Experimental studies of Debye-like process and structural relaxation in mixtures of 2-ethyl-1-hexanol and 2-ethyl-1-hexyl bromide

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Binary solutions of 2-ethyl-1-hexanol (2E1H) with 2-ethyl-1-hexyl bromide (2E1Br) are investigated by means of dielectric, shear mechanical, near-infrared, and solvation spectroscopy as well as dielectrically monitored physical aging. For moderately diluted 2E1H the slow Debye-like process, which dominates the dielectric spectra of the neat monohydroxy alcohol, separates significantly from the α-relaxation. For example, the separation in equimolar mixtures amounts to four decades in frequency. This situation of highly resolved processes allows one to demonstrate unambiguously that physical aging is governed by the α-process, but even under these ideal conditions the Debye process remains undetectable in shear mechanical experiments. Furthermore, the solvation experiments show that under constant charge conditions the microscopic polarization fluctuations take place on the time scale of the structural process. The hydrogen-bond populations monitored via near-infrared spectroscopy indicate the presence of a critical alcohol concentration, \( x_c \approx 0.5–0.6 \), thereby confirming the dielectric data. In the pure bromide a slow dielectric process of reduced intensity is present in addition to the main relaxation. This is taken as a sign of intermolecular cooperativity probably mediated via halogen bonds. © 2012 American Institute of Physics.

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I. INTRODUCTION

For the structure and dynamics of bio-macromolecules, water, and many glass forming liquids hydrogen bonds play an important role. However, even focusing on the probably simpler case of small-molecule glass formers, such as the classical glass formers propylene glycol or glycerol that feature several hydroxyl groups per molecule, it is often found that they exhibit a more complex behavior than molecular liquids devoid of hydrogen bonds: The behavior of such hydrogen-bonded liquids often displays deviations from various scaling properties and they are thus considered peculiar viscous liquids.\(^1\) Moreover, substances with only a single hydroxy group per molecule, such as the monohydroxy alcohols, reveal an even more interesting behavior. When monitoring their response using dielectric spectroscopy, not only the structural relaxation as well as faster modes can be detected but additionally an intense low-frequency absorption shows up. This relaxational feature, named after Peter Debye who formulated the theoretical description of its spectral shape almost 100 years ago,\(^2\) is known experimentally at least since the late 1920s.\(^3\) Despite considerable experimental\(^4\) and theoretical\(^5,6\) effort its microscopic nature had remained controversial for decades. Recently, with a renewed interest in these also technologically relevant solvents, monohydroxy alcohols have been explored using fresh approaches and witnessed a surge of notions and models\(^7–12\) aimed at understanding the specificities of these liquids.

One of the problems encountered when exploring the dielectric properties of pure monohydroxy alcohols is that their Debye-like response can heavily overlap with the structural relaxation and that the latter process accounts for typically only a few percent of the total relaxation strength. This unfavorable combination of properties rendered the clear-cut assignment of, e.g., calorimetric\(^13\) observations difficult and has long hampered substantial conceptual progress in the field.

If an insufficient spectral separation of Debye-like and α-process in monohydroxy alcohols is a concern, chemical mixing can provide a way out of this situation. In the literature, various binary, alcohol containing systems were explored ranging from the admixture of salts\(^5,14\) and nonpolar substances,\(^15,16\) which due to major differences in polarity to the alcohols often exhibit a limited mutual solubility, to the addition of other alcohols\(^17\) as well as of alkyl halides which usually circumvent that problem. Although alcohol solutions with alkyl bromides were investigated early on,\(^18–20\) and also more recently,\(^21,22\) their ability to facilitate a spectral separation of relaxation processes is systematically exploited only since a few years: Examples include mixtures of 5-methyl-2-hexanol with isoamylobromide,\(^23\) of n-butanol (BuOH) with \(n\)-bromobutane (BuBr),\(^24,25\) and of 2-ethyl-1-hexanol (2E1H) with BuBr.\(^21,26\) In the present article we continue along these lines by investigating solutions of 2E1H with 2-ethyl-1-hexyl bromide (2E1Br). In a first step, we will explore the dielectric properties of \((2E1H)_n(2E1Br)_{1−n}\) for the entire range of...
alcohol concentrations x near and above their calorimetric glass transition temperatures \( T_g \). These are 148 K for 2E1H and 131 K for 2E1Br.\(^{11,27}\)

For samples with intermediate alcohol concentrations we will report below that the Debye process is up to four decades slower than the structural one. We take advantage of this enormous spectral separation in such samples in order to show that their shear mechanical modulus reflects solely the structural relaxation. To this end we make use of a measuring technique which allows us to study the mechanical response over more than five decades in frequency.\(^{28}\) Furthermore, we employ a recent version of the Gemant-DiMarzio-Bishop model\(^{29–31}\) in order to clarify the interrelation of dielectric with shear mechanical properties.

Further insight can be gained from triplet state solvation dynamics experiments that were already applied to propanol,\(^{32}\) a short-chain monohydroxy alcohol. The dipolar probe used in the present work is sensitive to the electric modulus response of the solvent at the microscopic level.\(^{33}\) The results can thus be compared with shear modulus data or with the measured electric impedance represented in modulus form.\(^{34}\)

It is not clear which process dominates the physical aging of monohydroxy alcohols, because so far only somewhat incomplete or inconclusive dielectric measurements exist.\(^{35–37}\) The available data do not allow one to decide whether aging takes place on the \( \alpha \) time scale or on a somewhat longer scale. The currently studied equimolarly diluted alcohol is well suited to demonstrate unambiguously that physical aging is governed by the structural (or \( \alpha \)-) relaxation alone.

For several binary solutions of monohydroxy alcohols with alkyl bromides, such as (BuOH)\(_x\)(BuBr)\(_{1-x}\) and (2E1H)\(_x\)(2E1Br)\(_{1-x}\), the occurrence of a so-called critical concentration \( x_c \) was reported.\(^{24,26}\) This term is meant to imply that the shape and/or the time scale of the Debye process is more or less preserved when diluting a monohydroxy alcohol, in some cases even by 50%. We address the issue of a critical concentration \( x_c \) and its properties can be found in Ref. \(^{42}\) the is reported.\(^{24,26}\) For solvation dynamics experiments a small amount (10\(^{-4}\) mol) of quinoxaline (QX), purified by sublimation, was dissolved in a (2E1H)\(_{0.5}\)(2E1Br)\(_{0.5}\) mixture. The sample was placed in an optical cell containing UV-grade synthetic silica windows and it was vacuum sealed in a stainless steel frame. More information regarding the equipment and its properties can be found in Ref. \(^{42}\) The results were obtained as described in Ref. \(^{43}\), and for each temperature the T\(_1\) → S\(_0\) emission peak of QX was recorded 10 ms after the laser excitation.

III. RESULTS AND ANALYSIS

A. Dipolar dynamics probed by dielectric spectroscopy

In Fig. 1 we present the real and the imaginary parts of the dielectric constant for \( x = 0.69 \) and for \( x = 0.31 \). For the alcohol rich sample \( [x = 0.69, \text{ frames (a) and (b)}] \) a two-step behavior is obvious from \( \varepsilon' (\omega) \) and correspondingly two loss maxima are seen in \( \varepsilon'' (\omega) \). The low-frequency relaxation, corresponding to the Debye-like process, is considerably stronger and far less broadened than the \( \alpha \)-relaxation which shows up at higher frequencies. For the bromide rich sample \( [x = 0.31, \text{ frames (c) and (d)}] \) a two-step or two-peak pattern is revealed, again. However, here the \( \alpha \)-relaxation exhibits the larger amplitude. Another striking difference is seen in the overall relaxation strengths which appear almost independent of temperature for low \( x \), but for large \( x \) relaxation strength increases strongly upon cooling. A careful inspection of the data shows that the \( \alpha \)-relaxation is relatively insensitive to temperature for both concentrations, while the low-frequency dispersion gains significant strength as \( T \) is lowered. The various dependences of the relaxation strengths on temperature, composition, etc. are often expressed in terms of the Kirkwood factor,\(^{44}\) which, applied to the present data, underscores the significant differences in mutual molecular alignment associated with the \( \alpha \)-relaxation or with the Debye processes.
The solid lines are fits using Eq. (1).

The relaxation times and relaxation strengths data, similar fits were achieved for other concentrations and temperatures. The relaxation times and relaxation strengths thus obtained as a function of the alcohol concentration are summarized in Fig. 3. Figure 3(a) presents \( \tau_D \) and in Fig. 3(b) the \( \alpha \)-relaxation times \( \tau_\alpha \) are shown for several temperatures. In order to emphasize the common features in the concentration dependence, all the data are normalized to their values at \( x = 0 \). The already mentioned monotonic increase of \( \tau_D \) and \( \tau_\alpha \) with \( x \) is nicely borne out by Fig. 3. More strikingly, this plot demonstrates that two composition regimes can be distinguished: Below \( x \sim 0.5 \) the logarithm of \( \tau_D \) follows a stronger linear dependence than above \( x \sim 0.6 \), while for \( \log(\tau_\alpha) \) the dependence for \( x > 0.6 \) is stronger than it is for lower \( x \).

Consequently, the ratio of the two time scales is largest for \( x = 0.5-0.6 \). This statement can be quantified on the basis of the decoupling ratio

\[
d(x) = \log_{10}\frac{\tau_D(x)}{\tau_\alpha(x)}.
\]

The inset of Fig. 3 shows indeed a broad \( d(x) \) maximum near \( x = 0.6 \) indicative for a decoupling of time scales of...
about four decades. Such a tremendous separation and thus
the clear-cut resolution of Debye-like and α-relaxation void
of a significant spectral overlap facilitates the assignment and
interpretation of results obtained for roughly equimolar mix-
tures of 2E1H with 2E1Br. This will be exploited in the shear
relaxation devoid of the bromide atom.47–49 Hence, the in-
tensity of this band decreases linearly with increasing alcohol
concentration.

Further evidence for a change of behavior near
x ∼ 0.5–0.6 comes from the composition dependence of the
Cole-Davidson exponent γD which relates to the Debye-like
process, see Fig. 3(a). For x ∼ 0.5–0.6 both the α- and the
Debye-like relaxations are about equally strong, at least for
T = 170 K, see Fig. 2. Figure 3(c) documents that ΔεD shows a
crossover at x ∼ 0.5. On the other hand, the spectral
width (not shown) and the relaxation strength of the α-
relaxation [see Fig. 3(c)] interpolate linearly between those of
the pure substances without a sign of a peculiar behavior near
x ∼ 0.5–0.6.

B. Hydrogen bond populations probed
by near-infrared spectroscopy

In Fig. 4 NIR spectra of (2E1H)ₓ(2E1Br)₁₋ₓ are shown for
wavelengths ranging from about 1330 nm to about 1680
nm. All spectra were recorded at T = 300 K and were cor-
rected as detailed in Sec. II. For neat 2E1Br (x = 0, lower-
most curve) a series of bands is seen to exist. These bands
are assigned to combinations of stretching and bending vi-
brations involving carbon and hydrogen atoms47 that will be
termed CHₓ bands in the following. The sharp feature around
6000 cm⁻¹ is a combination band involving the α-CH₂ bands
that are located close to the bromide atom.47–49 Hence, the in-
tensity of this band decreases linearly with increasing alcohol
concentration.

Furthermore, with increasing x, additional bands appear
in the spectra that are due to the first overtones of the OH
stretching vibrations. The assignment of these bands (cf. the
arrows in Fig. 4) is illustrated in Fig. 5(b). The band around
1410 nm corresponds to OH species for which the protons are
not involved in hydrogen bonds and will be called in the fol-
lowing the “monomer” band (free OH group, so-called α
state, to be distinguished from the terminal OH group, called
β-state, according to the nomenclature of Graener et al.50). Since,
usually, the two species cannot be easily spectroscop-
ically differentiated they are commonly, though not com-
pletely unambiguously so, called the “monomer” band. The
small absorbance feature near 1430 nm, termed here as the
terminal band, reflects the vibration of that terminal OH group
which is hydrogen bonded via its proton (γ-state in Ref. 50).
The broad peak around 1590 nm is due to strongly hydrogen
bonded non-terminal OH groups and will be termed CHₓ bands
which OH overtones appear. The arrows highlight the approximate positions of the maxima corresponding to the so called monomer band (λ ∼ 1410 nm), the terminal band (λ ∼ 1430 nm), and the polymer band (λ ∼ 1590 nm).
The terminal band cannot be further resolved. The monomer band decreases, the number of hydrogen-bonded structures basically does not change and the terminal band intensity slightly decreases, the number of hydrogen-bonded structures basically stays constant down to \( x \approx 0.6 \). Therefore, the strong decrease of the polymer band observed here must be due to a decrease in the size of the supramolecular structures. For \( x < 0.6 \) no conclusions can be drawn, as the contribution of the terminal band cannot be further resolved. The monomer band seems to hint at another critical concentration around \( x \approx 0.25 \) as the slope in \( \Delta A_{\text{mon}}(x) \) changes once again.

To check our interpretation \((\text{BuOH})_x(\text{BuBr})_{1-x}\), a similar binary system was studied [see Fig. 5(b)]. Here, the same behavior of the differential absorbance is observed: the intensity of “monomer” band, as that of the terminal band, is essentially constant above an alcohol concentration of 0.5. The same critical butanol concentration was previously identified by dielectric spectroscopy. The similarity of the NIR results obtained for both the 2E1H and the BuOH mixtures indicates that the alcohol molecules, added to solutions above the critical concentration, become part of the existing hydrogen-bonded structures and increase the size (and not the number) of these objects.

### C. Frequency dependent shear response

In order to test the relationship of dielectric and viscoelastic properties in detail we performed measurements of the complex shear modulus \( G'(\nu) = G''(\nu) + i G''(\nu) \) for frequencies ranging from 0.1 Hz to about 10 kHz. For a sample with \( x = 0.53 \) the real part, \( G'(\nu) \), and the imaginary part, \( G''(\nu) \), are shown in Figs. 6(a) and 6(b), respectively. A high-frequency shear modulus of \( G_\infty \approx 1 \text{ GPa} \) can be read off from the data in Fig. 6(a) at the lowest temperature. In Fig. 6(b) several well resolved mechanical loss maxima show up. The arrows included in this figure indicate the positions of the dielectric loss peaks (corresponding to the \( \alpha \)-process) of the same sample. It becomes clear that the mechanical loss peaks appear at frequencies which are \( \tau_{\text{rel}}/\tau_{\text{shear}} \approx 5 \times \tau_{\text{rel}} \). Therefore, the strong increase in the size of the supramolecular structures. For \( x < 0.6 \) no conclusions can be drawn, as the contribution of the terminal band cannot be further resolved. The monomer band seems to hint at another critical concentration around \( x \approx 0.25 \) as the slope in \( \Delta A_{\text{mon}}(x) \) changes once again.

To check our interpretation \((\text{BuOH})_x(\text{BuBr})_{1-x}\), a similar binary system was studied [see Fig. 5(b)]. Here, the same behavior of the differential absorbance is observed: the intensity of “monomer” band, as that of the terminal band, is essentially constant above an alcohol concentration of 0.5. The same critical butanol concentration was previously identified by dielectric spectroscopy. The similarity of the NIR results obtained for both the 2E1H and the BuOH mixtures indicates that the alcohol molecules, added to solutions above the critical concentration, become part of the existing hydrogen-bonded structures and increase the size (and not the number) of these objects.

![Differential band intensities \( \Delta A \) for \((2E1H)(2E1Br)_{1-x}\) read out near the wavelengths marked by the arrows in Fig. 4.](image1)

![Differential band intensities \( \Delta A \) for \((2E1H)(2E1Br)_{1-x}\) read out near the wavelengths marked by the arrows in Fig. 4.](image2)

![Fig. 6. (a) Real part and (b) imaginary part of the frequency dependent shear modulus of \((2E1H)_{0.53}(2E1Br)_{0.47}\) measured for several temperatures. The arrows mark the frequency positions of the dielectric loss peaks corresponding to the structural relaxation. The dashed lines highlight the power laws characterizing the low-frequency response of “simple” liquids.](image3)
frequencies are typical when comparing (dielectric) susceptibilities with (mechanical) moduli. The shear data clearly demonstrate that a terminal relaxation mode is experimentally accessed in the investigated frequency window: In Fig. 6 the dashed lines indicate that in the low-frequency range the ν dependences of $G'(ν)$ and $G''(ν)$ for $T = 150$ K become identical with those expected for “simple” liquids (within the Maxwell model), i.e., $G'(ν) \propto ν^2$ and $G''(ν) \propto ν^{−1}$. In particular, for the data recorded at 160 K and 150 K it is evident that the Debye process in $(2E1H)_{0.5}(2E1Br)_{0.5}$ does not leave any measurable trace in the mechanical response above the resolution limit (10^7 Pa) available in the present work. This result is compatible with previous conclusions drawn for pure 2E1H.

A more detailed comparison of dielectric and shear mechanical responses, which allows one to check the compatibility of the peak maxima and in favorable cases also of the entire spectral shapes of $G'(ν)$ and $ε''(ν)$, is possible on the basis of a simple model. In its recently refined form this approach yields for the dielectric loss

$$ε''(ν) = \frac{Δ B^2(Δ) G''(ν)}{[1 + ΔB(Δ) G''(ν)]^2 + [ΔB(Δ) G''(ν)]^2} \tag{3}$$

with the abbreviation $B(Δ) = \frac{1}{4}[Δ_ε + \sqrt{Δ_ε^2 + 4Δ_ε/(ΔG∞)}]$ and Δ denoting the electro-viscoelastic constant which is considered a free parameter. We calculated $ε''(ν)$ from $G'(ν)$ on the basis of Eq. (3) with $Δ = 7 \times 10^{-10}$ Pa$^{-1}$ and present the results of this procedure as lines in Fig. 7 for $T = 150$ K (for which dielectric and rheological data are available). Excellent agreement of the calculated with the measured loss peak frequency and loss maximum is obtained, while the model underestimates the dielectric loss peak width somewhat. This way of analyzing the data confirms the correspondence of the mechanical response to the α-relaxation.

D. Physical aging

In Fig. 7 we show several dielectric spectra for $(2E1H)_{0.5}(2E1Br)_{0.5}$, a sample for which the time scale of the α-process reaches 100 s near $T_{g,α} \approx 132$ K. Reducing the temperature in steps of 5 K and starting from 152 K, equilibration of the loss spectra is attained practically instantaneously, except at the lowest temperature. Thermal stability of about ±0.02 K was typically reached within a time interval of 200 s. The immediate equilibration for all temperatures $T > 130$ K, which was confirmed by repeat runs at longer times, rules out that aging processes take place on the scale of $τ_α$. This confirms a previous report on pure 2E1H which, however, was unable to resolve the exact time scale of this physical aging process.

At a base temperature of 127 K, which is about 5 K below $T_{g,α}$, the loss data exhibit a pronounced shoulder in the frequency range of about 1 to 10 Hz which after waiting for about 1 day evolves into a well resolved secondary relaxation peak. This is due to the fact that at a given frequency the dielectric loss contribution arising from the structural relaxation successively decreases with time. After a jump from 129.5 K to 127 K, we monitored this reduction of $ε''$ for a frequency of 0.1 Hz in a time range from about $2 \times 10^5$ s to about $3 \times 10^7$ s and present our results in the inset of Fig. 8. One recognizes that at the longest times structural equilibrium is fully established. For the sake of simplicity the aging curve can be described using a Kohlrausch function $ε''(T) \propto \exp[-(t/τ_{age})^{β_{age}}]$. From a least-squares fit to the data we obtain an aging time $τ_{age} = 6.7 \times 10^4$ s and the corresponding stretching exponent is $β_{age} = 0.42$ yielding a mean
aging time of \( \langle \tau_{\text{age}} \rangle = \tau_{\text{age}} \Gamma (1/\beta_{\text{age}})/\beta_{\text{age}} \approx 2 \times 10^4 \) s with \( \Gamma \) denoting Euler’s Gamma function.

A slightly less complete set of data with re-equilibrating times extending only up to about 1.6 \( \times 10^5 \) s was recorded for neat 2E1H subsequent to stepping the temperature from 138 to 135 K. The aging time dependent dielectric loss is also shown in the inset of Fig. 8. Here a fit using a Kohlrausch function yields \( \tau_{\text{age}} = 2.4 \times 10^4 \) s and \( \beta_{\text{age}} = 0.38 \) leading to \( \langle \tau_{\text{age}} \rangle \approx 8.7 \times 10^4 \) s.

In Fig. 8 the aging times \( \langle \tau_{\text{age}} \rangle \) are compared with other dielectric relaxation times, \( \tau_D \) and \( \tau_\alpha \), collected for 2E1H and for (2E1H)\(_{0.5}(2E1Br)_{0.5} \). As shown by the dotted lines, the \( \tau_D \) and the \( \tau_\alpha \) times can be parameterized by a Vogel-Fulcher-Tammann law\(^{58}\) that is typically used to describe the temperature dependence of the relaxation times\(^{59}\) for molecular supercooled liquids,

\[
\tau = \tau_0 \exp [B/(T - T_0)].
\]

Here \( \tau_0^{-1} \) designates an attempt frequency and the coefficients \( B \) and \( T_0 \) determine the form of the \( \tau(T) \) curves. The parameters for \( x = 0.5 \) are \( \tau_{0D} \approx 1.7 \times 10^{-15} \) s, \( \tau_{0,\alpha} \approx 1.3 \times 10^{-14} \) s, \( B_D = 2700 \) K, \( B_\alpha = 1250 \) K, \( T_{0D} = 75 \) K, and \( T_{0,\alpha} = 98 \) K. For \( x = 1 \) the corresponding parameters were previously reported in Ref. 60.

Several features are important to note from Fig. 8: (i) Although \( \tau_D \) and \( \tau_\alpha \) display a tendency to merge towards low temperatures, they remain separated by more than three decades near \( T_{g,\alpha} \) for \( x = 0.5 \). (ii) For \( x = 1 \) the aging time \( \langle \tau_{\text{age}} \rangle \) is intermediate between \( \tau_\alpha \) and the extrapolated \( \tau_D \) which at 135 K are in close proximity. (iii) For \( x = 0.5 \), however, \( \langle \tau_{\text{age}} \rangle \) is fully compatible with the extrapolation of \( \tau_\alpha \) but not with that of \( \tau_D \), demonstrating that the \( \alpha \)-process governs the physical aging, also in monohydroxy alcohols. Hence, it is fully justified to call the \( \alpha \)-process the structural relaxation. (iv) In the inset one can observe that for \( x = 0.5 \) the aging curve reaches its saturation (i.e., the system becomes fully equilibrated) for a waiting time that is slightly above \( 10^5 \) s, which is still considerably below the extrapolated value for \( \tau_D \) \( (\approx 10^8 \) s) at this temperature. This implies that the conclusion drawn in item (iii) remains valid independent of the approach used for estimating \( \langle \tau_{\text{age}} \rangle \).

E. Solvation dynamics

\( T_1 \rightarrow S_0 \) emission spectra of QX in (2E1H)\(_{0.5}(2E1Br)_{0.5} \) were recorded for several temperatures between 112 and 152 K using a fixed acquisition time of 10 ms. This is significantly shorter than the phosphorescence lifetime of QX that is about 0.3 s. In order to determine the average emission energy \( \langle \nu_e \rangle \) each emitted spectrum was interpolated by a Gaussian function. The temperature dependence thus obtained for \( \langle \nu_e \rangle \) is plotted in Fig. 9.

At temperatures below 130 K the average emission energy, \( \langle \nu_e \rangle_0 \), is virtually temperature invariant. This indicates that the solvent dynamics is frozen in on the time scale of our isochronal experiment. For temperatures above about 130 K, a decrease of \( \langle \nu_e \rangle \) below \( \langle \nu_e \rangle_0 \) can be noticed. This continuous variation of the Stokes shift signals that the time scale of the polarization fluctuation in the local environment of QX decreases towards the value of the experimental time window (10 ms). Previous solvation dynamics investigations demonstrated that, for various chromophore/solvent combinations, this redshift \( (\langle \nu_e \rangle - \langle \nu_e \rangle_0 < 0) \) occurs close to the glass transition temperature of the molecular solvent.\(^{61}\) Indeed, the onset in the decrease of the emission energy \( \langle \nu_e \rangle \) measured for (2E1H)\(_{0.5}(2E1Br)_{0.5} \) (see Fig. 9) is very close to its \( T_{g,\alpha} \) \( (\approx 132 \) K).

In order to quantify the temperature evolution of the solvent dynamics we follow previous studies\(^{61,62}\) and consider the Stokes shift correlation function,

\[
C(t, T) = \frac{\langle \nu_e(t, T) \rangle - \langle \nu_e \rangle_\infty}{\langle \nu_e \rangle_0 - \langle \nu_e \rangle_\infty},
\]

in the form of a Kohlrausch stretched exponential,

\[
C(t, T) = \exp \left( -\frac{t}{\tau(T)\beta(T)} \right).\]

Using this expression the temperature variance of the energy shift can be written as

\[
\langle \nu_e(T) \rangle = \langle \nu_e \rangle_\infty + (\langle \nu_e \rangle_0 - \langle \nu_e \rangle_\infty) \exp \left( -\frac{t_0}{\tau(T)\beta(T)} \right)
\]

with \( t_0 = 10 \) ms denoting the experimental time scale.

The non-equilibrium polarization fluctuations of the mixture solvent are caused by a change in the electronic charge distribution (rather than in the electrical field) of the excited chromophore. Therefore, the solvation experiment probes an electric modulus response (instead of a susceptibility).\(^{32}\) In this sense, it is appropriate to compare the solvation results with the ones obtained via dielectric spectroscopy after converting the permittivity \( \varepsilon^* \) data to the electric modulus \( M^* = 1/\varepsilon^* \). Accordingly, \( \tau \) and \( \beta \) in Eq. (6) have to be replaced by \( \tau_M \) and \( \beta_M \) that are specific for this quantity.

To this end the dielectric data of (2E1H)\(_{0.5}(2E1Br)_{0.5} \) was transformed to the modulus representation and for every temperature a modulus time scale was extracted as \( \tau_M = 1/(2\pi\nu_M) \). Here \( \nu_M \) is the peak frequency in the
imaginary part, $M'(v)$, that corresponds to the $\alpha$-process. The results for $\tau_M(T)$, as shown in the inset of Fig. 9, were parameterized using Eq. (4) and yielded $\tau_0 = 5 \times 10^{-15}$ s, $B = 1200$ K, and $T_0 = 102$ K. Regarding the stretching parameter, the imaginary part of the modulus could be interpolated well by the Laplace transform of a Kohlrausch function and yielded $\beta_M = 0.33$, independent of the temperature in the range in which the solvation dynamics was monitored.

With these parameters at hand, $(\nu_e(T))$ can be calculated according to Eq. (6). In this expression, only one parameter, $(\nu_e)\infty$, is not already fixed by experiment. Using $(\nu_e)\infty = 20650$ cm$^{-1}$, it turns out that the calculation provides a good description of the energy shift probed in our solvation experiments, cf. Fig. 9. It should be emphasized that the modulus response that enters into these calculations corresponds to the structural relaxation.

IV. DISCUSSION

The time scale derived from the aging experiments is in excellent agreement with the structural relaxation times as documented for a sample with $x = 0.5$ in Fig. 8. Nevertheless, this agreement deserves comment because we compare results from dielectric linear-response experiments with those induced by a sizeable temperature step. By their very nature the latter experiments are nonlinear and this property applies also to aging measurements. Several methods have been devised for their description.63-66 For analyzing the present data, we simply quantify an aging time scale, $\tau_{age}$, based upon the stretched exponential decay outlined above. Any model of physical aging will predict that $\tau_{age}$ obtained in such a manner has to be intermediate between the equilibrium (linear) relaxation times at the temperatures before and after the $T$-jump, $\tau_e(T = 129.5$ K) $< \tau_{age} < \tau_T(T = 127$ K). This range is represented by an “error” bar in Fig. 8 and clearly demonstrates that $\tau_e$ rather than $\tau_T$ governs the process of physical aging.

It is also worthwhile to compare the present physical aging data with previous ones that were acquired using dielectric spectroscopy35, 36 or NIR spectroscopy.60 The NIR data representing the equilibration of the hydrogen-bonding distribution exists in the undiluted bulk phase, at low temperatures, specific monitored the equilibration of the hydrogen bond dynamics were performed at lower temperatures,7, 68, 71 and solvation.72 This very broad array of observations suggests that the hydrogen-bonded structures which exist in the undiluted bulk phase, at low temperatures, and at low pressures are what one could call “self stabilized,” a notion that in studies of hydrogen-bonded systems is well known as cooperative effect.73 Now as temperature or pressure are increased, or upon chemical dilution or via surface solvation, the supramolecular structures are destabilized considerably only beyond a certain threshold.

Examples for corresponding effects, reported in the present article, include changes in the concentration dependence of not only $\tau_D$, $\Delta \tau_D$, and $\gamma_D$ but also in $\tau_{\alpha}$, cf. Fig. 3. These observations hint at what was termed “critical concentration” $x_c$, a feature which could also be identified from our NIR measurements on (2E1H)$_{0.5}(2E1Br)_{0.5}$ and (BuOH)($BuBr)_{1-x}$ as shown in Fig. 5. A critical concentration, $x_c \approx 0.5$, below which the Debye-process turns nonexponential, was reported for 2E1H diluted in bromobutane as well.26

It is interesting to compare the concentration dependence of the decoupling ratio for various alcohol-solvent
mixtures. For (BuOH)$_x$(BuBr)$_{1-x}$ it was found that “the decoupling is smallest for the pure alcohol and increases up to almost a factor of $10^4$ in the dilute limit.”

V. SUMMARY

In the present article, we applied a multiphase of experimental techniques, including dielectric, near-infrared, shear mechanical, and solvation spectroscopy in order to study various relaxation phenomena in (2E1H)$_x$(2E1Br)$_{1-x}$. When supercooled, these mixtures of branched molecules turned out to be very resistant against crystallization. Therefore, the Debye-like and the structural relaxation could be traced over the entire concentration range using dielectric spectroscopy. We found smooth compositional variations in time scale, dielectric strength, and loss peak broadening as well as an indication of a critical concentration, $x_c \approx 0.5–0.6$.

This $x_c$ was confirmed by NIR measurements for (2E1H)$_x$(2E1Br)$_{1-x}$ and, in harmony with previous dielectric measurements, also for (BuOH)$_x$(BuBr)$_{1-x}$. Furthermore, near $x_c$ the Debye-like peak and the structural relaxation of (2E1H)$_x$(2E1Br)$_{1-x}$ display an enormous spectral separation of about four decades which facilitates the selective investigation of the various relaxation processes considerably. This selectivity was exploited by studying samples with $x \approx 0.5$ by means of various techniques: The shear mechanical measurements indicate that the Debye process shows no significant viscoelastic signatures and we find clear indications that the rheological response of this hydrogen-bonded system is similar to the one observed for simple liquids. The present solvation experiment, carried out close to the glass transition temperature, was found to monitor the polarization fluctuations corresponding to the $\alpha$-process. Finally, using dielectrically detected physical aging experiments we were able to demonstrate that re-equilibration subsequent to a temperature jump proceeds on the time scale of the structural relaxation and not on that of the Debye-like process.

All in all, the measurements carried out in the present work show that the Debye-like process can be studied profitably not only in neat monohydroxy alcohols but also using suitable diluents in which this process retains most of its characteristic features such as the absence of a detectable rheological signature and the noninvolvement in physical aging. Therefore, the present data conform to approaches recently advanced in order to rationalize the particular features of the Debye process. Moreover, it is not only interesting to study moderately diluted monohydroxy alcohols, as even in the highly diluted limit we find indications for Debye-like features in completely miscible systems such as $(2E1H)_x(2E1Br)_{1-x}$ or $(BuOH)_x(BuBr)_{1-x}$.

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12Substantial progress was achieved some years ago, see Ref. 11.


26$T_g$ for 2E1Br was estimated from the results of the present work as the temperature at which the dielectric relaxation time is $100 \text{ s}$.


See, e.g., Fig. 10-2 in J. D. Ferry, Viscoelastic Properties of Polymers (Wiley, New York, 1980), Chap. 10, Sec. A1.


