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Glass Transitions in Viscous Monohydroxy Alcohols: Calorimetry Versus Dielectric Relaxation

Li-Min Wang · Ranko Richert

Abstract An extensive comparison of the calorimetric and dielectric measurements of the glass transitions in both monohydroxy alcohols and other molecular liquids is presented, with only these alcohols displaying an additional pronounced dielectric Debye peaks. It is found that the calorimetric T_g's of the non-Debye liquids with moderate cooling and heating rates ($\pm 20\,\mathrm{K \cdot min^{-1}}$, for example) are slightly higher than the kinetic ones which are determined as the temperatures at which the relaxation time is 100 s. As the difference does not exceed 3 K, this relation of calorimetric and kinetic T_g's is used as 'standard.' Two kinetic glass transitions from the dielectric relaxation of Debye type monohydroxy alcohols are identified, and it is found that the Debye process is not the signature of the glass transition.

Keywords Calorimetry · Dielectric relaxation · Glass transition · Kinetics · Monohydroxy alcohols

1 Introduction

Dielectric relaxations are often used to study the structural relaxation of supercooled liquids and to determine the glass transitions. For the majority of glass forming liquids, the calorimetric glass transition temperature, $T_{\text{g-cal}}$, which is determined based on the onset temperature of the heat capacity jump from the glassy to the liquid state, is

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generally comparable to the kinetic one, $T_{\text{g-kin}}$, at which the average structural relaxation time approaches 100 s. However, for many monohydroxy alcohols and some other hydrogen bonding liquids, this correlation is more complicated. The dielectric spectra of generic glass-formers exhibit one primary or α-relaxation, which is non-exponential (non-Debye) in the supercooled liquid regime. By contrast, many monohydroxy alcohols have one pronounced Debye type (exponential) dielectric relaxation process and a smaller and faster non-Debye process [1,2]. We refer to the latter as 'Debye-type' liquids. The two dielectric relaxations in monohydroxy alcohols give rise to two distinct kinetic glass transitions, $T_{\text{g-kin-D}}$ and $T_{\text{g-kin-}\alpha}$, which correspond to the Debye peak and the non-Debye α-relaxation, respectively. However, heat capacity measurements on these alcohols do not exhibit two transitions. Therefore, it needs to be elucidated which dielectric relaxation is to be identified with the 'true' glass transition, and which is associated with the calorimetric T_g and with viscous flow.

The view that the Debye-type dynamics reflects the glass-transition dependent structural relaxation has been questioned in recent years [1–4]. Some basic observations concerning the Debye relaxations have shown that this peak is inconsistent with the characteristics of structural relaxations. For example, other measurements such as mechanical relaxation do not exhibit these exponential relaxation processes in the dynamics of glasses and supercooled liquids [5]. Additionally, the exponential behavior contrasts the well-established correlation linking the broadening parameter of relaxation times to the liquid fragility, which is based upon numerous non-Debye supercooled liquid dynamics [6].

In this article, the relationship of the calorimetric and the kinetic glass transitions is studied based on the generic (non-Debye) liquids. This is expected to set the 'standard' used to assess the two kinetic glass transitions found in the dielectric relaxation of Debye-type monohydroxy alcohols.

2 Results and Discussion

Figure 1 shows the calorimetric and kinetic glass-transition temperatures of a monohydroxy alcohol, 2-ethyl-1-hexanol. The value of $T_{\text{g-cal}}$ is determined by using the onset temperature of the heat-capacity jump from the glass to supercooled liquid state. Since $T_{\text{g-cal}}$'s of glass-forming liquids depend on both heating and cooling rates, all the $T_{\text{g-cal}}$'s used in this article are derived from cooling/heating rates of $\pm 20\,\text{K}\cdot\text{min}^{-1}$. It is important to set strict experimental conditions for a reliable comparison, because heat-capacity measurements from vacuum adiabatic calorimetry usually give $T_{\text{g-cal}}$ values much below those from the $\pm 20\,\text{K}\cdot\text{min}^{-1}$ cooling/heating rate case. All the calorimetric data here are from a Perkin-Elmer DSC-7 with temperature and energy corrected prior to the measurements [7]. The kinetic glass temperature is defined here as the temperature at which the relaxation time approaches 100 s. The Debye and non-Debye relaxation dynamics of monohydroxy alcohols are non-Arrhenius, and can be fitted well in the supercooled regimes with the Vogel-Fulcher-Tammann equation, $\tau = \tau_0 \exp[B/(T - T_0)]$, where τ_0, B and T_0 are constants and τ_0 is of the order of phonon times, $\sim 10^{-14}$ s. Therefore, both $T_{\text{g-kin-D}}$ and $T_{\text{g-kin-}\alpha}$ can be obtained with only a little extrapolation, shown as lines in Fig. 1. All the dielectric

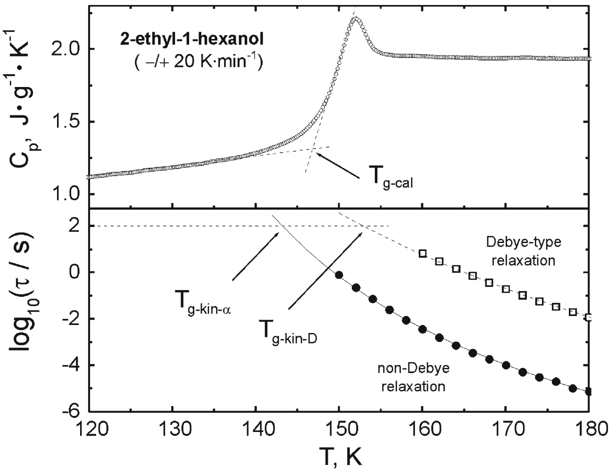

Fig. 1 Definitions of calorimetric and kinetic glass transition temperatures, $T_{g\text{-cal}}$ and $T_{g\text{-kin}}$. Dielectric measurements of monohydroxy alcohols exhibit two main relaxations, which correspond to two $T_{g\text{-kin}}$'s

data are from our dielectric apparatus with frequency-dependent impedance measurements using a Solartron 1260 gain-phase-analyzer equipped with a Mestec DM-1360 transimpedance amplifier and liquid nitrogen cooling system [2,4]. Therefore, errors originating from different measurement equipment are greatly reduced and a more decisive comparison of $T_{g\text{-cal}}$ and $T_{g\text{-kin}}$ is possible.

Figure 2 demonstrates the temperature-dependent dielectric constants and heat capacity of Debye and non-Debye-type liquids, 2-ethyl-1-hexanol (a) and 3-methylpentane (b). Two main relaxation processes are clearly observed in the dielectric measurements of the alcohol. The one with higher amplitude (and lower peak frequency) is identified to be of the Debye-type, and determines $T_{g\text{-kin-D}}$, while the other is a non-Debye process and corresponds to $T_{g\text{-kin-}\alpha}$. One can see that for Debye and non-Debye liquids, the calorimetric glass transition is more associated with the dispersive (non-Debye) dielectric relaxation feature.

We would like to address a more quantitative comparison by identifying the calorimetric and kinetic T_g. Figure 3 shows the results of some canonical non-Debye glass-forming liquids and monohydroxy alcohols. The measurements cover a wide range of types of organic non-Debye glass-forming liquids with regards to structure and dynamics: in structure, associating, polar, nonpolar, aromatic liquids are involved; and in dynamics, the fragility index m, which is defined as the slope at T_g of the logarithmic relaxation time as a function of the reduced temperature to T_g, spans from $m = 52$ (propylene glycol) to 145 (decalin) [7,8]. For *all* the non-Debye liquids, we found that the $T_{g\text{-cal}}$'s from $\pm 20\,\mathrm{K \cdot min^{-1}}$ calorimetry are 1–3 K higher than the kinetic ones, and generally, the $T_{g\text{-cal}} - T_{g\text{-kin}}$ difference varies with the liquid fragility. For the stronger liquids, propylene glycol and glycerol, the difference is within 1 K, while for fragile liquids such as decalin and propylene carbonate, the difference could reach from 2 to 3 K. Therefore, we conclude that for these experimental conditions, $T_{g\text{-cal}}$ is always slightly higher than $T_{g\text{-kin}}$, but the difference does not exceed 3 K.

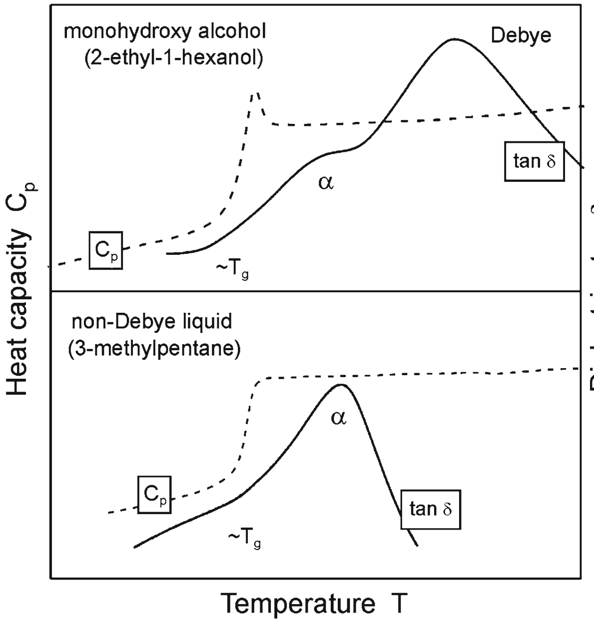

Fig. 2 Comparison of thermodynamic and dielectric spectra of Debye (2-ethyl-1-hexanol) and non-Debye-type (3-methylpentane) liquids. Two main relaxations are seen in the dielectric spectra of the monohydroxy alcohol. The dielectric results are represented as tan $\delta = \varepsilon''/\varepsilon'$,measured at a frequency of 1 kHz

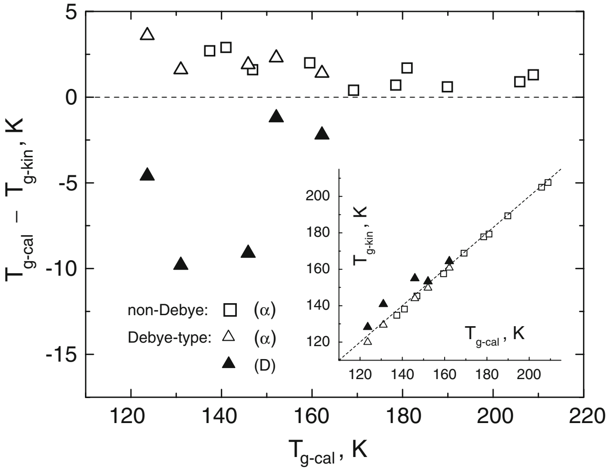

Fig. 3 Calorimetric and kinetic glass transition temperatures of non-Debye and Debye liquids. All $T_{\text{g-cal}}$'s are based on the cooling and heating rate of ±20 K · min^{-1}, and $T_{\text{g-kin}}$'s on isothermal dielectric measurements, and are determined with the temperatures at which dielectric relaxation times reach 100 s. Non-Debye liquids are: decalin, 2-ethylhexylamine, 3-methoxy-1-butanol, propylene carbonate, propylene glycol, di-*n*-butyl phthalate, decahydroisoquinoline, glycerol, 2,4-pentanediol, and 2-ethyl-1,3-hexanediol. The Debye liquids are: 2-methyl-1-butanol, 2-ethyl-1-butanol, 2-ethyl-1-hexanol, 5-methyl-2-hexanol, and 4-methyl-3-heptanol. Both lists are given in the order of increasing T_g

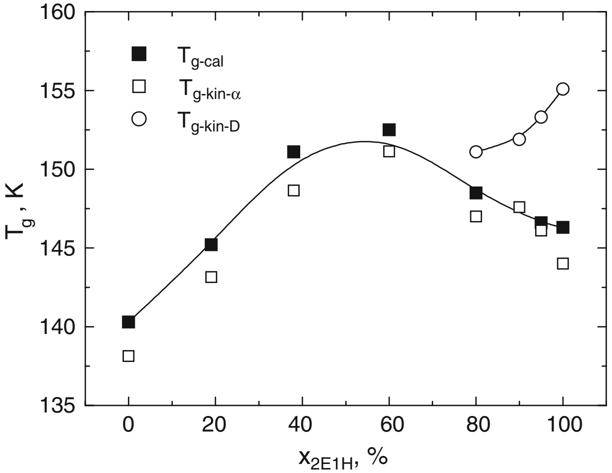

Fig. 4 Calorimetric and kinetic glass transition temperatures in mixtures of 2-ethyl-1-hexanol (2E1H) with 2-ethylhexylamine (2EHA) versus 2E1H mole fraction x_{2E1H}. Open symbols are for the kinetic T_g from dielectric relaxations at relaxation times of 100 s

The $T_{g\text{-cal}} - T_{g\text{-kin}}$ correlation for non-Debye liquids will help to check the two kinetic glass transition temperatures of monohydroxy alcohols, as seen in Fig. 3. It is clear that $T_{g\text{-kin-}\alpha}$ follows the rule of the non-Debye liquids. Some differences between $T_{g\text{-cal}}$ and $T_{g\text{-kin-}\alpha}$ might be a little larger than expected, which is due to errors in determining $T_{g\text{-kin-}\alpha}$ when the two relaxation processes are not well separated. As observed in Fig. 3, $T_{g\text{-kin-D}}$'s are generally higher than $T_{g\text{-cal}}$'s, and the difference is as high as 9.1 K for the case of 2-ethyl-1-hexanol. Also, no systematic dependence on fragility is detected.

It is, therefore, the non-Debye relaxation of the monohydroxy alcohols that really corresponds to the calorimetric glass transition. This result is consistent with other evidence that the non-Debye dielectric relaxation is more reasonably correlated with the viscous flow in monohydroxy alcohols [2]. Additional support for the conclusion comes from our recent measurements of the calorimetric and dielectric measurements of mixtures of 2-ethyl-1-hexanol with 2-ethylhexyamine through the entire concentration range, shown in Fig. 4 [9]. Here, we see that $T_{g\text{-kin-}\alpha}$'s from the non-Debye dielectric relaxations follow the concentration dependence of the $T_{g\text{-cal}}$'s, but $T_{g\text{-kin-D}}$'s based on the Debye relaxations do not.

It appears that the present method can be used as a tool for determining whether a dielectric relaxation process is associated with the calorimetric glass transition, structural relaxation, and viscous flow. It concerns two cases: (a) there are two or more main non-Arrhenius relaxations in the supercooled liquid regions, and (b) apparently, only one relaxation is detected, but it is the Debye-type. In addition to the pure liquid monohydroxy alcohols, the Debye-type relaxations were also detected in other mono-H-bonding liquids, such as secondary amides. Although no two main relaxations are visible, the Debye relaxations have to be questioned when we found that the $T_{g\text{-kin-D}}$ (161.6 K) from the Debye relaxation of N-ethylacetamide was a little higher than the calorimetric counterpart (160.4 K). Recent work revealed that a non-Debye-type relaxation (the 'true' structural relaxation) does exist with $T_{\text{g-kin-}\alpha}$ to be 158.2 K, although it is hard to be discerned [10]. This example shows that the method established in this work is quite reliable.

Finally, to our knowledge, this is the first such quantitative comparison under such strict experimental conditions, although other assessments have been reported earlier [11]. While the present definition of the kinetic glass transition temperature at $\tau = 100\,\text{s}$ appears somewhat arbitrary, its correlation with the calorimetric counterpart is quite good. By contrast, if it is defined at either 10 s or shorter or 1,000 s or longer, we found that the variance for the data of $T_{\text{g-cal}} - T_{\text{g-kin}}$ of organic glass formers is much larger. For example, when using 10 s to determine $T_{\text{g-kin}}$ instead of 100 s, the strong liquids will experience a substantial change and might be lower than $T_{\text{g-cal}}$, while the change is small for the fragile liquids. Therefore, for the molecular liquids, defining the kinetic glass temperatures using the 100 s criterion will generate the most systematic correlation with the calorimetric values of T_g, provided the latter are obtained from the experimentally most common cooling/heating rates of around $20\,\text{K} \cdot \text{min}^{-1}$.

3 Conclusion

Glass transition temperatures of supercooled liquids are assessed on the basis of two distinct criteria. The calorimetric glass transition is determined as the onset temperature $T_{\text{g-cal}}$ of the heat capacity step, while the kinetic value $T_{\text{g-kin}}$ is derived from a relaxation time reaching 100 s. The study focuses on monohydroxy alcohols, where the existence of two dielectric relaxation processes (a Debye and a non-Debye type peak) raises the question of which one to identify with the glass transition. If determined consistently, organic molecular liquids possessing a single relaxation peak exhibit $T_{\text{g-cal}}$ and $T_{\text{g-kin}}$ values that are highly correlated, albeit not equal. For the present conditions, we find $T_{\text{g-kin}} < T_{\text{g-cal}} < T_{\text{g-kin}} + 3$ K. Using this relation as a benchmark, we conclude that the prominent dielectric Debye peak of monohydroxy alcohols is not related to the calorimetric modes, while a much smaller amplitude dielectric signature of the glass transition can be identified at higher frequencies.

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