Diluent Effects on the Debye-Type Dielectric Relaxation in Viscous Monohydroxy Alcohols

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With the recognition that the Debye-type dielectric relaxation of liquid monohydroxy alcohols does not reflect the structural relaxation dynamics associated with the viscous flow and the glass transition, its behavior upon dilution is expected to differ from that of real α -processes. We have investigated the Debye-type dielectric relaxation of binary alcohol/alkane mixtures across the entire concentration range in the supercooled regimes. The focus is on 2-ethyl-1-hexanol in two nonpolar liquids, 3-methylpentane and squalane, which are more fluid and more viscous than the alcohol, respectively. The Debye relaxation is found to occur only for alcohol mole fractions x > 0.2 and is always accompanied by a non-Debye relaxation originating from the alcohol component. Prior to its complete disappearance, the Debye relaxation is subject to broadening. We observe that the Debye dynamics of 2-ethyl-1-hexanol is accelerated in the more fluid 3-methylpentane, while the more viscous squalane leads to longer Debye relaxation times. The present experiments also provide evidence that the breakdown of the Debye relaxation amplitude does not imply the absence of hydrogen-bonded structures.

1. Introduction

In supercooled liquids, dielectric relaxation experiments always observe the signature of viscous flow and the thermodynamic glass transition in terms of what is referred to as structural relaxation or α-process.¹⁻³ Particularly in glassforming materials, this structural dynamics is characterized by a non-Arrhenius temperature dependence of the relaxation time scales and by nonexponential (or non-Debye type) relaxation patterns.^{4,5} However, deviations from the above universal behavior are often observed in monohydroxy alcohols, where the prominent dielectric relaxation is a purely exponential (Debye) process. In many ways, this Debye process does not possess the features typical of α-relaxations in nonassociating liquids.^{6,7} These anomalies regarding the Debye peak are particularly obvious in the case of supercooled liquids, which has given rise to extensive disputes about its origin.⁸⁻¹⁵ So far, the understanding of these Debye relaxations which occur in many associating liquids has remained rather limited. In a number of models, the Debye relaxation has been taken as equivalent to the α -relaxation process of typical liquids, without appreciating the unique properties of this dielectric signal. In the numerous studies of alcohol dynamics performed at higher frequencies (higher temperatures) the observation of Debyetype dielectric loss peak was not unusual because even the dynamics of simple liquids are practically exponential at frequencies of several gigahertz or above. Nonetheless, complex dielectric behavior has been observed, and as many as three relaxation terms are used to describe the high-temperature dielectric relaxation. ^{10,15–18} By contrast, Debye-type relaxations in the supercooled regime of glass-forming liquids are the exception displayed only by some associating liquids, mainly monohydroxy alcohols, but never by a simple (nonassociating) molecular liquid. In what follows, we will use the term " α "relaxation for those structural relaxation processes which are similar to the typical dynamics seen in nonassociating liquids, with the properties that these structural relaxations are responsible for viscous flow as well as the calorimetric and mechanical

signatures of the glass transition. Because the Debye-type peak observed in many associating liquids occurs at lower frequencies, there is some structure (regarding polarization, hydrogen bonding, etc.) which persists for times longer than the " α "-process.

Recent studies on glass-forming H-bonded liquids have provided increasing evidence that the Debye-type relaxation in these systems is not the immediate signature of the structural relaxation and therefore only indirectly related to viscous flow and the glass transition. 19-23 The coupling model provides one additional item because it predicts the coincidence of the Johari-Goldstein secondary peak with the Debye process if the latter were the signature of structural relaxation.²⁴ In a recent publication we have compiled and discussed the numerous observations that argue in favor of the Debye relaxation not being the α-relaxation of monohydroxy alcohols.²⁵ The aim of compiling this information is to provide critical tests for existing and future models of this dielectric feature. For example, the models of H-bonds breaking and forming within linear chains was objected when two experimental results were reportedone being that the activation energies for this process differed widely among the isomeric octanols, reaching values which are far greater than the H-bond energy, 12 and the other the observation of the single relaxation time in binary n-alkanol systems.¹¹ Consequently, before making a conclusive judgment about the origin of the Debye relaxation, it is necessary to explore and characterize its unique dynamic characters. In the following, some of the typical dynamic properties of the Debye processes found in H-bonding liquids are listed. First, in pure liquids, the Debye relaxation cannot exist independently without being accompanied by a non-Debye "true" α-structural relaxation. Second, the Debye dynamics is invariably slower than the α -structural relaxation with certain coupling with the latter. Third, when mixing two Debye-type alcohols, the Debye relaxation persists through the entire concentration range. 15,26-28 Fourth, the Debye relaxation dynamics follows the ideal mixing rule in both supercooled region and at higher temperatures, while the typical structural relaxation dynamics follows nonideal behavior. 27,28 Fifth, it is found that the Debye relaxation frequency does not exceed $\sim\!10^{11}$ Hz in the high-temperature limit, 19,25,29 which is 2 orders of magnitude below typical phonon frequencies. The sixth and very important observation is that this dielectric Debye peak has no corresponding feature in mechanical or calorimetric data. 20,22,23,29,30 Therefore, it is obvious that this Debye relaxation requires an explanation that is specific for the dielectric polarization fluctuations and thereby different from the approach to the typical $\alpha\text{-processes}$ of simple liquids.

For binary molecular liquid mixtures of nonassociating miscible compounds, the signature of structural dynamics of the system is usually a single relaxation peak, positioned at a relaxation time intermediate between the two α -relaxations of the individual components, if the composition is not near a dilute limit.31-33 Because the Debye-type relaxation of associating liquids differs from the structural relaxation, it is interesting to ask how it evolves upon dilution in non-Debye liquids. For binary mixtures of one liquid having a Debye process with another liquid without such a process, a key question is whether the Debye-type relaxation undergoes a continuous transition into another relaxation or it breaks down and disappears at a certain concentration. In the past, the dielectric relaxation behaviors of mixtures of monohydroxy alcohols with alkanes or with polar non-Debye type liquids have been studied extensively both in the viscous and in the fluid regimes.^{34–39} Only a few reports have noted that at low alcohol content this Debye relaxation behaves unexpectedly where the dielectric strength drops rapidly. 40-43 In a systematic investigation of alcohols in alkanes, Denney and Ring suggested a continuous ring-chain transition of intermolecular configuration, 41 while Crossley, Glasser, and Smyth's investigation points toward the termination of this relaxation at low concentrations due to its involvement in H-bonded structures of some considerable size.⁴² In view of the distinct properties of the Debye and α -process dynamics, it is important to reconsider the fate of the Debye peak upon dilution.

In this paper, we focused on the dynamics of the Debye relaxation of monohydroxy alcohols in non-Debye liquids across the entire concentration range. We chose to use 2-ethyl-1-hexanol for the investigation of the dielectric spectra in two nonpolar liquids: 3-methylpentane and squalane. The temperature range covers the deeply supercooled states around the respective glass transition region, so that the Debye-type and non-Debye-type relaxations can be identified and separated with a minimum of ambiguity.

2. Experimental Section

The monohydroxy alcohol 2-ethyl-1-hexanol (2E1H, 99.6%) is employed in this study of the dielectric Debye relaxation. This alcohol is a good glass-former with the advantageous feature that the Debye relaxation and the α -relaxation are subject to a pronounced separation of time scales, with a ratio of over 3 decades near the glass transition temperature $T_{\rm g}=145~{\rm K}.^{19}$ Moreover, some dielectric properties of the liquid and its mixtures have been reported before, which allows us to compare our results with the previous studies. The selection of the two nonpolar liquids, 3-methylpentane (3MP, 99+%) and squalane (SQA, 2,6,10,15,19,23-hexamethyltetracosane, 99%), is based upon their dynamics being respectively faster and slower, compared with the alcohol. In terms of their $T_{\rm g}$ values, the liquids are characterized by $T_{\rm g}=78~{\rm K}$ (from calorimetric measurements 44,45 and dielectric results 46) for 3MP and $T_{\rm g}=$

160 K (from viscosity⁴⁷) and $T_{\rm g}=167$ K (from dielectric relaxation⁴⁸) for SQA. Compositions are reported in terms of their mole fractions. All liquids are purchased from Aldrich and used as received.

For these mixtures, two experimental setups are used for the dielectric measurements with different resolution and frequency range. The experiments for the mixtures of 2E1H with 3MP are conducted in a brass cell which is mounted on the cold stage of an evacuated closed-cycle He-refrigerator cryostat Leybold RDK 10-320, driven by a Leybold RW2 compressor, which has been described in ref 46. Using this setup, the low-temperature measurements are accessible for the 3MP-rich mixtures. Temperature is controlled with a Lakeshore model 340 temperature controller equipped with calibrated DT-470-CU diodes as sensors. Frequency-dependent impedance measurements were done by using an Andeen-Hagerling ultraprecision capacitance bridge AH-2700A with low-noise cables. Frequency scans range from 50 Hz to 20 kHz.

The dielectric measurements of the mixtures of 2E1H with SQA are conducted by holding the liquids between two brass electrodes, which are separated by thin Teflon stripes with thickness of 25 μ m 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 controller. Frequency-dependent impedance measurements were performed using a Solartron 1260 gain-phase-analyzer equipped with a Mestec DM-1360 transimpedance amplifier. In this measurement, frequency range scans from 0.1 to 10^6 Hz. Empty sample capacitors are used as the references in order to calibrate the frequency-dependent transimpedance $Z(\omega)$ of the DM-1360.⁴⁹

Although this study focuses on the Debye relaxation, other dielectric signals also need to be characterized. Up to four distinct loss features are considered in the mixtures: the dc conductivity, a Debye-type relaxation, and two primary (α) relaxation peaks. Johari—Goldstein-type β -relaxations have also been observed in some cases, but they will be disregarded in the following. We use the following fit function in order to quantify these processes:

$$\epsilon^{*}(\omega) = \epsilon_{\infty} + \frac{\Delta \epsilon_{\mathrm{D}}}{(1 + (i\omega\tau_{\mathrm{D}})^{\alpha_{\mathrm{D}}})^{\gamma_{\mathrm{D}}}} + \frac{\Delta \epsilon_{\mathrm{al}}}{(1 + (i\omega\tau_{\mathrm{al}})^{\alpha_{\mathrm{al}}})^{\gamma_{\mathrm{al}}}} + \frac{\Delta \epsilon_{\mathrm{ak}}}{(1 + (i\omega\tau_{\mathrm{ak}})^{\alpha_{\mathrm{ak}}})^{\alpha_{\mathrm{ak}}})^{\gamma_{\mathrm{ak}}}} + \frac{\sigma_{\mathrm{dc}}}{\epsilon_{0}i\omega}$$
(1)

Here, ϵ_{∞} is the dielectric constant in the high-frequency limit and $\Delta\epsilon_i$ is the relaxation strength of mode "i". The second, third, and fourth terms of this equation represent Havriliak—Negami (HN) functions. The second term described the Debye ("D") peak, but an HN function is used because the effect of mixing could result in the broadening of this process. ^{25,28} For the third and fourth terms, we use HN functions to reflect the asymmetrically broadened profiles of the α -relaxations of the alcohol ("al") and alkane ("ak") component, respectively. In these HN expressions, α and γ gauge the asymmetry and broadening of the loss profile. The dc conductivity is quantified by the parameter $\sigma_{\rm dc}$.

3. Results

Figure 1 presents the dielectric loss tangent (tan δ at a fixed frequency of $\nu_0 = 1$ kHz) of the mixtures of 2E1H with 3MP across the entire concentration range. At high and low concentrations of the alcohol, two main relaxations are dominant, while

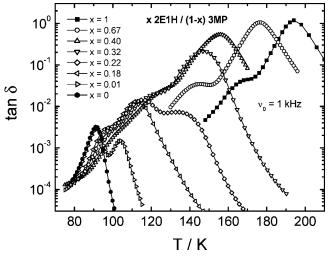


Figure 1. Dielectric loss tangent tan δ (at a fixed frequency of ν_0 = 1 kHz) of the mixtures of 2-ethyl-1-hexanol (2E1H) in 3-methylpentane (3MP) for various compositions. The Debye relaxation amplitude rapidly decreases and disappears between 30 and 20% alcohol mole fraction. The x_{2E1H} = 0.22 case shows the three distinct relaxations, with the low-temperature relaxation originating from 3MP, while the other two relaxations are from 2E1H.

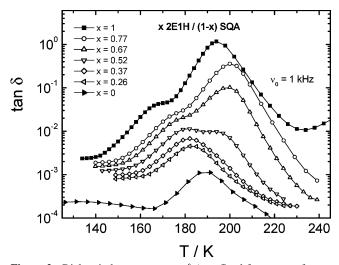


Figure 2. Dielectric loss tangent tan δ (at a fixed frequency of ν_0 = 1 kHz) of the mixtures of 2-ethyl-1-hexanol (2E1H) in squalane (SQA) for various compositions. The rapid breakdown of the Debye relaxation amplitude is seen at the medium concentrations.

in the medium range, three distinct relaxations are displayed simultaneously as seen for the $x_{2E1H} = 22$ mol % curve. Regarding the dominant or slowest relaxation of the mixtures, it is found that this peak decreases rapidly in intensity as an alcohol mole fraction of 20-30 mol % is approached. This slow process originates from the Debye relaxation of the alcohol, an assignment that has been made previously.³⁷ At low concentrations, two relaxations are still observed, but none of these peaks display Debye-type character. An analogous graph for the 2E1H/ SQA mixtures is provided in Figure 2. Again, the breakdown of the dominant relaxation amplitude is observed at intermediate concentrations. Unlike the 2E1H/3MP case, the dielectric α -peak of the nonpolar diluent cannot be observed at significant alcohol contents because the dielectric peak of SQA is in close proximity to the Debye signal of 2E1H and therefore obscured due to its very low dielectric strength.

Next, we characterize in more detail the different peaks observed in these mixtures. Figure 1 and the complete analysis of the temperature-dependent loss spectra show that the Debye

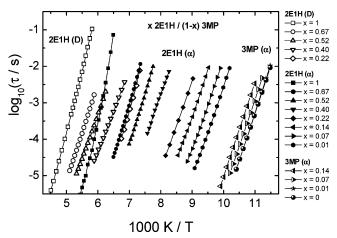


Figure 3. Activation plots of the characteristic relaxation times for the mixtures of 2-ethyl-1-hexanol (2E1H) and 3-methylpentane (3MP). The Debye relaxation dynamics of 2E1H are continually accelerated with increasing dilution, while the dynamics of 3MP slows down.

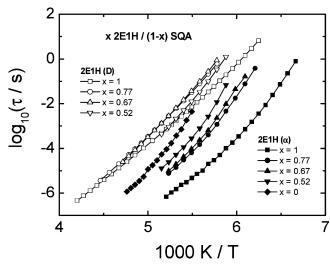


Figure 4. Activation plots of the characteristic relaxation times for the mixtures of 2-ethyl-1-hexanol (2E1H) and squalane (SQA). Note that the Debye relaxation dynamics of 2E1H is not subject to a monotonic change with concentration.

and the α -structural relaxations of the pure alcohol shift toward the dynamics of 3MP with dilution, while the relaxation of the pure 3MP moves in the opposite direction. Accordingly, the slowest relaxation peak in these mixtures is of the Debye nature, the middle relaxation corresponds to the α -relaxation of the alcohol, and the fastest to the structural relaxation of 3MP. The fit parameters for the dielectric strength ($\Delta\epsilon$) and the shape exponents (α , γ) support this identification of the three processes. Our results for the pure compounds agree with earlier measurements 19,46 and serve as reference. Near the glass transition temperature, for example, we find $\Delta\epsilon \approx 21.3$ and $\alpha = \gamma = 1$ for the Debye peak of 2E1H and $\Delta\epsilon \approx 0.4$, $\alpha = 0.5$, and $\gamma = 0.6$ for the α -relaxation of 2E1H. For 3MP near its $T_{\rm g}$, we obtain $\Delta\epsilon \approx 0.01$, $\alpha = 0.92$, and $\gamma = 0.42$ for the α -relaxation of 3MP.

The average dielectric relaxation times of the Debye and the α -relaxation from 2E1H in the two nonpolar liquids, 3MP and SQA, are exhibited in Figure 3 and Figure 4. Upon being diluted in 3MP, both the Debye and the α -relaxations of 2E1H shift toward higher frequencies, indicating an acceleration due to the addition of a more fluid component. At the same time, the relaxation times of 3MP gradually increase toward the alcohol values. In SQA, however, the two relaxations of 2E1H shift

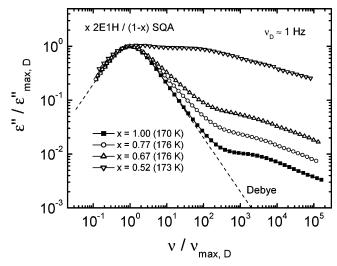


Figure 5. Dielectric loss curves for 2-ethyl-1-hexanol (2E1H) in squalane (SQA) at various concentrations and at temperatures at which the Debye frequency is near $\nu_D=1$ Hz. Amplitude and frequency scales have been normalized to generate identical values for the peak of the Debye process. The graph demonstrates that some broadening of the "Debye" peak occurs as its amplitude approaches zero.

toward longer time scales, equivalent to the slowing down of the dynamics by adding a more viscous component. These observations reflect the common behavior of viscosity of n-alcohols in alkanes. 50 Although the concentration dependences of the dynamics of the two alcohol peaks, Debye and α , appear similar, their spectral separation is not entirely concentration invariant.

4. Discussion

4.1. Broadening of the Debye Relaxation. Previous dielectric studies concerned with supercooled mixtures of a monohydroxy alcohol with a more fluid nonpolar liquid have discussed one Debye or near Debye-type peak and another higher frequency relaxation. Although the high-frequency relaxation is occasionally attributed to two contributions, distinct assignments regarding their origins have not been provided. In the present case, see for example Figure 1, the high-frequency or low-temperature side of the Debye process displays two distinct relaxation processes, which we identify as the α -relaxation peaks of the two compounds.

Both mixtures, 2E1H/3MP and 2E1H/SQA, display a clear Debye-type loss peak, not only for the very high alcohol fraction compositions. However, these features disappear at intermediate mole fractions of $x_{2E1H} \approx 0.2$ or below for the 2E1H/3MP case. As its amplitude becomes small, it is found that the peak is subject to broadening from a pure Debye case ($\alpha = 1, \gamma = 1$) to a Cole-Davidson profile ($\alpha = 1, \gamma < 1$) and eventually to an HN type peak ($\alpha < 1, \gamma < 1$). Figure 5 presents an example of this evolution of the Debye relaxation of 2E1H in SQA. The data analysis for the $x_{2E1H} = 32\%$ solution (where the Debye relaxation has almost disappeared) indicates that what has been a pure Debye profile is now described well with the HN parameters $\alpha = 0.95$ and $\gamma = 0.65$, indicating significant deviations from the pure Debye mode. The results for the mixtures of 2E1H and 3MP also support that the Debye relaxation broadens increasingly below 30% alcohol mole fraction. Relative to higher temperature dielectric measurements where deviations from the Debye shape remain small for any relaxation process, 39,51 the present results for the deeply supercooled systems reveal this correlation between amplitude and broadening quite clearly.

Recent dielectric studies of mixtures of two Debye-type monohydroxy alcohols have also observed that the "Debye" relaxation does not remain purely exponential in the mixtures but is subject to only slight broadening around 50% mole fraction. As a result, concentration fluctuations appear to contribute less to the broadening of the Debye relaxation than to the structural relaxation processes, 28 consistent with the present observations. By contrast, mixtures of non-Debye liquids display much more pronounced concentration fluctuation effects regarding the width of their α -relaxations.⁵² The insensitivity of the prominent dielectric signal in monohydroxy alcohols to concentration fluctuation is most certainly a consequence of whatever makes this process Debye-like in pure alcohols. Apparently, these dielectric processes do not couple to or they average over the dynamic heterogeneities of supercooled liquids.53,54

The present findings also emphasize that the Debye-type relaxation feature of associating liquids does not occur without an associated non-Debye (α -) relaxation at higher frequencies. The observation holds not only for solutions but equally for pure glass-forming Debye-type liquids at low temperature. 8,14,22,23 On the other hand, the existence of the α -relaxation is not affected by the breakdown of the Debye relaxation.

4.2. Disappearance of the Debye Relaxation. Figure 1 has clearly displayed that below 20 mol % of the alcohol the relaxation has disappeared while the α -structural relaxation still persists. Here we will discuss the breakdown scenarios of the Debye relaxation in more detail under various conditions, which can be categorized into two parts: in pure liquids and in binary systems.

For pure monohydroxy alcohol liquids, factors like strong steric hindrance, the formation of network structure from multi-H-bonding, and crystallization have been made responsible for the elimination of the Debye peak. It has been proposed that the strong steric hindrance leads to the disappearance of the Debye feature. 12,14 Our dielectric measurements of a secondary alcohol, 4-methyl-3-heptanol, demonstrated that a clear but very weak Debye peak occurs, accompanied by an α-relaxation near the glass transition temperature $T_{\rm g}$ (100 s) = 160 K. In the case of a tertiary alcohol, 2,3-dimethyl-3-pentanol, we hardly discerned a Debye relaxation in its supercooled regime. Note that tertiary alcohols have marginal glass-forming ability and strong tendency to form plastic crystals, which tends to limit the width of the supercooled liquid range. Compared with the primary alcohols, the weaker Debye relaxation strength of the secondary and tertiary alcohols is likely to originate from the stronger steric hindrance to the development of extended H-bonding. Also, the formation of 3-D network in liquids also destroys the Debye relaxation. For example, it was found that the dielectric spectrum of diols displays a process that becomes more Debye like the larger the spatial separation of the two -OH groups is.⁵⁵ As another example, for pure liquids whose molecules include -OH and -O- groups, like 3-methoxy-1-butanol and 2-isopropoxyethanol, we did not find a Debye relaxation but an asymmetrically broadened relaxation typical of nonassociating liquids. Finally, crystallization studies of the 2-propanol on the Debye relaxation found that the Debye peak is subject to a gradual broadening until it disappears at complete crystallization.⁵⁶

Now, we consider the dielectric strength of the Debye relaxation as a function of alcohol concentration in binary systems and its disappearance at a finite concentration. The dielectric results of 2E1H in 3MP indicate that the Debye relaxation reaches zero amplitude at \approx 20 mol % 2E1H. In early studies of the dielectric relaxation of mixtures of 1-propanol

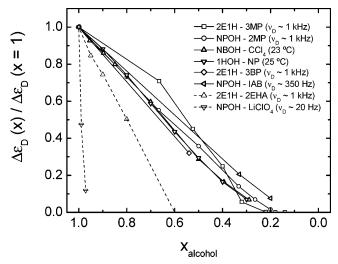


Figure 6. Normalized Debye relaxation strengths of different monohydroxy alcohols as a function of mole fraction. The alcohols are 2-ethyl-1-hexanol (2E1H), 1-propanol (1POH), 1-butanol (1BOH), and 1-heptanol (1HOH). The nonpolar diluents are 3-methylpentane (3MP), 2-methylpentane (2MP), CCl₄, and *n*-pentane (NP). The polar diluents are 3-bromopentane (3BP), isoamyl bromide (IAB), and 2-ethylhexylamine (2EHA), as well as the addition of LiClO₄. Data for 1POH/2MP is from ref 41, for 1POH/IAB from ref 37, for 1BOH/CCl₄ from ref 57, for 1HOH/NP from ref 39, and for 2E1H/2EHA from ref 52. The data with 1 mol % of LiClO₄ is from ref 59 at $T \approx 123$ K, and the data of 2.87 mol % is based on dielectric modulus data from ref 58 and dielectric susceptibility data of pure 1POH from ref 19 at 143.3 K.

with 2-methylpentane, Denney and Ring have stated that "it was apparent, however, that the nature of the solution must change drastically between about 30 and 15 mol % npropanol". 41 This observation is entirely analogous to our present results. To make this effect clearer, we show in Figure 6 the Debye amplitude behavior of monohydroxy alcohols in various mixtures vs composition. For the cases of alcohols in alkanes, several examples are compiled in Figure 6, such as 1-propanol in 2-methylpentane, 41 1-butanol in CCl₄, 57 and 1-heptanol in *n*-pentane.³⁹ It is deduced from Figure 6 that, for these solutions where the alcohols and alkanes are all small molecules, the common feature is that the dielectric strength of the Debyetype relaxations decrease linearly with the concentration of alcohols, 42,51 reaching zero near 20% mole fraction of the alcohol. Regarding our Debye relaxation results of 2E1H in SQA, the behavior is similar to the 3MP case if compared on a weight fraction basis.

In the mixtures with polar liquids, the dielectric behaviors of monohydroxy alcohols is partly obscured by the high dielectric signal of the polar component.⁴³ An example included in Figure 6 is 1-propanol in isoamyl bromide.³⁷ The interesting feature of this polar diluent is that the breakdown of the Debye relaxation is similar to the nonpolar cases. This suggests that the breakdown process in polar liquids is not very different from the behavior in alkanes. Recent measurements on solutions with an associating but non-Debye liquid, 2-ethylhexylamine (2EHA), found that the Debye relaxation disappeared at around 60 mol % 2E1H.²³ Beyond that concentration, only a single non-Debye type dielectric relaxation is detected in the supercooled liquid region. Earlier studies of 1-propanol in glycerol and 1,3butanediol have also demonstrated that lowering the 1-propanol concentration leads to a rapid disappearance of the Debye relaxation.35

In Figure 6 we also include the fate of the Debye relaxation induced by the addition of ions, based on the data of 1-propanol

with LiClO₄. 58,59 It is seen that LiClO₄ has the most pronounced effect on the Debye relaxation intensity. Regarding dynamics, it was observed that addition of LiClO₄ leads to a slight acceleration of the Debye process and the slowing down of the α -relaxation of 1-propanol. Additionally, obvious broadening of the Debye relaxation is detected in the ionic solutions. 58,59 On the other hand, the addition of ions was found to give rise to the increase of the viscosity η of the systems. 58,60 This result is in excellent agreement with the argument that only the α -relaxation of alcohols is associated with the viscous flow of liquids.

On the basis of the analysis provided in Figure 6, the elimination of the Debye relaxation already at a high alcohol concentration requires the dilution with strongly associating character. Debye peaks in mixtures with nonassociating liquids, polar or nonpolar, display the disappearance of their amplitude at a common finite value for the alcohol mole fraction, around x = 0.2. This is different from the effects seen in binary systems without a Debye process,61,62 where the dielectric strength of the polar component vanishes only when its concentration tends to zero. Mixtures of liquids that involve Debye peaks at sufficient alcohol content not only cease to show this peak below about 20% alcohol mole fraction, but the structural relaxations from alcohols and alkanes can be independently identified in the absence of the Debye process. That two α -peaks can be observed in an up to 20% mole fraction mixture indicates that the liquids do not mix homogeneously on the molecular level, indicative of the importance of hydrogen bonding even at these low concentrations. Even in the dilute limit of 2E1H in 3MP (see the x = 0.01 curve in Figure 1), the H-bonding effects can be observed, which lead to the formation of stable clusters with low dipole moments. 46,63,64

According to the above observations, the disappearance of the Debye process by dilution does not necessarily imply the disintegration of the H-bonded structures formed in associating liquids. The basis for this notion is the occurrence of two separate α-relaxation peaks in a concentration range where the Debye peak is not observed. On the basis of experimental evidence, molecular binary systems which do not involve an associating compound display only one α-process (possibly widened by concentration fluctuations), provided the miscibility on a molecular level. 31,33,52 Accordingly, the observation of two peaks in simple supercooled mixtures of intermediate composition can be viewed as a hint toward phase separation. Phase separation in mixtures of polar and nonpolar liquid on a mesoscopic rather than macroscopic level usually requires the addition of surfactants. Examples are "oil-in-water" type micellar structures or propylene glycol in decalin as a case of glassforming reverse-micellar microemulsion system.^{65–67} Because primary monohydroxy alcohols have surfactant character,⁶⁸ reverse-micellar like structures might be a possibility for alcohols or alcohol/alkane mixtures to mesoscopically phase separate polar from nonpolar moieties, which is favorable over a molecular mixture in case the energy gain exceeds the entropic cost of such structures.⁵⁸

4.3. Coupling of Debye and α -Relaxation Dynamics. The change of the Debye relaxation time with dilution is also quite interesting. In studying the mixture of 1-propanol (20 mol %)— isoamyl bromide systems, Denney found for the Debye peak that "the relaxation time corresponding to the alcohol is longer in the mixture than in the pure alcohol although the relaxation time for the latter is greater than that for the pure halide by more than 100 times".³⁴ It implied that the slow Debye relaxation of 1-propanol is slowed down further in the solution,

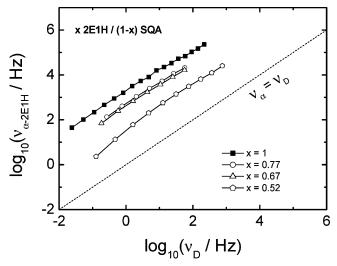


Figure 7. Correlation of the Debye (ν_D) and α-relaxation (ν_α) peak frequencies for 2-ethyl-1-hexanol (2E1H) upon being diluted in squalane (SQA). The dashed line represents the identity $\nu_\alpha = \nu_D$. The graph shows the approach of the two dynamics as the Debye relaxation intensity decreases.

apparently by adding a liquid with faster dynamics. However, viscosity measurements on the binary mixtures observed a monotonic decrease of η from the *n*-alkanol-rich to the alkane halide-rich composition.⁶⁹ Compared to the Debye peak of 1-propanol, other independent measurements also support that the single dielectric process of pure isoamyl bromide is indeed faster in this (ref 34) temperature range. 20,62,70,71 Instead of the above approach, let us now compare the true α -relaxation dynamics of the two compounds. Experimental measurements have established the $T_{\rm g}$ of the pure 1-propanol to be 96 K, 72 which is lower than that of the isoamyl bromide with $T_{\rm g} = 105$ K (differential thermal analysis and viscosity⁷³). Furthermore, the two liquids have similar fragility values of m = 40 for 1-propanol²⁰ and m = 53 for isoamyl bromide.⁶² It thus turns out that the α-relaxation dynamics of 1-propanol is actually faster than that of the halide, and therefore the structural relaxation time of this alcohol is inevitably slowed down upon adding isoamyl bromide. This observation implies that the relation of the α -relaxation times of the two components, but not the Debye process time scale, is the decisive factor in determining the change in viscosity and primary relaxation times in such mixtures. Again, the conclusion from the above considerations is that the Debye relaxations is not the immediate signature of the structural relaxation of the alcohol. In solutions as well as pure alcohols, the Debye dynamics remains correlated with the α -relaxation time of the alcohol, but it is not a decisive factor regarding other than dielectric properties.

To study the coupling of the Debye and the corresponding α -structural relaxation of the alcohol, a plot of the Debye vs the α -relaxation time of 2E1H in SQA is presented in Figure 7. Here, we introduce a decoupling coefficient d to describe the separation of the two relaxations, defined as

$$d = \nu_{\rm q} / \nu_{\rm D} \tag{2}$$

where $\nu_{\rm D}$ and ν_{α} are the respective peak relaxation frequencies of the Debye and the α -relaxation of the alcohol. According to this definition, high d values represent the large separation of the two relaxations, with observed values for d ranging from 14 to 2000. Since the Debye dynamics is invariably slower than the structural relaxation, this coefficient d is always greater

than unity. Figure 7 demonstrates that with dilution of 2E1H in SQA the decoupling coefficient decreases, indicative of the approaching of the two relaxations. Considering the results in Figures 3 and 4, it is more exact to say that increasing dilution of the alcohol moves the Debye relaxation more toward the structural relaxation time. Actually, the decrease of the extent of decoupling between the two relaxations has also been exhibited in the mixtures of two monohydroxy alcohols, 28 where around a 50:50 composition the decoupling coefficient has reached its lowest value. A closer look at Figure 7 shows that near the breakdown concentration (x = 0.52) of the Debye relaxation d is close to 100. It is worthwhile to point out that this value is exactly the decoupling coefficient of pure monohydroxy alcohols in the limit of high temperatures, ¹⁹ where the amplitude reaches zero for different reasons. This similarity of the dilution-induced and temperature-induced breakdown of the Debye feature warrants future exploration.

Whether the Debye relaxation is being accelerated or slowed down in nonpolar liquids is determined by the relative values of the two α-relaxation times, while changes in the degree of decoupling can be an additional factor. At high concentration of alcohols where the decoupling coefficient is almost unchanged compared with that of the pure liquid, the acceleration or the slowing down of the α-relaxation of the alcohols in solutions determines the change of the Debye relaxation time. At low concentration, the decoupling degree can decrease, and this leads to the relative movement of the Debye relaxation toward the α-relaxation time of the alcohol. Under this condition, there are two different scenarios. If the dynamics of the α-relaxation of the alcohol is slower than that of the nonpolar liquids, the Debye relaxation will be accelerated across the entire concentration range until its complete breakdown, which has been exhibited in the alcohol-containing mixtures.^{37,43} On the other hand, if the dynamics of the α -relaxation of the alcohol is faster than that of the nonpolar liquids, the α -peak of the alcohol will certainly be slowed down in the solution. At the same time, the decreasing decoupling (d) implies that the Debye peak moves toward the α -process, possibly leading to an acceleration (see the low concentration of x = 52 mol % alcohol in Figure 4) or to a slowing down.^{34,37} On the basis of these analyses, it is easy to explain the "anomalous behavior" of the Debye relaxation of 2E1H in SQA in Figure 4, where the Debye relaxation dynamics is slowed down at the high alcohol concentrations before the trend reverses direction.

To conclude this section, the diluent effect on the Debye relaxation time in mixtures remains to be determined by the viscosity or $\alpha\text{-relaxation}$ time scale of the alcohol, which in turn is modified in either direction by the diluents viscosity or $\alpha\text{-relaxation}$ time. Therefore, diluting 2E1H by the more fluid 3MP or by the more viscous SQA leads to the Debye peak of 2E1H being shifted in different directions. The relative position of the Debye peak appears not to be relevant for this mixing effect, but its position tends to track the change of the $\alpha\text{-process}$ of the alcohol.

5. Summary and Conclusions

We have studied the dielectric relaxation behavior of supercooled 2-ethyl-1-hexanol when mixed with glass-forming alkanes, one being more fluid (3-methylpentane) and one being more viscous (squalane) than the alcohol. The alcohol of this study displays the pronounced Debye-type dielectric loss peak typical of many associating liquids in their supercooled regime. The focus of this work is on the amplitude, the spectral width, and the relaxation time of the Debye process and its dependence on adding nonpolar diluents.

Consistent with observations regarding pure alcohols, the Debye-type process in alcohol/alkane mixtures is always accompanied by a lower amplitude, higher frequency relaxation which displays the typical characteristics of a structural or α -process. Naturally, the dielectric strength ($\Delta \epsilon$) of the Debye peak is diminished upon adding a nonpolar diluent. However, as its amplitude approaches zero, the originally Debye-type loss peak broadens asymmetrically before it disappears altogether. More interestingly, the breakdown of the amplitude does not occur trivially at zero alcohol mole fraction x, but rather at finite values around x = 20%. Therefore, a minimum alcohol content in these mixtures is required in order to sustain the dielectric Debye process. This level might indicate a percolation threshold for some long-ranged interaction required for the occurrence of the Debye process. In the absence of the Debye peak, two α-relaxations remain observable, indicative of the alcohol and the alkane not forming a homogeneous mixture on the molecular level. Instead, a mesoscopic phase separation as in micellar systems remains, which in turn suggests that hydrogen bonded structures exist without giving rise to a Debye process. Therefore, the disappearance of the Debye process by dilution does not indicate the disintegration of the H-bonded structures formed in these liquids.

Regarding the relaxation times in the binary systems compared to the pure compounds, we find that the α -relaxation time scale of the diluent relative to the α -relaxation (not Debye) time of the alcohol determines whether the alkane leads to slower or faster alcohol dynamics. The time scale of the Debye process is not relevant for this mixing effect; it rather follows the change of the alcohols α -peak (with possible changes in their spectral separation). That only the α -peaks (or equivalently the viscosities) govern the direction of change immediately explains the apparent paradox observed by Denney, that "the relaxation time corresponding to the alcohol is longer in the mixture than in the pure alcohol although the relaxation time for the latter is greater than that for the pure halide by more than 100 times".³⁴ If the true α -relaxation time instead of the Debye time had been used for comparing the dynamics of 1-propanol and isoamyl bromide, the observed behavior would have been readily expected.

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References and Notes

- (1) Angell, C. A.; Ngai, K. L.; McKenna, G. B.; McMillan, P. F.; Martin, S. W. J. Appl. Phys. **2000**, 88, 3113.
 - (2) Ngai, K. L. J. Non-Cryst. Solids 2000, 275, 7.
 - (3) Menon, N.; Nagel, S. R. Phys. Rev. Lett. 1994, 73, 963.
- (4) Disorder Effects on Relaxational Processes; Richert, R., Blumen, A., Eds.; Springer: Berlin, 1994.
- (5) Ediger, M. D.; Angell, C. A.; Nagel, S. R. J. Chem. Phys. 1996, 100, 13200.
- (6) Böhmer, R.; Ngai, K. L.; Angell, C. A.; Plazek, D. J. J. Chem. Phys. **1993**, 99, 4201.
 - (7) Murthy, S. S. N. J. Mol. Liq. 1989, 40, 261.
- (8) Hassion, F. X.; Cole, R. H. *Nature (London)* **1953**, *172*, 212. (b) Hassion, F. X.; Cole, R. H. *J. Chem. Phys.* **1955**, *23*, 1756.
- (9) Brot, C.; Magat, M.; Reizisch, L. Kolloid Z. 1953, 134, 101. (b) Brot, C.; Magat, M. J. Chem. Phys. 1963, 39, 841.
 - (10) Garg, S. K.; Smyth, C. P. J. Phys. Chem. 1965, 69, 1294.
- (11) Bordewijk, P.; Gransch, F.; Böttcher, C. J. F. J. Phys. Chem. 1969, 73, 3255.
- (12) Dannhauser, W. J. Chem. Phys. 1968, 48, 1918. (b) Johari, G. P.; Dannhauser, W. Phys. Chem. Liq. 1970, 2, 37.
- (13) Sagal, M. W. J. Chem. Phys. 1962, 36, 2437. (b) Minami, R.; Itoh, K.; Sato, H.; Takahashi, H.; Higasi, K. Bull. Chem. Soc. Jpn. 1981, 54,

- 1320. (c) Mandal, H.; Frood, D. G.; Habibullah, M.; Humeniuk, L.; Walker, S. J. Chem. Soc., Faraday Trans. 1 1989, 85, 3045.
- (14) Kalinovskaya, O. E.; Vij, J. K. J. Chem. Phys. 2000, 112, 3262.
 (b) Johari, G. P.; Kalinovskaya, O. E.; Vij, J. K. J. Chem. Phys. 2001, 114, 4634.
- (15) Petong, P.; Pottel, R.; Kaatze, U. J. Phys. Chem. A 1999, 103, 6114.
 (b) Kaatze, U. J. Non-Cryst. Solids 2002, 305, 19.
- (16) Barthel, J.; Bachhuber, K.; Buchner, R.; Hetzenauer, H. Chem. Phys. Lett. 1990, 169, 369.
 - (17) Sato, T.; Chiba, A.; Nozaki, R. J. Chem. Phys. 2000, 113, 9748.
 - (18) Kilp, H.; Garg, S. K.; Smyth, C. P. *J. Chem. Phys.* **1966**, *45*, 2799.
 - (19) Wang, L.-M.; Richert, R. J. Chem. Phys. 2004, 121, 11170.
- (20) Hansen, C.; Stickel, F.; Berger, T.; Richert, R.; Fischer, E. W. J. Chem. Phys. **1997**, 107, 1086.
- (21) Kudlik, A.; Tschirwitz, C.; Benkhof, S.; Blochowicz, T.; Rössler, E. Europhys. Lett. 1997, 40, 649.
 - (22) Murthy, S. S. N.; Tyagi, M. J. Chem. Phys. 2002, 117, 3837.
 - (23) Wang, L.-M.; Richert, R. J. Phys. Chem. B 2005, 109, 11091.
 - (24) Ngai, K. L. J. Phys.: Condens. Matter 2003, 15, S1107.
 - (25) Wang, L.-M.; Richert, R. J. Chem. Phys. 2005, 123, 054516.
 - (26) Denney, D. J.; Cole, R. H. *J. Chem. Phys.* **2005**, *123*, 054516 (26) Denney, D. J.; Cole, R. H. *J. Chem. Phys.* **1955**, *23*, 1767.
- (27) Mashimo, S.; Umehara, T.; Redlin, H. J. Chem. Phys. 1991, 95,
 - (28) Wang, L.-M.; Richert, R. J. Phys. Chem. B 2005, 109, 8767.
- (29) Angell, C. A. In *Hydrogen-Bonded Liquids*; NATO ASI Series C, Vol. 329; Dore, J. C., Teixeira, J., Eds.; Kluwer Acad. Pub.: Dordrecht, 1980
- (30) Litovitz, T. A.; McDuffie, G. E. J. Chem. Phys. 1963, 39, 729.
- (31) Crossley, J.; Tay, S. P.; Walker, M. S.; Walker, S. J. Chem. Phys. 1978, 69, 1980.
- (32) Naoki, M.; Matsumoto, K.; Matsushita, M. J. Phys. Chem. 1986, 90, 4423.
 - (33) Johari, G. P.; Goldstein, M. J. Chem. Phys. 1970, 53, 2372.
 - (34) Denney, D. J. J. Chem. Phys. 1959, 30, 1019.
- (35) McDuffie, G. E.; LaMacchia, J. T.; Conord, A. E. J. Chem. Phys. 1963, 39, 1878.
 - (36) Johari, G. P.; Smyth, C. P. J. Am. Chem. Soc. 1969, 91, 6215.
 - (37) Daumezon, P.; Heitz, R. J. Chem. Phys. 1971, 55, 5704.
 - (38) Shinomiya, K.; Shinomiya, T. Bull. Chem. Soc. Jpn. 1990, 63, 1093.
- (39) Schwerdtfeger, S.; Kohler, F.; Pottel, R.; Kaatze, U. J. Chem. Phys. 2001, 115, 4186.
 - (40) Phillips, C. S. E. Nature (London) 1950, 166, 866.
 - (41) Denney, D. J.; Ring, J. W. J. Chem. Phys. **1963**, *39*, 1268.
- (42) Crossley, J.; Glasser, L.; Smyth, C. P. J. Chem. Phys. **1971**, *55*, 2197. (b) Glasser, L.; Crossley, J.; Smyth, C. P. J. Chem. Phys. **1972**, *57*, 3977
 - (43) Murthy, S. S. N.; Tyagi, M. J. Solution Chem. 2002, 31, 33.
 - (44) Finke, H. L.; Messerly, J. F. J. Chem. Thermodyn. 1973, 5, 247.
- (45) Yamamuro, O.; Takahara, S.; Inaba, A.; Matsuo, T.; Suga, H. J. Phys.: Condens. Matter 1994, 6, L169.
- (46) Shahriari, S.; Mandanici, A.; Wang, L.-M.; Richert, R. J. Chem. Phys. 2004, 121, 8960.
- (47) Deegan, R. D.; Leheny, R. L.; Menon, N.; Nagel, S. R.; Venerus, D. C. *J. Phys. Chem. B* **1999**, *103*, 4066. This $T_{\rm g}$ value is based on the viscosity data at 10^{13} P.
- (48) Richert, R.; Duvvuri, K.; Duong, L.-T. J. Chem. Phys. 2003, 118, 1828.
 - (49) Richert, R. Rev. Sci. Instrum. 1996, 67, 3216.
 - (50) Sastry, N. V.; Valand, M. K. J. Chem. Eng. Data 1996, 41, 1421.
- (51) Noreland, E.; Gestblom, B.; Sjoblom, J. J. Solution Chem. 1989, 18, 303.
 - (52) Duvvuri, K.; Richert, R. J. Phys. Chem. B 2004, 108, 10451.
 - (53) Ediger, M. D. Annu. Rev. Phys. Chem. 2000, 51, 99.
 - (54) Richert, R. J. Phys.: Condens. Matter 2002, 14, R703.
 - (55) Davidson, D. W. Can. J. Chem. **1961**, *39*, 2139.
- (56) Sanz, A.; Jimenez-Ruiz, M.; Nogales, A.; Martin y Marero, D.; Ezquerra, T. A. *Phys. Rev. Lett.* **2004**, *93*, 015503.
- (57) Wong, N. M.; Drago, R. S. J. Phys. Chem. 1991, 95, 7542.
- (58) Floriano, M. A.; Angell, C. A. J. Chem. Phys. 1989, 91, 2537.
- (59) Power, G.; Johari, G. P.; Vij, J. K. J. Chem. Phys. 2002, 116, 4192.
- (60) Sare, E. J.; Angell, C. A. J. Solution Chem. 1973, 2, 53.
- (61) Denney, D. J.; Ring, J. W. J. Chem. Phys. 1966, 44, 4621.
- (62) Kalinovskaya, O. E.; Vij, J. K. J. Chem. Phys. 1999, 111, 10979.
- (63) Czarnecki, M. A. J. Phys. Chem. A 2000, 104, 6356.
- (64) Murdoch, K. M.; Ferris, T. D.; Wright, J. C.; Farrar, T. C. J. Chem. Phys. **2002**, 116, 5717.
- (65) Angell, C. A.; Kadiyala, R. K.; MacFarlane, D. R. J. Phys. Chem. 1984, 88, 4593.
 - (66) Green, J. L. J. Phys. Chem. 1990, 94, 5647.
 - (67) Wang, L.-M.; He, F.; Richert, R. Phys. Rev. Lett. 2004, 92, 095701.

- (68) Kahlweit, M.; Strey, R.; Busse, G. J. Phys. Chem. 1991, 95, 5344.
 (69) Anson, A.; Garriga, R.; Martinez, S.; Perez, P.; Gracia, M. J. Chem. Eng. Data 2005, 50, 1478. (70) Denney, D. J. J. Chem. Phys. 1957, 27, 259.

- (71) Berberian, J. G.; Cole, R. H. J. Am. Chem. Soc. 1968, 90, 3100.
 (72) Richert, R.; Angell, C. A. J. Chem. Phys. 1998, 108, 9016.
 (73) Carpenter, M. R.; Davies, D. B.; Matheson, A. J. J. Chem. Phys. **1967**, 46, 2451.