in the mixture of 53 mol % of 2M1B is not as high as that of their components. At  $T_g$ , the ratio  $\nu_\alpha/\nu_D$  for the mixture is 350, while it is 900 and 2000 for the individual components 2M1B and 2E1H, respectively.<sup>29</sup> Clearly, the separation of Debye and  $\alpha$ -relaxation becomes smaller than that of the pure liquids. For the 50 mol % IPOH/DM1O system, it can be concluded that the mixture should have a smaller separation than those in IPOH and DM1O, where the values of  $\nu_\alpha/\nu_D$  are 160 and 14, respectively.<sup>26,29</sup> Therefore, the Debye and  $\alpha$ -relaxation dynamics cannot be separated easily in the IPOH/DM1O mixtures.

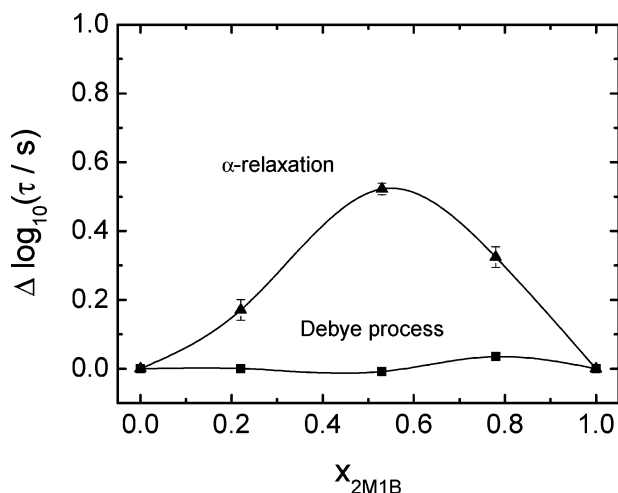
## 4. Discussion

**4.1. Persistence of the Debye Mode in Mixtures.** Understanding the exponentiality or Debye character of liquid dynamics at low temperatures (supercooled liquid state) is a challenge because this property is not immediately compatible with the disordered nature of supercooled liquids.<sup>7,40</sup> Debye processes appear to be a particular feature of the dielectric behavior of some associating liquids, without the occurrence of equivalent exponential processes in other relaxation measurements, like mechanical<sup>17</sup> and solvation<sup>41</sup> experiments.

Debye type liquid dynamics has been reported for some pure systems, such as monohydroxy alcohols and *N*-monosubstituted amides, like *N*-methylformamide.<sup>42</sup> Also, Debye behavior in mixtures of two structurally similar small-molecule monohydroxy alcohols has been observed in the supercooled liquid state.<sup>32</sup> However, no detailed quantitative analysis has been made available on the properties of these relaxations in the dielectric dynamics of monohydroxy alcohol mixtures.<sup>43</sup> On the basis of the results of Figure 3 and Figure 4, it turns out that only a marginal broadening occurs upon mixing, with  $\alpha'$  remaining within the 0.97–1.00 range for all compositions. We conclude that the basic nature of this Debye process persists across the entire composition range in this mixture. Similar preliminary results are obtained by recent dielectric measurements on the mixtures of 2-ethyl-1-hexanol with *N*-methylacetamide and of *N*-methylacetamide with *N*-ethylacetamide.<sup>44</sup> Therefore, the persistence of the Debye character of the dominant dielectric loss peak appears to be a general phenomenon, provided that the individual components show this feature. Naturally, the Debye mode can be suppressed via the introduction of a non-Debye liquid or ionic electrolytes.<sup>12,45,46</sup>

Given the mixing phenomenology of other nonassociating simple liquids, the persistence of a single time constant across a significant mole fraction range in binary systems is remote from being trivial. Two-component liquids, even if highly miscible, develop concentration fluctuations as an additional source of environmental fluctuations and relaxation time dispersion. Therefore, liquid mixtures typically exhibit a broader distribution of relaxation times within the intermediate composition range, equivalent to a broader dielectric loss peak or lower stretching exponent  $\beta$ .<sup>47</sup> An inspection of Figure 4 reveals that at  $T = 160$  K, the Debye peaks of pure 2M1B and 2E1H are 3.8 orders of magnitude apart regarding their respective  $\tau_D$  values. In this situation, any structural relaxation would show considerable excess broadening, as documented for the primary relaxation mode in terms of  $\alpha(x)$  in Figure 3. The absence of concentration fluctuation effects might be considered a hint toward long-range coupling and the resulting concerted motion of charges being involved in this dielectric feature.

The purely exponential loss peak of some monohydroxy alcohol mixtures has been discussed earlier with the aim to clarify the mechanism of their dielectric dynamics. The Debye mode has always been associated with the dynamics of hydrogen bonds.<sup>20,32</sup> More specifically, the Debye peak is “attributed to a relaxation mechanism of H-bond breaking and reforming”, while the smaller and faster process is related “to the OR group motions within the H-bonded chains”.<sup>19</sup> In mixtures, the absence of a distribution of relaxation times has led Bordewijk et al. to rejecting the idea of linear chains.<sup>33</sup> Instead, a single kind of highly dipolar cyclic multimers was proposed as the origin of the Debye process in monohydroxy alcohols. Even at present, the existing models for the mechanism responsible for the Debye dynamics are not consistent with all the relevant observations regarding the behavior of this dielectric loss peak.



**Figure 7.** Excess logarithmic relaxation time  $\Delta \log \tau$ , calculated as the difference between the experimental data and the ideal mixing prediction (see Figure 3) for mixtures of 2-methyl-1-butanol (2M1B) with 2-ethyl-1-hexanol (2E1H). The abscissa scales the mole fraction  $x$  of 2M1B. These results show that the Debye dynamics follows the ideal mixing law for  $\log \tau$ , while the  $\alpha$ -relaxation displays nonideal behavior.

#### 4.2. Mixing Behavior of Dynamics and Thermodynamics.

On the basis of the data of Figure 4, we construct in Figure 7 a plot of excess relaxation dynamics,  $\Delta \log \tau$ , as a function of composition, where  $\Delta \log \tau$  is the difference between the experimental relaxation time and that expected for the case of ideal mixing (dashed lines in Figure 4). This graph shows more clearly that the Debye relaxation follows the ideal mixing law of eq 4, while the  $\alpha$ -relaxation deviates significantly. Detailed investigations of the Debye relaxation in viscous monohydroxy alcohols leave little doubt that this dielectric mode is not the immediate signature of structural relaxation.<sup>12,17,18,26–29</sup> The present results provide yet another piece of evidence, showing that the dielectric Debye dynamics differs qualitatively from phenomenology of structural relaxation.

The ideal mixing behavior of Debye type dynamics in the two present supercooled liquid systems is not readily expected. Previous studies of alcohol mixtures at higher temperatures have attributed ideal behavior to the similarities of the liquid structure and relaxation mechanism.<sup>34,43</sup> In these experiments, methanol is mixed with ethanol and 1-propanol, and the three liquids indeed may be considered structurally similar. However, in our binary system 1-propanol with 3,7-dimethyl-1-octanol, the molecular structures differ considerably, and structural similarity is obviously not required to generate ideal mixing behavior of  $\log(\tau_D)$  versus  $x$ . As an alternative, we suggest that this ideal mixing behavior is a feature inherent in the Debye process of many alcohols, irrespective of structural compatibility.

Let us now turn to the mixing behavior of the dielectric  $\alpha$ -relaxation dynamics. Hanna et al. studied the dielectric dynamics of mixtures among small molecule diols including ethane-1,2-diol, propane-1,3-diol, butane-1,4-diol, and pentane-1,5-diol, all of which do not exhibit the Debye mode typical of the monohydroxy alcohols.<sup>48</sup> Although these diols are structurally similar, analyzing their data in terms of logarithmic relaxation time versus mole fraction yields clear deviations from the ideal mixing linearity with positive excess  $\log(\tau_{mix})$ . This is qualitatively similar to the mixing results of the structural relaxation ( $\alpha$ ) dynamics in Figure 7.

The amount of available dielectric data on the structural process of other monohydroxy alcohol mixtures across wide concentration ranges is very limited. Therefore, we resort to

viscosity data, which is directly related to structural dynamics.<sup>49</sup> First, we examine the viscosity results for mixtures of monohydroxy alcohol systems.<sup>50–53</sup> Plots of  $\log(\eta)$  as a function of mole fraction for these literature data all demonstrate non-ideal mixing with convex curves, equivalent to the  $\alpha$ -relaxation trace in Figure 7. Also, the extent of deviation from linearity in a  $\log(\eta)$  versus  $x$  plot increases with increasing structural difference of two components. For any pair of two adjacent liquids within the homologous 1-alkanol series (1-propanol and 1-butanol,<sup>52</sup> for instance), the curvature remains very small. For other more different pairs of 1-alkanols, however, the convex behavior is quite pronounced. This suggests that the logarithmic viscosity of the binary mixtures of 1-alkanols generally fails to obey an ideal mixing law. The analogous behavior can be found for the viscosity of the binary mixtures within the series of  $n$ -alkanes.<sup>54–56</sup> Therefore, the nonideal mixing behavior of  $\log(\tau_\alpha)$  for the dielectric  $\alpha$ -relaxation in Figure 7 agrees well with that of the viscosity and with relaxation data for systems which do not possess a dielectric Debye peak.

The above conclusions regarding the mixing behavior is supported by thermodynamic quantities in binary liquid systems. Benson and co-workers have measured the isothermal excess heats of mixing among 1-alkanol<sup>57</sup> and 1-alkane<sup>58</sup> systems, both showing significant positive endothermic excess enthalpy  $\Delta H_{mix}$ . The excess heat of mixing increases with increasing structural difference of the liquids and, most strikingly, the excess heat of mixing among the 1-alkanol series does not differ significantly from that among the 1-alkane system. Thus, it is legitimate to conclude that the mixing behaviors of the two systems are very similar with respect to both dynamics and thermodynamics. The small difference of  $\Delta H_{mix}$  values for 1-alkanol and 1-alkane systems suggests that hydrogen bonds have little effect on these mixing enthalpies.

Finally, an important parameter in characterizing supercooled liquid dynamics, the glass-transition temperature  $T_g$ , also needs to be addressed. In the context of dynamics, it is common practice to assign to  $T_g$  the temperature at which the average relaxation time is 100 s. For our alcohol mixture, this will result in two values, corresponding to the Debye and the  $\alpha$ -relaxation. Treatments of the mixing behavior of  $T_g$  are still limited to phenomenology.<sup>59,60</sup> Glass-transition temperatures derived from the  $\tau_\alpha = 100$  s criterion are not expected to display a simple mole fraction dependence, since already  $\log(\tau_\alpha)$  itself is nonlinear in  $x$ . Actually, Lesikar's differential thermal analysis measurements of  $T_g$  in a series of binary mixtures of 1-alkanols from methanol to  $n$ -octanol has clearly revealed an increasing deviation from the ideal mixing behavior when the structural difference among the two components is increased.<sup>59</sup> These studies also indicate differences in the structure of methanol and ethanol relative to the longer 1-alkanol cases, perhaps explaining that these two simple alcohols do not share the occurrence of a Debye process.<sup>61–63</sup> In general, also the linear mixing law for  $\log(\tau_D)$  of the Debye peak will not translate into a linear variation of the temperature,  $T_D$ , at which the Debye time reaches the  $\tau_D = 100$  s threshold. Therefore, we consider the linearity of  $T_D$  versus  $x$  for our 2M1B/2E1H system a coincidence. We wish to emphasize that the  $T_D$  defined via the Debye relaxation time  $\tau_D = 100$  s is not a glass transition, because the Debye process does not involve structural dynamics. Accordingly,  $T_D$  will not be observed in a calorimetric measurement, since the Debye process does not contribute significantly to the heat capacity.

In summary, the mixing behavior of the structural or  $\alpha$ -relaxation of the primary monohydroxy alcohols in our

experiments (Figure 3 and Figure 7) is entirely consistent with that of other dynamic and thermodynamic properties, while that of the dielectric Debye mode is not. Again, it is confirmed that the dominant dielectric Debye mode in monohydroxy alcohols is a feature of charge dynamics which is decoupled from structural relaxation.

**4.3. Origin of Debye Dynamics.** It is an interesting observation that  $\log(\tau_D)$  for the Debye peak is linear only with respect to the mole fraction, but not with respect to volume or weight fractions. This suggests that the Debye relaxation of mixtures is only an average based on the number of molecules or hydroxyl groups, regardless of the molecular weight or length of the alkyl chain. On the other hand, it is the molecular weight that greatly influences the structural relaxation and the glass-transition temperature. The absence of significant concentration fluctuation effects on the Debye peak of the mixture (i.e., the lack of excess broadening at intermediate concentrations) can be understood to indicate large-scale spatial averaging, for example, by long-range coupling of the charges that are being displaced. Any more localized process should be subject to concentration fluctuations and result in concomitant relaxation time dispersion at intermediate mole fractions. Although the present alcohol mixture results do not provide a direct hint toward the mechanism of this dielectric process, the findings will serve as a critical test for future models, which will need to be consistent with ideal mixing regarding  $\log(\tau_D)$  versus  $x$ .

To explain the dielectric behavior of monohydroxy alcohols, special molecular structures have been proposed: linear chains, cyclic multimers,<sup>23–25</sup> and clusters.<sup>64</sup> In view of the decoupling of the prominent dielectric mode from structural relaxation, the idea of self-micellization proposed by Floriano and Angell is particularly appealing.<sup>12</sup> This picture implies assemblies with the polar hydroxyl groups inside and the nonpolar alkyl chains pointing outward, analogous to water-in-oil microemulsions. The tendency to form micellar structures exists naturally only for monohydroxy alcohols, for which the  $-\text{OH}$  group is sterically accessible for the formation of micelles. Diols, polyols, and cases where the  $-\text{OH}$  group is sterically hindered would not display the Debye feature, in agreement with experimental findings. Because of the spatial separation of polar and nonpolar moieties inherent in this view, Maxwell–Wagner<sup>65</sup> type polarization effects may become important. A further interesting aspect of this micellar picture is the immediate explanation of the low dielectric strength of the  $\alpha$ -process, because alkyl chain motion about a relatively immobile hydroxyl end would be the dominant contribution.

## 5. Concluding Remarks

We have measured the dielectric loss of mixtures of some primary monohydroxy alcohols in their supercooled state. The prominent Debye type dielectric peak observed for several of these alcohols displays ideal mixing behavior, that is,  $\log(\tau_D)$  depends linearly on the mole fraction  $x$ . In the same system, the much smaller dielectric  $\alpha$ -process is subject to a nonlinear composition dependence of  $\log(\tau_\alpha)$ , consistent with this higher frequency process being the signature of structural relaxation. The linearity of  $\log(\tau_D)$  versus  $x$  is not a result of similar molecular structures within the mixture but is also observed for the case of mixing alcohols as different as 1-propanol and 3,7-dimethyl-1-octanol. As a result of observing that the Debye peak persists across the entire composition range, it appears that this process is not sensitive to the inevitable concentration fluctuations of highly miscible binary systems. In contrast, the dielectric  $\alpha$ -process shows the typical excess relaxation time

dispersion at intermediate concentrations. This constitutes yet another piece of evidence which rules out that the Debye peak is the immediate dielectric signature of structural relaxation. The challenge emerging from these results is to find a mechanism that explains the phenomenology of this dielectric feature with Debye character.

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