Communication: Slow supramolecular mode in amine and thiol derivatives of 2-ethyl-1-hexanol revealed by combined dielectric and shear-mechanical studies

K. Adrjanowicz,[1,2,a)] B. Jakobsen,[1] T. Hecksher,[1] K. Kaminski,[3] M. Dulski,[3] M. Paluch,[3] and K. Niss[1]

[1]*Department of Sciences, DNRF Centre "Glass and Time," IMFUFA, Roskilde University, P.O. Box 260, DK-4000 Roskilde, Denmark*
[2]*NanoBioMedical Centre, Adam Mickiewicz University, ul. Umultowska 85, 61-614 Poznan, Poland*
[3]*Institute of Physics, University of Silesia, ul. Uniwersytecka 4, 40-007 Katowice, Poland*

In this paper, we present results of dielectric and shear-mechanical studies for amine (2-ethyl-1-hexylamine) and thiol (2-ethyl-1-hexanethiol) derivatives of the monohydroxy alcohol, 2-ethyl-1-hexanol. The amine and thiol can form hydrogen bonds weaker in strength than those of the alcohol. The combination of dielectric and shear-mechanical data enables us to reveal the presence of a relaxation mode slower than the α-relaxation. This mode is analogous to the Debye mode seen in monohydroxy alcohols and demonstrates that supramolecular structures are present for systems with lower hydrogen bonding strength. We report some key features accompanying the decrease in the strength of the hydrogen bonding interactions on the relaxation dynamics close to the glass-transition. This includes changes (i) in the amplitude of the Debye and α-relaxations and (ii) the separation between primary and secondary modes. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4935510]

Among different types of the intermolecular interactions, hydrogen bonds play an exceptional role in biology and practical applications. They are responsible for unique chemical and physical properties of polar substances such as water, alcohols, polyols, sugars, or their aqueous solutions.[1–3] The behaviour of hydrogen bonding liquids is often more complex and distinct from liquids with non-hydrogen bonding interactions. Their structure and dynamics are affected by the formation/reorganization of the extended hydrogen bonding networks of different sizes and geometries. In the highly viscous regime, this can bring about a breakdown of the otherwise general dynamic scaling rules (i.e., isochronal superposition or density scaling) and a variety of anomalous behaviour with decreasing temperature and increasing pressure.[4–10]

Monohydroxy alcohols are a special class of hydrogen bonding systems. The dynamics of supercooled monohydroxy alcohols has a very distinct feature which has received a lot of attention, namely, the so-called Debye relaxation.[11–13] This is a slow mode which is often very intense in the dielectric signal sometimes completely covering the signal of the α-relaxation.[12,14–17]

Experimental observations have revealed that this mode has an exponential character, hence the name Debye relaxation. The prominent dielectric amplitude of the Debye relaxation in monohydroxy alcohols cannot be explained exclusively from the molecular dipole moment, but it is due to hydrogen bonding associations (chains, rings, or other units) that induce changes in the orientational correlations of dipoles.[18–21] It was earlier believed that the Debye relaxation

was only seen in the dielectric signal but with improved experiments and data analysis it has over the last 10-15 years been detected also by other experimental techniques, such as mechanical spectroscopy, dynamic light scattering, and nuclear magnetic resonance.[22–26]

The origin of the Debye relaxation in monohydroxy alcohols has been hotly discussed and intensively upgraded throughout the last century.[27] Today the consensus is that the process is due to slow dynamics in supramolecular hydrogen bonded structures. However, there is still controversy about the mechanisms for the relaxation. The prevailing picture today is that the Debye relaxation can be viewed as a sequential rearrangement of the chain structures, analogous to what happens for polymeric aggregates,[28] either by self-restructuring transient chain-like dynamics (end-to-end vector migration)[22] or the fluctuation of the net Kirkwood factor aided by recombination of chain-like structure.[29]

The size and the architecture of the intermolecular hydrogen bonding network depend on the molecular structure. It is believed that terminal hydroxyl group facilitates long chain-like structures, whereas intermediate attachment of the hydroxyl group to the alkyl chain creates steric hindrance and favors ring-like morphology.[29–32] In the dielectric spectra, ring structures are manifested by a decrease of the Debye relaxation's strength. Moreover, remarkable changes in the chain-ring equilibrium altering the general behaviour of Debye process (its time scale or separation from the structural dynamics) can also be tuned by high external field, chemical modification of the alkyl tail, or mixing with various polar, non-polar, or ionic components.[32–39] It is also well-known that removal of hydrogen bonds by chemical modification or applying pressure eliminates the Debye mode and restores

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a)Electronic address: kadrjano@us.edu.pl
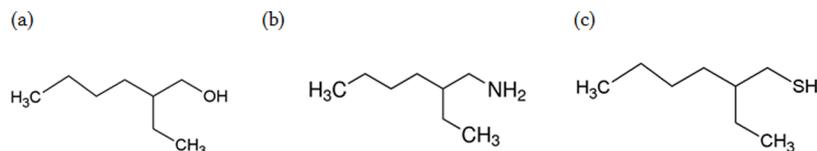
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FIG. 1. Chemical structures of (a) 2-ethyl-1-hexanol, (b) 2-ethyl-1-hexylamine, (c) 2-ethyl-1-hexanethiol.

the characteristic features in the relaxation dynamics of non-hydrogen bonding liquids. (e.g., Refs. 40 and 41). For a recent review on the Debye mode, see Böhmer *et al.*[27]

The slow supramolecular mode has been mainly documented for monoalcohols but very little studied for other types of hydrogen bonding liquids.[42,43] However, supramolecular hydrogen bonding structures can potentially be created by halogens, amines, and perhaps thiols as well. Their effective strength is expected to decrease in the same order as the difference in electronegativity of the constituting atoms.[3]

The aim of this work is to systematically study the effect of varying the strength of the hydrogen bonding interactions on the viscous liquid dynamics. We have performed detailed dielectric and shear-mechanical studies for amine and thiol derivatives of 2-ethyl-1-hexanol. Combining the two experimental techniques makes it possible to provide unique information about the relaxation dynamics of the investigated samples.

As illustrated in Fig. 1, the studied samples have the same alkyl backbone as 2-ethyl-1-hexanol but differ in the type of donor-acceptor combination. This relatively small substitution has a big impact on the strength of the intermolecular interactions, and potentially on the overall hydrogen bonding architecture, and the dynamics of the investigated liquids.

The monohydroxy alcohol 2-ethyl-1-hexanol represents a strongly hydrogen bonding system (calculated bond length 1.7 Å), 2-ethyl-1-hexylamine creates moderately strong

$N–H \cdots N$ bonding (bond length 2.4 Å), while the bonds in 2-ethyl-1-hexanethiol $S–H \cdots S$ are only barely stronger than van der Waals interactions (bond length > 3 Å).[44] In fact, 2-ethyl-1-hexylamine was earlier reported to be non-hydrogen bonding and without Debye relaxation, as concluded from the dielectric studies of the binary mixtures (2-ethyl-1-hexylamine with 2-ethyl-1-hexanol).[33,35]

We have measured the complex frequency-dependent dielectric permittivity $(\epsilon^*(\nu) = \epsilon'(\nu) + i\epsilon''(\nu))$ and shear modulus $(G^*(\nu) = G'(\nu) + iG''(\nu))$ over a broad range of temperature and characteristic relaxation times. Viscoelastic properties were measured by using the piezoelectric shear modulus gauge (PSG) method.[45] The experimental details can be found in the supplementary material.[46]

In Figs. 2 and 3, we present dielectric and shear mechanical data for the amine and thiol derivatives of 2-ethyl-1-hexanol. Both data sets show an α-relaxation with the characteristic slowing down upon cooling. A clearly resolved β-relaxation is seen in both dielectric and mechanical spectra for 2-ethyl-1-hexylamine while a β-relaxation is seen by both techniques as a pronounced shoulder in 2-ethyl-1-hexanethiol. A more detailed comparison of the dielectric and shear-mechanical α- and β-relaxations is given in the supplementary material.[46] In the following paragraphs, we will analyze the data in more detail, focusing on subtle signatures of a slow supramolecular relaxation mode.

The first hint of dynamics slower than the α-relaxation is seen as a shoulder on the low-frequency side of the dielectric
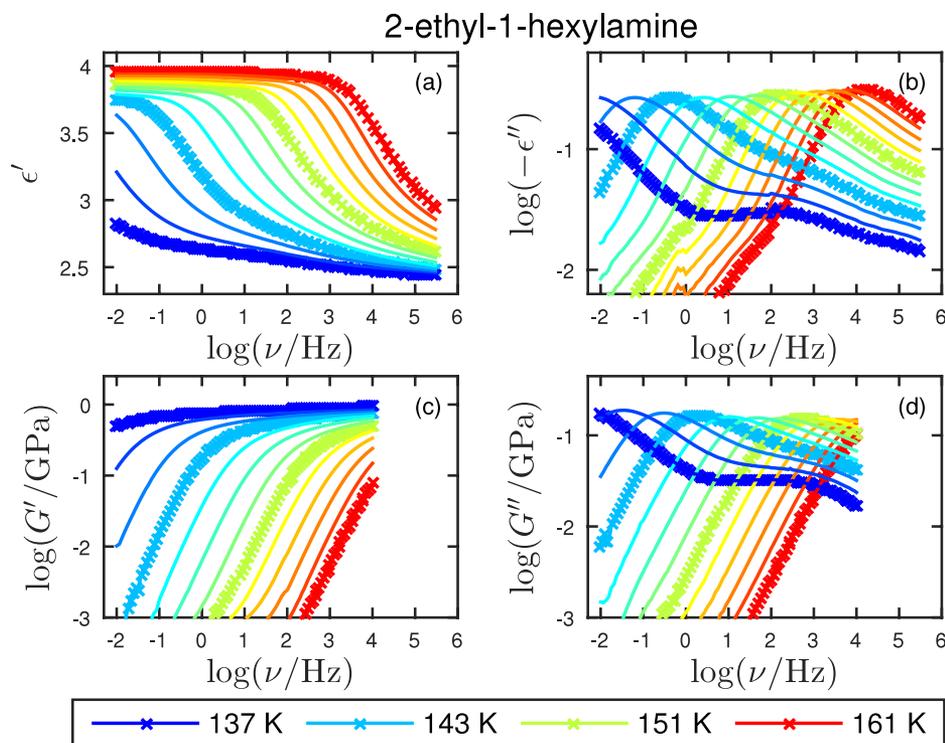

FIG. 2. Frequency dependent dielectric and shear mechanical data for 2-ethyl-1-hexylamine: (a) real ε' and (b) imaginary ε'' parts of complex dielectric permittivity, (c) real G' and (d) imaginary G'' parts of complex shear modulus measured upon cooling from 161 to 137 K with steps of 2 K.
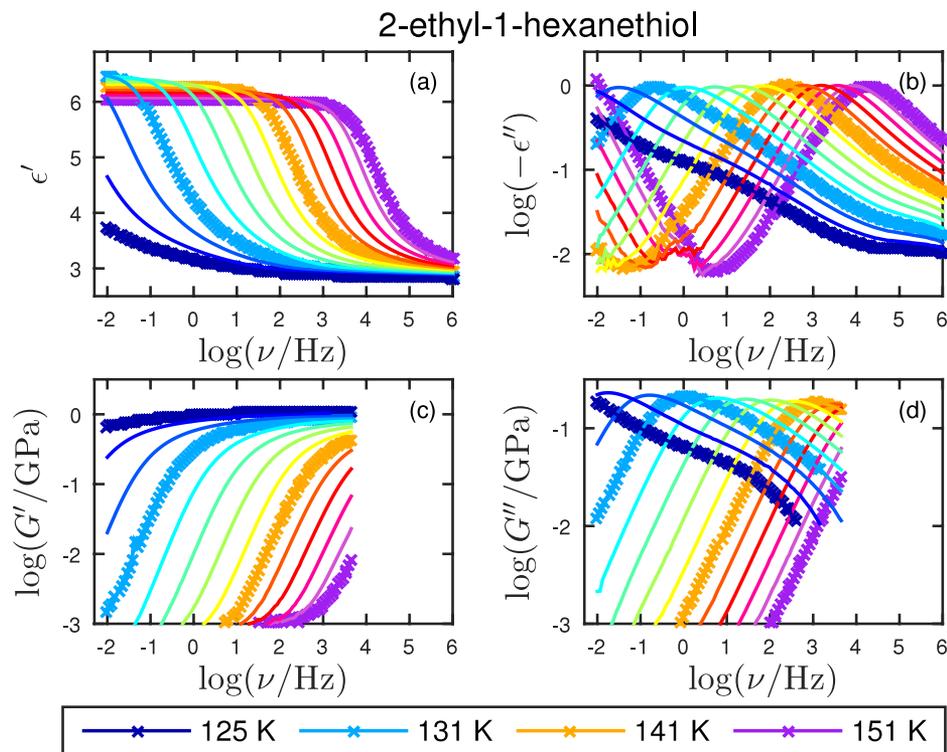
FIG. 3. Frequency dependent dielectric and shear mechanical data for 2-ethyl-1-hexanethiol: (a) real ε' and (b) imaginary ε'' parts of complex dielectric permittivity, (c) the real G' and (d) imaginary G'' parts of complex shear modulus measured upon cooling from 151 to 125 K with steps of 2 K.

spectra of the amine (Fig. 2(b)). However, a much more striking observation is the anomalous temperature dependence of the strength of the α-relaxation. Typically, on lowering the temperature, the dielectric strength $\Delta\epsilon$ of the α-relaxation increases because of the thermal energy and density effects ($\Delta\epsilon \propto \mu^2 \rho / k_B T$). In contrast to this, the dielectric strength of the α-relaxation decreases with decreasing temperature for 2-ethyl-1-hexylamine (Fig. 2(a)). This anomalous behaviour of $\Delta\epsilon$ is a clear indication of changes in the orientational correlations of the dipoles. The dielectric signature of the α-relaxation is smaller than expected from the dipole moment in monohydroxy alcohols with a pronounced dielectric Debye relaxation, indicating that the existence of a Debye relaxation leads to a smaller amplitude of the α-relaxation. This suggests that the decreasing amplitude of the α-relaxation in 2-ethyl-1-hexylamine upon cooling is due to an increased influence of a Debye process. For the very weakly hydrogen bonding 2-ethyl-1-hexanethiol, there is no visible low frequency feature, but it is difficult to conclude anything because the signal is dominated by dc-conductivity (Fig. 3(b)). In this case, the α-relaxation has the standard temperature dependence, as well as an overall larger amplitude of the α-relaxation.

In Figs. 4(a) and 4(b), the normalized dielectric and shear-mechanical loss spectra for amine and thiol are presented. Spectra recorded at slightly different temperatures were compared in order to match approximately the same α-relaxation time (for clarity in the supplementary material[46] we also show raw data, see Fig. S2). Presenting experimental results in this way highlights subtle signatures of the supramolecular mode in both response functions. In the dielectric signal of the amine, this appears as barely perceptible slow relaxation as mentioned above. In the shear-mechanical spectra, it is seen as the deviation from the pure viscous behavior expected in simple liquids at low frequencies.

The storage and loss moduli for a simple viscoelastic material as, e.g., described by the classical Maxwell model obey the unique power law $G'(\nu) \propto \nu^2$ and $G''(\nu) \propto \nu^1$ in the low frequency regime.[49] A crossover from an intermediate to the terminal power law reported for short-chain polymers, polymeric liquids, or monoalcohols ($\nu^{0.7}$) is an evidence of an additional slow supramolecular organization/dynamics.[23–25,42,50]

In the present study, due to resolution limits of the PSG technique, we were not able to clearly observe the change of the frequency dependence of G' and G'' at modulus values lower than 1 MPa. However, the power law of the low-frequency part of the mechanical loss shear spectra for amine ($\nu^{0.85}$) and thiol ($\nu^{0.93}$) shows that they display an intermediate behavior between the one reported for non-associating and associating liquids. A similar observation comes from the real part of the shear modulus, as presented in Fig. 4(c). For comparison, we have included the shear-mechanical data from Refs. 23 and 47 for 2-ethyl-1-hexanol and polyphenyl ether (5PPE) which represent two limiting cases, i.e., a strongly hydrogen bonding liquid and a van der Waals bonded simple Roskilde-type[51,52] liquid. In Fig. 4(d), we present the shear viscosity data (calculated as $\eta'(\nu) = G''(\nu)/\nu$) normalized by the respective steady-state viscosity values determined from the Maxwell expression ($\eta_0 = G_\infty \tau_M \simeq G_\infty / (2\pi\nu_{max})$). The ν_{max} value is taken to be the position of the shear mechanical loss maximum. The temperature dependence of the infinite frequency shear modulus (G_∞) was determined for each liquid separately by fitting the mechanical data to the alpha-beta model.[53,54] Normalized shear viscosity data for 5PPE were included to demonstrate viscoelastic behaviour expected for liquids without supramolecular organization. At the other extreme, we show 2-ethyl-1-hexanol with the relative viscosity increase by a factor of almost 10.[23] As can be seen,
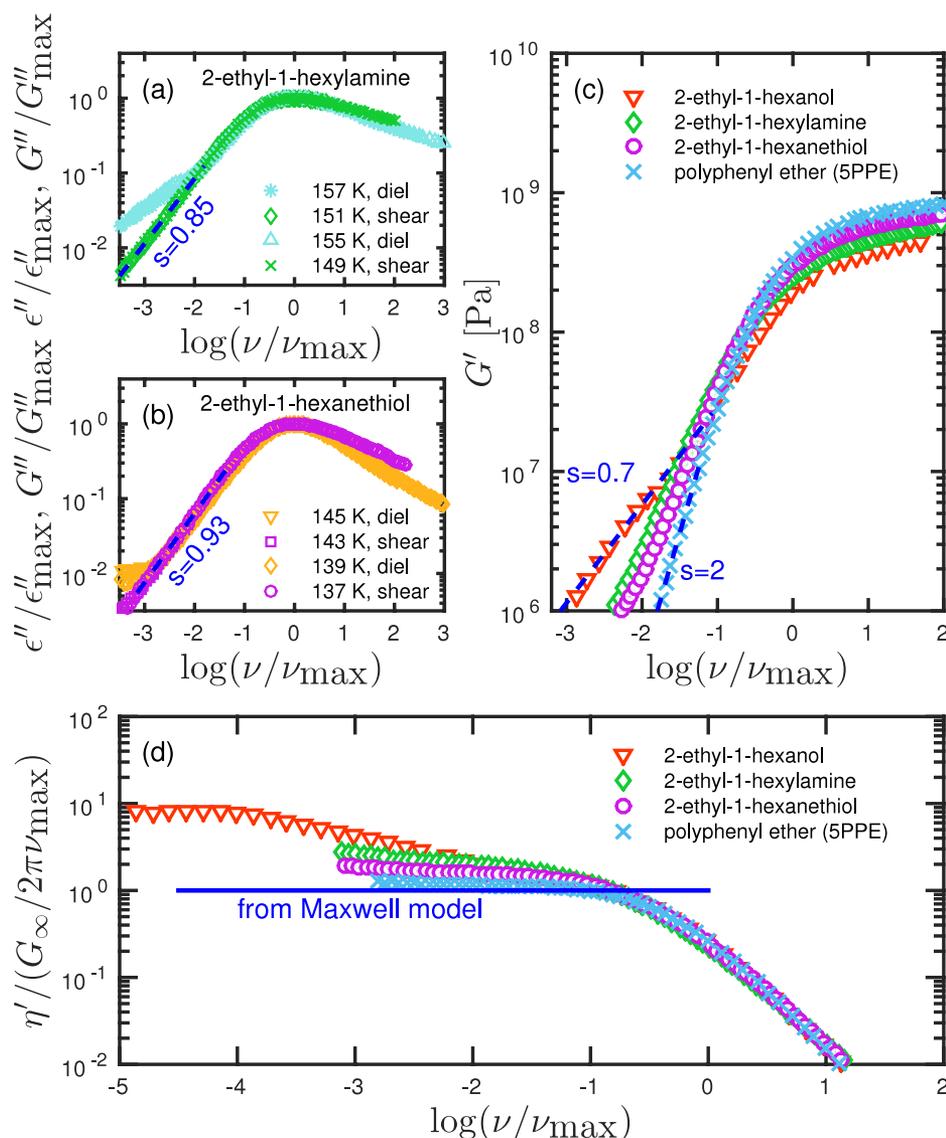
FIG. 4. Comparison of the amine and thiol analogues of isooctanol. Dielectric and shear loss spectra for (a) 2-ethyl-1-hexylamine and (b) 2-ethyl-1-hexanethiol were taken at different temperatures but for approximately the same structural relaxation time. Data were normalized by values corresponding to their maximum peaks positions. (c) Real part of the shear modulus G' plotted versus scaled frequency and (d) dynamic shear viscosity normalized by the viscosity predicted from the Maxwell relation for 2-ethyl-1-hexanol, 2-ethyl-1hexylamine (T = 149 K), 2-ethyl-1-hexanethiol (T = 137 K), and van der Waals liquid 5PPE (T = 260 K). At selected temperatures, the position of the shear peak maximum (ν_{max}) is approximately the same for all materials. Dashed lines indicate slopes. Shear-mechanical data for 5PPE are from Ref. 47 and can be found in Glass and Time data repository.[48] The frequency dependent shear-modulus data for 2-ethyl-1-hexanol are taken from Ref. 23.

amine and thiol show a slight enhancement of the viscosity at the low-frequency part. This deviation from the simple viscous flow mechanism suggests the existence of additional dynamics on a much slower time scale. The increase is not as spectacular as for the monoalcohol analogue (by a factor of 2 and 4, respectively) but still clear and systematic.

The qualitative differences in the relaxation behavior of the studied samples are illustrated in Fig. 5. Shear-mechanical (Fig. 5(a)) and dielectric (Fig. 5(b)) data for alcohol, amine, and thiol were taken from different temperatures to match the same characteristic time scale of the α-process. Substituting the –OH group by an –NH$_2$ or an –SH group systematically reduces the separation between α- and β-relaxations clearly seen in the shear mechanical data. This suggests a connection between the hydrogen bonding structure and the β-relaxation. In contrast, a complete lack of correlation between α- and β-relaxations for a series of octanol isomers was reported recently in the literature.[37] In the dielectric spectra, there is a remarkable enhancement in Debye relaxation strength accompanied by a decrease of the α-relaxation signal when going from weaker to stronger hydrogen bonds. Moreover, the

amplitude of the α-relaxation goes in the opposite direction of the size of the dipole moment, indicating a difference in the molecular correlations of the three samples.

Interestingly, there is no significant change in the time scale separation between Debye and α-relaxations. Typically, diluting or modifying the position of the hydroxyl group in the alkyl chain backbone produces differences in the separation between the alpha- and the Debye processes.[25,35]

The combined dielectric and shear mechanical results presented in the preceding paragraphs clearly show that there is a slow relaxation (Debye) mode in the amine. For the thiol, the signatures are subtle; however, it seems suggestive that there is also a slow process in the thiol even if it is weak in strength. Changes in the relaxation dynamics of the glass-forming liquid due to removing hydrogen bonds, diluting, or playing with the molecular structure are nothing new. However, our results highlight the exact effect of manipulating purely with the character of the hydrogen-bonding interactions in a neat system without changing the molecular structure.

The mechanical signal of the Debye process seen in Figures 4(c) and 4(b) decreases rather smoothly following
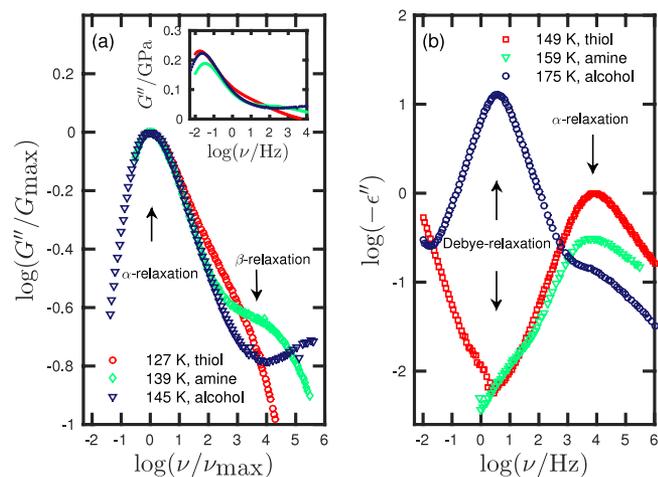
FIG. 5. Comparison of the shear-mechanical and dielectric loss spectra with approximately the same relaxation time for 2-ethyl-1-hexanol, 2-ethyl-1-hexylamine, and 2-ethyl-1-hexanethiol. (a) Normalized shear-mechanical loss spectra taken from the region close to T_g. Inset shows the raw data. (b) Dielectric loss spectra taken from higher temperatures where the Debye and α-processes are detectable. Shear and dielectric data for 2-ethyl-1-hexanol are from Ref. 14 and were taken from the Glass and Time data repository.[48]

the decreasing strength of the hydrogen bond. We interpret this as a sign of decreasing strength of the supramolecular structures involved in the Debye relaxation. Meanwhile, the time scale separation between the α-relaxation and the Debye relaxation does not change. This is at odds with the common observation where decrease in the intensity of the dielectric Debye relaxation is followed by a decreased separation between the alpha and the Debye relaxation (e.g., Ref. 25). The invariant time scale separation could suggest that the size of the supramolecular structures is comparable in the three systems, but this is very speculative. On the other hand, the dielectric Debye signal decreases abruptly when going from the alcohol to the amine. By taking into account the spatial geometry of the $-NH_2$ group (two protons available for the hydrogen bonding), we hypothesize that the amine molecules will mostly prefer compact circular architectures, or that their chain-like associates tend to fold. This might significantly reduce, or even cancel the overall dipolar contribution coming from the supramolecular structures. To substantiate this hypothesis, we have performed theoretical calculations based on the DFT method of the effective dipole moment of different chain configurations of 2-ethyl-1-hexanol and 2-ethyl-1-hexylamine. More details are given in the supplementary material.[46] The calculations show that for a similar supramolecular structure the two substances have dipole moments of similar order of magnitude. From this, we conclude that the large difference in strength of the Debye relaxation must be due to a different morphology of the involved structures.

To summarize, by combining dielectric and mechanical results with the recently established method of analyzing mechanical signal of the hydrogen bonding chain-like associates in monoalcohols, we were able to provide unique evidence of the slow supramolecular mode for other type of low-molecular-weight hydrogen bonding liquids. Replacing the $-OH$ group by $-NH_2$ or $-SH$ group changes the strength

and morphology but maybe not the size of the supramolecular structures. The present study provides a new piece for the puzzle on the nature of the slow supramolecular modes. It also shows the interplay between inter-molecular interactions and relaxation dynamics of glass-forming liquids.

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[44] The geometries of 2-ethylohexanol, 2-ethylhexylamine, and 2-ethylhexanethiol molecules, as well as the 5-molecular systems in the ring and the chain configurations, were optimized using Becke's hybrid exchange and correlated three-parameter with the Lee-Yang-Parr correlation functional (B3LYP) at standard Gaussian basis sets 6-31G(d,p). These calculations were carried out in the gas phase using density functional theory (DFT) approach and the Gaussian09 software package.

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[54] We obtain the following values: $G_\infty = 0.7$ GPa for 2-ethyl-1-hexylamine at 160 K, $G_\infty = 0.79$ GPa for 2-ethyl-1-hexanethiol at 137 K, $G_\infty = 0.97$ GPa for 5PPE at 260 K. Dielectric and shear mechanical data for amine and thiol derivatives of 2-ethyl-1-hexanol can be found in "Glass and Time" data repository.