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Insights on the origin of the Debye process in monoalcohols from dielectric spectroscopy under extreme pressure conditions

D. Fragiadakis, C. M. Roland, and R. Casalini[a]
Chemistry Division, Naval Research Laboratory, Washington, DC 20375-5342, USA

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The dielectric spectra of most simple liquids are characterized by two relaxation processes: (i) the α-process, an intense, broad non-Debye relaxation with a non-Arrhenius temperature dependence and (ii) a β process, evident mainly below the glass transition and having nearly Arrhenius temperature behavior. However, the dielectric spectra of monoalcohols show three processes: two that resemble those of normal liquids and a third very intense Debye peak at lower frequencies, which is non-Arrhenius. Interestingly, this third process is not observed with other techniques such as light scattering and mechanical spectroscopy. There is a disagreement in the literature concerning the nature of this third relaxation. We investigated 2-ethyl-1-hexanol under high pressures (up to ~ 1.4 GPa) over a broad range of temperatures. The Debye process, which is the slowest, is strongly affected by pressure. At higher pressures the relaxation times and intensities of the two non-Arrhenius relaxations become more nearly equal. In light of these results, we propose a modified interpretation of the relaxation processes and their underlying structures in monoalcohols. © *2010 American Institute of Physics*. [doi:10.1063/1.3374820]

I. INTRODUCTION

The broad frequency range of dielectric spectroscopy makes it an experimental technique particularly suited for the study of dynamic processes in supercooled liquids, polymers, glasses, etc. Dielectric relaxation measurements are usually correlated with those obtained by methods, such as mechanical (e.g., rheology) and optical (e.g., Brillouin scattering) spectroscopies. Differences in the spectra obtained using different methods can be caused by the different observables probed by each. For example, secondary relaxation processes, such as the Johari–Goldstein process,[1,2] are usually well resolved in dielectric relaxation spectra, but are not so readily evident in mechanical and light scattering experiments. In fact, the motions underlying secondary dielectric relaxations do not necessarily require a displacement of the surrounding molecules and thus may not induce a local pressure or density change, which are the main observables for mechanical and optical methods. On the other hand, processes involving mutual interactions and requiring a cooperative rearrangement of molecules (or polymer segments), such as structural relaxation, are detected by all techniques. This is why the glass transition temperature T_g when defined in terms of the relaxation time, e.g., $\tau(T_g)=100$ s, is about the same when determined by different methods.

One interesting example of a relaxation process observed by dielectric relaxation but absent from mechanical and light scattering measurements is found in monoalcohols. The dielectric spectra of most monoalcohols show an intense Debye process ($\phi(t)\sim\exp(-t/\tau)$) at frequencies lower than the primary α-relaxation that is not detected in mechanical,[3] optical,[4] or calorimetry[5] measurements. The first widely accepted interpretation of this Debye process was by Cole and co-workers,[6] who reported the presence of three separate processes in the dielectric spectra of n-propanol; we will refer to these (in order of increasing frequency) as process I, a Debye relaxation function that has a Vogel–Fulcher–Tammann (VFT) temperature dependence (defined below, it refers to an increase in the apparent activation energy with decreasing temperature); process II, a weaker peak that also shows VFT behavior; and process III, observed only below T_g or at very high frequency and having Arrhenius behavior.[7] In the interpretation of Cole and co-workers, the Debye process I arises from the reorientation of a molecule's hydroxyl dipole, which requires breaking of the intermolecular hydrogen bond and subsequent formation of a new H bond with a different molecule. They interpreted process II as the reorientation of the oxygen alkyl chain dipole of the CO group.[6] Their interpretation implies that the Debye process comprises structural relaxation, which is noteworthy, since structural relaxation is almost invariably non-Debye, excepting only a few cases and only at high temperatures ($T>1.3T_g$). Usually the structural relaxation function has the stretched exponential form, $\phi(t)\sim\exp[(-t/\tau)^{\beta_{\mathrm{KWW}}}]$ with $0<\beta_{\mathrm{KWW}}\leq 1$. Generally, β_{KWW} is anticorrelated with the deviation from Arrhenius-like behavior;[8] therefore, VFT behavior for a Debye-like structural relaxation is an unusual combination of properties.

The Debye process is not apparent in the spectra of polyalcohols, which can form networks of H bonds; examples include glycerol, sorbitol, threitol, and xylitol.[9] However, it is important to point out that process I is not present for all molecules having one hydroxyl group. It is absent in monohydroxy molecules that cannot form intermolecular H bonds due to steric hindrances, resulting from a bulky chemical structure. Examples include salol[10] and

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[a]Electronic mail: riccardo.casalini@nrl.navy.mil.

1-phenyl-1-propanol.[11] The latter has the same structure as 1-propanol, apart from the substitution of a phenyl group for an H atom. Another sign of a relationship between process I and intermolecular H bonding is the decrease in the intensity (dielectric strength) of the Debye peak by dilution of the H bonds.[12–14] For several mixtures of monoalcohols with nonassociated liquids, the Debye process depends linearly on the OH concentration, disappearing entirely around an alcohol volume fraction of ~0.2.[15] However, there does not appear to be any particular critical value for the loss of process I, i.e., different diluents have different abilities to disrupt the H bonds. For example, in mixtures of *n*-butyl alcohol (BuOH) and *n*-bromobutane (BuBr) (only the former capable of H bonding), the dielectric strength of the Debye process disappears entirely only for pure BuBr.[14] The most pronounced effect on the intensity of the Debye process seems to be that of the addition of ionic species; adding 2.87 mol % of $LiClO_4$ to BuOH decreases the Debye intensity by almost 90%.[15,16]

The dilution of H bonds affects not only the intensity of process I but also its separation from process II. When mixed with a more viscous solvent, the peaks get closer [e.g., 2-ethyl-1-hexanol (2E1H) /squalane[15]], while less viscous solvents tend to increase the separation (as seen, for example, in BuOH/BuBr[14] and 2E1H/3-methylpentane.[15] This behavior is in accord with the observation that process II is coupled to the viscosity.[15]

Hansen and co-workers[4] found that the relaxation time of process II in *n*-propanol correlates well with the structural relaxation times determined from light scattering spectroscopies as well as with the viscosity. Their work makes a very strong case for the identification of processes II and III as the structural and Johari-Goldstein (JG), respectively. This interpretation of process II as the α relaxation had been proposed previously, from a comparison of mechanical and dielectric data for the same liquid.[16] This interpretation was seemingly confirmed by comparisons of shear mechanical and dielectric spectra of 2E1H and 2-butanol,[3] in which processes I and II are well separated (approximately three orders of magnitudes). Process I is absent from the mechanical spectra, and a good correlation was found between the temperature dependence of the mechanical α process and the dielectric process II. Aging experiments on 2E1H found no change in process II over the time scale of process I.[17] Modulated calorimetry spectra of 2E1H show a single peak in the heat capacity (corresponding to the α-process), having a peak frequency and peak shape close to that of process II.[5] It should be noted that from recent measurements on 5-methyl-2-hexanol, the use of calorimetric or mechanical measurements to interpret dielectric relaxation times has been called into question.[18]

In the current literature, it is still disputed whether the Debye process is the α-process,[19,18] and if not, what is the underlying molecular motion that is active only in response to an electric field.[12] In this work, we studied the monoalcohol 2E1H using dielectric spectroscopy at high pressure to gather new information and insight into the nature of process I and its relationship to process II. This material is of particular interest since it has been the subject of several recent investigations and these two processes are well resolved.[3,15,17,12] A previous investigation at high pressures on 1-propanol[20,21] only analyzed process I. It was found that process I no longer exhibits Debye relaxation behavior at high pressure; there is an increased decrement in the loss on the high frequency side of the peak with increased pressure.[21] There have been several investigations of the effect of pressure on the static dielectric constant (i.e., ε_0) in alcohols.[20,22,23] The dielectric constant is found to increase with pressure at constant temperature (i.e., increasing density), as expected from the classical theory of Kirkwood and Onsager.[24] These studies concluded that pressure not only changes the density but also perturbs the structure of H-bonded liquids. This perturbation seems to be larger for monoalcohols than for polyalcohols. The perturbation of the H-bonded structure by pressure has been confirmed by other results for other relaxation properties: (i) their nonconformity to thermodynamic scaling of the α-relaxation times;[25] (ii) their nonconformity to isochronal superposition of the α-peak;[26–29] (iii) an increase in the fragility, in contrast to the behavior of nonassociated liquids;[26,30,31] and (iv) an increase in the time scale separating cooperative and noncooperative processes, with consequently better resolution of the latter.[26,29,32] The last point is of particular interest because pressure can help discriminate between different secondary processes;[2,32] very generally, more intermolecularly cooperative motions exhibit greater sensitivity to pressure. In the present paper, we present new dielectric spectroscopy measurements on 2E1H at high pressures (up to ~1.4 GPa), discuss them in relation to previous literature results, and propose a possible mechanism for the Debye peak.

II. EXPERIMENTAL

The 2-ethyl-1-hexanol was obtained from Aldrich, USA ($\geq$99.6%) and used as received. For the dielectric measurements, we used a Novocontrol Alpha analyzer in combination with an IMass time domain dielectric analyzer. The measurements at atmospheric and high pressure were made using the same dielectric cell, which consisted of an air capacitor ($C_g=25.5$ pF) enclosed in flexible Teflon® tubing filled with the sample. This arrangement allows precise measurement of absolute values of the dielectric permittivity since the capacitor cell geometry is fixed. In a conventional parallel plate capacitor arrangement, the electrode spacing changes with pressure.

For the measurements at atmospheric pressure, a Delta Design oven was used, with a nitrogen atmosphere; temperature control$\leq$0.1 °C. The high pressure apparatus consisted of (i) a high pressure vessel from Harwood, Inc. (Walpole, MA), containing the dielectric cell surrounded by a pressurizing fluid (for these measurements a blend of approximately equal amounts of pentanes, hexanes and heptanes); (ii) an oven (Tenney, Inc., USA) to control the temperature of the pressure vessel; and (iii) a hydraulic system used to generate the pressure, consisting of two pumps (Superpressure to 200 MPa and Enerpac to 275 MPa), in combination with an intensifier (Harwood, 1.4 GPa). The pressure was measured with a transducer (Sensotec, OH, USA) and a pressure gauge

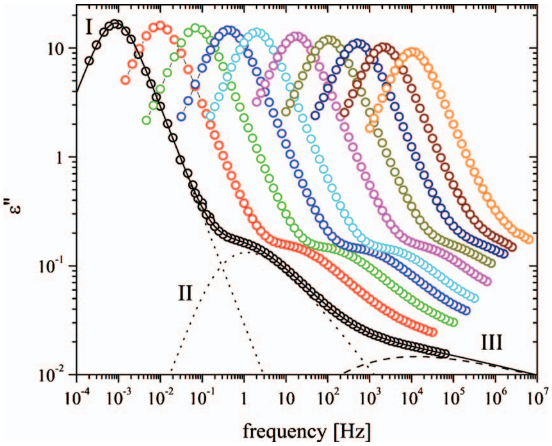

FIG. 1. Representative dielectric loss spectra of 2E1H at atmospheric pressure (from left to right: $T=-121.5, -116.2, -111.5, -106.2, -101.7, -94.2, -86.5, -78.7, -71.1, -60.5$ °C). For the spectra at -121.5 °C, the fit (solid line) represents the superposition of three processes (dotted lines), with details given in the text.

(Heise, CT, USA). Pressure-volume-temperature (PVT) measurements employed a Gnomix apparatus (200 MPa), modified to reach subambient temperatures.

III. RESULTS

Representative dielectric loss spectra of 2E1H at atmospheric pressure are shown in Fig. 1. At lower frequency there is an intense Debye peak (process I), separated by about three decades of frequency from process II, which is an order of magnitude less intense. At higher frequency, the much broader process III is observed close to and below the glass transition. This general behavior is in accord with previously measurements for this alcohol.[3,15,17,12] The spectra at high pressure show similar behavior, with the three processes clearly resolved; measurements at $T=-79.3$ °C are displayed in Fig. 2. It is evident that the separation and intensity of the peaks is strongly affected by high pressure. Processes I and II are much closer in frequency and intensity compared to atmospheric pressure.

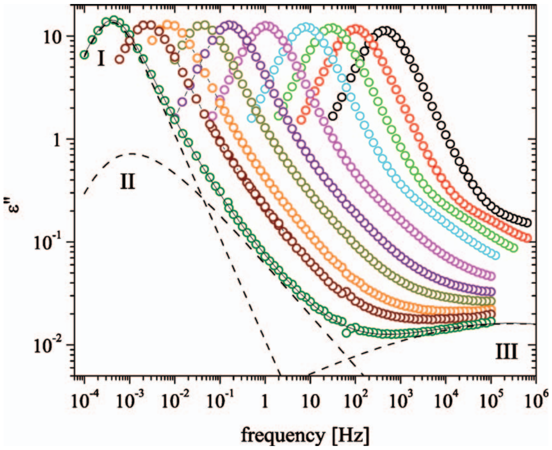

FIG. 2. Representative dielectric loss spectra of 2E1H at $T=-79.3$ °C (from right to left: $P=22.5, 101.7, 171.4, 245.7, 352.6, 435.8, 489.1, 575.5, 632.3$ MPa). For the spectra at 632.3 MPa, the fit (solid line) is the superposition of three processes (dotted lines); see text for details.

Fits of the spectra were made using the superposition of three relaxation functions, a Debye, a Kohlrauch–Williams–Watts (KWW)[24] and a Cole–Cole (CC)[24] relaxation function

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon_{\mathrm{I}}}{1+i\omega\tau_{\mathrm{I}}} + \Delta\varepsilon_{\mathrm{II}} L_{i\omega}\left[-\frac{d\varphi_{\mathrm{II}}(t,\tau_{\mathrm{II}})}{dt}\right] + \frac{\Delta\varepsilon_{\mathrm{III}}}{(1+i\omega\tau_{\mathrm{III}})^{\alpha_{\mathrm{CC}}}}$$
$$\text{with} \quad \varphi_{\mathrm{II}}(t,\tau_{\mathrm{II}}) = \exp[-(t/\tau_{\mathrm{II}})^{\beta^{\mathrm{II}}_{\mathrm{KWW}}}], \tag{1}$$

where $L_{i\omega}$ indicates the Laplace transform, ε_∞ is the high frequency permittivity, τ_i is the relaxation time, $\Delta\varepsilon_i$ is the dielectric strength, α_{CC} is the shape parameter for process III, and $\beta^{\mathrm{II}}_{\mathrm{KWW}}$ is the KWW parameter for process II. The Laplace transform of the KWW function was done numerically using the method of McDonald[33] implemented in the GRAFITY software.[34] Examples of the fits are seen in Figs. 1 and 2 (solid line) for the spectra at the lowest temperature ($T=-121.5$ °C) and highest pressure (632.3 MPa), respectively. Since the intensity of process III is much smaller so that the peak is not clearly resolved, for the spectra in which the relaxation times of processes I and II were <1 s, the fitting was done using the superposition of only those two peaks. For different combinations of T and P, we found that $\beta^{\mathrm{II}}_{\mathrm{KWW}}$ is a function of $\log(\tau_{\mathrm{II}})$, with larger $\beta^{\mathrm{II}}_{\mathrm{KWW}}$ for larger τ_{II} (inset in Fig. 12). This behavior is opposite to what is observed for the α process in other materials, and we did not find it mentioned in other publications. Measurements over a broader range of frequency would be necessary to better evaluate whether some contribution to this broadening at long τ_{II} could be due to a larger separation from process III.

Since processes I and II are close in frequency (especially under some conditions of T and P), it is reasonable to ask whether a linear superposition is correct, or should the temporal span of process II be limited to the onset of process I. In other words, are the two processes independent or is process II the precursor of process I? To examine this second possibility, we used the ansatz introduced by Williams and Watts for the case of α and β processes in polymers,[35]

$$\varepsilon^*(\omega) = \varepsilon_\infty + \Delta\varepsilon_{\mathrm{I}} L_{i\omega}\left[-\frac{d\varphi_{\mathrm{I}}(t,\tau_{\mathrm{I}})}{dt}\right] + \Delta\varepsilon_{\mathrm{II}} L_{i\omega}\left[-\frac{d[\varphi_{\mathrm{I}}(t,\tau_{\mathrm{I}})\varphi_{\mathrm{II}}(t,\tau_{\mathrm{II}})]}{dt}\right] + \frac{\Delta\varepsilon_{\mathrm{III}}}{(1+i\omega\tau_{\mathrm{III}})^{\alpha_{\mathrm{CC}}}} \quad \text{with} \quad \varphi_{\mathrm{I}}(t,\tau_{\mathrm{I}}) = \exp(-t/\tau_{\mathrm{I}}), \tag{2}$$

where the symbols have the same meanings as in Eq. (1). We found that fitting using Eq. (2) gave parameters that differ only a few percent from those determined with Eq. (1). Thus, the two descriptions are essentially equivalent and in the following we limit our analysis to Eq. (1).

Figure 3 compares the dielectric spectra measured at 0.1 MPa and at 1.14 GPa, but at different temperatures such that the loss peak maxima are at approximately the same frequency (given in the caption). While in the spectrum at

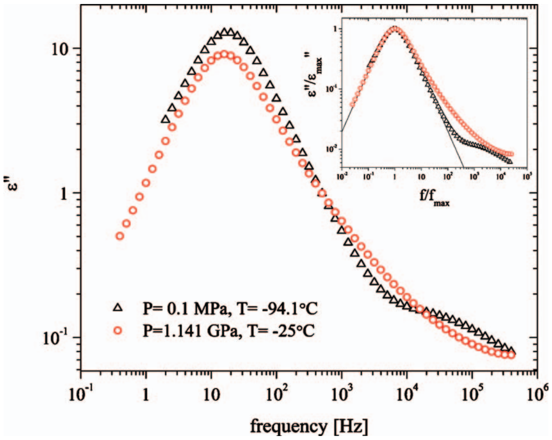

FIG. 3. Comparison of the dielectric loss spectra at atmospheric and high pressure. In the inset is the dielectric loss normalized by its maximum vs the normalized frequency ($f_{\max}(0.1\ \mathrm{MPa},-94.1\ ^\circ\mathrm{C})=13.0\ \mathrm{Hz}$, $f_{\max}(1.141\ \mathrm{GPa},-25\ ^\circ\mathrm{C})=9.13\ \mathrm{Hz}$). For comparison, a Debye relaxation function (solid line) is included.

atmospheric pressure processes I and II are resolved, in the spectrum at lower T and higher P there is only one distinct maximum. This behavior is opposite to that observed for the α and β processes in H-bonded materials such as glycerol,[26] salol,[27] and tripropylene glycol.[32] In these alcohols, the α and β processes (both JG and non-JG) become more separated with increasing pressure. In fact, as stated above, the pressure dependence generally reflects the degree of cooperativity of the process, with more local relaxations being less pressure dependent. The behavior in Fig. 3 implies that process I, being less sensitive to pressure, is more "local" than process II.

The temperature dependence at atmospheric pressure of the relaxation times τ_{I} and τ_{II} is described by the VFT equation[36]

$$\tau(T) = \tau_\infty \exp\left(\frac{DT_0}{T-T_0}\right), \tag{3}$$

where D is the fragility parameter, T_0 is the Vogel temperature, and τ_∞ is the limiting relaxation time at high T. τ_{I} and τ_{II} are shown in Fig. 4, together with the fits to Eq. (3) (solid lines; parameters given in the caption). From the fit parameters, we calculate the temperature at which $\tau_{\mathrm{II}}=10^2$ s, $=142\pm5$ K. This is close to that reported previously.[15,17,12] The temperature dependence of τ_{II} is stronger than that of τ_{I} so that the extrapolated VFT functions would cross or the two processes would merge at very long τ.

A quantity used to describe the pressure dependence of liquids is the activation volume $\Delta V^{\#}$ defined as

$$\Delta V^{\#} = -RT\frac{\partial \log(\tau)}{\partial P}, \tag{4}$$

where R is the gas constant. $\Delta V^{\#}$ is found to have values close to the molecular volume (or segmental volume for polymers).[37] However, only for a few liquids and generally over a limited range of pressure can the behavior of τ be described with a constant value of $\Delta V^{\#}$. As seen in Fig. 5, the isothermal pressure dependence of both τ_{I} and τ_{II} in 2E1H increases (larger activation volume) with increasing pressure.

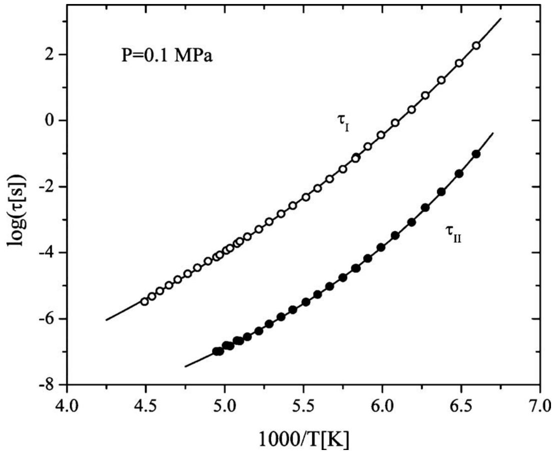

FIG. 4. Temperature dependence of the relaxation times for processes I and II at atmospheric pressure. The solid lines are the fits to the VFT function [Eq. (3)], with $\log(\tau_0^{\mathrm{I}})=-12.9\pm0.1$, $D^{\mathrm{I}}=29\pm1$, $T_0^{\mathrm{I}}=82.6\pm1$ K; $\log(\tau_0^{\mathrm{II}})=-12.5\pm0.1$, $D^{\mathrm{II}}=11.7\pm0.4$, and $T_0^{\mathrm{II}}=105\pm1$ K.

To account for this changing $\Delta V^{\#}$, Johari and Whalley introduced an empirical equation,[38]

$$\tau(P) = \tau_0 \exp\left(\frac{D_P P_0}{P_0-P}\right), \tag{5}$$

where τ_0 is the relaxation time at zero pressure, and D_P and P_0 are constants, the latter the pressure at which τ should diverge.

The fit of Eq. (5) using a temperature-invariant value of D_P (solid lines in Fig. 5, parameters in Table I) describes the relaxation data well in the vicinity of the glass transition with some deviation at short τ. This could indicate a crossover to a different low pressure behavior, as found for other materials.[39,40] However, the data do not extend sufficiently to high frequency for an analysis of the crossover in this case.

A standard definition of the glass transition temperature T_g in relaxation measurements is the temperature at which the structural relaxation time equals 100 s. Since our data do not all extend to such a long time, it is useful to define a temperature T_a at which $\tau=10^{-2}$ s; this allows comparison to literature data without any extrapolations (since

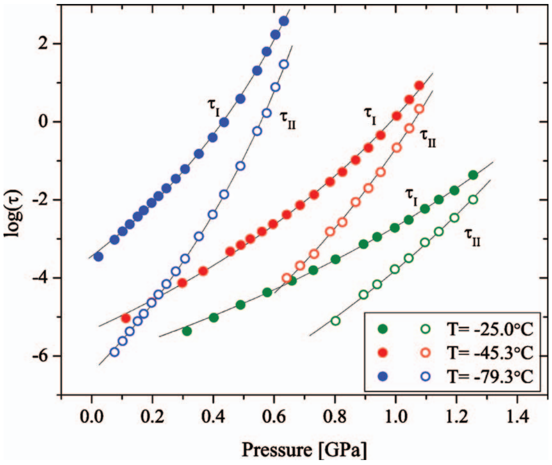

FIG. 5. Pressure dependence of the relaxation times for processes I and II at three different temperatures.

TABLE I. Fit parameters [Eq. (5)] for the data in Fig. 5. These fits are plotted in Fig. 5.

T (C)	$\log(\tau_0^{\mathrm{I}}[s])$	D_P^{I}	P_0^{I} (MPa)	$\log(\tau_0^{\mathrm{II}}[s])$	D_P^{II}	P_0^{II} (MPa)
−25.0	-14.9 ± 0.5	20.6 ± 1	3680 ± 110	-21.8 ± 0.9	30.4 ± 1.9	3745 ± 140
−45.3	-14.2 ± 0.5	20.6 ± 1	2660 ± 70	-21.2 ± 0.9	30.4 ± 1.9	2810 ± 94
−79.3	-12.3 ± 0.4	20.6 ± 1	1570 ± 45	-19.6 ± 0.9	30.4 ± 1.9	1701 ± 66

$T_a > T_g$, generally $dT_a/dP < dT_g/dP$). By combining the isobaric and isothermal data, we determined the pressure dependence of T_a (inset in Fig. 6): $\partial T_a^{\mathrm{I}}/\partial P|_{P=P_{\mathrm{atm}}}=89$ K/GPa and $\partial T_a^{\mathrm{II}}/\partial P|_{P=P_{\mathrm{atm}}}=108$ K/GPa. The latter is significantly higher than the dT_g/dP reported for n-propanol (=70 K/GPa),[20,41] glycerol (40 K/GPa),[26] and sorbitol (43 K/GPa),[42] but close to the value for tripropylene glycol (109 K/GPa).[31] These pressure coefficients are all substantially smaller than for nonhydrogen bonded liquids (o-terphenyl, propylene carbonate, etc.), for which $dT_g/dP > 240$ K/GPa.[37]

A metric often used to quantify the change in the activation energy at constant pressure is the steepness index or fragility

$$m_P = \left.\frac{\partial \log(\tau)}{\partial T_g/T}\right|_{T=T_g}, \tag{6}$$

where m_P and $\Delta V^{\#}$ are related by[43]

$$m_P = \frac{1}{R}\frac{\Delta V^{\#}|_{\tau=\tau_g}}{\left.\frac{\partial T}{\partial P}\right|_{\tau=\tau_g}} \tag{7}$$

from which it is possible to calculate the pressure dependence of the steepness index. For nonassociated liquids, m_P is a decreasing function of pressure, as expected from their conformity to the thermodynamic scaling.[30] Hydrogen bonded materials, on the other hand, show an increasing fragility with pressure.[26,31] For the 2E1H, we find that m_P for both processes I and II increases with pressure. Over the studied range of pressures, m_P^{II} is always larger than m_P^{I}.

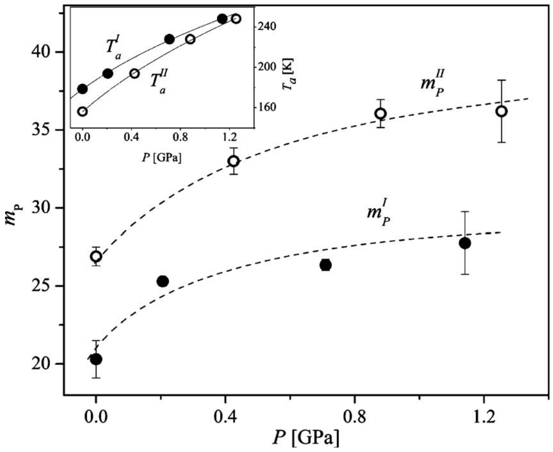

FIG. 6. Pressure dependence of the steepness index calculated using Eq. (7) for $\tau=10^{-2}$ s for processes I and II. The dotted lines are guides to the eye. The inset shows the pressure dependence of the temperature T_a at which the relaxation time is equal to 10^{-2} s.

As a consequence of the larger fragility and activation volume of process II, it tends to move closer to the peak for I with decreasing T and increasing P. The data suggest that at certain conditions the two relaxation times for the two processes will be equal, $\tau_{\mathrm{I}}=\tau_{\mathrm{II}}=\tau^*$. Interestingly, τ^* appear to decrease with increasing pressure, as seen by plotting $\log(\tau_{\mathrm{II}})$ versus $\log(\tau_{\mathrm{I}})$ (Fig. 7); this plot shows that the separation of the two processes is reduced at higher pressure. Such behavior is different from that of the normal mode in polymers, for which the separation from the α-process is independent of pressure, whereby a plot of the normal mode relaxation time versus τ_α for different T and P superimpose.[44] Using Eqs. (3) and (5) with the obtained fit parameters, the merging relaxation time τ^* was calculated as a function of T and P (Fig. 8). The τ^*'s for the two isotherms at higher T denoted in Fig. 7 show that an extrapolation using this different representation gives a similar value. At atmospheric pressure τ^* is extremely large ($>10^9$ s), falling well into the glassy state and thus experimentally inaccessible. With increasing pressure τ^* decreases, with $\tau^* \sim 1$ s at P=1.5 GPa. The behavior of $\log(\tau^*)$ versus T or P are very similar; in fact, the dependence of T^* on P^* is essentially linear (top inset in Fig. 8). Such behavior has not been seen previously for other alcohols.

The effect of volume on the dynamics is more amenable to interpretation than that of pressure. Toward this end, it is necessary to know the equation of state (EOS) in order to calculate the specific volume V for any condition of T and P. $V(T,P)$ for 2E1H is shown in Fig. 9. The behavior is similar to that of other simple liquids and polymers, with no discontinuities or changes in slope indicative of a phase change. The data can be described by the Tait EOS

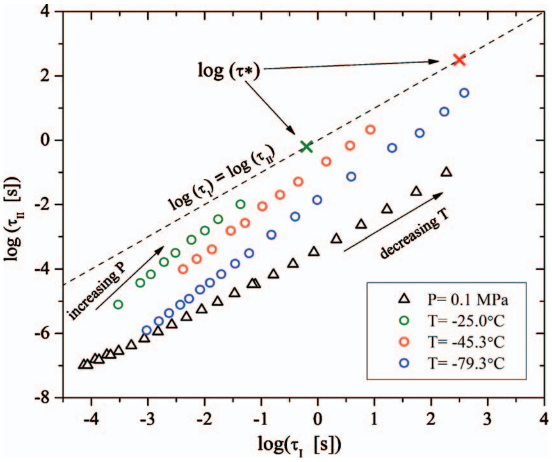

FIG. 7. Relaxation time of process II vs the relaxation time of process I at atmospheric pressure and for three isotherms The dotted line represents the condition at which the two relaxation times are equal. The crosses denote the relaxation times for the two lower temperature isotherms.

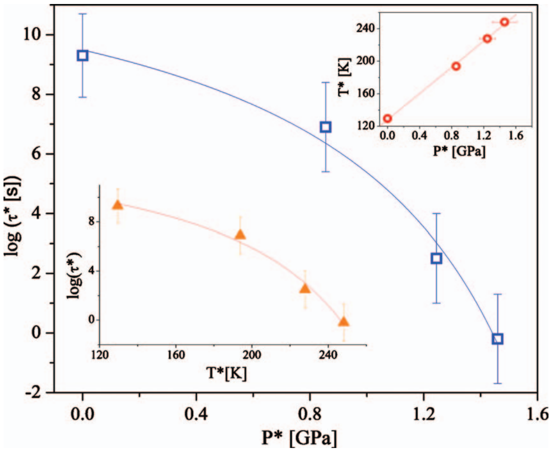

FIG. 8. Relaxation time corresponding to $\tau_I=\tau_{II}=\tau^*$ as a function of pressure (main figure) and temperature (lower inset). The behaviors are similar, as shown by the linear dependence of these quantities for $\tau_I=\tau_{II}=\tau^*$ (top inset); the solid line is the fit $T^*(\mathrm{K})=(128\pm 3)+(81\pm 3)P^*(\mathrm{GPa})$.

$$V(T,P)=V_0\exp(a_0T)\left\{1-C\ln\left[1+\frac{P}{b_0\exp(-b_1T)}\right]\right\}, \tag{8}$$

where V_0, a_0, b_0, b_1, and C (=0.0894) are constants. For 2E1H we obtain $V_0=1.1729\pm 1\times 10^{-4}$ cm^3/g, $a_0=(8.873\pm 0.008)\times 10^{-4}$ C^{-1}, $b_0=137.5\pm 0.1$ MPa, and $b_1=(6.19\pm 0.02)\times 10^{-3}$ C^{-1} (fits are shown as the solid lines in Fig. 9).

Using this EOS, we calculated the dependence of the relaxation times I and II on volume (Fig. 10). For both processes the volume change required to change the relaxation time at constant temperature is much larger than the corresponding volume change at constant pressure. This indicates that the relaxation times are more sensitive to changes in the thermal energy than to the volume changes accompanying variations in T. We can quantify these dependences from the ratio of the isochoric and isobaric activation energies E_V/E_P [where $E_P=R\partial\log(\tau)/\partial(1/T)|_P$, $E_V=R\partial\log(\tau)/\partial(1/T)|_V$].

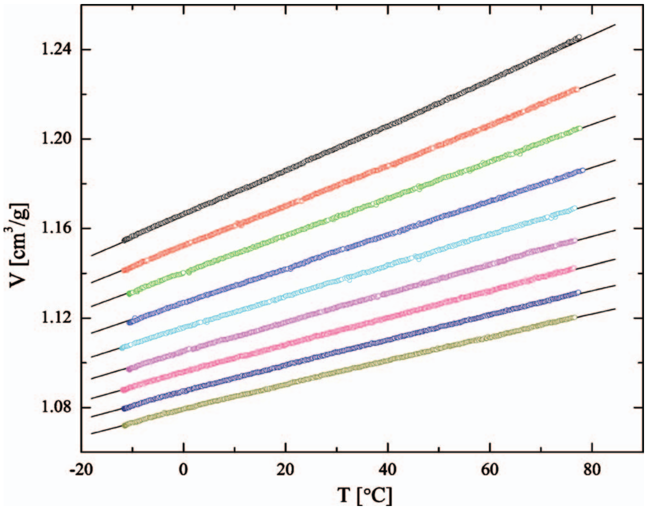

FIG. 9. Specific volume of 2E1H as a function of T at nine pressures: 10, 30, 50, 75, 100, 125, 150, 175, and 200 MPa. The solid lines represent fits to the Tait equation [Eq. (8)].

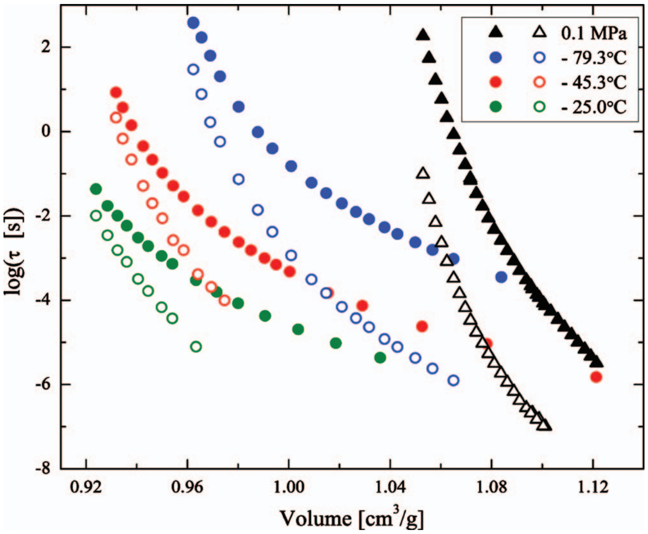

FIG. 10. Volume dependence of the relaxation times for processes I (solid symbols) and II (open symbols) at three temperatures (circles) and at atmospheric pressure (triangles).

For the limiting cases of τ depending only on T or V, $E_V/E_P=1$ and $E_V/E_P=0$, respectively. If T and V exert the same influence, $E_V/E_P=0.5$. For 2E1H, we find that for processes I and II, $(E_V/E_P)^{\mathrm{I}}=0.76$ and $(E_V/E_P)^{\mathrm{II}}=0.67$. These values fall between those for structural relaxation in other hydrogen bonded liquids with more than one hydroxyl group (e.g., glycerol $E_V/E_P=0.97$, sorbitol $E_V/E_P=0.87$, propylene glycol $E_V/E_P=0.88$, dipropylene glycol $E_V/E_P=0.86$, and tripropylene glycol $E_V/E_P=0.83$) and those of nonassociated materials (*ortho*-terphenyl $E_V/E_P=0.55$, salol $E_V/E_P=0.43$, propylene carbonate $E_V/E_P=0.64$, and phenylphthalein-dimethylether $E_V/E_P=0.53$).[37] We attribute this intermediate behavior to the ability of 2E1H to form some aggregated H-bonded structure (chains, micelles, etc.), but lacking more than one hydroxyl per molecule, there is no H-bond network.

We also find that, unlike nonassociated liquids, 2E1H does not conform to thermodynamic scaling, whereby τ is a function of the product variable TV^{γ},[25] for either process I or II. This is consistent with the observed increase in fragility with pressure (Fig. 6), since the conformity to thermodynamic scaling requires a negative pressure coefficient for m_p.[30]

Temperature and pressure strongly affect not only the time constants for the dynamics (i.e., τ) but also the intensity ($\Delta\varepsilon$) of both. In Fig. 11 the dielectric strength of process I is plotted versus τ_I after normalization by the density. When the relaxation time is changed by varying T, the expected increase in $\Delta\varepsilon_I/\rho$ with increasing τ (decreasing T) is observed; however, $\Delta\varepsilon_I/\rho$ is nearly constant when τ_I is changed by varying P at constant T. Consequently, for the conditions of high P and T, $\Delta\varepsilon_I/\rho$ is about half its value at atmospheric pressure and low T.

For process II the normalized dielectric strength versus τ_{II} is shown in Fig. 12. The behavior is almost opposite to that of process I: $\Delta\varepsilon_{II}/\rho$ slightly decreases with T at atmospheric pressure, but increases when P is increased at constant T. These differing behaviors are brought out in Fig. 13 in a plot of the ratio $\Delta\varepsilon_I/\Delta\varepsilon_{II}$ versus τ_I. The ratio $\Delta\varepsilon_I/\Delta\varepsilon_{II}$

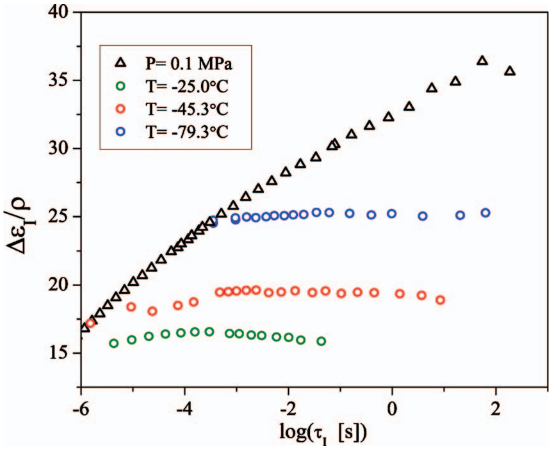

FIG. 11. Dielectric strength $\Delta\varepsilon_I$ normalized by the density vs the relaxation time of process I for the isobar at atmospheric pressure (triangles) and three isotherms (circles).

increases with decreasing T and decreases with increasing P; thus, at very high P process II could become dominant. Also shown in the figure is the value of τ^*, suggesting that at this merging condition the ratio $\Delta\varepsilon_I/\Delta\varepsilon_{II}$ would be nearly zero.

IV. DISCUSSION

The relaxation spectra of 2E1H are strongly affected by pressure and temperature, with changes in both the dielectric strength and frequency of the two dominant processes. These changes can be attributed to the differences in the number of hydrogen bonds. The dependences of the "glass transition" and fragility are both consistent with the behavior observed for other hydrogen bonded materials, with a decrease in H bonds at higher pressure. However, 2E1H has the interesting feature of two dominant processes with non-Arrhenius temperature dependences. Their nature is open to question, in particular, which process underlies structural relaxation of the material.

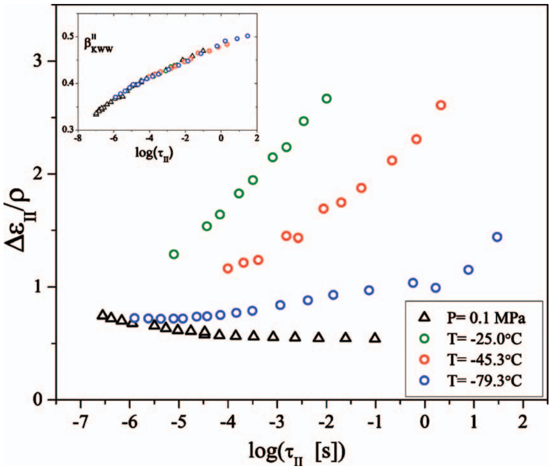

FIG. 12. Dielectric strength normalized by the density vs the relaxation time of process II at atmospheric pressure (triangles) and at three temperatures (circles). The inset shows the Kohlrausch exponent as a function of the relaxation time of process II. The symbols are the same for the inset and the main figure.

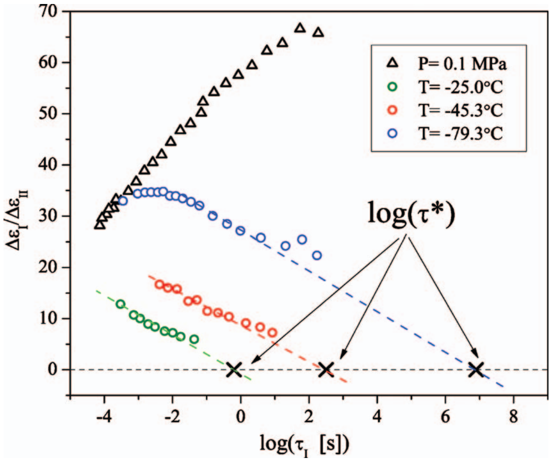

FIG. 13. The ratio of the dielectric strengths of processes I and II vs the relaxation time of process I.

The two processes are not independent, as made evident by the effect of T and P on the dielectric strengths and relaxation times. Consequently, the classification of either one as the structural relaxation process may not be correct. A possible interpretation of the high pressure behavior can be given in terms of a change in the molecular associations. It is well accepted in literature that the hydrogen bonds between hydroxyl groups in monoalcohols give rise to various molecular arrangements, with a consequent heterogeneous distribution of hydrocarbons and hydroxyl groups. However, there is no agreement on the detailed nature of these structures for any of the alcohols. For the case of methanol and ethanol, H-bonded chains are believed to be the dominant structure, although investigations using various techniques [X-ray diffraction, NMR, IR/Raman, molecular dynamic (MD) simulations] have failed to yield any consensus on the exact structure, with some results suggesting alternative structures such as micelles or winding chainlike architectures.[45]

One interesting case is 1-octanol, which has been investigated extensively because it serves as a model system for lipid molecules in biological membranes. The structure proposed for 1-octanol, supported by X-ray scattering,[46] 1H NMR,[47] and MD simulations,[48] consists of micellar aggregates with a polar core of up to 10–15 hydroxyl groups. These are bonded together in mostly linear structures, with a nonpolar shell of the alkyl chains radiating outwards. This

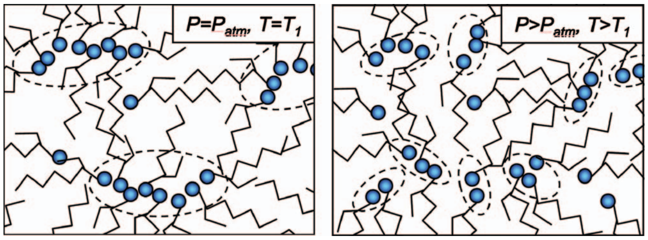

FIG. 14. Sketch of the proposed structure of 2E1H at ambient and at high pressures, based on structure proposed for 1-octanol by MacCallum and Tieleman (Ref. 48). The circles represent the hydroxyl groups and the zigzag lines the alkyl groups. The dashed lines indicate the strongly correlated H-bonded clusters.

morphology is depicted in Fig. 14. This same structure was also proposed by Floriano and Angell to explain the dielectric Debye relaxation in *n*-propanol.[16] There seems to be general agreement that linear primary alcohols tend to arrange in chainlike clusters. Alcohols with hydroxyl groups farther from the end of the chain are less prone to chainlike arrangements, instead forming shorter chains and rings. Even in the more favorable cases, the maximum number of molecules in a cluster is limited to about 10.[49–51] As pointed out by Dannhauser,[51] ring clusters would have a dipole moment nearly equal to zero, which in terms of the classical theory of Kirkwood and Fröhlich[24] results in a correlation factor $g < 1$. For the case of 2E1H, the large dielectric constant ($g > 1$) is an indication of mainly parallel ordering of the permanent dipoles, consistent with the presence of chainlike clusters.

High T and high P reduce the extent of hydrogen bonding with a consequent decrease in the size and number of H-bonded chain clusters and less local ordering of the dipoles. The observed P and T behavior of process I is qualitatively in agreement with the interpretation of this process as involving clusters; to wit, $\Delta\varepsilon_{\mathrm{I}}$ at constant τ_{I} is smaller at higher P and T. The fact that this process is not observed by mechanical or light scattering spectroscopies can be explained by the motion being internal to the cluster, and thus not involving cooperative rearrangement of many molecules. Such internal motion could be the rotation of a molecule around its chain cluster axis, which would still change substantially the total dipole of the cluster. In fact, when the chain cluster is formed by molecules disposed to one side, the dipole moment will be much larger than if the molecules were arranged on both sides in alternating fashion. Rotation of the latter would not require the breaking of any H bonds, but would be coupled to the viscosity of the surrounding medium, which is controlled by the alkyl chains. This motion would be analogous to that of a polar probe orienting in a nonpolar matrix that relaxes faster than the probe itself. Interestingly, for such a case it is found that the probe relaxes exponentially (Debye behavior) since the surroundings are dynamically homogeneous, (the "hydrodynamic rotational regime").[52] To our knowledge, an interpretation of process I in terms of such motion has not been described in the literature.

Since process II is known to be strongly correlated with the viscosity and with density fluctuations (i.e., light scattering), its nature is consistent with motion of the alkyl chains of bonded and nonbonded molecules (which should be very similar). With increasing pressure, the two processes move closer because smaller clusters relax faster. The "merging" would coincide with conditions at which the formation of chain clusters is no longer favorable; only rings and isolated molecules are possible, similar to what is observed for biomembranes.[53] Some hint of this transition is seen in the changes in $\partial P/\partial T|_V$ with T and found to correspond to changes in the static dielectric constant for some alcohols.[54] However, to our knowledge, sufficient dielectric measurements are not available, so it is unknown whether there is any change in the intensity of the two processes. Further investigations along this line could be very fruitful.

V. CONCLUSIONS

Broadband dielectric spectroscopy measurements over a broad range of pressures and temperatures on the monoalcohol 2E1H reveal interesting new features. (i) The relaxation time of process II is more strongly dependent on pressure than process I and, consequently, the two processes merge at high pressures. (ii) Process II becomes more intense with increasing pressure relative to $\Delta\varepsilon$ of process I. This implies that at extreme pressures the situation reverses, with process II becoming dominant. (iii) The merging temperature T^* depends linearly on pressure (Fig. 8, inset).

The observed changes are consistent with a decrease in H bonds with increasing pressure. Based on the structural evidence reported in literature as discussed above, it seems likely that the local organization is strongly inhomogeneous, with the alcohol molecules organized in nearly linear clusters of a small number of molecules (<20). We ascribe process I to the rotation of the alcohol molecules around the chain axis, which would act as a local probe slower than the viscous surrounding medium and dominated by the alkyl chains and the unbonded chains, both of which are responsible for process II. With increasing pressure the chains become progressively smaller and, consequently, the intensity of process I decreases relative to that of process II.

The merging of the two processes could therefore be the indication of a "phase" transition similar to that observed in biomembranes.[53] This potentially has important implications for biological applications of alcohols. Further studies using higher pressures and other experimental techniques will be required to clarify this aspect of the behavior.

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