

## Broadband dynamics in neat 4-methyl-3-heptanol and in mixtures with 2-ethyl-1-hexanol

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The relatively small dielectric Debye-like process of the monohydroxy alcohol 4-methyl-3-heptanol (4M3H) was found to depend slightly on the intramolecular conformation. Proton and deuteron nuclear magnetic resonance demonstrate that the hydroxyl dynamics and the overall molecular dynamics take place on similar time scales in contrast to the situation for the structural isomer 2-ethyl-1-hexanol (2E1H) [S. Schildmann *et al.*, J. Chem. Phys. **135**, 174511 (2011)]. This indicates a very weak decoupling of Debye-like and structural relaxation which was further probed using volume expansivity experiments. Shear viscosity as well as diffusometry measurements were performed and the data were analyzed in terms of the Debye-Stokes-Einstein equations. In mixtures of 4M3H with 2E1H the Debye-like process becomes much stronger and for 2E1H mole fraction of more than 25% the behavior of this alcohol is rapidly approached. This finding is interpreted to indicate that the ring-like supramolecular structures in 4M3H become energetically unfavorable when adding 2E1H, an alcohol that tends to form chain-like molecular aggregates. The concentration dependence of the Kirkwood factor in these mixtures displays a high degree of similarity with experimental results on monohydroxy alcohols in which the pressure or the location of the OH group within the molecular structure is varied. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4821229>]

### I. INTRODUCTION

In recent years, the Debye-like relaxation in monohydroxy alcohols has been scrutinized by numerous studies, in continuation of activities that started a long time ago.<sup>1,2</sup> The hydrogen bonds that are present in these liquids are thought to favor supramolecular association and are held responsible for the typically strong electrical absorption known as Debye relaxation. This relaxational feature reflects an underlying single exponential dynamics which is slower than the structural relaxation. A prominent Debye relaxation is, phenomenologically, similarly displayed by water<sup>3</sup> and a few other hydrogen bonded systems.<sup>4</sup> However, for some monohydroxy alcohols<sup>5-9</sup> a Debye-like feature is observed that is only about as strong or even weaker than the structural relaxation. Hence, the question arises whether or not the microscopic mechanisms giving rise to this small Debye-like feature are analogous to those leading to strong Debye peaks.

Dannhauser addressed this issue already in the 1960s by studying a large variety of isomeric aliphatic octanols.<sup>5</sup> It was found that the strength of the overall relaxation depends strongly on the position of the hydroxyl group within the molecule. With an OH group in a terminal site, large relaxation strengths  $\Delta\epsilon$  can be detected, while "shifting" this group to the central part of the molecule leads to a marked decrease of  $\Delta\epsilon$ . These findings are generally interpreted to indicate that a non-terminal OH group is effectively screened by the non-polar alkyl chain part of the molecule thereby dis-

favoring intermolecular association characterized by a large effective dipole moment.

Monohydroxy alcohols with strong Debye peaks, such as 2-ethyl-1-hexanol (2E1H), have been studied using a variety of techniques not only including dielectric work<sup>10-13</sup> but also specific heat,<sup>14</sup> mechanical,<sup>11</sup> nuclear magnetic resonance (NMR),<sup>15-17</sup> and infrared spectroscopy.<sup>18</sup> For monohydroxy alcohols with a small Debye-like feature such as 4-methyl-3-heptanol (4M3H), dielectric<sup>5,6,9,19-21</sup> and calorimetric measurements<sup>19,22,23</sup> have been performed but work using other methods is scarce.<sup>24</sup>

Apart from using dielectric spectroscopy, in the present work we report on the shear viscosity and volume expansivity of 4M3H and study this substance using several NMR techniques including relaxometry, diffusometry, and echo spectroscopy. The combination of these experimental methods allows us to work out common features and differences exhibited by 4M3H in comparison with alcohols showing a large Debye-type dielectric absorption such as 2E1H.

Additional insights into the nature of small Debye-like features can be expected by mixing an alcohol such as 4M3H with another one such as 2E1H, which exhibits a strong Debye relaxation. Therefore, we also report on our dielectric results on 4M3H-2E1H mixtures covering the entire concentration range. The idea of mixing two alcohols is by no means new<sup>25,26</sup> and was often applied to find out whether or not ideal mixing behaviors regarding the structural and/or the Debye-type of relaxations exist.<sup>27-29</sup> However, to our

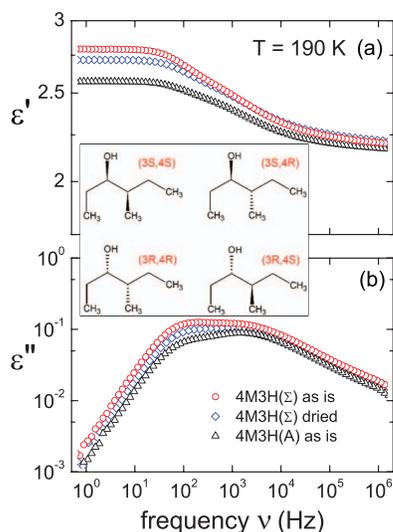


FIG. 1. Dielectric response of 4M3H from different suppliers. The liquid obtained from Alpha-Aesar (data taken from Ref. 9) shows a significantly smaller Debye process as compared to that obtained from Sigma-Aldrich. Drying the latter using a molecular sieve reduces the Debye relaxation strength, but only slightly. The four diastereomers of 4M3H are schematically depicted in the inset. The erythro (or syn) diastereomers are sketched on the left-hand side and the threo (or anti) conformers are sketched on the right-hand side.

knowledge, composition variation was so far not exploited to track the evolution of the dipolar dynamics in mixtures of liquids exhibiting vastly different strengths in their Debye(-like) relaxations.

While the main motivation of the present work is to explore the consequences of the molecular structure on *supramolecular* association phenomena, it is worth mentioning that 4M3H exhibits also an interesting intramolecular complexity, see the inset of Fig. 1. Both the methyl group as well as the hydroxyl group represent a chirality center, so that the 4M3H molecule exists in four diastereomeric forms.<sup>30–32</sup> Some of them act as pheromones among insects. For instance, the (3*S*,4*S*) species has been recognized as aggregation pheromone of the elm bark beetle, if not inhibited by the presence of (3*R*,4*S*) or (3*R*,4*R*) species,<sup>33</sup> while somewhat different observations were made for the almond bark beetle.<sup>34</sup> On the other hand, (3*R*,4*S*)-4M3H is used as trail pheromone by some ants.<sup>35</sup> For 2E1H no such biological relevance seems to be known.<sup>36</sup>

Since it is well conceivable that the *intramolecular* conformation close to the hydroxyl group can affect the sterical hindrance experienced by the OH group, it is necessary to address this point in the present work. To anticipate our result, it is found that the strength of the Debye-like feature in 4M3H does indeed depend slightly on the *intramolecular* conformation. By using chemicals from different suppliers this result was discovered, however, only relatively late in the course of this work, i.e., after some sub-projects described in this article were already completed. Therefore, the use of 4M3H from a specific supplier for a given sub-project did not follow a plan.

## II. EXPERIMENTAL DETAILS

2E1H (stated purity of 99.6%) was obtained from Sigma-Aldrich. 4M3H with a stated purity of 99% was received from Sigma-Aldrich and from Alpha-Aesar; whenever deemed necessary, the samples are labeled using the letters  $\Sigma$  and A, respectively. Unless stated otherwise, the samples were used as received. Dielectric measurements and  $^{13}\text{C}$  NMR on pure 4M3H were carried out using liquids from both sources. 4M3H(A)<sup>37</sup> was used for the deuteron NMR experiments performed at a Larmor frequency  $\omega_D = 2\pi \times 46$  MHz. Proton spin-lattice relaxation times and translational self-diffusion coefficients  $D_t$  were measured at  $\omega_H = 2\pi \times 54$  MHz for 4M3H( $\Sigma$ ). To obtain  $D_t$ , we performed Hahn echo and stimulated-echo experiments in a static magnetic field gradient of  $(20 \pm 2)$  T/m using the procedures described in more detail in Ref. 17.

$^{13}\text{C}$  high-resolution NMR at 75 MHz was carried out to determine the ratio of the erythro [also called “syn,” i.e., (3*S*,4*S*) or (3*R*,4*R*)] to threo [also called “anti,” i.e., (3*S*,4*R*) or (3*R*,4*S*)] conformers in our samples. Using chemical shift data published for the various diastereomers,<sup>30</sup> we find that the erythro:threo ratio is 1:0.6 for 4M3H( $\Sigma$ ) (or syn fraction 0.63) and 1:0.72 (or syn fraction 0.58) for 4M3H(A).

For the deuteron NMR measurements 4M3H(A) was labeled at the hydroxyl group by repeated dissolution in  $\text{D}_2\text{O}$  and subsequent distillation, thereby achieving an isotopic purity of 98%. Details regarding the deuteron experiments are described elsewhere, see, e.g., Refs. 11, 16, and 17. The setup employed for the dielectric non-equilibrium measurements is described in Ref. 38. In these measurements the time evolution of the real part of the dielectric constant is monitored after a nonlinear temperature step of  $\sim 2$  K. If the molecular polarizability is temperature independent at the monitoring frequency, the measured quantity is proportional to the density and hence to the dynamic thermal volume expansivity. This method determines the terminal relaxation rate<sup>38</sup> which in general is smaller than the corresponding loss peak frequency.

When studying the concentration dependent dielectric response of binary 4M3H-2E1H mixtures 4M3H( $\Sigma$ ) was utilized.<sup>39</sup> 4M3H( $\Sigma$ ) was also used for the shear viscosity measurements. In the temperature range  $165 \text{ K} < T < 215 \text{ K}$  viscosities,  $\eta$ , were obtained from the DC (low-frequency) limit of the imaginary part of the shear modulus divided by frequency with  $\eta'(\omega) = G''(\omega)/\omega$  and  $\eta = \lim_{\omega \rightarrow 0} \eta'(\omega)$ . In the temperature range  $187 \text{ K} < T < 220 \text{ K}$  the shear viscosity was determined from the Helmholtz resonance in the aperture of a bulk transducer.<sup>40</sup>

## III. EXPERIMENTAL RESULTS

### A. Neat 4M3H

#### 1. Dielectric spectroscopy

In a recent broadband dielectric study we used 4M3H(A).<sup>9</sup> In Fig. 1 we reproduce a spectrum from that work taken at 190 K. Here the Debye-like feature is rather weak. Then 4M3H( $\Sigma$ ) was measured and, as Fig. 1 shows,

here the Debye-like process was found to be somewhat more prominent. A quantitative analysis was carried out in terms of a superposition of two Cole-Davidson functions: One accounting for the structural relaxation, index  $\alpha$ , and another one accounting for the Debye-like feature, index  $D$ . With  $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$  the difference of static and high-frequency permittivity, denoting the relaxation strength,  $\tau$  the relaxation time, and  $\nu$  as the measuring frequency we have

$$\varepsilon^*(\nu) = \varepsilon_\infty + \frac{\Delta\varepsilon_D}{(1 + 2\pi i\nu\tau_D)^{\gamma_D}} + \frac{\Delta\varepsilon_\alpha}{(1 + 2\pi i\nu\tau_\alpha)^{\gamma_\alpha}}. \quad (1)$$

Here,  $\gamma_{\alpha,D} < 1$  is the Cole-Davidson exponent<sup>41</sup> which describes the broadening of the corresponding contribution. For  $\gamma_{\alpha,D} = 1$  the spectral form characteristic of a Debye relaxator (indicative for single exponential relaxation) is recovered. Although it was found previously that the  $\alpha$ -process in monohydroxy alcohols with a strong and well resolved Debye process can be described using a Cole-Cole expression,<sup>42</sup> for 4M3H the Cole-Davidson function, Eq. (1), seems to give consistently better results<sup>9,21</sup> and therefore we use this expression here.

For 4M3H( $\Sigma$ ) we find  $\Delta\varepsilon_D/\Delta\varepsilon_\alpha = 0.47$  and  $\tau_D/\tau_\alpha = 6.3$ , while  $\Delta\varepsilon_D/\Delta\varepsilon_\alpha = 0.32$  and  $\tau_D/\tau_\alpha = 6.8$  are found for 4M3H(A), revealing that the relaxation time ratio is almost unaffected unlike what is observed for the (ratio of) relaxation strengths. We first checked whether this significant difference in the relaxation strengths,  $\Delta\varepsilon_D$ , could arise from differences in contamination with water. Due to its large dipole moment one may expect that water enhances the dielectric response so that 4M3H( $\Sigma$ ) could be contaminated more strongly. However, a Karl Fischer titration revealed that the water content of 4M3H(A) (found to be 0.13%) is comparable to that of 4M3H( $\Sigma$ ) (0.11%). Then, we dried the latter liquid using a molecular sieve with a pore size of 4 Å thereby reducing the water content about 100-fold to 13.2 ppm. This drying procedure indeed led to a reduction of the strength of the Debye-like feature, see Fig. 1, so that now  $\Delta\varepsilon_D/\Delta\varepsilon_\alpha = 0.38$ . But Fig. 1 also shows that the dried 4M3H( $\Sigma$ ) sample still exhibits a stronger Debye-like feature than 4M3H(A). This suggests that the difference in the  $\Delta\varepsilon_D/\Delta\varepsilon_\alpha$  ratio of the untreated samples is *not* predominantly due to differing water contents. So presumably, the differences in the amounts of the different stereoisomers, as reported in Sec. II, affect the  $\Delta\varepsilon_D/\Delta\varepsilon_\alpha$  ratio.

The fact that 4M3H( $\Sigma$ ) with its larger syn fraction has the larger Debye-like feature can be interpreted in two ways, (i) either in terms of a single-molecule picture, e.g., if the different conformers have different dipole moments, or (ii) in terms of a supramolecular picture.

Option (i) means that the syn conformer should have a larger dipole moment. Indeed, the finding of different molecular dipole moments for different diastereomers is not uncommon.<sup>43</sup> However, from simple bond moment calculations<sup>44</sup> we estimate that the syn configuration of 4M3H should have a slightly smaller dipole moment than the anti conformer. Therefore, it is worthwhile to consider also the second option. (ii) In terms of a supramolecular picture several possibilities come to mind, even if one assumes that just dimeric species exist. One could either argue with ring-like

clusters in mind or in terms of more open supramolecular structures. The latter seems unlikely because for the anti conformer the OH group is certainly sterically screened somewhat less and hence should give rise to a slightly larger Debye process, unlike to what is observed experimentally. Therefore, we are left to consider that the anti conformer allows for a more efficient ring-dimer-like packing.

## 2. Proton and deuteron spin-lattice relaxation times

For the elucidation of the molecular site specific dynamics of monohydroxy alcohols it has turned out useful to compare proton with deuteron NMR spectroscopy.<sup>15,17,45</sup> By performing <sup>2</sup>H-NMR measurements on OD labeled 4M3H one is selectively sensitive to the dynamics of the hydroxyl group. In <sup>1</sup>H-NMR on fully protonated 4M3H only one out of the 18 molecule's protons reflects the OH group. Hence, such experiments will essentially yield information regarding the alkyl part of 4M3H.

Fig. 2 shows our results on the two hydrogen isotopomers, i.e., the spin-lattice relaxation times <sup>1</sup>H- $T_1$  and <sup>2</sup>H- $T_1$ , both obtained for Larmor frequencies near  $\omega_L = 2\pi \times 50$  MHz. It is seen that for both probe nuclei  $T_1$  passes through a minimum near 254 K at which the molecular relaxation time is estimated to be  $\tau_{\text{NMR},T_1} \approx 0.616/\omega_L \approx 2$  ns. This similarity in time scales and thus minimum temperatures is to be contrasted with an about 20 K difference in the <sup>1</sup>H- $T_1$  versus <sup>2</sup>H- $T_1$  minima found from NMR measurements of 1-butanol<sup>15,16</sup> and of 2E1H.<sup>17</sup> For 2E1H this more than 20 K

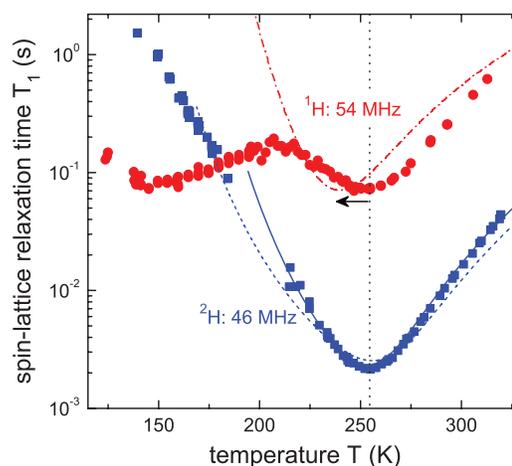


FIG. 2. The squares represent deuteron spin-lattice relaxation times of OD-labeled 4M3H as recorded at 46 MHz. A minimum is observed for  $T = 254$  K. Due to very short spin-spin relaxation times no  $T_1$  data could be taken for temperatures between 185 and 215 K. The circles represent proton spin-lattice relaxation times of fully protonated 4M3H as recorded at 54 MHz. These latter data display two minima, one at 254 K, showing that the dynamics of the OD group and that of the overall molecular motion are very similar. A second minimum is observed for <sup>1</sup>H- $T_1$  near 150 K which indicates the freezing of the threefold motion of methyl groups on the time scale of nanoseconds. The solid line is calculated using Eq. (2) in conjunction with Eq. (3). For comparison, the dashed line reflects the <sup>2</sup>H- $T_1$  behavior of OD-labeled 2E1H and the dashed-dotted line reflects the <sup>1</sup>H- $T_1$  behavior of fully protonated 2E1H (both taken from Ref. 17). The arrow emphasizes that unlike for 4M3H for 2E1H the minimum temperatures of the proton and the deuteron spin-lattice relaxation times do not agree with each other, but differ by about 20 K.

difference in the  $^1\text{H}$ - $T_1$  minimum temperatures is highlighted by the arrow. Hence, the coincidence of the  $^1\text{H}$ - $T_1$  versus  $^2\text{H}$ - $T_1$  minimum temperatures for 4M3H is not at all trivial. Unlike 4M3H, these other two monohydroxy alcohols show very intense Debye (-like) processes which, furthermore, are a factor of 100 to 1000 slower than the structural relaxation. For 4M3H the  $\tau_D/\tau_\alpha$  ratio is only  $\sim 3$ -5 at temperatures at which the structural relaxation times are in the nanosecond range.<sup>9</sup>

Near the minimum of the spin-lattice relaxation time, the  $^1\text{H}$ - $T_1$  times of 4M3H are considerably longer than those measured using the deuteron probe, as also observed for 2E1H.<sup>17</sup> This is due to differences in the dipolarly dominated proton-proton versus the quadrupolar coupling strength. Furthermore, the  $^1\text{H}$ - $T_1$  times exhibit another minimum near 150 K. Again in close analogy to findings for 2E1H,<sup>17</sup> this low-temperature minimum can be attributed to the slow-down of the threefold rotation of the methyl groups which contain half of the protons of 4M3H. The fact that protons located at different molecular sites contribute to the  $^1\text{H}$ - $T_1$  times inhibits a straightforward quantitative analysis of their temperature dependence.

For the deuteron spin-lattice relaxation times a more detailed analysis was performed. Here we used the model of Bloembergen, Purcell, and Pound<sup>46</sup>

$$\frac{1}{T_1} = \frac{2(\Delta\delta_Q)^2}{15} [J(\omega) + 4J(2\omega)], \quad (2)$$

which expresses the spin-lattice relaxation rate in terms of the spectral density  $J(\omega)$  provided that the fluctuating part  $\Delta\delta_Q$  of the anisotropy parameter  $\delta_Q = 3e^2qQ/(4\hbar)$  is known.<sup>47</sup> For  $J(\omega)$  we chose the Cole-Davidson form<sup>48</sup> which has a rather different appearance than the expression in Eq. (1) and is given by

$$J(\omega) = \frac{\sin[\beta_{\text{CD}} \arctan(\omega\tau)]}{\omega(1 + \omega^2\tau^2)^{\beta_{\text{CD}}/2}}. \quad (3)$$

Here,  $\beta_{\text{CD}} < 1$  is a measure for the nonexponentiality of the structural relaxation.

Using this approach, i.e., Eqs. (2) and (3) in conjunction with dielectric time constants, e.g., from Ref. 9, a good description of the experimental data is obtained for temperatures near the deuteron  $T_1$  minimum, see Fig. 2. The resulting parameters will be presented and discussed in Sec. IV A below.

While spin-lattice relaxometry is most sensitive to molecular dynamics taking place on nanosecond time scales, deuteron stimulated-echo experiments enable one to detect motions in the range of milliseconds to seconds.<sup>49</sup> We performed the corresponding experiments using OD labeled 4M3H(A) yielding two-time reorientational correlation functions. The stretching parameters characterizing these functions turned out to lie in the range from 0.3 to 0.5, a quite typical finding.<sup>17,49</sup> The temperature dependence of the correlation times resulting from these experiments will also be presented in Sec. IV A below.

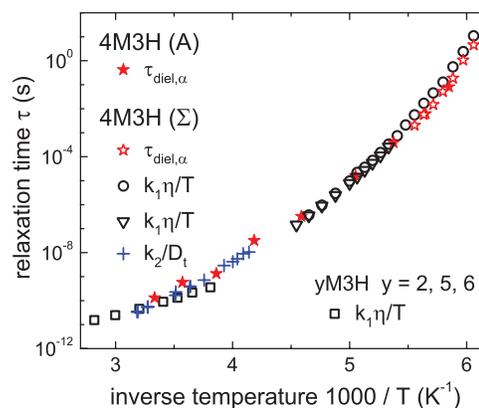


FIG. 3. Dielectric relaxation times for the  $\alpha$ -process of 4M3H( $\Sigma$ ) (open stars, present work) and of 4M3H(A) (filled stars, Ref. 9). The circles and triangles reflect shear viscosities determined from  $G''$  and using the Helmholtz resonance, respectively (present work). The squares are calculated using the shear viscosities reported by Johari and Dannhauser<sup>50</sup> for several octanol isomers that differ from 4M3H only by the position of the methyl group. To allow for a comparison with the dielectric time constants the viscosity data are presented as  $k_1\eta/T$  with  $k_1 = 2 \times 10^{-6}$  K/Pa, cf. Eq. (4). The translational self-diffusion coefficients measured in this work are presented as  $k_2/D_t$  with  $k_2 = 10^{-20}$  m<sup>2</sup>, cf. Eq. (5).

### 3. Viscosity measurements and field-gradient diffusometry

In Fig. 3 we present viscosity data and compare them with dielectric and diffusivity results. Both sets of viscosity data (those determined from  $G''$  and those from the Helmholtz resonance), which were measured for a temperature range overall covering  $165 \text{ K} < T < 220 \text{ K}$  in the course of the present work, agree very well with each other. Fig. 3 contains also shear viscosity data from the literature that were measured at higher temperatures ( $262 \text{ K} < T < 345 \text{ K}$ ) for a family of octanol isomers including 2-methyl-3-heptanol, 5-methyl-3-heptanol, and 6-methyl-3-heptanol, labeled in Fig. 3 as yM3H.<sup>50</sup> These substances were reported to display practically identical ambient pressure viscosities in the specified temperature range. Fig. 3 shows that the viscosity of these isomers is compatible with that extrapolated for 4M3H.

In Fig. 3 the viscosities are presented in the following form: They are divided by temperature and shifted by a constant factor  $k_1$  which is chosen such that best agreement with respect to the dielectric  $\alpha$ -relaxation times  $\tau_\alpha$  is obtained in a broad temperature range. It is obvious that the shifted viscosity data and  $\tau_\alpha$  display a very similar temperature dependence. Based on the Debye-Stokes relation such an agreement allows one to estimate the mean hydrodynamic radius,  $R_H$ , of the reorienting moieties via<sup>1</sup>

$$\tau_\alpha = \frac{4\pi}{k_B} R_H^3 \frac{\eta}{T}. \quad (4)$$

From  $k_1 = 4\pi R_H^3/k_B = 2 \times 10^{-6}$  K/Pa (as utilized in Fig. 3), one obtains  $R_H \approx 1.6 \text{ \AA}$  which is a factor of 2 smaller than the van der Waals radius  $R_{\text{vdW}} = 3.33 \text{ \AA}$  estimated for the 4M3H molecule.<sup>51</sup> Using  $\tau_D \approx 6 \times \tau_\alpha$  instead of  $\tau_\alpha$  in Eq. (4) the hydrodynamic radius becomes  $\approx 3 \text{ \AA}$ . The good agreement of this number with  $R_{\text{vdW}}$  could be coincidence

because it was not<sup>16,17</sup> observed for other monohydroxy alcohols.

We compared the viscosities with the translational self-diffusion coefficients  $D_t$  that we measured for 4M3H. The latter are plotted in Fig. 3 again in a scaled form as  $k_2/D_t$ . The factor  $k_2$  was chosen to obtain a good overall agreement with the viscosity (and dielectric time constant) data. Combining the Stokes-Einstein relation<sup>52</sup>

$$\frac{1}{D_t} = \frac{6\pi}{k_B} R_H^* \frac{\eta}{T} = \frac{\tau_\alpha}{k_2}, \quad (5)$$

with Eq. (4) the hydrodynamic radius of the diffusing moieties can be estimated. From the constant  $k_2 = 2R_H^3/(3R_H^*) = 1 \times 10^{-20} \text{ m}^2$  used in Fig. 3, one obtains  $R_H^* \approx 1.5 \text{ \AA}$ . This value is compatible with  $R_H$ , hence much smaller than the van der Waals radius. This kind of deviation between simple estimate and experimental determination was found also for 2E1H.<sup>17</sup>

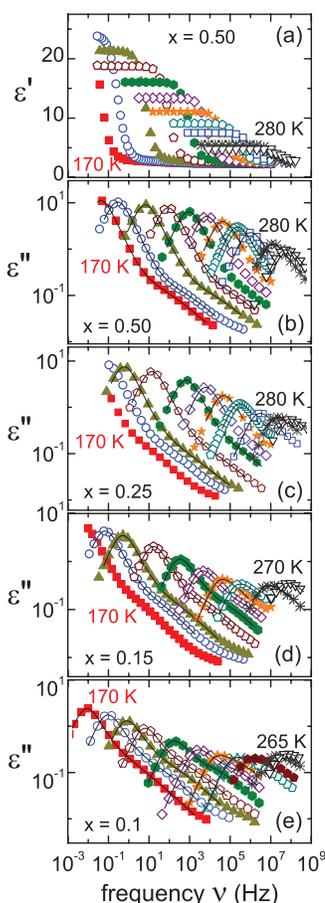


FIG. 4. Dielectric spectra of  $(4M3H)_{1-x}(2E1H)_x$  mixtures measured at (a) and (b) 280, 265, 255, 245, 235, 225, 215, 205, 195, 185, 175, and 170 K; (c) 280, 265, 250, 235, 225, 215, 205, 190, 180, 175, and 170 K; (d) 270, 250, 230, 220, 210, 200, 190, 180, 175, and 170 K; (e) 265, 250, 235, 225, 215, 205, 195, 185, 180, 175, and 170 K. The solid lines represent fits based on Eq. (1).

## B. Dielectric spectroscopy of 4M3H mixed with 2E1H

The real part  $\epsilon'(\nu)$  and the imaginary part  $\epsilon''(\nu)$  of the dielectric constant were measured for a number of  $(4M3H)_{1-x}(2E1H)_x$  samples with molar fraction  $x = 0, 0.05, 0.10, 0.15, 0.25, 0.50, 0.75, 0.87$ , and 1 covering a frequency range from  $10^{-2}$  to  $10^9$  Hz. In Figs. 4(a) and 4(b) we show  $\epsilon'(\nu)$  and  $\epsilon''(\nu)$ , respectively, of  $(4M3H)_{0.5}(2E1H)_{0.5}$ . In both frames one recognizes that two relaxation processes exist, the structural relaxation at higher and the Debye process at lower frequencies. It is remarkable that the real part,  $\epsilon'(\nu)$ , displays a very long low-frequency plateau. This means that the AC-conductivity in this monohydroxy alcohol mixture is very much smaller than observed for other types of organic glass formers. Moreover, the static permittivity,  $\epsilon_s$ , exhibits an enormously pronounced, but monotonic temperature dependence. Usually for neat monohydroxy alcohols the peak of the dielectric loss shows a continuous slight decrease with temperature up to  $T \approx 250$  K and then drops more steeply. This kind of “250 K anomaly” was also observed for  $(4M3H)_{1-x}(2E1H)_x$  mixtures with 2E1H concentrations  $x = 0.75, 0.87$ , and 1 that are not shown in Fig. 4 and for a range of other monohydroxy alcohols.<sup>9</sup> For  $(4M3H)_{0.25}(2E1H)_{0.75}$ , cf. Fig. 4(c), the loss peaks do not show this feature but merely level off in the high-frequency/high-temperature range. For lower concentrations [ $x = 0.15$  in Fig. 4(d) and for  $x = 0.10$  in Fig. 4(e)] the peaks become even larger at the highest temperatures. Finally, for  $x = 0.05$  the static susceptibilities, see Fig. 5(a), and also the dielectric loss peak amplitudes, see Fig. 5(b), display a strong increase. In this respect, the behavior of  $(4M3H)_{0.95}(2E1H)_{0.05}$  resembles that of pure 4M3H.<sup>9</sup> However, one also recognizes that in the audio-frequency range the Debye process for the  $x = 0.05$  sample is much more prominent than the structural relaxation, in contrast to what has been observed for neat 4M3H.<sup>9</sup>

We analyzed the data for all concentrations  $x$  quantitatively in terms of Eq. (1) and will discuss the results in Sec. IV below. However, a good survey of the overall

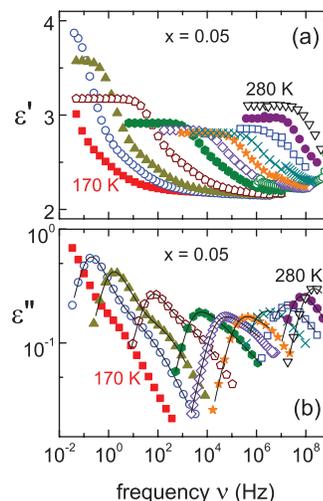


FIG. 5. (a) Real part and (b) imaginary part of the dielectric constant of  $(4M3H)_{0.05}(2E1H)_{0.95}$ . Measurements were taken at 280, 265, 250, 235, 225, 215, 205, 190, 180, 175, and 170 K. The solid lines represent fits using Eq. (1).

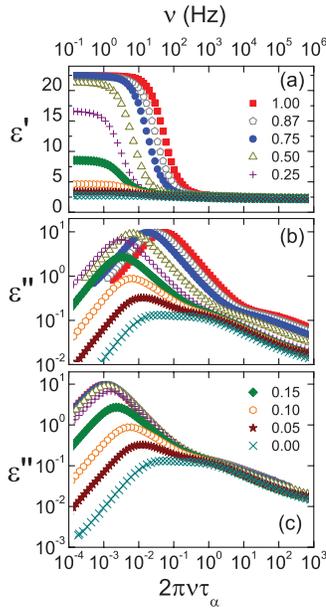


FIG. 6. (a) Dielectric constant and (b) dielectric loss spectra of all studied  $(4M3H)_{1-x}(2E1H)_x$  samples at 185 K. The concentration dependence of the relaxation processes is clearly revealed. (c) The data shown in frame (b) are rescaled to the  $\alpha$ -relaxation time of each sample  $\tau_\alpha$ . One recognizes that the amplitude of the  $\alpha$ -process changes very little over the entire concentration range.

behavior can be gained by focusing on a single temperature and showing the results from all samples in a common plot. In Figs. 6(a) and 6(b)  $\varepsilon'(\nu)$  and  $\varepsilon''(\nu)$ , respectively, are compiled for  $T = 185$  K. One observes that the  $\alpha$ -process, i.e.,  $\log \tau_\alpha(x)$  evolves smoothly with  $x$ , reflecting the differing glass transition temperatures of 2E1H ( $T_g = 146$  K)<sup>53</sup> and 4M3H ( $T_g \approx 162$  K).<sup>19,23</sup> For  $x \leq 0.15$  the peak frequencies of the  $\alpha$ -process almost coincide.

Reducing the 2E1H concentration from  $x = 1$  to 0.5, also the Debye process shifts smoothly to lower temperatures, but otherwise it is practically unaffected. Diminishing  $x$  further,  $\Delta\varepsilon_D$  drops precipitously and at least for  $x < 0.25$  the time scales  $\tau_D$  and  $\tau_\alpha$  tend to approach each other. The trends in  $\tau_D/\tau_\alpha$  are, however, more clearly revealed when scaling the dielectric loss curves to superimpose the peak frequency of the  $\alpha$ -relaxation. In Fig. 6(c) one indeed recognizes immediately that the time scale decoupling of the two processes, and hence the ratio  $\tau_D/\tau_\alpha$ , is constant for  $x \geq 0.25$ , but that for lower 4M3H concentrations the dynamic decoupling tends to vanish.

## IV. DISCUSSION

### A. Relaxation dynamics of neat 4M3H

In an Arrhenius plot, Fig. 7, we compile relaxation times from dielectric spectroscopy, from NMR measurements, and from calorimetry. Dealing first with the dielectric results, it is useful to point out that for 4M3H( $\Sigma$ ) time constants were obtained from fits using Eq. (1), while for 4M3H(A) the data were collected from the literature.<sup>9,19</sup> One recognizes that the Debye relaxation times of 4M3H from the various sources agree very well with each other, and good agreement is also noted for the  $\alpha$ -times, as already indicated in Fig. 3. In the

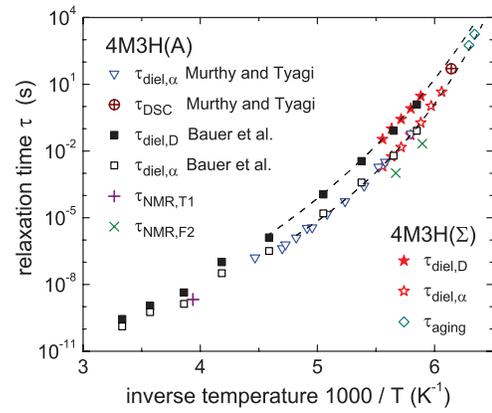


FIG. 7. Relaxation map of 4M3H including data on 4M3H( $\Sigma$ ) from this work (dielectric equilibrium measurements; volume expansion experiments; deuterium spin-lattice relaxometry; stimulated-echo spectroscopy). For comparison, the literature data obtained from dielectric measurements on 4M3H(A) (Bauer *et al.*<sup>9</sup>; Murthy and Tyagi<sup>19</sup>), and differential scanning calorimetry (DSC, Ref. 19) are included. The dashed lines are fits of dielectric data for 4M3H( $\Sigma$ ) using Eq. (6) covering time scales in the range from  $10^{-6}$  to  $10^4$  s using the parameters given in the text.

deeply supercooled state the temperature dependence of the Debye as well as of the  $\alpha$ -relaxation times can both be described using a Vogel-Fulcher law

$$\tau = \tau_0 \exp\left(\frac{B}{T - T_0}\right). \quad (6)$$

From fits to the  $\tau > 10^{-6}$  s data in Fig. 7, and in good agreement with Ref. 9 we obtain  $\tau_{0,\alpha} = 1.1 \times 10^{-13}$  s,  $B_\alpha = 1490$  K, and  $T_{0,\alpha} = 117$  K for the  $\alpha$ -process and  $\tau_{0,D} = 2 \times 10^{-15}$  s,  $B_D = 2400$  K, and  $T_{0,D} = 101$  K for the Debye process. In Fig. 7 both dependences are represented by dashed lines and are seen to provide a good description of the data. The longest time scales ( $\sim 1700$  s) measured in the present work stem from the dielectrically detected dynamic volume expansivity experiments. Close to time scales of  $10^4$  s  $\tau_\alpha$  and  $\tau_D$  tend to merge. However, one should keep in mind that the longest relaxation times provided from aging measurements need not be directly comparable to the relaxation times obtained from dielectric loss peak frequencies. The aging points represent a different response function than the pure dielectric function and do not need to have identical relaxation times.<sup>54</sup> Furthermore, the points represent an upper bound of the relaxation time as obtained by a loss peak since the terminal relaxation rate is smaller than the loss peak rate. There is evidence though that the terminal relaxation rate of the dielectric response and the volume relaxation are close or identical<sup>38</sup> and thus the aging points  $\tau_{\text{aging}}$  may be regarded as an upper limit to the dielectric relaxation time  $\tau_{\text{diel},\alpha}$ .

The calorimetric relaxation time determined near  $T_g$  in Ref. 19 appears to be compatible with both dielectric time scales. Another calorimetric study<sup>22</sup> reported a glass transition temperature which is about 9 K lower than all the other determinations of  $T_g$ . This data point is not included in Fig. 7.

On the basis of the dielectric  $\alpha$  relaxation times of 4M3H(A) reported in Ref. 9 we calculated the spin-lattice relaxation time  $T_1$  using Eqs. (2) and (3), while treating the width parameter  $\beta_{CD}$  and the fluctuating part of the quadrupolar coupling  $\Delta\delta_Q$  as fitting parameters. Focusing on the

temperature range  $T > 210$  K, at which interference from the  $\beta$ -process is minimal, the best fit as shown in Fig. 2 as solid line yields  $\beta_{CD} = 0.50 \pm 0.05$  and  $\Delta\delta_Q = 2\pi \times (152 \pm 2)$  MHz. The latter parameter is practically identical to that of the coupling  $\delta_Q$  and to the corresponding parameters for 2E1H.<sup>17</sup> The dashed line in Fig. 2 reflects the fit to the deuteron spin-lattice relaxation times of 2E1H as measured at the same Larmor frequency of 46 MHz. As compared to 2E1H the minimal  $T_1$  ( $\sim 2$  ms) is slightly shorter for 4M3H, indicating a broader distribution of  $\alpha$ -relaxation times for 2E1H<sup>55</sup> in accord with a (smaller than for 4M3H) width parameter  $\beta_{CD} = 0.35$  reported for 2E1H.<sup>17</sup> However, the error margin of  $\beta_{CD}$  given above for 4M3H may not be fully adequate if  $T_1$  data at temperatures below 210 K are taken into account. Then also smaller width parameters could emerge from the analysis. Quantitative estimates are difficult, however, because of the possible interference of the  $\beta$ -process which is not easily quantified in NMR terms.<sup>56</sup>

Returning to Fig. 7 we have included only the relaxation times resulting (in model-free ways) from the relation  $\tau = 0.62/\omega_L$  exploited at the temperature of the  $T_1$  minimum and from the decay of the stimulated-echo functions recorded for an evolution time of  $10 \mu\text{s}$ . Both types of NMR time constants agree reasonably well with  $\tau_\alpha$  as determined from dielectric spectroscopy but they are considerably shorter than  $\tau_D$ . This is in accord with previous findings which indicate that NMR is not directly sensitive to the Debye process.<sup>15,17</sup>

## B. Mixing effects

To quantify the observations made for the dielectric data in Fig. 6 in terms of the parameters appearing in Eq. (1), we present  $\Delta\epsilon_D$ ,  $\gamma_D$ ,  $\tau_D/\tau_\alpha$ , and  $\tau_\alpha$  in Fig. 8 for 185 K and, additionally,  $\Delta\epsilon_D$ ,  $\tau_D$ , and  $\gamma_D$  for 200 K. The remaining parameters are  $\Delta\epsilon_\alpha$  – which is essentially independent of the concentration  $x$ , cf. Fig. 6(c) – and  $\gamma_\alpha(x)$  which is  $0.60 \pm 0.03$  at 185 K (not shown).

Focusing first on  $\Delta\epsilon_D(x)$ ,  $\gamma_D(x)$ , and  $\tau_D(x)/\tau_\alpha(x)$  one recognizes from Fig. 8 that two concentration regimes can be distinguished. For  $x \geq 0.25$  the parameters are essentially those found for neat 2E1H. But for smaller 2E1H concentrations the relaxation strength of the Debye process drops precipitously [note the logarithmic ordinate axis in Fig. 8(a)], its spectral width increases, Fig. 8(b), and the  $\tau_D/\tau_\alpha$  ratio is reduced by a factor of more than 10, see Fig. 8(c). For  $x = 0$  no width parameter  $\gamma_D$  can be given, since for the corresponding fits, owing to the very small intensity of the corresponding feature, the assumption was made that it is characterized by a Debye shape.<sup>9,21</sup> While the parameters discussed above hint at a “critical concentration” of  $x_c = 0.20 \dots 0.25$  (highlighted by the dotted lines in Fig. 8) such a change of behavior is not observed from the essentially linear concentration dependence of  $\log_{10}\tau_\alpha$ , cf. Fig. 8(d). Only the samples with  $x \leq 0.05$  deviate slightly from this approximately linear, sometimes called “ideal mixing” behavior.

Also for the Debye process of the binary systems 2-methyl-1-butanol (2M1B) and 2-ethyl-1-hexanol as well as for 1-propanol and 3,7-dimethyl-1-octanol ideal mixing be-

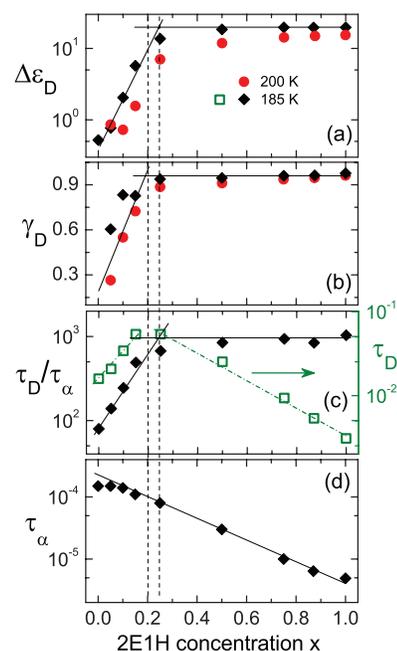


FIG. 8. Dependence of various parameters on the molar 2E1H concentration  $x$  as obtained from fits using Eq. (1): (a) relaxation strength  $\Delta\epsilon_D$  of the Debye-like process, (b) its shape parameter,  $\gamma_D$ , of the Debye-like process, (c) time scale of the Debye-like process,  $\tau_D$ , as well as time scale separation of Debye-like and  $\alpha$ -process,  $\tau_D/\tau_\alpha$ , and (d) structural relaxation times  $\tau_\alpha$ . The solid lines are guides to the eye. The dotted vertical lines mark the composition range in which the  $x$ -dependent behavior changes markedly.

haviors were reported.<sup>28</sup> All four of these monohydroxy alcohols show quite pronounced Debye processes. For the present mixture, which involves also a liquid with a weak Debye-like feature, striking deviations from ideal mixing are obvious from  $\log_{10}\tau_D(x)$ , see Fig. 8(c), as well as from  $\Delta\epsilon_D(x)$ , see Fig. 8(a).

In fact  $\Delta\epsilon_D(x)$  resembles the behavior reported for mixtures of the isomeric hexanols 4-methyl-2-pentanol (4M2P) and 2-ethyl-1-butanol (2E1B).<sup>29</sup> Depending on temperature 2E1B shows a 20%–30% larger  $\Delta\epsilon_D$  than 4M2P. In their Fig. 6, Gong *et al.* report that upon mixing  $\Delta\epsilon_D$  is roughly constant down to a 2E1B concentration of  $\sim 25\%$  and then decreases.<sup>29</sup> Interpreting this as a critical concentration, its numerical value even coincides with that for the present system. The currently studied 4M3H-2E1H mixture is to be distinguished from the 4M2P-2E1B mixture in the sense that the strength  $\Delta\epsilon_D$  of the neat alcohols 4M3H (for which the OH group is sterically more screened than in 4M2P) and 2E1H differs by a factor of  $\approx 40$ .

Another difference between the two binary systems is that for a given temperature, the relaxation time  $\tau_D$  shows a monotonic variation with concentration in the 4M2P-2E1B mixture<sup>29</sup> while in 4M3H-2E1H  $\tau_D(x)$  is maximum for  $x \approx x_c$ , see Fig. 8(c). Gong *et al.* studied mixtures of 2E1H with 2M1B and their Fig. 8 shows a monotonic compositional variation, albeit for  $\Delta\epsilon_D$ .<sup>29</sup> Whether  $\tau_D$  also exhibits a non-monotonic variation for the 2E1H-2M1B mixtures is not obvious from Ref. 29.

Referring to  $\Delta\epsilon_D(x)$ , see Fig. 8, we suggest that the pronounced increase of the relaxation strength when

coming from the 4M3H side, i.e., for increasing 2E1H concentration means that the ring-like dimeric or multimeric structures dominating in the neat liquid are destabilized. In other words, they are broken up by the presence of 2E1H. Obviously this process is quite efficient because it leads to an almost exponential increase of  $\Delta\epsilon_D(x)$  up to  $x \approx 0.2$ , see Fig. 8(a). On the other hand, coming from the 2E1H side, at 185 K the general dielectric behavior, and hence the presumed chain-like structures, are preserved in the relatively “diluted” mixtures near the critical concentration. Preservation of  $\Delta\epsilon_D$  over about three quarters of the molar concentration range is also indicated by the results for 4M2P-2E1B mixtures.<sup>29</sup> We find this observation quite surprising and will offer some rationalization in terms of the Kirkwood factors to be discussed next.

### C. Temperature and concentration dependent dielectric relaxation strength

The analysis of our dielectric data, cf. Fig. 4 and Fig. 5, using Eq. (1) yields the dielectric relaxation strengths in a wide concentration range. Taking into account the limiting permittivities  $\epsilon_s$  and  $\epsilon_\infty$  we calculated the Kirkwood factor<sup>57</sup>

$$g_K = \frac{9\epsilon_0 k_B T (\epsilon_s - \epsilon_\infty)(2\epsilon_s + \epsilon_\infty)}{n\mu^2 \epsilon_s(\epsilon_\infty + 2)^2} \quad (7)$$

by assuming that the molecular dipole moment  $\mu = 1.68$  (Ref. 5) as well as the number density  $n = 3.8 \times 10^{21} \text{ cm}^{-3}$  (Ref. 58) are both similar for 4M3H and 2E1H (regarding  $n$ , see also the discussion below). The results for  $g_K$  are compiled in Fig. 9(a). For neat 4M3H one recognizes that  $g_K$

displays a shallow minimum near 220 K and that  $g_K < 0.5$  in the entire accessible temperature range.<sup>9,21</sup> For 2E1H, on the other hand,  $g_K$  is always larger than unity reaching values larger than 4 at low temperatures. As a function of concentration there is a smooth change of behavior between that of neat 4M3H and that of neat 2E1H. For 2E1H concentrations in the range  $x \approx 0.5 \dots 1$  there is little overall variation in the temperature dependence of  $g_K$ . However, it is interesting to observe that for  $x = 0.5$  in the 190 ... 240 K range the temperature dependence of  $g_K$  becomes more pronounced than for pure 2E1H. Finally, for mixtures with  $x < 0.2$  a minimum in  $g_K$  develops for 215 K  $< T < 240$  K and, e.g., for  $x = 0.1$ , values larger than  $g_K = 1$  are reached at low temperatures.

Overall the  $g_K$ -pattern revealed by varying the composition of a binary mixture resembles that reported in two other types of studies. In the first kind of these investigations the position of the hydroxyl group within an octanol molecule was successively changed from a terminal position to a site more in the “middle” of the alkyl chain.<sup>5</sup> The general similarity of these and the present results for  $g_K(T)$  implies that it is essentially the average distance of the OH group from a terminal position which governs the temperature evolution of the dielectric strength.

In the second kind of study, monohydroxy alcohols displaying a small Debye process at ambient pressure were investigated for varying degrees of compression.<sup>59,60</sup> Increasing the pressure exerted, e.g., on 4M3H up to several hundred MPa a  $g_K(T)$  dependence was found which resembles that of 2E1H.<sup>21</sup> In particular, Fig. 9(a) showing  $g_K(T)$  with  $x$  as a parameter resembles  $g_K(T)$  with pressure as a parameter, see, e.g., Refs. 21 and 59.

Let us now discuss these findings in the light of a statement made in Ref. 60. There it is emphasized that “low dipole moment complexes ( $g < 1$ ) are less dense than non-associated molecules ( $g \approx 1$ ), which are in turn less dense than high dipole moment complexes ( $g > 1$ ).” In accord with this statement, from preliminary scattering experiments it is found<sup>61</sup> that 2E1H is significantly more dense than 4M3H. Hence, indeed, increasing the overall density of 4M3H either by compression or by admixing a “densifier” such as 2E1H should have a similar effect, in accord with experimental findings.

Returning to the observation that  $\Delta\epsilon_D(x)$  or  $g_K$  is preserved in  $(4M3H)_{1-x}(2E1H)_x$  upon chemical dilution down to  $x_c \approx 0.25$  [at least for  $T \leq 200$  K, Fig. 9(b)] this suggests that 2E1H’s “high-density” supramolecular structure is relatively stable if 4M3H molecules are dispersed as (non-self associating species) within 2E1H. Such a situation would imply that only below a percolation threshold, roughly marked by  $x_c$ , dimeric and maybe larger “low-density” clusters of 4M3H form in significant fractions. This conjecture calls for temperature and concentration dependent structural measurements which are currently underway.

## V. CONCLUSIONS

To summarize, we studied pure 4M3H using a variety of techniques including equilibrium and out-of-equilibrium dielectric experiments, the latter probing the dynamic volume expansion, shear viscosimetry, as well as several NMR

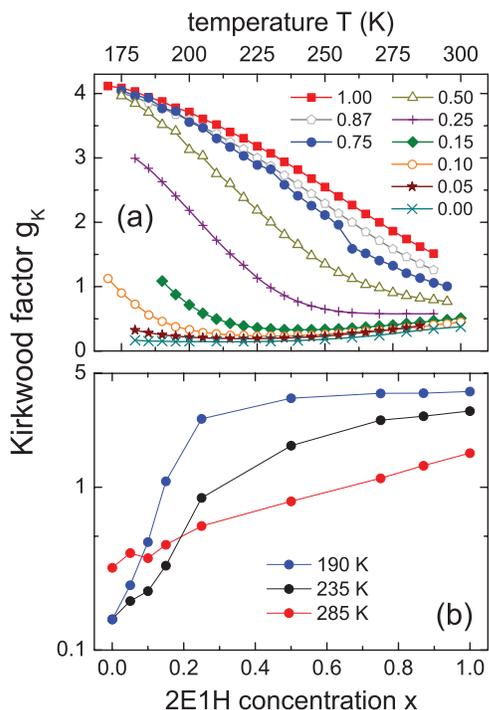


FIG. 9. (a) Temperature dependence of the Kirkwood factor calculated from Eq. (7) for all 4M3H( $\Sigma$ ) based  $(4M3H)_{1-x}(2E1H)_x$  mixtures measured in the present work. The lines are drawn to guide the eye. Frame (b) shows the Kirkwood factor  $g_K(x)$  for several temperatures.

techniques such as  $^1\text{H}$ ,  $^2\text{H}$ , and  $^{13}\text{C}$  spin-lattice relaxometry, field-gradient diffusometry, and deuteron stimulated-echo spectroscopy. This allowed us to obtain detailed insights into the dynamics of 4M3H and to track the molecular relaxation times over a wide temperature range.

Combining  $^{13}\text{C}$ -NMR with dielectric spectroscopy we find that the amplitude of the weak Debye-like feature of 4M3H depends slightly on its diastereomeric configuration. This is presumably because the anti conformer packs more efficiently in ring-dimer-like associates than the syn conformer does. The relaxation strength of the  $\alpha$ -process and the time scales  $\tau_\alpha$  and  $\tau_D$  are obviously essentially unaffected by the intramolecular configuration.

The combination of  $^1\text{H}$ - with  $^2\text{H}$ -NMR revealed that the dynamics of the hydroxyl group and that of the alkyl part of the 4M3H molecule are very similar as indicated by the (identical!) temperatures at which the  $T_1$  minima show up for the two probe nuclei. This behavior is to be contrasted with that of 2E1H. There, on the nanosecond scale set by the  $T_1$  experiment, the dynamics of the OH group slows down at a temperature 20 K above that at which the alkyl chain slows down. This difference in behavior of the two octanol isomers obviously reflects different kinds of intermolecular association. While for 2E1H relatively large supramolecular objects induce a pronounced time scale separation and a large Debye process, for 4M3H only the effects of smaller, presumably ring-like moieties can be detected.

In accord with previous studies on other monohydroxy alcohols, we find for 4M3H that field-gradient diffusometry, analyzed in combination with viscosity data, is essentially sensitive to single-molecule properties indicative for the transient character of the supramolecular objects. The “usual” relaxation dynamics of the  $\alpha$ -process was also revealed by deuteron stimulated-echo experiments.

Finally, we studied a large number of  $(4\text{M3H})_{1-x}(2\text{E1H})_x$  mixtures in a range of up to 12 decades in frequency. This allowed us to track the evolution of 4M3H's weak Debye-like feature into the strong Debye process characteristic of 2E1H. Already for molar 2E1H concentrations of  $\sim 20\%$  the low-temperature  $\Delta\varepsilon_D$  and  $\tau_D/\tau_\alpha$  behavior of the mixture is practically indistinguishable from that of neat 2E1H, while  $\tau_D$  shows a maximum near the critical concentration of  $x_c \sim 20\%$ . Presumably related, albeit less pronounced departures from ideal mixing behaviors were recently reported also for isomeric hexanol mixtures.<sup>29</sup> For  $(4\text{M3H})_{1-x}(2\text{E1H})_x$  at low  $x$  and  $T \leq 200$  K we concluded that the ring-like 4M3H associates are very efficiently destabilized by the presence of small amounts of 2E1H.

Analyzing the dielectric  $(4\text{M3H})_{1-x}(2\text{E1H})_x$  data in terms of the Kirkwood factor  $g_K(x, T)$ , a pattern emerged that was compared to previous work on pure monohydroxy alcohols. In one regard<sup>5</sup> our study indicated that it is essentially the mean position of the hydroxyl group which governs the temperature evolution of the overall dielectric strength. We also found that in terms of the static dielectric response the addition of 2E1H to 4M3H has similar effects than the application of external pressure.<sup>21,59</sup> Hence 2E1H seems to act as a compaction agent for 4M3H, a conjecture calling for a direct experimental check.

## ACKNOWLEDGMENTS

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