

Entropic Nature of the Debye Relaxation in Glass-Forming Monoalcohols

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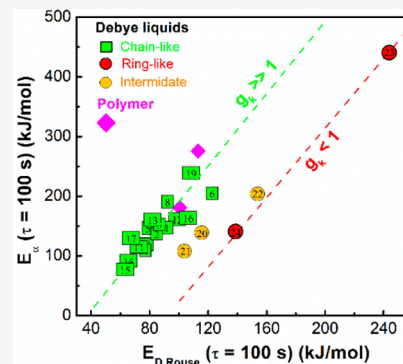


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Supporting Information

ABSTRACT: The dynamics and thermodynamics of the Debye and structural (α) relaxations in isomeric monoalcohols near the glass transition temperature T_g are explored using dielectric and calorimetric techniques. The α relaxation strength at T_g is found to correlate with the heat capacity increment, but no thermal signals can be detected to link to the Debye relaxation. We also observed that the activation energy of the Debye relaxation in monoalcohols is quantitatively correlated with that of the α relaxation at the kinetic T_g , sharing the dynamic behavior of the Rouse modes found in polymers. The experimental results together with the analogy to the Rouse modes in polymers suggest that the Debye process in monoalcohols is an entropic process manifested by the total dipole fluctuation of the supramolecular structures, which is triggered and driven by the α relaxation.



As the structural α relaxation is invariably observed in the supercooled liquid regimes by various relaxation spectroscopic techniques,^{1–4} an extra Debye-type relaxation is frequently detected in the dielectric relaxation of monoalcohols and secondary amides, showing a slower dynamics than that of the α relaxation.^{5–9} The study of the Debye relaxation is vital to understand the complicated molecular configurations and motions underlying hydrogen-bond interactions as well as the glass transition problem.^{10–14} Additionally, insight into the Debye relaxation in monoalcohols is expected to provide guidance for design and analysis of molecules with complex hydrogen-bond aggregations such as water and proteins.^{15,16}

However, the physical origin of the Debye relaxation remains to be clarified. The transient chain model suggested that the Debye relaxation involves the reorientation of the end-to-end dipole vector, as achieved by the self-restructuring of the hydrogen-bonded chain accompanied by the attachment and detachment of hydrogen bonds.^{17,18} Later, it was found that the ring–chain transformation occurs at the timescale of the Debye relaxation, and the Debye relaxation is viewed as the fluctuations of the Kirkwood–Fröhlich correlation factors g_K .¹⁹ The Debye relaxation was also, recently, explored by the depolarized light scattering, emphasizing the linking of the motions of supramolecular hydrogen-bonded chains responsible for the Debye relaxation to those of the α relaxation, which shows dynamic anisotropy.²⁰ It is hence expected that the Debye relaxation might be an athermal process. Meanwhile, the Debye relaxation is kinetically typified by thermal activation with a remarkable temperature dependence of the relaxation time, showing strong energy barriers.^{21–23} It appears that the rationalization of the phenomenon of the Debye

relaxation requires the comprehensive understanding of its thermodynamic connections; yet, thermodynamic studies of the Debye relaxation remain rare.²⁴ Here, the thermodynamics and dynamics involved in the glass transitions of eight hexanol isomers were investigated using calorimetric and dielectric measurements.²⁵ The absence of thermal contributions to the Debye relaxation is confirmed. The strong dependence of the kinetic activation energy of the Debye relaxation on that of the α relaxation is elucidated. The results conclude that the Debye relaxation is, in nature, an entropy-driven process.

Eight *n*-hexanol isomers including four primary monoalcohols (2-methyl-1-pentanol (2M1P, $\geq 99\%$), 3-methyl-1-pentanol (3M1P, $\geq 99\%$), 4-methyl-1-pentanol (4M1P, $\geq 97\%$), 2-ethyl-1-butanol (2E1B, $\geq 98\%$)), and four secondary monoalcohols (3-methyl-2-pentanol (3M2P, $\geq 99\%$), 4-methyl-2-pentanol (4M2P, $\geq 98\%$), 2-methyl-3-pentanol (2M3P, $\geq 99\%$), and 2-hexanol ($\geq 98\%$)) were purchased from Sigma-Aldrich and used without further purification. The calorimetric measurements were conducted using a PerkinElmer diamond differential scanning calorimetry (DSC) equipped with a liquid nitrogen cooling system.²⁶ Specimens sealed in aluminum pans were subjected to a cooling–heating cycle process around their glass transition temperatures T_g with a fixed scan rate of 20 K/min. The heat-capacity increments $\Delta C_p(T_g)$ were determined

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by the differences in C_p between the supercooled liquids and glasses at T_g .

The dielectric measurements were performed using a Novocontrol broadband dielectric spectrometer (Concept 80) equipped with a liquid nitrogen cooling system.²⁷ Specimens held between two brass electrodes separated by two Teflon strips (a thickness of 25 μm) were isothermally measured in the frequency range from 0.1 Hz to 10 MHz. The temperature was controlled using a nitrogen gas cryostat (Novocontrol Quatro) with an accuracy of ± 0.1 K. The dielectric data were analyzed using Debye and Havriliak–Negami (HN) equations together with a conductivity term,²⁸

$\epsilon^*(\omega) = \epsilon_\infty + \sum_i \frac{\Delta\epsilon_i}{[1 + (i\omega\tau_i)^{\alpha_i}]^{\gamma_i}} + \frac{\sigma_{dc}}{i\epsilon_0\omega}$, where ϵ_∞ is the high-frequency dielectric constant, $\Delta\epsilon_i$ represents the dielectric relaxation strength, τ_i is the dielectric relaxation time, α_i and γ_i are the profile shape parameters of the relaxation dispersion, and σ_{dc} represents the dc conductivity. $\alpha_i = \gamma_i = 1$ restores the Debye mode. To increase the accuracy of the α relaxation parameters, two methods were used. Initially, the combination of the Debye and HN equations is used for the whole imaginary loss spectra (Method 1).²⁹ Alternatively, the α relaxation is extracted by subtracting the fitted Debye relaxation from the dielectric constant and loss (Method 2). In particular, the α relaxation strength determined from the HN fitting of the imaginary spectra is examined by subtracting the Debye relaxation strength from the total strength in the real part, which can be accurately determined by subtracting the high-frequency dielectric constant (ϵ_∞) from static dielectric constant (ϵ_0) at a certain temperature,³⁰ neglecting the impact of secondary relaxations.

Figure 1 presents the dielectric loss spectra normalized by the Debye relaxation frequency ($\nu_D \sim 1$ Hz) for (a) primary

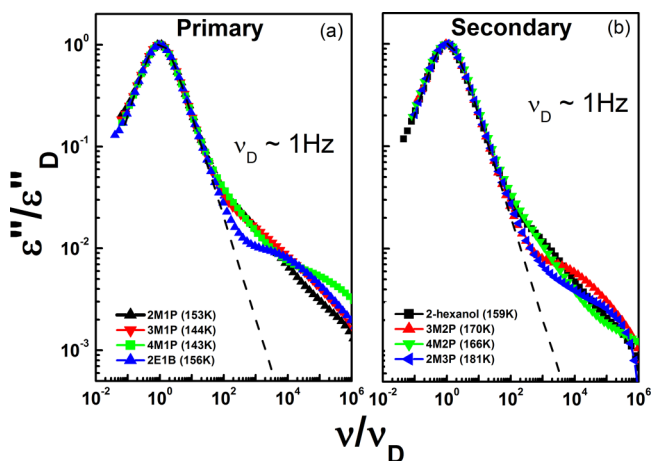


Figure 1. Normalized dielectric loss (ϵ'') spectra for (a) primary and (b) secondary hexanol isomers measured at various temperatures.

and (b) secondary hexanol isomers. The dashed lines depict the profile of the Debye relaxation. The relaxation strength data of the Debye and α relaxations are listed in the Supplementary Table 1. Two different methods mentioned in the experimental section were used to yield the α relaxation strength $\Delta\epsilon_\alpha(T_g)$ of the isomers, which gave comparable results, as seen in Figure S1. Figure 2 demonstrates the calorimetric data around the individual glass transition for the eight isomers. Interestingly, 2M1P is found to have the largest $\Delta C_p(T_g)$ and approximately the largest $\Delta\epsilon_\alpha(T_g)$ among the

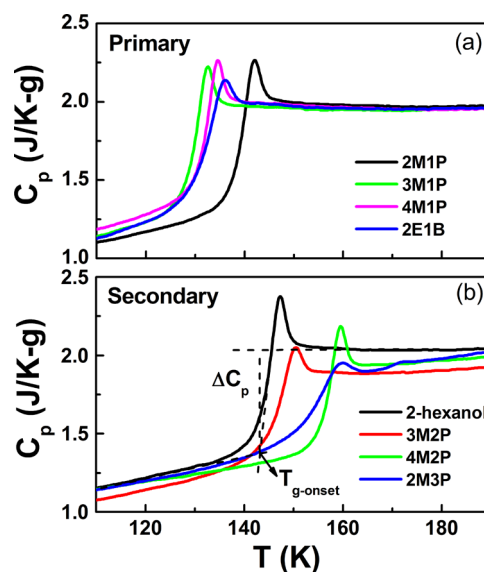


Figure 2. Thermal glass transition heat capacities C_p of eight hexanol isomers using a fixed cooling and heating rate of 20 K/min for (a) primary and (b) secondary monoalcohols.

primary alcohols. By contrast, 2M3P exhibits both the smallest $\Delta C_p(T_g)$ and $\Delta\epsilon_\alpha(T_g)$ in the group of secondary alcohols. The aforementioned test results might imply some correlation between $\Delta C_p(T_g)$ and $\Delta\epsilon_\alpha(T_g)$ in the isomeric hexanols. However, no correlation between $\Delta\epsilon_D(T_g)$ and $\Delta C_p(T_g)$ can be detected.

Figure 3 shows the reciprocal temperature dependence of the Debye and α relaxation times. The solid lines represent the Vogel–Fulcher–Tammann (VFT) fits, $\log_{10} \tau = A + B/(T -$

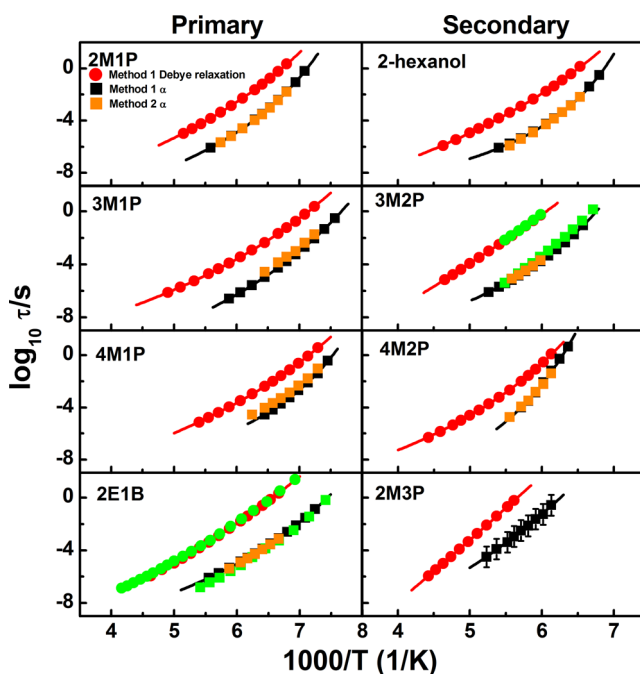


Figure 3. Reciprocal temperature dependence of the dielectric Debye and α relaxation times of eight hexanol isomers. The solid line represents the VFT fitting. Red and black points were calculated using Method 1, orange points were obtained from Method 2, and green points are from the published data.^{25,31}

T_0), where τ is the relaxation time, A , B , and T_0 are constants. The dynamic separations of the Debye and α relaxations in the timescale at T_g are noticeable in 2E1B, 3M2P, and 2M3P. In contrast, the two dynamics of 4M2P tend to merge in the vicinity of T_g . For comparison, data from the literature are also added.^{25,31}

Furthermore, we examined the relationship between $\Delta C_p(T_g)$ and $\Delta \varepsilon_\alpha(T_g)$ for more monoalcohols and non-Debye polyalcohols, as shown in Figure 4. For comparison, the

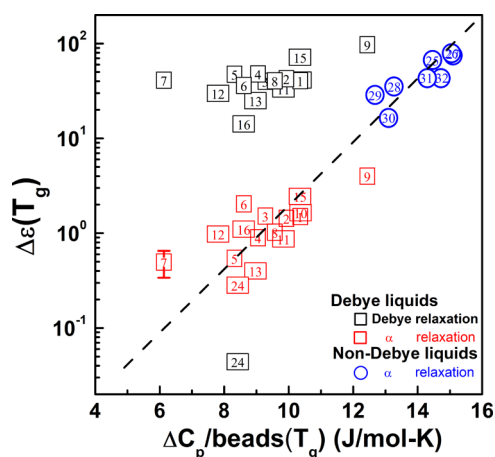


Figure 4. Dependence of the relaxation strength on the normalized heat capacity increment at the glass transition temperature T_g for Debye and non-Debye liquids. Hexanol isomers are numbered 1–8, and other Debye liquids are numbered 9–24. Details of the serial numbers are available in the Supplementary Table 1.

effect of different numbers of atomic groups on $\Delta C_p(T_g)$ needs to be compensated and, thus, the number of beads is used to normalize $\Delta C_p(T_g)$, as proposed by Wunderlich to represent the number of molecular degrees of freedom.^{32,33} The quantity refers to the number of atoms or rigid groups, which can rotate or reorientate such as $-\text{CH}_2-$ or the phenyl group. Such a practice has been applied to various glass formers.³⁴ Experimental measurements of the dielectric relaxation and calorimetric glass transition in polyalcohols always reported larger $\Delta \varepsilon_\alpha(T_g)$ and $\Delta C_p(T_g)$ than those of monoalcohols.^{35–37} Studies of nonassociated polar liquids also revealed the correlation of the dielectric constant and liquid–solid C_p difference.³⁸ However, these reported conclusions are in a qualitative fashion. Here, for the first time, we show the quantitative correlation for the family of alcohols by using the concept of beads to normalize the heat-capacity increments of glass transition. Considering the fact that $\Delta C_p(T_g)$ is proportional to the increase in the mean-square entropy fluctuation at T_g ,³⁹ and $\Delta \varepsilon_\alpha(T_g)$ addresses roughly the intermolecular potential,⁴ their correlation in glass-forming alcohols thus implies the dependence of the intermolecular potential on entropy fluctuation due to hydrogen-bond interactions. This correlation also provides new evidence of linking glass-transition thermodynamics and kinetics. Note that this correlation is only applicable for alcohols, and not universal when compiling the data of $\Delta \varepsilon_\alpha(T_g)$ and $\Delta C_p(T_g)$ for other types of liquids, reminiscent of the reported correlation of $T_g \Delta C_p$ and the number of beads,⁴⁰ where one master curve does not cover all types of glass-forming liquids. The data of Debye relaxation strength $\Delta \varepsilon_D(T_g)$ are also noted; no prominent tendency of the $\Delta \varepsilon_D(T_g)$ with $\Delta C_p/\text{beads}(T_g)$ is

seen, suggesting the thermal irrelevance to the Debye relaxation dynamics. This is not surprising when considering the fact that the nonexponential parameter β in Debye liquids, as determined by the enthalpy method, is far from unity for the Debye relaxation but shows remarkable agreement with those of the dielectric α relaxation.²⁵ The results indicate the Debye relaxation is not involved in the thermal glass transition. Similarly, early studies of the dynamic heat capacity measurements of 2-ethyl-1-hexanol at the fixed frequency $\nu = 10$ Hz did not detect the Debye relaxation.²⁴ It is therefore confirmed that the Debye relaxation does not make any contribution to the thermal glass transition.

Figure 5 presents the activation energies of the Debye and α relaxations at the kinetic T_g for the monoalcohols. The

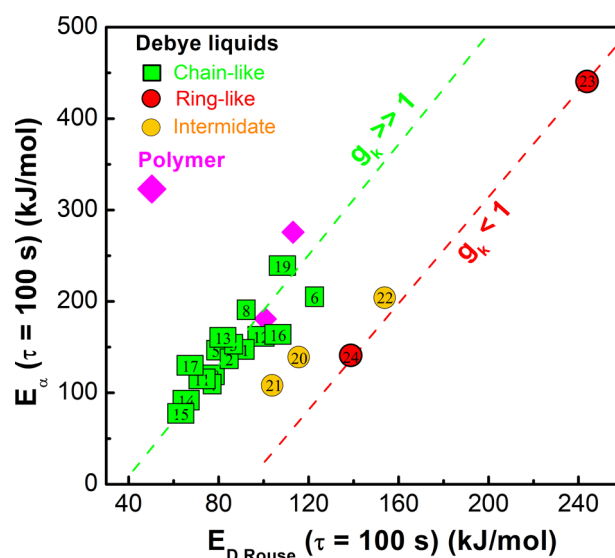


Figure 5. Correlation of activation energies between Debye and α relaxations for Debye liquids and polymers at the relaxation time 100 s. The solid lines serve as guides only. Data of polymers DCIIR and DPIB from the ref 46 are added. The sequence numbers in the figure are consistent with those in the Supplementary Table 1.

activation energies are calculated from the data in Figure 3 and references through the equation^{41,42} $E_{D,\alpha} = R \left(\frac{d \ln \tau}{d(1/T)} \right) \Big|_{\tau=100s}$, which are available in the Supplementary Table 1. Close inspection found that the alcohols can be well divided into two groups on the basis of the calculated Kirkwood factor g_K at the glass transition. g_K is a critical factor to evaluate the supramolecular structure induced by hydrogen bonds,¹⁹ for which $g_K > 1$ corresponds to the chainlike supramolecular structures while $g_K < 1$ holds for the ringlike ones.^{29,43} Alcohols with chainlike supramolecular structures featured by $g_K \gg 1$ show a linear relation that has a larger E_α -axis intercept than that of the linear relation of alcohols with ringlike ones manifested by $g_K < 1$ such as 4-methyl-3-heptanol ($g_K = 0.2$)²⁹ and 2-hexyl-1-decanol ($g_K = 0.27$).⁴⁴ Some alcohols fall into the area between the two lines. It appears that the distinct supramolecular structures formed by hydrogen bonds give rise to the different activation correlation between the Debye and α relaxations. Albeit recent studies have reported the correlations of the Debye and α relaxations,^{20,45} the quantitative correlation between the Debye and α relaxations established in the present work allows us to make a detailed comparison with the Rouse

modes and α relaxations in polymers. Using the thermal activation data of polymers DPIB (polyisobutylene doped with 1 wt % *p*-tert-octylphenolic resin) and DCIIR (chlorinated butyl rubber doped with 1 wt % *p*-tert-octyl phenolic resin),⁴⁶ the activation energies of the Rouse modes and α relaxation were calculated at the relaxation time 100 s. Interestingly, we found that the Debye relaxation and Rouse modes have extremely similar activation correlation with their corresponding α relaxations, revealing a new feature existing commonly for the two dynamics, in addition to the earlier observations of the weaker temperature dependence relative to their α relaxations and the exponential parameter of $\beta = 1$.^{47,48} Rouse dynamics and the corresponding α relaxation have been reported to share the same friction factor, and⁴⁹ the same conclusion was also recently suggested for the Debye and α relaxations in monoalcohols.⁵⁰

The Rouse modes in polymers have been widely known to be an entropic process,^{51–53} as interpreted in terms of a bead-spring model.⁵⁴ Figure 5 appears to provide new evidence of the dynamic similarity of the Debye relaxation in monoalcohols and the Rouse modes in polymers by correlating their activation energies with those of the α relaxations. Together with the experimental identification of the athermal process for the Debye relaxation, the analogy of the Debye process in monoalcohols as transient chains to the Rouse modes in polymers leads us to identify the former to be entropic in origin. The transient chain model also emphasized that the Debye relaxation is associated with the self-restructuring of hydrogen-bonded chains,¹⁷ implying an entropic behavior. Entropic processes are often found in protein dynamics⁵⁵ as well as some phase transitions,^{56,57} and thus the identification of the entropic nature for the Debye relaxation dynamics would help understand the molecular motions in hydrogen-bonded supramolecular structures. It is suggested that the Debye relaxation in monoalcohols is mainly self-driven by the changes of the configurational entropy of the supramolecular structures, showing strong correlation with the α relaxation.

In summary, we investigate the dielectric and enthalpy relaxations of isomeric hexanols using the calorimetric and dielectric spectroscopies. When extending to more monoalcohols and polyalcohols, for the first time two critical features of the Debye liquids are found, one being the prominent correlation of the α relaxation strength and the normalized heat-capacity increment at the glass transition, and the other the strong dependence of the Debye activation energies on those of the α relaxations. The new finding leads to the conclusion that the Debye relaxation in monoalcohols is an entropic process in nature, which is triggered and driven by the α relaxation contributed by the configuration changes of hydrogen-bonded supramolecular structures.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.0c01499>.

α relaxation strength of eight hexanol isomers calculated at the glass transition by the two methods listed in the experimental section (Figure S1); thermodynamics and kinetics data of monoalcohols, polyalcohols, and polymers (Supplementary Table 1) (PDF)

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Notes

The authors declare no competing financial interest.

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