

Effect of Compression on the Relationship between Viscosity and Dielectric Relaxation Time in Hydrogen-Bonded Primary Alcohols

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High pressure viscosity and dielectric measurements were carried out on two monohydroxy alcohols, 2-ethyl-1-hexanol and 5-methyl-2-hexanol, at room temperature. Analysis of the dielectric relaxation times versus viscosity revealed the breakdown of the Einstein-Debye relation above some characteristic pressure. The failure of the Einstein-Debye relation is a manifestation of pressure induced changes of supramolecular hydrogen bonded structures which occur in these liquids.

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The glass transition, attained by decreasing temperature or increasing the system density, remains far from being completely clarified. One of the most important factors governing the dynamics of liquids on approaching the glassy state is the character of intermolecular interactions. It is a well-known fact that van der Waals materials often exhibit completely different properties than hydrogen bonded or ionic liquids. Monohydroxy alcohols are a family of hydrogen bonded materials with unique features. Contrary to other small molecular liquids, two relaxation modes, instead of the single structural relaxation peak, are commonly identified in dielectric spectra of many primary alcohols. The slower of the two is usually dominating and exhibits exponential (Debye-like) behavior. The Debye process is often strongly overlapped with a faster and much weaker structural relaxation process. However, the most intriguing feature of the Debye relaxation found in monohydroxy alcohols is that this process is experimentally observed only by means of dielectric spectroscopy. Other experimental methods do not provide any evidence of the existence of this process. Moreover it has been suggested that the faster dielectric relaxation process should be identified with structural relaxation [1–27]. Because of these experimental problems, the molecular origin of the Debye relaxation still remains an open question, and different models have been proposed [1–3,6,7,25,28–31]. The only consensus concerning the nature of the Debye process in monohydroxy alcohols is that “hydrogen bonding will need to be an essential ingredient of the explanation” [17]. Very recently, the transient chain model suggesting existence of H-bonded chains which are similar to polymer chains, was described and tested [18,20–22,24,32,33]. According to this model, the “inner” hydrogen-bridged hydroxyl groups, are temporarily held together by electrostatic forces. These forces are responsible for segregation of the polar groups from the nonpolar alkyl chains. Motions of the chain (contributing to the Debye relaxation) are induced by attachment and detachment of the molecules at its other end [22]. However, the H-bond switching rate is much faster

than the relaxation time of the Debye process and coincides with the structural relaxation time [32]. Nevertheless, there still remain a number of unanswered questions about the dynamics of both the Debye and structural relaxations, in particular, the effect of temperature and pressure as well as the molecular architecture on the time scale which separates these two processes [19–23,25,32,33].

Recent, preliminary results obtained from dielectric pressure measurement of two alcohols, 2-ethyl-1-hexanol (2E1H, linear formula $\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{OH}$) and 5-methyl-2-hexanol (5M2H, linear formula $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CHOHCH}_3$), showed that pressurization strongly modifies the molecular dynamics of these liquids [19,20,23,25]. At elevated pressure the maxima of both processes, i.e., the Debye and the structural relaxations, approach each other, and above ca. 0.5 GPa only the single non-Debye relaxation peak is observed [19,23,25]. Also the temperature behavior of the relaxation dynamics of the Debye process exhibits characteristic changes with pressurization, and for pressures of ca. 1.57 GPa T_g -scaled relaxation times of the main relaxation process are characterized by the same value of the steepness index as the T_g -scaled structural relaxation times at ambient pressure [23,25]. Moreover, in the case of 2E1H it was demonstrated that the Debye-like process satisfies the thermodynamic scaling only in the low pressure region up to ca. 0.5 GPa, whereas the breakdown of the scaling is observed above this pressure [34].

The vitrification process of a liquid is manifested by the dramatic slowing down of molecular relaxation dynamics. To investigate the underlying microscopic origin of this slowing down, the most often used approach is to study the temperature dependence of transport properties (e.g., viscosity η , self-diffusion constant D , and structural relaxation time τ_α) at ambient pressure. For many years it has been commonly accepted that η is simply proportional to the structural relaxation time. This proportionality is described by the Einstein-Debye (ED) equation [35,36]

$$\eta = (k_B T / V) \tau_\alpha, \quad (1)$$

where k_B is Boltzmann's constant, T is the temperature, and V is the molecular volume. Also, the Maxwell model for viscoelastic liquids establishes the relationship between η and τ_α , with the infinite frequency shear modulus, G_∞ , as the constant of proportionality:

$$\eta = G_\infty \tau_\alpha. \quad (2)$$

Consequently, one could expect that both η and τ_α should change in the same manner with temperature. However, some deviations from this proportionality have been reported in the literature, indicating decoupling of τ_α from η . It is commonly observed that the ratio $\eta/T\tau_\alpha$ remains constant only at high temperatures (for low values of η and short relaxation times) and, on approaching to the glassy state, starts to increase up to ca. one order of magnitude at the glass temperature, T_g [37–39]. This breakdown of the ED relation was explained as a consequence of the diverging length scale of the cooperative dynamics on approaching T_g [40]. In the case of a few monohydroxy alcohols it was showed that η is closely related to the structural process [12,16] and the ED relation is reasonably well fulfilled.

Because of the experimental difficulties, up to now most of the experimental tests of the validity of the ED equation have been performed for various temperatures but only at ambient pressure. In general, there are two distinct effects responsible for slowing down of the molecular dynamics as the temperature of the liquid is lowered: the available thermal energy of molecules decrease, making it more difficult for molecules to surmount minima in the potential energy surface; this trapping of configurations slows the dynamics. Simultaneously, there is a volume decrease, which causes steric constraints of the motions. Consequently, both η and τ_α measured at ambient pressure are influenced by the respective contributions of thermal energy and density. Then the question arises whether the correlation between η and τ_α described by the ED relation is maintained during pressurization, when only intermolecular distances are changed. Very few high pressure studies of the ED relation were performed only for dibutylphthalate [41] and propylene carbonate [42]. For both liquids it was reported that the proportionality between η and τ_α remains valid under compression. The lack of signs of the breakdown of the ED relation in dibutylphthalate were explained by the relatively weak intermolecular cooperativity found in this material, even close to T_g [41].

It is a well-known fact that compression can markedly modify supramolecular hydrogen bonded structures which are present in associated materials. Thus, a fundamental question arises immediately: to what extent compression affects the relationship between η and τ , captured by the Einstein-Debye relation. For the first time we present results of high pressure measurements (up to ca. 1.5 GPa)

of η in two monohydroxy alcohols: 2-ethyl-1-hexanol and 5-methyl-2-hexanol. These results are compared with the high pressure isothermal dielectric relaxation times, measured up to ca. 1.7 GPa. Analysis of the dielectric relaxation times versus viscosity revealed the breakdown of the Einstein-Debye relation above some characteristic pressure. This effect is the more spectacular in the case of 2E1H. The η measurements were carried out in a sapphire cell using the “rolling ball method” [43]. The anvils were half-inch sapphire spheres with a 3.5 mm flat culet. Gaskets were made of CuBe and provided with a 1.3 mm hole with 0.5 mm depth, in which the speed of a tungsten carbide ball of typically 100 μm diameter was observed at various inclination angles between 10° and 20°. The force of up to 5 tons was provided by a VX2 Paris-Edinburgh cell [44]. Pressures were measured using the fluorescence of a BaFCl:Sm²⁺ crystal inside the pressure chamber using a pressure coefficients of +1.1 nm/GPa [45]. Experimental details will be published elsewhere. The experimental setup for dielectric measurements was described in [41].

Representative dielectric loss spectra of 2E1H measured isothermally at room temperature are shown in Fig. 1. The pronounced relaxation process becomes visible in the experimental window only above ca. 470 MPa and its maximum moves toward lower frequencies with increasing pressure. Contrary to the data at ambient pressure, the shape of the main relaxation process observed at high pressures clearly exhibits the nonexponential behavior. As mentioned above, this broadening of the shape of the loss peak is due to overlapping of the Debye and structural relaxation peaks [19,23].

The pressure dependence of η measured in both alcohols at $T = 20^\circ\text{C}$ is presented in Fig. 2. η increases dramatically on approaching the glass transition. Similarly, as in the case of propylene carbonate, the inflection point is visible during pressurization [42]. It was shown that this

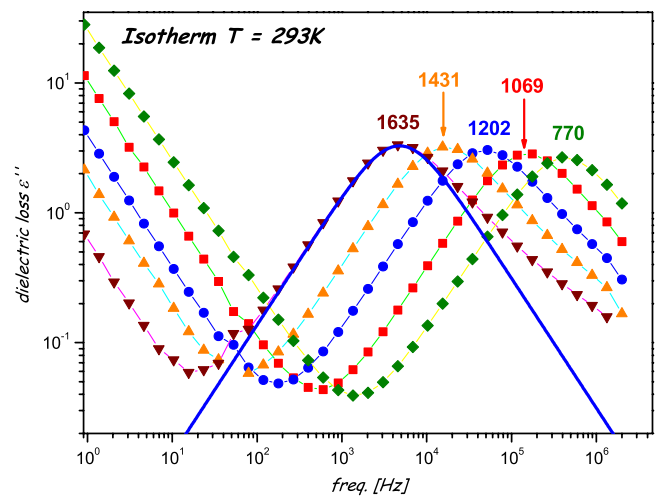


FIG. 1 (color online). Representative dielectric loss spectra measured for 2E1H at $T = 20^\circ\text{C}$. Numbers are pressure values in MPa. The solid line indicates a single exponential process.

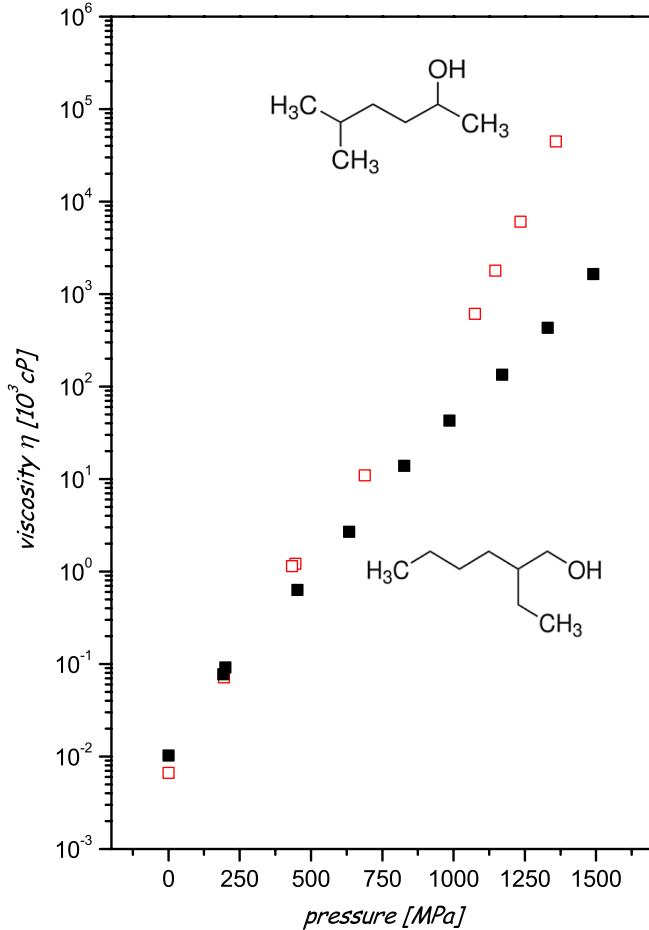


FIG. 2 (color online). Pressure dependence of the η in 2E1H (black solid squares) and in 5M2H (red hollow squares), both measured at $T = 20^\circ\text{C}$.

inflection η corresponds to a minimum in the activation volume, ΔV , during compression. Since ΔV is proportional to the product of compressibility, κ_T , and the apparent activation energy at constant volume, E_V , the inflection point is due to the crossover from the low pressure region where κ_T depend more strongly on densification than E_V to the high pressure region with opposite pressure dependence of κ_T and E_V [42].

A striking difference between the pressure behavior of η and τ becomes visible when the data presented in Fig. 2 are compared with dielectric relaxation times, determined as the inverse of the frequency of the maximum in the loss peak ($\tau = 2\pi/f_{\text{max}}$) (see Fig. 3). In addition, dielectric relaxation times for the structural and the Debye process as well as the structural relaxation time from shear measurements (scaled to the dielectric relaxation time, according to calculations presented in [33,46]) [16] are depicted in Fig. 3. It is obvious from inspection of the data in Fig. 3(a) that only at low pressures up to ca. 550 MPa (marked by the vertical arrow) do dielectric relaxation times and the viscosity of 2E1H seem to have similar pressure dependences. Above this characteristic pressure strong decoupling

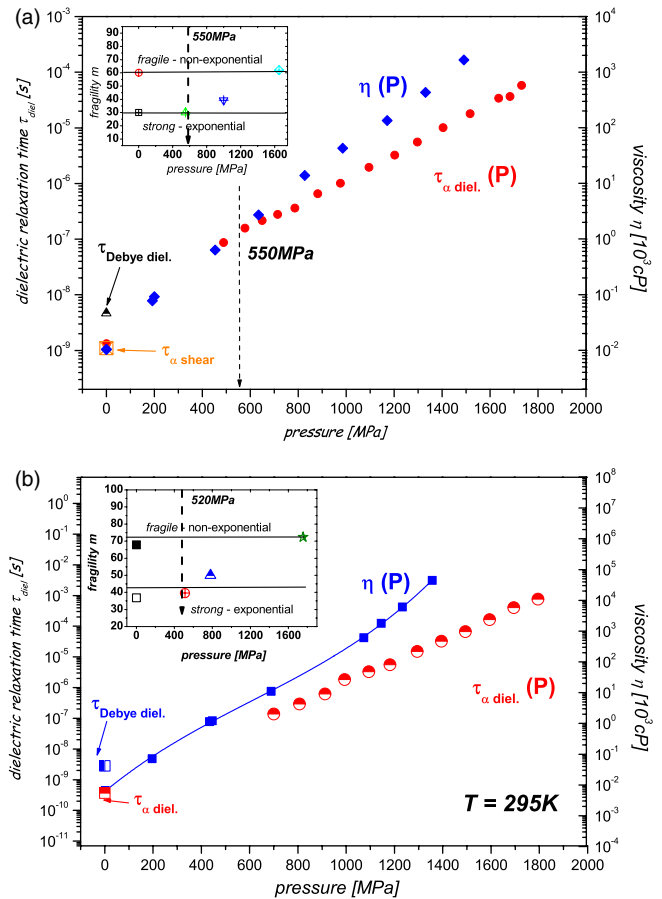


FIG. 3 (color online). The dielectric relaxation times (solid circles) and the viscosity (solid squares) for (a) 2E1H and (b) 5M2H as a function of pressure at $T = 20^\circ\text{C}$ and $T = 22^\circ\text{C}$, respectively. The ordinary scales have the same expanse, demonstrating conformance of the ED relation at low pressure and breakdown of this relation above ca. 550 MPa in 2E1H. Insets present pressure dependences of the fragility for the main relaxation process in both alcohols.

between η and τ is observed. The breakdown of the ED relation is also visible for the second monohydroxy alcohol [see Fig. 3(b)]. It has to be emphasized that the pressure for which this decoupling takes place surprisingly coincides with the pressure above which the value of the steepness index of the main relaxation process in both alcohols starts to increase [insets in Fig. 3(a) and 3(b)]. Moreover, as shown recently in the case of 2E1H, the so-called thermodynamic scaling holds only up to the characteristic pressure of ca. 550 MPa [34].

The decoupling of η from τ and, consequently, the breakdown of the ED relation clearly indicates an essential role of pressure in modifying transport properties in both primary alcohols. As presented in Fig. 4(a), in which ambient pressure $\log\tau_{\text{Debye}}$ and $\log\tau_\alpha$ are plotted as a function of $\log\tau_{\text{shear}}$ for 2E1H, the shear relaxation times have the same temperature dependence as the structural and the Debye relaxation times (the scaling exponents are

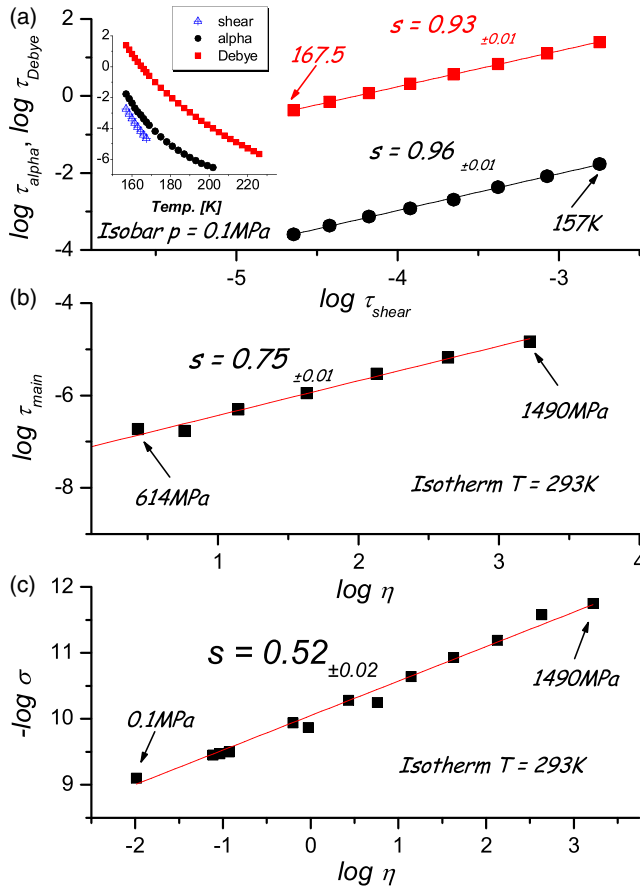


FIG. 4 (color online). Dependence of (a) $\log \tau_{\alpha}$ (dielectric) and $\log \tau_{\text{Debye}}$ (dielectric) vs $\log \tau_{\text{shear}}$ at $p = 0.1 \text{ MPa}$ in temperature range from 157 up to 167.5 K, (b) $\log \tau_{\text{main}}$ (dielectric) vs $\log \eta$ in the pressure range from 614 up to 1490 MPa, and (c) $-\log \sigma$ vs $\log \eta$ at elevated pressure in pressure range from 0.1 up to 1490 MPa, both for $T = 20^\circ \text{C}$ in 2E1H. Inset in (a) depicts temperature dependence of dielectric structural and Debye relaxation times and shear relaxation times collected at ambient pressure.

$s = 0.96 \pm 0.01$ and 0.93 ± 0.01 , respectively). It has to be emphasized that the correspondence between τ_{α} and τ_{shear} perfectly agrees with recent results of Preuß *et al.* [33,46]. These authors proposed an electrical circuit for describing the frequency-dependent behavior of glass-forming liquids. They used this circuit to calculate the mechanical from the dielectric response and vice versa, demonstrating that there is good agreement between the calculations and experimental data. These calculations clearly show that the structural relaxation process visible in the shear modulus spectra of primary alcohols can be identified with the structural relaxation process observed in dielectric spectra. On the other hand, the dependence of dielectric $\log \tau_{\text{main}}$ vs $\log \eta$, presented in Fig. 4(b) clearly shows that both τ and η have different pressure dependences with $s = 0.75 \pm 0.02$. Also the protonic dc conductivity, σ , can be used to monitor transport properties of liquids. The Stokes-Einstein (SE) equation describes

the ionic motions according to $D = kT/6\pi\eta r$, in which D is the diffusion coefficient and r is approximately the ionic radius. In order to relate σ to the diffusion, the Einstein-Nernst equation, $\sigma/D = ne^2/kT$, is used. Combining these two equations one arrives at the simple relation $\sigma\eta = \text{const}$. However, as presented in Fig. 4(c), in which $-\log \sigma$ vs $\log \eta$ for 2E1H is plotted, the ionic conductivity measured at elevated pressure is also strongly decoupled from η with $s = 0.52 \pm 0.02$.

Thus, our results clearly show that, contrary to ambient pressure data, compression above some characteristic pressure causes a decoupling between the main dielectric relaxation process and η . As mentioned earlier, during isothermal densification the Debye and the structural relaxation peaks start to overlap and, consequently, only a single, the non-Debye relaxation process is visible in dielectric spectra [19,31]. However, as demonstrated by Fragiadakis *et al.* [19], the amplitude and shape of this relaxation at high pressure is only slightly different as compared to the Debye process at ambient pressure. This indicates that the Debye relaxation remains the dominating process even at elevated pressure. However, whereas at ambient pressure the relation between both the τ_{α} and τ_{Debye} versus τ_{shear} can be described by the ED equation, the breakdown of this relation is observed during pressurization. Although, due to strong overlapping between the Debye and the structural relaxation peaks, it is impossible to estimate precisely the pressure changes of the shape of the dielectric loss peak, it can be expected, as already observed for pressurized glycerol or propylene glycol, that densification will dramatically broaden the relaxation function [47]. Such broadening is usually interpreted as a fingerprint of a significant modification of the H-bonded structures, which are present in associated materials, including monohydroxy alcohols. Also isobaric loss spectra, collected at ambient pressure, exhibit noticeable, although more subtle changes of shape with varying temperature. Thus, a breakdown of the ED relation is expected, in general, both for isothermal and isobaric data. However, as depicted in Fig. 4(a), in this limited range of shear relaxation times no decoupling between dielectric and mechanical relaxation times was detected at ambient pressure. It suggests that temperature variation alone at constant pressure does not modify significantly supramolecular hydrogen bonded structures, which are present in the monohydroxy alcohols. It has to be noted also that the satisfactory correspondence between the $\eta(P)$ and $\tau(P)$ dependences is observed only in a limited, low-pressure range. This leads to the conclusion that in this pressure range the H-bonded architecture remains only slightly influenced by compression. However, above some characteristic pressure, ca. 550 MPa, a significant departure from the ED relation is observed. It indicates a dramatic change of supramolecular structures above this pressure, e.g., by shortening of the transient chains, as suggested previously

[19,23]. This finding agrees with the fact that the increase of the steepness index describing the temperature dependence of τ occurs at the same pressure in which breakdown of the thermodynamic scaling has been found.

All these results demonstrate that compression plays a crucial role in the modification of hydrogen-bonded structures of the investigated primary alcohol. Moreover, it is worth noting that the dynamics of these structures do not change monotonically with compression but dramatic changes are observed only above some characteristic pressure. Further tests of the relation between the dielectric relaxation time and η at different thermodynamic conditions, especially during compression, for other monohydroxy alcohols will be essential for understanding the dynamics of hydrogen bonded structures in associated materials.

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