Watching Hydrogen-Bonded Structures in an Alcohol Convert from Rings to Chains
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Phys. Rev. Lett. 109, 167802 — Published 18 October 2012
DOI: 10.1103/PhysRevLett.109.167802
Watching Hydrogen Bonded Structures in an Alcohol Convert from Rings to Chains

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(Physical Review Letters)

Abstract

In hydrogen bonded liquids including monohydroxy alcohols, the prominent Debye process that often dominates the dielectric relaxation behavior is associated with hydrogen bonding, but its microscopic origin has remained unclear to date. High electric field impedance spectroscopy on 5-methyl-3-heptanol reveals a field induced change in the Kirkwood-Fröhlich correlation factor, $g_K$, viewed as evidence for an electric field driven conversion from ring to chain type hydrogen bonded structures. The concomitant rearrangement of the chain structure is observed to occur on the time scale of the Debye process, suggesting that the Debye peak of monohydroxy alcohols originates from a fluctuation of the net dipole moment via $g_K$ of the chain structures on a time scale that is largely controlled by viscosity.

PACS numbers: 77.22.Gm, 61.20.Qg, 64.70.pm, 77.22.–d
A significant driving force behind dielectric studies of water, alcohols, and other hydrogen bonded liquids is the goal of understanding the role of the hydrogen bond in these materials [1,2,3]. The prominent dielectric Debye process observed in many monohydroxy alcohols is a particularly characteristic feature that is generally associated with hydrogen bonded structures [4,5]. Such a polarization fluctuation that occurs with a single time constant is especially unusual in the case of glass-forming alcohols in their viscous regime [6,7], as most other supercooled liquids display significant relaxation time dispersions [8,9]. Although this Debye process in supercooled monohydroxy alcohols is responsible for the majority of the dielectric relaxation amplitude, it is well established that it is not the direct signature of structural relaxation. Instead, more reliable indicators of the primary (α) mode of structural relaxation such as mechanical [10] and enthalpy [11] relaxations are often a factor of 100 to 1000 faster than the Debye process [12]. A small dielectric signature of the α process is usually found within the dielectric spectrum of such alcohols [13], but its amplitude is very small compared with expectations based upon the dipole density.

While it has been clearly established that the Debye peak is not the immediate signature of structural relaxation [6,10,7,11,12,13,14,15], the microscopic origin of this dominant dielectric process is not at all clear. However, that this Debye type peak is linked to hydrogen bonded structures within the liquid has remained largely accepted and is supported by 'prepeaks' in the static structure factor of hydrogen bonded liquids [16,17]. The most important information on such supramolecular structures has been derived from the Kirkwood-Fröhlich correlation factor [1,2,18,19]. This factor, \( g_K \), gauges the average alignment of neighboring dipoles and thus the strength of the effective dipole moment relative to the true molecular dipole [1,2]:

\[
g_K = \frac{\mu_{\text{eff}}^2}{\mu^2} = 1 + z\langle \cos \theta \rangle .
\] (1)
Here, \( z \) is the average number of neighbors and \( \langle \cos \theta \rangle \) is the averaged cosine of the angle between neighboring dipoles. In practice, one uses Kirkwood-Fröhlich's generalization of Onsager's relation between dielectric constant \( \varepsilon_s \) and net dipole moment \( \mu_{\text{eff}} \) to obtain \( g_K \) from the knowledge of the dipole moment \( \mu \) of the molecule [2]. For many monohydroxy alcohols, \( g_K \) values in excess of unity are frequently observed, with the tendency to approach unity as the temperature is increased [2,18,19,20]. The interpretation of \( g_K > 1 \) and the concomitant high static dielectric constant is a preference for parallel alignment of neighboring dipoles, brought about by the hydrogen bond connectivity of the dipole bearing hydroxyl groups which then form chain-like structures. Accordingly, no such prominent Debye type process and large correlation factor is observed for diols [21], polyalcohols [22], or monohydroxy cases in which the hydrogen bonding capability is sterically hindered [23].

While the above \( g_K > 1 \) situation is found for numerous alcohols, their mixtures [24], and other hydrogen bonding liquids [25], some monohydroxy alcohols display \( g_K < 1 \), indicative of anti-parallel dipole alignment [2,18,19,20]. Particularly noteworthy is the series of octanol isomers studied by Dannhauser [18,19], who demonstrated that a methyl-group position can alter the correlation factor from \( g_K > 4 \) to \( g_K < 0.1 \). We have re-measured the dielectric spectra of the j-methyl-3-heptanol isomer series for \( j = 3, 4, 5, \) and \( 6, \) with all compounds (3M3H, 4M3H, 5M3H, 6M3H) obtained from Sigma-Aldrich and used as received. The dielectric relaxation measurements are based upon a Solartron SI-1260/DM-1360 gain/phase analyzer system and a Novocontrol Quatro temperature controller as described previously [12]. An isochronal (\( \nu = 1 \) kHz) plot of those results are shown in Fig. 1, indicating that the methyl group position greatly affects the amplitude and peak frequency of the Debye process (D), whereas the signatures of structural relaxation (\( \alpha, \beta \)) remain quite methyl-position invariant.
According to Dannhauser [18], the 5-methyl-3-heptanol isomer of that series displays a strong temperature dependence of the correlation factor $g_K$, which drops from 1.56 at $T = 180$ K to 0.67 at $T = 200$ K. The concomitant change in relaxation strength, $\Delta \varepsilon = \varepsilon_s - \varepsilon_\infty$, by more than a factor of 2 across the same $\Delta T = 20$ K range can be seen in Fig. 2, which includes $g_K$ values [18]. The interpretation of this result is based upon the model that cooling shifts the equilibrium of chain and ring type structures towards chains, thereby increasing $\Delta \varepsilon$ because chains and rings are associated with correlation factors $g_K > 1$ and $g_K \approx 0$, respectively [18,19]. Such a sensitivity of this chain/ring equilibrium constant implies that the free energy difference between those two configurations has to be small. Because the two structures differ considerably in their net dipole moment, one can imagine that the equilibrium constant is also a matter of the strength of an external electric field. The remainder of this Letter is devoted to exploring such a field effect.

Our experimental approach to high-field impedance data is based on the SI-1260 gain/phase analyzer, with the generator voltage amplified by a factor of 100 via a Trek Model PZD-350 high-voltage four-quadrant amplifier and connected to the 'high potential' side of the sample capacitor. That potential is measured via the voltage monitor signal (1V/100V) of the PZD-350 which is routed into the 'V1' input of the SI-1260. The 'low potential' side of the capacitor is connected to ground via a shunt of impedance $Z_s$, determined by a resistor $R_1 = 100 \, \Omega$ and a capacitor $C_1 = 100 \, \text{nF}$ in series and another resistor $R_2 = 10 \, \text{k}\Omega$ in parallel with the $R_1C_1$ branch. The increase of $Z_s$ towards lower frequencies by a factor of 100 helps to counteract the reduction of the voltage across the shunt when the current becomes very small due to low frequencies. The voltage drop across this shunt is fed into a home built buffer amplifier ($V_{\text{out}} = V_{\text{in}}$ for frequencies $\nu < 800$ kHz) that sustains 500 V$_p$ at the input and thus protects the SI-1260 against sample failure. The output of this amplifier gauges the current through the sample and is connected to the 'V2' input of the SI-1260. The analyzer determines the input voltages $V_1$
and \( V_2 \) at high and low field sine amplitudes for a given set of frequencies at zero bias voltage. The voltage across the capacitor is given by \( V_1 - V_2 \), the current through the sample is \( V_2/Z_s \). The components are calibrated using a disk capacitor with 20 mm diameter and a Teflon sheet of 25 \( \mu \)m thickness between the electrodes and linearity of the measurement system has been verified. For the sample measurement the stainless steel electrodes are spaced 25 \( \mu \)m apart by four Teflon strips of low surface area, the cell is filled with the liquid, and cooled in a Novocontrol Quatro \ell-N_2\) system.

Fig.3 compares the permittivity (\( \varepsilon' , \varepsilon'' \)) of 5-methyl-3-heptanol at \( T = 195 \text{ K} \) obtained at a peak field of \( E_0 = 170 \text{ kV/cm} \) with its low field (linear response) counterpart. Note that we use the notation \( \varepsilon' \) and \( \varepsilon'' \) also for results that are obtained outside the regime of linear response, with the understanding that these are apparent rather than true permittivity values. The obvious effect of the high field is to raise the permittivity for frequencies \( \omega < 1/\tau_D \), where \( \tau_D \) is the time constant of the Debye relaxation (the \( \alpha \) and \( \beta \) peak remain unresolved on the linear scale). Also, the peak frequency appears to be shifted to lower values, perhaps a result of a field induced increase in viscosity. The low-frequency non-linear dielectric effect amounts to \( \Delta \varepsilon/E^2 = +1\times10^{-15} \text{ m}^2/\text{V}^2 \).

We interpret this feature as a field induced increase of the correlation factor \( g_K \), resulting from shifting the chain/ring equilibrium towards the species with higher dipole moment, i.e., towards a preference of chain structures. The energy \( \mu g^{1/2}E \approx 80 \text{ J mol}^{-1} \) associated with a chain's dipole subject to a field \( E \) is around 1\% of the free energy \( (\Delta G = -7 \text{ kJ mol}^{-1}) \) estimated for ring formation [18], and thus a realistic value for shifting the dielectric constant a few percent. In further support of this picture, we note that the present field effect differs qualitatively from other non-linear dielectric effects: Langevin type dielectric saturation will always decrease permittivity [2], the increases in permittivity induced by energy absorption from the field are observed only at frequencies \( \omega > 1/\tau_D \) [26]. Because the present field effect increases \( \varepsilon' \) at low frequencies at which \( \varepsilon'' \approx 0 \), saturation or energy absorption
are not involved in this situation. More importantly, monohydroxy alcohols that display a pronounced Debye peak due to a high value of \( g_K \) show a reduction of \( \varepsilon_s \) consistent with saturation, even at fields as high as 453 kV/cm [26]. Consistent with previous studies of non-linear dielectric effects [27,28], the latter notion suggests that the effect observed in Fig. 3 is not only the alignment of existing chains, but an increase of chain numbers on the expense of rings. Accordingly, only hydrogen bonded liquids with a pronounced \( dg_K/dT \) slope and with \( g_K \) not too far from unity (e.g., chain/ring equilibria with little free energy difference) will show the present field effect. Accordingly, it is expected that significantly higher fields are needed to induce similar effects in the other isomers, 3M3H, 4M3H, and 6M3H.

Next, we ask whether a time scale for the ring/chain conversion can be inferred from the present experiments, as the kinetics had not been addressed thus far [18,19]. We emphasize again that the high field is applied via a sinusoidal voltage, \( E(t) = E_0\sin(\omega t) \), instead of a dc-voltage bias, which implies that the field induced modification needs to develop in the course of a half-wave \((= \pi/\omega)\) to modify the apparent permittivity. If the time required for this conversion process were significantly slower than the Debye time, \( \tau_D \), an increase of \( \varepsilon' \) at frequencies \( \omega \ll 1/\tau_D \) would be expected. If, on the other hand, the ring/chain conversion were fast compared with \( \tau_D \), then the relative increase of \( \varepsilon \) would appear with uniform magnitude across the Debye peak frequency range. This situation would occur if the conversion time were closer to the \( \alpha \)-process time scale \(( \tau_\alpha < \tau_D/10)\). The experimental results for the frequency dependence of the field induced relative increase of time dependent permittivity are depicted in Fig. 4. The dependent variable is

\[
\Delta \ln(\varepsilon' - \varepsilon_\infty) = \frac{\varepsilon'_{hi} - \varepsilon'_{lo}}{\varepsilon'_{lo} - \varepsilon_\infty},
\]

(2)

where 'hi' and 'lo' refer to 170 and 28 kV/cm, respectively, and \( \varepsilon_\infty \) is the dielectric constant in the limit of high frequency. The value of \( \varepsilon_\infty \) is subtracted because practically no field dependence is expected for
electronic polarizability. The results in Fig. 4b show that the quantity Δln(ε′−ε∞) decreases strongly from its plateau value at 4.5 % as the frequency approaches the Debye peak frequency (half height points in Fig. 4a). From this observation we conclude that the time scale associated with ring/chain conversion is very close to the Debye time τD. The negative Δln(ε′−ε∞) values originate from a small field induced increase of the Debye time, see also Fig. 3, an effect that appears to depend strongly on temperature. A more quantitative assessment of these kinetics will be possible when applying the time-resolved analogue [26] of these high-field experiments.

What can we learn regarding the origin of the dielectric Debye peak in monoalcohols and similar liquids? If the rings convert to chains on a time scale that is somewhat longer than the Debye time, it is likely that chains also reconfigure their structure on the same time scale that is largely governed by viscosity. Therefore, we view the Debye process as the signature of end-to-end vector fluctuations of chains, equivalent to fluctuations of their net correlation factor, gK. We envision that the chain structure changes from extended to more compact or curled topologies with a concomitant change in its net dipole moment, rather than a reorientation of a static structure. The analogy to polymer normal modes has been suggested previously by Gainaru et al. [29], where the end-to-end vector migration is assumed to result from attachment/detachment events at the chain ends. Our vision of chain-gK fluctuations is more similar to the model of sequential reorientations of molecules in chains developed by Levin and Feldman [30]. These chain structure changes may in part be promoted by chain scission and recombination of chain fragments, but details of the importance of the limited chain lifetime are not known. However, as correctly pointed out by Levin and Feldman [30], a considerable lifetime of dipole correlations are required for a sensible connection between chain structures and Debye process.

Due to the hydrodynamic aspects of the motion that affects the end-to-end distance and orientation, the correlation time of the chains gK will be governed for the most part by viscosity and its temperature
dependence. As a result, the activation traces of Debye and \( \alpha \) peaks are approximately parallel. Some added temperature effect may result from the temperature dependent partitioning into different chain lengths, rings, and other structures. Because the process is slow compared with the primary structural relaxation process as seen by mechanical or enthalpic modes [10,11,15], dynamical heterogeneities will have averaged out and only a single time constant prevails, i.e. the Debye nature of this polarization process originates from the environmental fluctuation being fast compared with \( \tau_0 \) [31].

Within this picture, the dielectric signature of the primary structural relaxation is very small because it originates from alkyl chain motion with some coupling to the hydroxyl dipole and/or from the small dipole moment that is oriented perpendicular to the chain [29]. As the hydroxyl dipole moment is orientationally locked into the chain structure, the dielectric amplitude associated with structural relaxation remain well below the expectation based on dipole density and the picture of independently reorienting dipoles.

In summary, we have observed a positive non-linear dielectric effect in viscous 5-methyl-3-heptanol, indicative of an electric field driven conversion from the non-polar ring structure towards more linear chains with a concomitant increase in the Kirkwood-Fröhlich correlation factor, \( g_K \), and in the dielectric amplitude of the Debye process. Because this effect occurs selectively for those monohydroxy alcohols for which the correlation factor is near unity and sensitive to temperature, the observation is supportive of Dannhauser's ring/chain equilibrium model for explaining the change from \( g_K < 1 \) to \( g_K > 1 \) as a function of temperature or methyl group position within the isomeric series of octanols. The main thrust of the present work stems from observing the kinetics of the ring/chain conversion and the result that it occurs on the time scale of the Debye process, the prominent dielectric polarization that is considerably slower than the primary structural relaxation and characteristic of many monohydroxy alcohols and some other hydrogen bonding liquids. We conclude that the Debye
peak is the signature of fluctuations of both length and orientation of the end-to-end vector of chain-like structures, equivalent to fluctuations of the chains Kirkwood-Fröhlich correlation factors.

This material is based upon work supported by the National Science Foundation under Grant No. CHE 1026124.
REFERENCES


Figure Captions

FIG. 1. (color online) Dielectric loss of four octanol isomers, 3M3H, 4M3H, 5M3H, and 6M3H, measured at a frequency of $\nu = 1$ kHz versus temperature. While the primary ($\alpha$) and secondary ($\beta$) structural relaxations occur at similar temperatures for all four isomers, the Debye process (D) position and amplitude changes systematically with the methyl group position.

FIG. 2. (color online) Dielectric loss spectra of 5M3H for temperatures between 215 K and 180 K as indicated. The considerable decrease of the Debye peak amplitudes with temperature leads to Kirkwood-Fröhlich factors, $g_K$, that change from above to below unity upon warming.

FIG. 3. (color online) : Storage ($\varepsilon'$) and loss ($\varepsilon''$) components of dielectric permittivity of 5M3H at a temperature $T = 195$ K. Dashed blue curves are for a low field of $E_0 = 28$ kV/cm, the red solid curves were obtained with a field amplitude of $E_0 = 170$ kV/cm. The effect of the higher field is to increase the steady state dielectric constant and to shift the peak frequency slightly to lower values.

FIG. 4. (color online) (a) Dielectric permittivity, $\varepsilon'$, versus frequency for 5M3H at the temperatures $T = 205, 200, 195, \text{ and } 190$. (b) Field induced effect on the curves in (a) in terms of $\Delta \ln(\varepsilon' - \varepsilon_\infty)$, the relative change of the permittivity (after subtracting its high frequency limit $\varepsilon_\infty$) induced by a field of $E_0 = 170$ kV/cm relative to the $E_0 = 28$ kV/cm case.
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Figure 1
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Figure 2

5-methyl-3-heptanol

$g_K = 0.41$

$g_K = 0.85$

$g_K = 1.56$

$v [\text{Hz}]$

Figure 2
Figure 3
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Figure 4

(a) ε'

(b) Δ ln(ε' - ε∞)

5-methyl-3-heptanol

ν [Hz]