Glass Transition and Dielectric Relaxation in Viscous Monohydroxy Alcohols

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The calorimetric glass transition temperature, T_g, which is determined based on the onset temperature of the heat capacity jump from glass to supercooled liquids, is generally comparable to the kinetic one, at which the average relaxation time approaches 100 s. However, notable discrepancies are often observed in monohydroxy alcohols when the kinetic T_g's are determined from the Debye-type dielectric relaxations. A question rises as to whether the Debye-type dielectric relaxations in the monohydroxy alcohols are associated with the calorimetric glass transition and viscous flow. Here we presented an extensive comparison of the thermal and dielectric measurements of the glass transitions in both monohydroxy alcohols and non-Debye liquids. It is found that the calorimetric T_g's of the non-Debye liquids with moderate cooling and heating rates (-/+20 K/min, for example) are slightly greater than the kinetic ones, and the difference is not greater than 3 K, while in the monohydroxy alcohols, the kinetic T_g's from the dielectric Debye relaxation times are much greater and, the difference could be as high as 10 K. Further analyses of the dielectric spectra of the monohydroxy alcohols reveal that the Debye-type relaxations are always companied with a non-Debye relaxation process. The dynamics of the non-Debye relaxations is faster, and the kinetic T_g's from the relaxations corresponds to the calorimetric ones very well. The results provided evidence that the Debye-type dielectric relaxations in the monohydroxy alcohols could not be accounted for as the glass-transition dependent structural relaxations.