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ORIGINAL CONTRIBUTION

Oscillatory shear and high-pressure dielectric study of 5-methyl-3-heptanol

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Abstract The monohydroxy alcohol 5-methyl-3-heptanol is studied using rheology at ambient pressure and using dielectric spectroscopy at elevated pressures up to 1.03 GPa. Both experimental techniques reveal that the relaxational behavior of this liquid is intermediate between those that show a large Debye process, such as 2-ethyl-1-hexanol, or a small Debye-like feature, such as 4-methyl-3-heptanol, with which comparisons are made. Various phenomenological approaches assigning a time scale for the rheological signature of supramolecular dynamics in monohydroxy alcohols are discussed.

Keywords Rheology · Dielectric spectroscopy · Hydrogen bonds · Monohydroxy alcohols

Introduction

As powerful experimental techniques, broad band dielectric and shear mechanical spectroscopies are well known to provide important insights into the dynamics of complex liquids [1–3]. As interesting examples of such liquids, the Debye-like relaxation not only in monohydroxy alcohols [4] but also in other classes of supramolecular liquids [5–8] is currently receiving a great deal of attention. The insights obtained by studying these substances can also enhance the understanding of the properties of other (hydrogen-bonded) systems including water and bio-macromolecules. While the Debye-like relaxation was long believed to be experimentally accessible only via dielectric [9, 10] and related spectroscopies [11–13], recent investigations demonstrate that also nuclear magnetic resonance [14], oscillatory shear [15], quasi-elastic neutron scattering [16], and even structural studies [17] may be sensitive to this feature.

It is known since long that in these complex liquids, the strength of the Debye-like dielectric relaxation depends sensitively on the architecture of the constituting monohydroxy alcohol molecules, notably on the position of the hydroxyl group within them, with the isomeric heptanols and octanols being particularly thoroughly studied in this context [18–23]. Building upon seminal earlier work [18, 19], this sensitivity to the molecular structure was recently reemphasized in a high-field dielectric study of the series of *j*-methyl-3-heptanol (*j*M3H) liquids with $j=3$, 4, 5, and 6 [24, 25]. In these liquids, only the position of the methyl group varies: it may sterically shield the OH group more—like in 3M3H and 4M3H for which a Debye-like dielectric feature is largely absent—or less—like in 6M3H. The latter substance displays an intense Debye peak, comparable to that of 2-ethyl-1-hexanol (2E1H), a monohydroxy alcohol that has recently attracted considerable interest [14, 15, 26–32].

It was suggested to classify these materials into group I or group II liquids depending on whether they possess a strong or a weak Debye-like process, respectively [18, 33]. In other words, the question is whether the orientational correlation within the monohydroxy alcohol liquids as measured by the Kirkwood factor, $g_K=1+z\langle\cos\theta\rangle$, is small or large [34]. Here,

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This is a special issue in honor of Prof. Dr. Friedrich Kremer on the occasion of his 65th birthday.

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$\langle \cos\theta \rangle$ corresponds to the mean angle enclosed by dipole moment vectors averaged over a coordination shell containing z molecules. Typically, one has $g_K>1$ if mutually parallel dipolar alignment prevails, while $1>g_K>0$ is often considered to arise from antiferroelectric or ring-like dipole correlations. Thus, $g_K=1$ may either correspond to uncorrelated dipolar arrangements or occur if parallel and antiparallel relative orientations are suitable mixed.

In molecular terms, group I monohydroxy alcohols are thought to feature chain-like supramolecular association which, like in type A polymers [35–38], lead to sizeable (dielectric) normal modes, while for group II monohydroxy alcohols, ring-like multimeric structures are held responsible for a nearly complete cancelation of supramolecular contributions to the dielectric response.

The 5M3H liquid, which is in the focus of the present work, presents a particularly interesting *intermediate* case as is also evident from the dielectric loss spectra shown in Fig. 1. It is well documented, albeit not evident from Fig. 1, that the Kirkwood factor of 5M3H is very small ($g_K \approx 0.6$) near ambient temperature [18] and that it reaches values close to $g_K \approx 1.6$ upon approaching its glass transition temperature, $T_g=162$ K [24, 25]. Near 190 K and at ambient pressures, the Kirkwood factor $g_K=1$ is crossed rather steeply. This was interpreted in terms of a conversion from ring-like to chain-like supramolecular structure upon cooling [18], but analogous effects can also be induced by application of large external electrical fields [24]. In the present article, we reexamine the $g_K=1$ crossing of 5M3H using high-pressure dielectric experiments, extending Johari and Dannhauser investigation [39] to higher pressures by a factor of more than 2 as well as to somewhat lower temperatures. These extensions are necessary to explore the intermediate character of 5M3H more thoroughly.

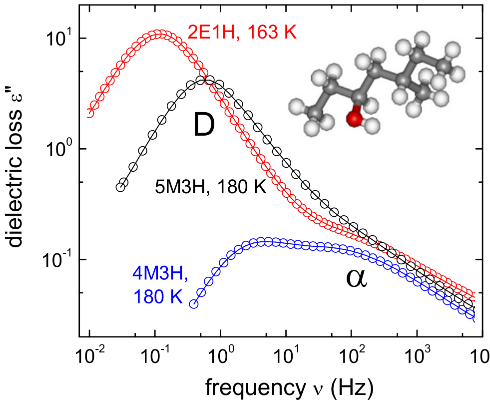

Fig. 1 Dielectric loss spectra of the octanols 4M3H, 5M3H, and 2E1H. The temperatures are chosen such that the dielectric α-relaxation frequency is close to 100 Hz. The strengths of the dielectric Debye process (D) of the various liquids differ significantly, but not their α-relaxation intensity. A sketch of the 5M3H molecule is shown as *inset*

Variously pronounced supramolecular features were recently reported from rheological measurements on different monohydroxy alcohols [15]: While for 2E1H a shear mechanical spectrum similar to that of covalently bonded oligomers (of, e.g., polystyrene [40, 41]) was obtained, the supramolecular rheological signature of 4M3H was rather faint. Hence, it is most interesting to explore whether or not an intermediate mechanical behavior is found using the shear response of 5M3H.

Experimental details

5M3H (purity ≥99 %) was purchased from Sigma-Aldrich and used as received. High-pressure dielectric experiments up to 1.03 GPa were carried out in the frequency range from 10^{-1} to 10^6 Hz using the setup described previously [42]. Measurements of the complex shear mechanical modulus, $G^*(\nu)=G'(\nu)+iG''(\nu)$, were conducted using an ARES G2 rheometer from TA Instruments, covering a frequency range from 10^{-1} to 100 Hz, and a piezoelectric shear modulus gauge technique, covering a frequency range from 10^{-3} to 10^4 Hz, also earlier described [15, 43].

Rheological experiments: results and analyses

In Fig. 2a, we present the in-phase or storage component of the mechanical shear modulus, $G'(\nu)$, of 5M3H. One recognizes that as a function of temperature and frequency, the magnitude of $G'(\nu)$ changes by several orders of magnitude. In particular, the slope of the curves varies, and near temperatures of 170 K, $G'(\nu)$ turns flat. At the lowest T, this indicates the high-frequency shear modulus, G_∞, which was used to normalize the data in Fig. 2a, b. Assuming that G_∞ and the shape of the overall shear mechanical spectrum is essentially independent of temperature in the 20 K interval covered by the present experiment, one can collapse all the data onto a master curve. The corresponding procedure is illustrated in Fig. 2b where the curves from Fig. 2a were shifted horizontally along the frequency scale in order to achieve best overlap, well known as frequency temperature superposition (FTS). Before turning to a discussion of the shift factors, let us emphasize that Fig. 2b demonstrates nicely that the obtained master curve for 5M3H is indeed intermediate between those previously published for 4M3H (black open triangles) and for 2E1H (black open circles dashed line) [15]. This result shows that the intermediate behavior seen in dielectric spectroscopy, cf. Fig. 1, is also borne out rheologically, further vindicating the assertion [15] that the strength of the dielectric Debye process is reflected in the intensity of its normal-mode-like mechanical signature as well. It is worthwhile to emphasize that this observation does not only largely confirm the

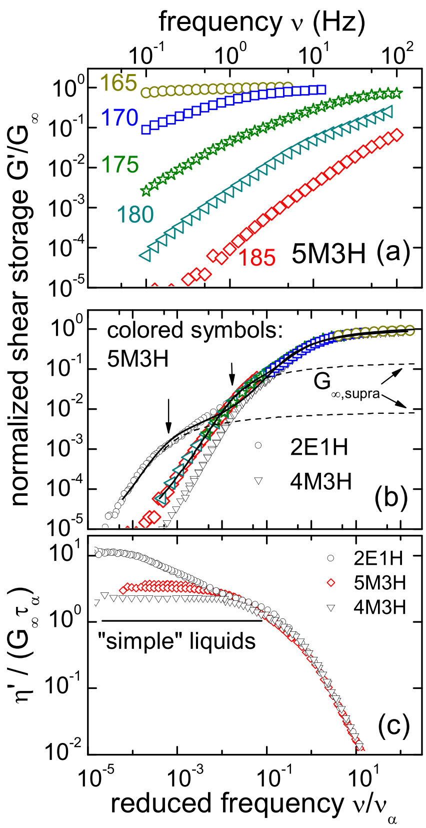

Fig. 2 **a** Normalized mechanical storage modulus, $G'(\nu)/G_\infty$ of 5M3H. The *numbers* refer to temperatures in Kelvin. **b** Master curve obtained by shifting the data shown in frame (**a**) only along the frequency axis. The mechanical data of 4M3H and 2E1H are taken from ref. 15. The *larger* and *smaller arrows* indicate the estimated terminal relaxation modes for 2E1H and 5M3H, respectively. The *solid lines* are interpolations of the 2E1H and 5M3H data using Eq. (1). The *dashed lines* highlight the spectral contribution of the supramolecular relaxation which for large ν saturates at $G_{\infty,\mathrm{supra}}$. **c** Dynamic shear viscosity $\eta'=G''/(2\pi\nu)$ normalized by the expectation from the Maxwell relation. One recognizes that also in this representation, 5M3H displays an intermediate behavior. Furthermore, the results for the alcohols are compared to corresponding data (schematically represented as *solid line*) obtained for small-molecule glass formers devoid of a Debye process. For details and references to the original "simple" liquids data, see ref. 45-46

overlooked previous indications [44], but it supersedes previous beliefs that signatures of the Debye process are invisible to mechanical spectroscopy.

The shift factors obtained from the scaling procedure illustrated in Fig. 2b can be exploited to evaluate the temperature dependence of the mechanical relaxation times. However, this holds only if frequency temperature superposition is applicable. A priori, it is not clear, however, whether this condition is fulfilled because we emphasized above that the supramolecular association in 5M3H is subject to a relatively strongly temperature dependent ring–chain equilibrium. In Fig. 3, we collect the shift factors τ_{rheo} and compare them with the absolute time constants τ_{PSG} from measurements using the piezoelectric shear modulus gauge technique [43]. Excellent agreement of the time scales determined from both techniques is obtained. This demonstrates that the ring–chain equilibration does not affect the scaling procedure significantly. In hindsight, this can be rationalized by noting that the mechanical data were all recorded at temperatures much smaller than that corresponding to the $g_K=1$ crossing at which the changes in the supramolecular structure are expected to be most pronounced.

In Fig. 2c, the shear data for the three monohydroxy alcohols, given in a viscosity representation, are compared with results for substances devoid of a (dielectric and/or mechanical) Debye process. These substances are here designated as "simple liquids," see ref.[45, 46] for details. For these liquids, the Maxwell relation connects the low-frequency viscosity, η_0, associated with the macroscopic flow with the relaxation time, $\tau_{\mathrm{Maxwell},1}$, and the high-frequency shear modulus, G_∞, according to $\eta_0=G_\infty\tau_{\mathrm{Maxwell},1}$ [47]. Fig. 3 demonstrates that this relation, when applied to monohydroxy alcohols, provides time scales $\tau_{\mathrm{Maxwell},1}$ that are slightly larger than $\tau_{\max}$ as obtained from the peak maximum in the shear loss, $G''(\nu)$. However, as is most obvious for the 2E1H data in Fig. 2c, the main contribution to the static (or low shear rate) viscosity, $\eta(\nu\rightarrow 0)$, is provided by the supramolecular relaxation modes.

Thus, following considerations known from polymer science, one may estimate a mechanical relaxation time, $\tau_{\mathrm{Maxwell},2}$, if one replaces G_∞ in the Maxwell relation by the much smaller shear modulus $G_{\infty,\mathrm{supra}}$ associated with the supramolecular hydrogen-bonded aggregates, cf. Fig. 2b [48][1]. $G_{\infty,\mathrm{supra}}$ was determined by parameterizing the G' data using a sum of two Cole–Davidson functions [49, 50]

$$G'(\nu)=\mathrm{Re}\left\{G_{\infty,\mathrm{supra}}\left[1-\frac{1}{\left(1+2\pi i\nu\tau_{\mathrm{supra}}\right)^{\gamma_{\mathrm{supra}}}}\right]+G_{\infty,\alpha}\left[1-\frac{1}{\left(1+2\pi i\nu\tau_{\mathrm{rheo},\alpha}\right)^{\gamma_\alpha}}\right]\right\}, \tag{1}$$

which describes the data quite well, see Fig. 2b. In Eq. (1), the two indices correspond to the supramolecular and the structural process, respectively, and the parameters $\gamma_{\mathrm{supra}}\approx\gamma_\alpha=0.25\pm0.05$ are measures for the width of the distribution of relaxation times underlying the different processes. The results for $\tau_{\mathrm{Maxwell},1}=\eta_0/G_\infty$ and for $\tau_{\mathrm{Maxwell},2}=\eta_0/G_{\infty,\mathrm{supra}}$ are included in Fig. 3 and will be discussed further below.

Dielectric high-pressure experiments: results and analyses

In Fig. 4, we present dielectric loss spectra obtained at 265, 223, and 203 K for various pressures ranging up to 1,031 MPa. One recognizes how, under isothermal conditions, the loss peaks shift to lower frequencies as the liquid is

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[1] Here, we considered an additive approach $G_\infty=G_{\infty,\mathrm{supra}}+G_{\infty,\alpha}$ similar to the one expressed by Eq. 8.8.6 in [48]

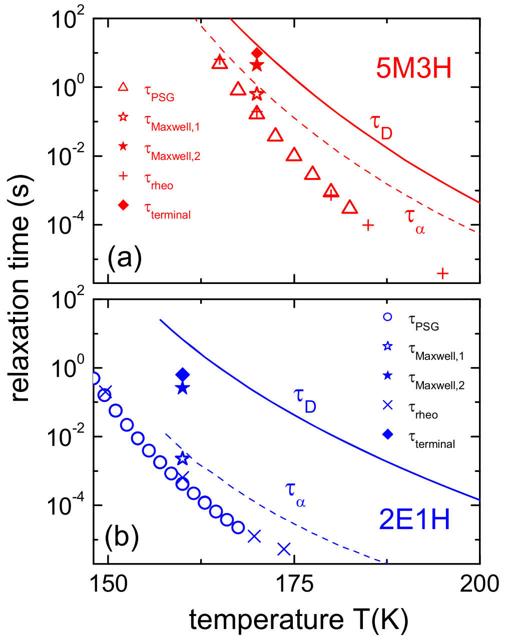

Fig. 3 Temperature-dependent shear relaxation times of **a** 5M3H (*red triangles*: PSG technique, current work; *red crosses*: rheometer, current work) and **b** 2E1H (*blue circles* and *blue crosses*, taken from ref. 15). The *diamonds* reflect the time scales of the terminal relaxation modes indicated by the *arrows* in Fig. 2b. The *stars* are calculations based on the Maxwell relation: the *open symbols* refer to $\tau_{\mathrm{Maxwell},1}=\eta_0/G_\infty$ and the *filled symbols* to $\tau_{\mathrm{Maxwell},2}=\eta_0/G_{\infty,\mathrm{supra}}$, respectively. The *lines* represent dielectric time constants for the α process (*dashed lines*) and for the Debye process (*solid lines*) taken from Refs. 25[6]

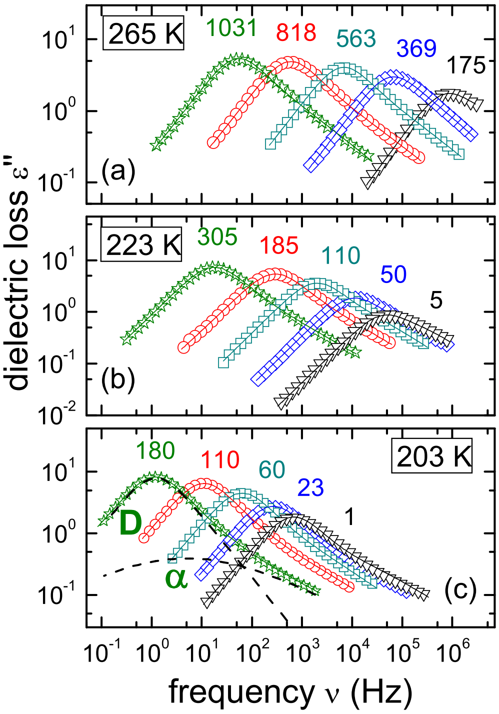

Fig. 4 Dielectric loss spectra of 5M3H as a function of frequency measured isothermally for **a** T=265 K, **b** 223 K, and **c** 203 K for several pressures (the *numbers* refer to pressures in megapascal). The *lines* are least-square fits using Eq. (2). For the dielectric loss measured at 203 K and 180 MPa, the individual contributions of Debye and α-relaxation are highlighted by the *dashed lines*

compressed. The data displayed in Fig. 4 (and another set obtained at 213 K, not shown) as well as the spectra provided in Fig. 1 were fitted using a sum of a Debye (index D) and a Cole–Cole function (involving a shape parameter α) [2][51]

$$\varepsilon*(\nu)=\varepsilon_\infty+\frac{\Delta\varepsilon_{\mathrm{D}}}{1+2\pi i\nu\tau_{\mathrm{D}}}+\frac{\Delta\varepsilon_\alpha}{1+(2\pi i\nu\tau_\alpha)^\alpha}. \tag{2}$$

Here, τ_α and τ_{D} denote the relaxation times and $\Delta\varepsilon_\alpha$ and $\Delta\varepsilon_{\alpha,\mathrm{D}}$ the relaxation strengths of the dielectric α- and Debye processes, respectively, and ε_∞ is the high-frequency contribution.

The relaxation strength and time scale parameters obtained from the fits to the 5M3H spectra are summarized in Fig. 5. In panels (a) and (b), we show the pressure dependence of τ_{D} and τ_α, respectively. Where overlap exists, excellent agreement with data from Johari and Dannhauser is noted [39]. In Fig. 5, we reproduce the time scales which these authors obtained at 226.8, 239.6, 248.4, 256.6, and 267.4 K.

One recognizes that the slope, $\partial\log_{10}\tau/\partial p$, of the $\tau(p)$ curves decreases for increasing temperatures. In other words, with R denoting the ideal gas constant, the activation volume [52]

$$\Delta V_{\alpha,D}=\ln(10)RT\left(\frac{\partial\log_{10}(\tau_{\alpha,D}/\mathrm{s})}{\partial p}\right)_T, \tag{3}$$

becomes smaller upon heating. Interestingly, for the α and the Debye process, the same activation volumes, $\Delta V=\Delta V_{\mathrm{D}}\approx\Delta V_\alpha$, are obtained within experimental error. This implies that $\tau_{\mathrm{D}}/\tau_\alpha$ should not depend on pressure. As a function of temperature, we find a linear decrease of ΔV from 65 ± 8 cm^3/mol (corresponding to ~110 Å^3/molecule) at 203 K to 25 ± 5 cm^3/mol (or ~42 Å^3/molecule) at 265 K, similar to the values for 4M3H [42]. For 5M3H, the pronounced temperature dependence of ΔV contrasts with the behavior of 2E1H. Here, from the data obtained in ref. 28 and reproduced in Fig. 5a, b, a temperature-independent ΔV=22 ± 3 cm^3/mol is obtained in the 211 to 250 K range. For comparison, it is interesting to note that on the basis of a van der Waals radius of 3.33 Å [53] for each of the isomeric octanol species, an equivalent sphere molecular volume of ~95 cm^3/mol (~157.5 Å^3/molecule) is theoretically estimated.

As summarized in Fig. 5c, different trends in the pressure dependence of the various alcohols are obtained for the strength ratio $\Delta\varepsilon_D/\Delta\varepsilon_\alpha$. While for 2E1H [28] $\Delta\varepsilon_D/\Delta\varepsilon_\alpha$ decreases with

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[2] Instead of a Cole–Cole, also the Cole–Davidson function and generalized approaches were tested. However, the Cole–Cole function gave consistently the most reliable results in particular also for the 265 K isotherm. The α was treated as a free parameter and was found typically found in the range from 0.4 to 0.8.

increasing pressure and for 4M3H [42] this ratio increases with increasing pressure, for 5M3H, a relatively weak pressure dependence is found which in fact saturates beyond about 500 MPa.

This intermediate behavior of 5M3H is not only borne out by $\Delta\varepsilon_D/\Delta\varepsilon_\alpha$, i.e., by a static quantity, but also by the time scale ratio τ_D/τ_α. Under isothermal conditions, for 2E1H, this ratio increases upon compression; for 4M3H, it decreases; and for 5M3H, however, it is virtually pressure independent. These trends were already pointed out in ref. 42 taking data from ref. 39 into account. The present data extend the statement that the time scale ratio is constant ($\tau_D/\tau_\alpha = 8 \pm 3$) up to pressures exceeding 1,000 MPa. More generally, these results confirm that increasing $\Delta\varepsilon_D/\Delta\varepsilon_\alpha$ ratios are typically associated with decreasing τ_D/τ_α ratios.[3]

To express the changes of the mutual arrangement of the molecular dipoles, based on the dielectric constant ε_s, it is useful to calculate the Kirkwood factor

$$g_K = \frac{9\varepsilon_0 k_B T}{n\mu^2}\frac{(\varepsilon_s-\varepsilon_\infty)(2\varepsilon_s+\varepsilon_\infty)}{\varepsilon_s(\varepsilon_\infty+2)^2}. \tag{4}$$

Here, $\mu = 1.68$ D is the molecular dipole moment (assumed to be independent of pressure) and the number density, $n = \rho N_A/M$, is obtained from the pressure- and temperature-dependent density ρ.[4] Furthermore, k_B is Boltzmann's constant, ε_0 is the permittivity of free space, M is the molar mass of 5M3H, and N_A denotes Avogradro's number. It is important to note that ε_s and ε_∞ are the low- and high-frequency limits of the dielectric constants estimated from the fits to the *overall* $\varepsilon'(\nu)$ spectra.[5] The Kirkwood factors g_K thus calculated are presented in Fig. 6 and compared with results from previous dielectric studies of 5M3H that focused on ambient [25] or high pressures [39].

A glance at Fig. 6 reveals that under high-pressure conditions, Kirkwood factors that agree excellently with previous determinations are found [39]. At the highest pressures and thus longest Debye relaxation times, τ_D, a trend toward saturation of g_K is obvious for the present data, in harmony with observation made in Fig. 5c for $\Delta\varepsilon_D/\Delta\varepsilon_\alpha$.

In previous investigations, the role of the $g_K = 1$ crossing was emphasized, as it indicates an equilibrium of molecular associates characterized by either $g_K < 1$ (ring-like structures) or $g_K > 1$ (chain-like structures) [18]. In isobaric studies, the temperature derivative $|dg_K/dT|$ should thus be particularly large in order to change this ring-to-chain equilibrium sensitively by even small external perturbations; for 5M3H, it was found that $dg_K/dT|_{g=1}$ is -0.044×10^{-3} K^{-1} at $T \approx 192$ K [24]. In order to enable a direct comparison of the previous isobaric with the present high-pressure isothermal Kirkwood factors, like in a previous publication, see, e.g., Fig. 10 in ref. [23], we have chosen to represent g_K as a function of the Debye relaxation times τ_D.

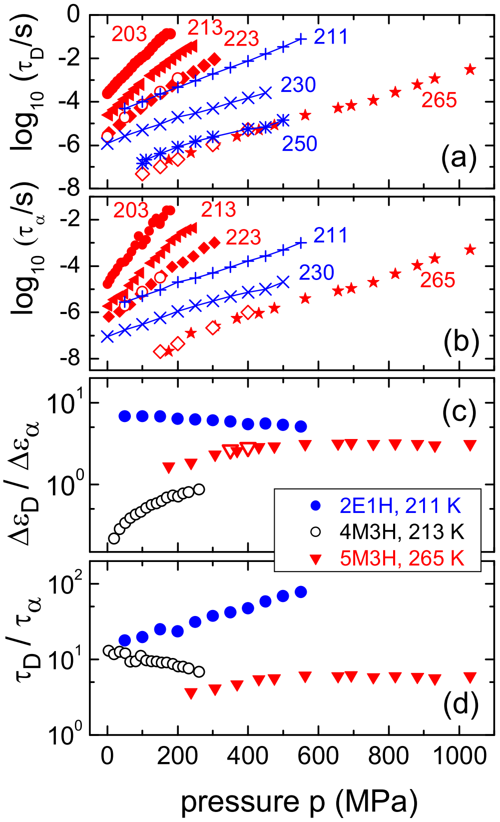

Fig. 5 **a**, **b** the pressure dependence of the relaxation times τ_D and τ_α, respectively, obtained for 5M3H from this work (*filled symbols*) and from Ref. 39 (*circles* for T=226 K and *open diamonds* for T=257 K). Time scales for 2E1H (*blue lines* and *crosses*, Ref. 28) are included for comparison. **c**, **d** the pressure-dependent relaxation strength ratio, $\Delta\varepsilon_D/\Delta\varepsilon_\alpha$, and time scale ratio, τ_D/τ_α, respectively, are shown for 5M3H from this work (265 K, *filled red triangles*) and from Ref. 39 (266 K, *open red triangles*). The present data indicate that for 5M3H, $\Delta\varepsilon_D/\Delta\varepsilon_\alpha$ and τ_D/τ_α saturate at sufficiently high pressures. By contrast, the $\Delta\varepsilon_D/\Delta\varepsilon_\alpha$ ratios determined for 2E1H (*blue dots*, from Ref. 28) and 4M3H (*black circles*, from Ref. 42), both referring to lower temperatures, show decreasing and increasing ratios, respectively, as pressure is increased and opposite behavior is displayed by τ_D/τ_α

Discussion and concluding remarks

Returning to the dielectric loss spectra shown in Fig. 1, it is remarkable that while the Debye (-like) process displays pronounced variations with molecular structure, the α-relaxation strengths are largely independent of that structure when comparing them under iso-τ_α conditions. The latter observation is easy to rationalize because any multimeric association does hardly affect the alcohol's intramolecular C–O bond which essentially is responsible for those dipole moment contributions that are not directed along the contour of the supramolecular

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[3] Also, 2M3H conforms to this trend, see ref. 36.

[4] See Table V and Eq. 1 in ref. 20.

[5] In ref. 25, it was emphasized that particularly for g_K values smaller than about unity, their numerical values can sensitively depend on the choice of ε_∞.

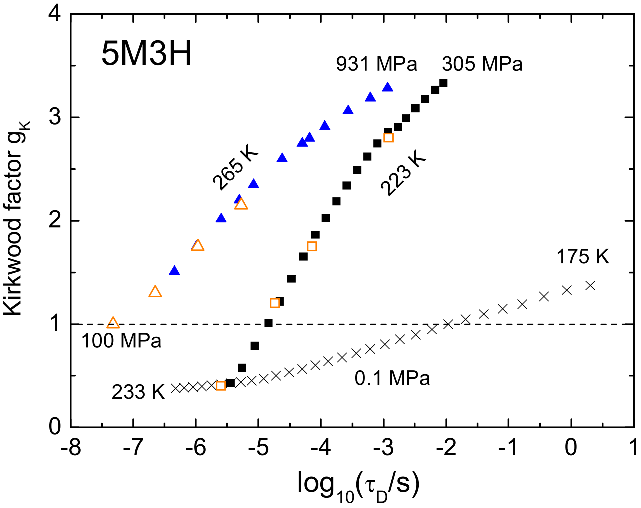

Fig. 6 Kirkwood factor g_K determined using Eq. (4) for 5M3H isothermally pressurized from this work (*filled symbols*) and from Ref. 39 (*open symbols*). Results obtained from temperature-dependent measurements at ambient pressure (*crosses*) are also included. These data are in good agreement with those from previous investigations [24]. The *dashed line* marks $g_K = 1$

structure [14, 54]. Of course, if the electrical dipole moment is intentionally altered, e.g., by exploiting (in other materials) sulfur substitution along the alkyl chain of a monohydroxy alcohol, changes in the strength of the α-relaxation are expected and were indeed observed experimentally [55].

The phenomenon that $g_K = 1$ is crossed while changing various external-state variables is not restricted to 5M3H. It is also shown by other neat alcohols such as, e.g., 2-methyl-2-hexanol [23] and 2-butyl-1-octanol [17, 56]. A ring-to-chain equilibrium may also be expected to appear when mixing the ring-former 4M3H with the chain-former 2E1H. Crossings of $g_K = 1$ with pronounced dg_K/dT slopes were indeed observed in an ambient-pressure study of mixtures of these two monohydroxy alcohols [32]. We wish to point out that whether g_K increases or decreases upon compression is not necessarily well defined for a given monohydroxy alcohol, but may depend on temperature as well. Here, 1-heptanol is an interesting example [22]: Below about 50 °C, the total dielectric strength diminishes with increasing pressure, while above this temperature, it increases with increasing pressure.

Our current dielectric studies confirm that under isothermal conditions, the relation that an increasing $\Delta\varepsilon_D/\Delta\varepsilon_\alpha$ ratio is typically accompanied by a decreasing τ_D/τ_α ratio, see Fig. 5c, d. However, we have also observed that for 2E1H, with its large $\Delta\varepsilon_D/\Delta\varepsilon_\alpha$ and τ_D/τ_α ratios, a more pronounced mechanical low-frequency feature emerges.

Figure 3 compares the temperature-dependent structural relaxation times revealed by dielectric and rheological measurements for 2E1H and 5M3H. Here, the open symbols represent the inverse frequency of the characteristic shear modulus loss peaks, and they appear smaller than the dielectric τ_α (schematically plotted in Fig. 3 as dashed line), in accord with previous observations for monohydroxy alcohols [48] and other supercooled liquids [57].

Since the dielectric time constants for the Debye process τ_D are also available for 2E1H and 5M3H (see the solid lines in Fig. 3 representing data taken from refs. 25 and 48), it is worthwhile to compare them with various "characteristic" time scales associated with the low-frequency process that can be determined from the present shear relaxation experiments. On the one hand, most *dielectric* studies—including the present one—identify the Debye and the structural relaxation as distinct spectral processes [58], in accord with analyses of dielectric results on diluted monohydroxy alcohols, see, e.g., [31, 59, 60]. On the other hand, a standard procedure is yet to be established for parameterizing the spectral shape of the supramolecular *rheological* relaxation of monohydroxy alcohols, mainly due to the scarcity of experimental investigations accessing it.

The simplest approach may be to consider additivity of two rheological contributions, as expressed by Eq. (1). As demonstrated by Behrends and Kaatze, close to room temperature, the complete low-frequency flank of the ultrasonic absorption peak of 1-dodecanol can be well described by adding two monodispersive (Debye-like) processes [44]. However, when applied to the shear modulus response of deeply supercooled 2E1H, this simple procedure does not provide a satisfactory description (not shown). It is worth noting that the separation between the characteristic frequencies for the slow mode and the structural peak maximum is below one decade for 1-decanol and other monohydroxy alcohols at room temperature at which the data in ref. 44 were taken,[6] while for 2E1H below 200 K, this separation exceeds a factor of 1,000, see Fig. 2b.

Many structural studies of monohydroxy alcohols indicate the formation of chain-like clusters. Therefore, one alternative is to adopt theoretical concepts applied to covalently bonded (polymeric) chains [15]. In this case, the time scales governing the supramolecular dynamics should be distributed. However, the viscosity or the characteristic time scale and amplitude of end-to-end dipole fluctuations are largely controlled by the *terminal* relaxation mode of the polymer, i.e., by a single time scale. Based upon this consideration, for 2E1H and 5M3H, one may identify the terminal mode via the lowest frequency at which deviations from a simple power-law behavior occur in $G'(\nu)$, see the arrows in Fig. 2b. The terminal time scales, τ_{terminal}, thus estimated are plotted as full diamonds in Fig. 3. One observes that they are smaller, albeit not entirely different from τ_D as extracted on the basis of the dielectric spectra.

Finally, in Fig. 3, we also included the results obtained for $\tau_{\text{Maxwell,1}}$ and $\tau_{\text{Maxwell,2}}$ as open and filled stars, respectively. One recognizes that $\tau_{\text{Maxwell,2}}$ is clearly larger than $\tau_{\text{Maxwell,1}}$ (or τ_α), and it appears to be only slightly smaller than τ_{terminal}. All in all, the time scale of the terminal shear relaxation mode

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[6] See Table 2 in ref. 44

seems to provide the best agreement when compared with the time scale of the dielectric Debye process, in particular, when considering that often the shear dynamics is somewhat faster than the dielectric one [57].

To conclude, we have seen that in all respects examined in the current article, 5M3H shows a behavior that is intermediate between that of monohydroxy alcohols with a strong Debye process (like 2E1H) or with a weak Debye-like feature (like 4M3H). This concerns the intensity of the viscoelastic normal mode, of the dielectric Debye process, as well as of the evolution of the dielectric relaxation strength and time scale ratio upon compression. For 5M3H, $\Delta\varepsilon_D/\Delta\varepsilon_\alpha$ and τ_D/τ_α are both relatively insensitive to high pressures when probed under isothermal conditions.

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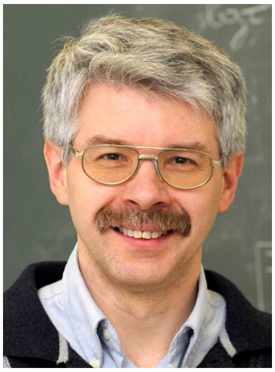

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