

## Debye Type Dielectric Relaxation and the Glass Transition of Alcohols

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Many hydrogen-bonded liquids, especially glass-forming cases, display a dielectric relaxation behavior that differs qualitatively from that of other simple liquids. The majority of models aimed at explaining this unusual dielectric behavior associate the prominent Debye process with structural relaxation, viscous flow, and the glass transition. We perform dielectric and calorimetric studies of glass-forming mixtures of 2-ethylhexylamine and 2-ethyl-1-hexanol across the entire composition range. The kinetic glass transition temperature derived from the large dielectric Debye peak decreases, whereas that of the much smaller and asymmetrically broadened peak increases upon addition of amine. Only the latter feature coincides with the calorimetric glass transition results, implying that molecular structure and dielectric polarization fluctuate on time scales that can differ by orders of magnitude in many hydrogen-bonding liquids.

In many of the biologically and technically important fluids, hydrogen-bonding is a significant aspect of intermolecular interactions.<sup>1</sup> Hydrogen-bonds affect the structure, the thermodynamics, and the dynamics of such liquids. Due to the polar nature of these systems, dielectric relaxation is a common technique for studying the behavior of water, alcohols, and other protic liquids regarding the dynamics.<sup>2,3</sup> In a number of cases, the lowest frequency dielectric loss signal exhibits Debye character instead of a relaxation time dispersion<sup>4–6</sup> and an amplitude that exceeds the value expected on the basis of the molecular dipole moments.<sup>7</sup> To explain these well documented features for this important class of liquids, various models have been proposed: chainlike,<sup>8</sup> cyclic,<sup>9</sup> or other structural units,<sup>10</sup> where correlated dipole orientations are responsible for the large polarities and hydrogen-bonding or the size of the structural unit is assumed to result in the existence of only a single relaxation time. Common to the majority of these models is that the prominent Debye type dielectric process remains to be associated with molecular reorientation and structural relaxation.<sup>8,11–17</sup> A generally accepted explanation for this exceptional behavior of many hydrogen-bonded liquids is not yet available, and our understanding of hydrogen-bonded liquids in general must be considered incomplete until this problem is solved. Therefore, a decisive scrutiny of the relation between the Debye process and structural modes is required. In this Letter, we show that this dielectric polarization process occurs on time scales that can be much slower than those of the structural relaxation and viscous flow. We demonstrate this separation of polarization fluctuations from the molecular motion for viscous monohydroxy alcohol/amine mixtures, where the effects are particularly obvious.

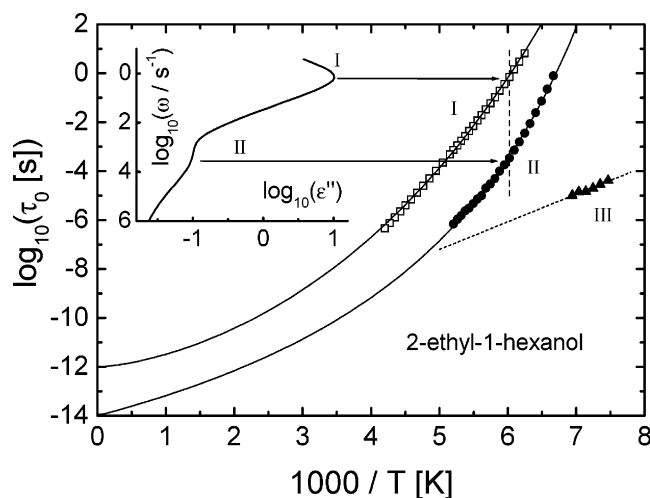
Glass-forming materials are those for which crystallization is avoided and further cooling eventually results in solidification by a gradual increase of the viscosity rather than by a phase transition.<sup>18</sup> Simple supercooled liquids as well as many glass-forming monohydroxy alcohols exhibit a super-Arrhenius or

Vogel–Fulcher–Tammann (VFT) type temperature dependence of their characteristic relaxation times  $\tau_0$ .<sup>19–21</sup>

$$\log_{10}(\tau_0/\text{s}) = A + B/(T - T_0) \quad (1)$$

The deviation from an Arrhenius behavior implied in eq 1 with  $T_0 > 0$  is usually accompanied by a dispersion regarding the relaxation times.<sup>22</sup> The dielectric signature of such a dispersion is a loss profile  $\epsilon''(\omega)$ , which spreads over a wide range of frequencies relative to the Debye type case.<sup>3,18</sup> This effect is most pronounced in the viscous regime near the glass transition temperature  $T_g$ , whereas deviations from the Debye type loss remain small when the dynamics approach gigahertz frequencies.<sup>23</sup> Dynamic processes with a single relaxation time (Debye type) are only rarely observed in the deeply supercooled state of a liquid,<sup>22</sup> and most exceptions from this rule are monohydroxy alcohols.<sup>4,5,6</sup>

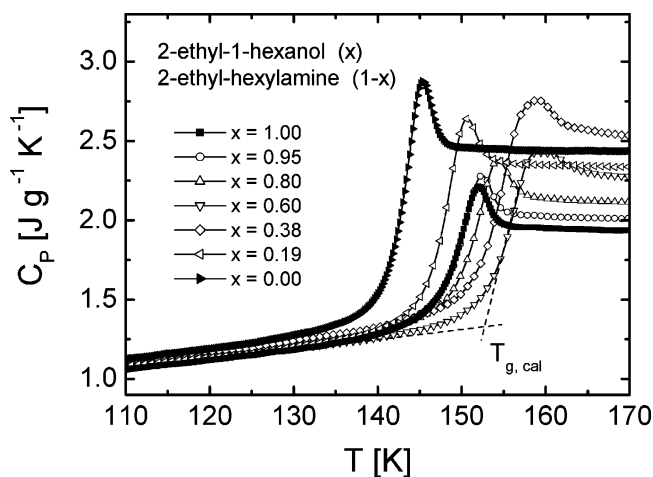
Observations regarding the unusual behavior of the Debye peak of many monohydroxy alcohols date as far back as 1963, when Litovitz and McDuffie have noted that the occurrence of a Debye type dielectric relaxation and a significant separation of the dielectric and mechanical time scales are correlated features.<sup>24</sup> An explanation was not provided, but the authors note that “This point warrants further investigation”.<sup>24</sup> Calorimetric assessments of  $T_g$  agree more with the kinetic ( $\tau_g = 100$  s) criterion applied to a smaller higher frequency peak rather than to the prominent Debye peak.<sup>19,25</sup> Simultaneous measurements of dielectric relaxation and photon correlation spectroscopy in 1-propanol indicate that density–density correlation times coincide with a faster and smaller asymmetrically broadened process, whereas there is little overlap with the Debye peak.<sup>26</sup> Additionally, the commonly observed correlation<sup>22</sup> between fragility index  $m$  (gauging the deviation from Arrhenius behavior) and stretching exponent  $\beta$  (indicating the degree of nonexponentiality of the correlation function) is strongly violated by the Debye peak,<sup>5</sup> whereas the smaller peak follows the expected trend.<sup>26</sup> Similarly, the separation between the Johari–



**Figure 1.** Activation traces of the three dielectric loss peaks of 2-ethyl-1-hexanol (2E1H). Symbols are experimental results, lines are guides only. The inset shows the loss spectrum at  $T = 166$  K (equivalent to the dashed vertical line in main figure) and identifies the correlation with the activation traces.

Goldstein peak and the primary process as predicted from the Coupling Model points to the smaller instead of the Debye type peak being the  $\alpha$ -relaxation.<sup>27,28</sup> According to a typical case shown in Figure 1, the peak designated “I” dominates the dielectric loss spectrum, but all characteristic signatures of supercooled liquid dynamics are exhibited by peaks “II” and “III”. Note that the amplitude of peak II is often only a few percent of the total dielectric signal. It is also observed that the Debye time of peak I remains a factor of 100 slower than typical structural relaxation times if extrapolated to infinite temperatures<sup>6,29</sup> and that the secondary peak III fails to merge with the large peak I in the regime of microsecond dynamics.<sup>26</sup> Despite these observations, the prominent Debye process is still being associated with structural relaxation features in hydrogen-bonding liquids.<sup>8,11–17</sup> The aim of the present study is to tell unambiguously which of the two dielectric peaks, the large Debye process (peak I) or the smaller asymmetrically broadened process (peak II), is the signature of structural relaxation.

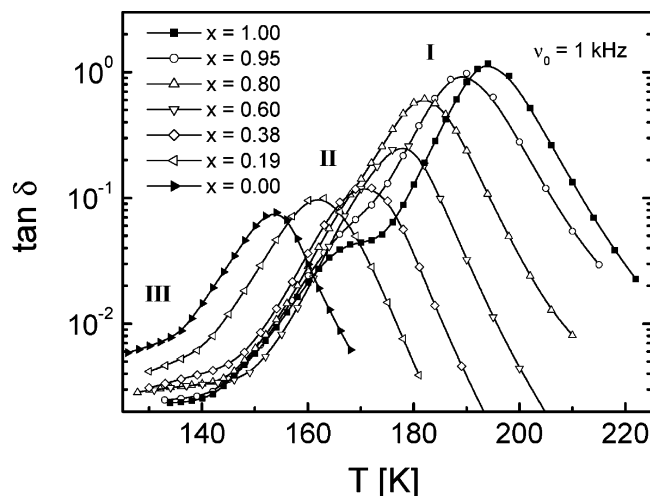
The glass transition at  $T_g$  identifies the temperature below which larger scale molecular motion and structure remain frozen. Therefore,  $T_g$  is one of the main properties used to characterize a glass-forming liquid in its viscous regime.<sup>30</sup> There are different experiments from which values of  $T_g$  can be inferred: calorimetric techniques based upon the heat capacity ( $C_p$ ) step at  $T_{g,cal}$ , viscosity ( $\eta$ ) measurements, and kinetic approaches where  $T_{g,kin}$  is inferred from relaxation time ( $\tau_0$ ) data.<sup>31</sup> Because no phase transition is involved, the typical criteria for identifying  $T_g$  are based upon somewhat arbitrary threshold values: the onset temperature of the heat capacity step  $C_p(T)$ , or a viscosity value  $\eta_g = \eta(T_g) = 10^{12}$  Poise =  $10^{11}$  Pa s, or a relaxation time limit  $\tau_g = \tau(T_g) = 10^2$  s. The two latter criteria are connected via Maxwell’s relation  $\eta = \tau G_\infty$ , with  $G_\infty \approx 1$  GPa being typical for molecular glass-formers near  $T_g$ .<sup>32</sup> The dielectric signature of molecular reorientation in polar supercooled liquids is a loss peak (primary or  $\alpha$ -process) that is broad and asymmetric in an  $\epsilon''(\omega)$  versus  $\log(\omega)$  graph, and possibly an additional smaller (secondary or  $\beta$ ) peak of the Johari–Goldstein (JG) type that persists in the glassy state.<sup>33–35</sup> Therefore, dielectric and structural relaxation times usually coincide and the temperature  $T_{g,kin}$  at which the dielectric relaxation time reaches 100 s is often in good agreement with the calorimetry result  $T_{g,cal}$ .



**Figure 2.** Differential scanning calorimetry results ( $\pm 20$  K/min) in terms of the heat capacity  $C_p$  versus temperature for mixtures of 2-ethyl-1-hexanol (2E1H) with 2-ethylhexylamine (2EHA). The various symbols are for different mole fractions of 2E1H ( $x$  mol) in 2EHA ( $1 - x$  mol) as indicated in the legend. Solid symbols indicate the pure liquids. These results are used to derive the calorimetric glass transition temperatures  $T_{g,cal}$ .

It might appear straightforward to identify the two possible kinetic values of  $T_g$  by applying the  $\tau_g = 100$  s criterion to peaks I and II and to compare these values with the calorimetric approach to  $T_g$ . Because calorimetric and kinetic values of  $T_g$  never coincide perfectly,<sup>36</sup> comparing  $T_{g,cal}$  with the kinetic counterparts for the two dielectric peaks as done previously<sup>19</sup> might not be considered entirely decisive. As an alternative, the present work focuses on the composition dependence of the various  $T_g$  values, i.e., on their derivatives with respect to the mole fractions. Differential scanning calorimetry (DSC) is a widely accepted technique for determining the glass-transition without limitations regarding particular classes of materials. DSC scans (Perkin-Elmer DSC-7) have been performed to quantify  $T_{g,cal}$  of glass-forming mixtures of 2-ethylhexylamine (2EHA, Aldrich 98%) and 2-ethyl-1-hexanol (2E1H, Aldrich 99+%) across the entire composition range. The  $C_p(T)$  traces obtained for cooling/heating rates of  $\pm 20$  K/min for the pure materials and for five intermediate mole fractions are shown in Figure 2. From these curves,  $T_{g,cal}$  values are determined from the onset temperature of the  $C_p$  increase upon heating.

Isothermal frequency scans for measuring the dielectric relaxation behavior in terms of  $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$  have been performed using a Solartron SI-1260 gain/phase analyzer equipped with a DM-1360 transimpedance amplifier for frequencies 10 mHz to 10 MHz. The sample temperature was controlled by a Novocontrol Quatro I-N<sub>2</sub> gas thermostat. A fraction of the actually collected dielectric data is compiled graphically as  $\tan \delta = \epsilon''/\epsilon'$  versus temperature in Figure 3. In the alcohol rich composition regime, three peaks (I–III) can be identified and their appearance is similar to those of many monohydroxy alcohols. Peak I is a pure Debye process, peak II is asymmetrically broadened and the much smaller peak III is very broad but symmetric. Peaks I and II both follow super-Arrhenius or VFT type temperature dependences, whereas peak III exhibits Arrhenius behavior. For lower alcohol content,  $x_{2E1H} < 0.8$ , only peaks II and III can be resolved; i.e., the Debye process disappears. To determine kinetic  $T_g$  values from the dielectric results, the isothermally recorded susceptibilities  $\epsilon''(\omega)$



**Figure 3.** Dielectric loss tangent,  $\tan \delta$  (measured at a frequency of 1 kHz), versus temperature for mixtures of 2-ethyl-1-hexanol (2E1H) with 2-ethylhexylamine (2EHA). The various symbols are for different mole fractions of 2E1H ( $x$  mol) in 2EHA ( $1 - x$  mol) as indicated in the legend. Solid symbols indicate the pure liquids. Roman numbers indicate the three distinct peaks of the alcohol rich mixtures, a Debye peak (I), an asymmetric smaller peak (II), and a symmetric very small peak (III).

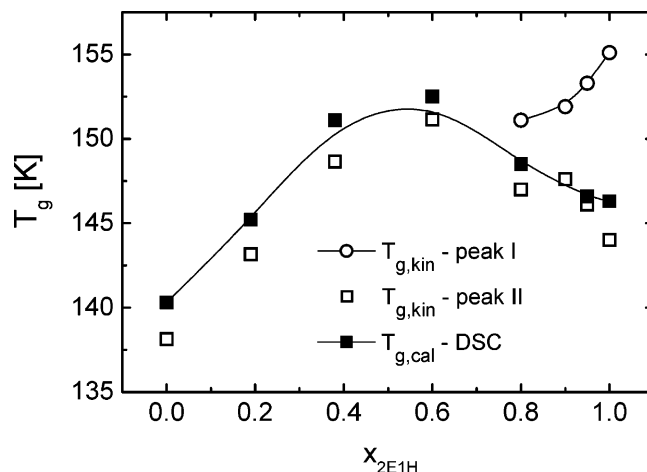
are subject to fits according to

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon_I}{1 + i\omega\tau_I} + \frac{\Delta\epsilon_{II}}{[1 + (i\omega\tau_{II})^\alpha]^\gamma} + \frac{\Delta\epsilon_{III}}{1 + (i\omega\tau_{III})^\alpha} + \frac{\sigma_{dc}}{\epsilon_0 i\omega} \quad (2)$$

where the rhs terms are the infinite frequency dielectric constant  $\epsilon_\infty$ , a Debye (D) process, a Havriliak–Negami (HN) process, a Cole–Cole (CC) process, and a term that accounts for dc conductivity. The individual relaxation strengths,  $\Delta\epsilon_I > \Delta\epsilon_{II} > \Delta\epsilon_{III}$ , and the relaxation time constants,  $\tau_I > \tau_{II} > \tau_{III}$ , are identified by the peak index I, II, or III. The exponents quantify the symmetric ( $\alpha$ ) and asymmetric ( $\gamma$ ) broadening. The steady-state dielectric constant is given by the sum  $\epsilon_s = \epsilon_\infty + \Delta\epsilon_I + \Delta\epsilon_{II} + \Delta\epsilon_{III}$ . In this analysis, we focus on the results for  $\tau_I(T)$  and  $\tau_{II}(T)$  using VFT fits to obtain  $T_{g,kin}$  values for peaks I and II.

The main result of this study is presented in Figure 4, showing the glass transition temperatures  $T_{g,cal}$  and the comparison with  $T_{g,kin}$  values for peak I and peak II. The conclusion from this graph is immediately clear: The composition dependence and even the absolute values for the calorimetric and kinetic  $T_g$ 's agree if (and only if) the dielectric peak II is considered. In contrast, peak I exhibits the reverse trend regarding the slope,  $dT_g/dx$ , with respect to the mole fraction  $x$ . Compared with previous assessments, this conclusion does not rely on the values of  $T_g$ , but rather on the sign of the slope  $dT_g/dx$ . We consider this an unambiguous identification of peak II instead of peak I being associated with features such as structural relaxation, viscous flow, and the glass transition.

We support the above conclusion by inspecting the amplitudes of peak III as a function of temperature. For all compositions, peak III displays the characteristic properties of a Johari–Goldstein type secondary or slow  $\beta$ -relaxation.<sup>28</sup> It has been observed in numerous examples that the relaxation strength of the JG peak,  $\Delta\epsilon_{III}$ , increases with temperature more rapidly above  $T_g$ .<sup>26,28,34,37</sup> According to the present results, this further signature of  $T_g$ , the temperature at which the slope  $d\Delta\epsilon_{III}/dT$  changes, follows the composition dependence of the other two



**Figure 4.** Comparison of the dielectric and calorimetric glass transition temperatures  $T_g$  for mixtures of 2-ethyl-1-hexanol (2E1H) with 2-ethylhexylamine (2EHA) as a function of composition in terms of the mole fraction  $x_{2E1H}$  of 2E1H. Solid squares are  $T_{g,cal}$  values derived from the onset temperatures of the data in Figure 2. Open squares and circles refer to the  $T_{g,kin}$  results ( $\tau_g = 100$  s) for the dielectric loss peak II and peak I, respectively.

values,  $T_{g,cal}$  and  $T_{g,kin}$  derived from peak II. Similar to the trend of the calorimetric  $T_{g,cal}$  in Figure 2, the temperature of the  $\Delta\epsilon_{III}(T)$  kink increases and then decreases along the composition scale, in support of peak II rather than peak I being associated with structural relaxation. Furthermore, similar  $T_{g,cal}$  maxima have been reported for other amine/alcohol mixtures.<sup>38,39</sup>

What is the relevance of deciding which dielectric peak to link to structural relaxation and viscous flow? Using the Debye type peak I as an indicator of the time scale of nondielectric relaxation phenomena in a given material can lead to the glass transition temperature  $T_g$  being offset by as much as 12 K or to the time constant  $\tau$  being displaced from the true value by a factor as high as 2000.<sup>6</sup> Also, peak I suggests the absence of a relaxation time dispersion, whereas the true primary relaxation is subject to a significant asymmetric broadening. Solvation dynamics experiments<sup>40,41</sup> deserve special attention in this respect, because both dipolar and nondipolar (mechanical) solute/solvent combinations are being used for studying the solvent response to the optical transitions of the chromophore. For the case of viscous 1-propanol, the time scales of dipolar and mechanical solvation have been observed to reflect the spectrally separated dielectric peaks I and II, respectively.<sup>42</sup> Another very important implication of peak II instead of peak I being related to structural relaxation is the need for a new model for rationalizing the dielectric Debye mode in a number of monohydroxy alcohols which is compatible with the observation of unexpectedly slow polarization fluctuations reflected in peak I.

In summary, we have exploited the composition dependent glass transition temperature for mixtures of 2-ethylhexylamine and 2-ethyl-1-hexanol to perform an unambiguous identification of the dielectric peak which may be considered the direct result of structural relaxation. Strong evidence is found that a kinetic approach to  $T_g$  is bound to fail if based upon the Debye type dielectric process observed in many alcohols. The conclusion of this study is that the prominent dielectric signal (peak I) with Debye character does not coincide with structural relaxation. It is rather a relaxation phenomenon that is observed only by dielectric measurements (and related techniques which are sensitive to polarization fluctuations) without exhibiting a resolved analogous mechanical or calorimetric signature. Accordingly, a rationale for this dielectric loss peak of substantial

amplitude will have to explain the displacement of charge that is not directly correlated with the (faster) motion of the molecules. Structural relaxation can still be identified in these hydrogen-bonding liquids via dielectric relaxation techniques, but it appears only as a small (few percent relaxation strength) higher frequency feature (peak II).

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