Test of the Einstein-Debye Relation in Supercooled Dibutylphthalate at Pressures up to 1.4 GPa

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Broadband dielectric measurements were carried out on di-n-butyl phthalate (DBP) under isothermal conditions at hydrostatic pressures up to 1.6 GPa. A comparison of the dielectric relaxation times with the viscosity revealed that no breakdown of the Einstein-Debye relation is induced by high compression. This absence of any decoupling is attributed to the weak intermolecular cooperativity of DBP and its negligible change with pressure. Because of the latter, the dielectric spectra conform to time-pressure superpositioning.

Relaxation and transport phenomena in supercooled liquids and polymer melts remain intriguing and important issues in the physics of soft condensed matter. In the last decade, there has been much discussion concerning the relationship between the viscosity, η, and the relaxation times of liquids as determined by various dynamical probes. A focus of the debate is the Einstein-Debye (ED) relation [1,2]:

$$\eta = \left(\frac{kT}{V}\right)\tau_r, \qquad (1)$$

where τ_r denotes the rotational relaxation time and V is a molecular volume. Although this equation was derived for Brownian particles that have dimensions larger than molecules, it is often utilized to characterize molecular motions in neat liquids and of probes surrounded by host molecules of similar or smaller size.

Chang and Sillescu [3] examined the behavior of the quantity $\eta/T\tau_{\mathrm{diel}}$ over a broad range of temperatures, where the viscosity and dielectric relaxation time, τ_{diel}, changed by more than 10 orders of magnitudes, for various low molecular weight glass forming liquids (o-terphenyl, salol, phenolphthaleine dimethyl ether, cresolphthaleine dimethyl ether, glycerol, and m-tricresylphosphate). They found that the ratio $\eta/T\tau_{\mathrm{diel}}$ was constant at high temperatures, for which the fluids have low viscosities. However, upon approach to the glass transition, this ratio systematically increased, with its value rising as much as 1 order of magnitude at the glass transition temperature, T_g. The breakdown of the ED relation near T_g is referred to as a decoupling phenomenon. Decoupling between the viscosity and the reorientational times, τ_{DLS} obtained from light scattering was also seen in OTP by Fischer and co-workers [4], who suggested that the temperature dependence of the characteristic length for the dynamic glass transition is reflected in the temperature variation of the ratio $\eta/T\tau_{\mathrm{DLS}}$.

There are other examples of decoupling of dynamic variables. Rössler [5] observed breakdown of the Stokes-Einstein relation between the translational diffusion constant and reorientational correlation times measured by dielectric, NMR, and photon correlation spectroscopes for 1,3,5-tri-α-naphthyl benzene. They noted that the onset of the deviation occurred in the vicinity of the critical temperature, T_c, predicted by mode-coupling theory.

Recently, Behrens et al. [6] compared η with shear relaxation times obtained from dynamic mechanical spectroscopy for di-n-butylphthalate (DBP). The ratio $\eta/T\tau_{\mathrm{mech}}$ is invariant to temperature accounted for by the invariance of the mechanical loss dispersion to temperature (i.e., time-temperature superpositioning was obeyed). A strong correlation between viscosity and dielectric relaxation times (covering 12 decades) in DBP was reported by Dufour and co-workers [7].

Chang and Sillescu [3] discussed the decoupling phenomena as being due to the spatial heterogeneity inherent to supercooled liquids. However, as they point out, this would not account for decoupling between the viscosity and dielectric relaxation times, since both are "local" processes. An alternative explanation has been presented, based on the idea that different dynamic variables experience different degrees of intermolecular cooperativity [8]; hence, upon approach to T_g, their variation with temperature can differ.

Up to now, the Einstein-Debye relation has been tested using only experimental data obtained from temperature dependent measurements at ambient pressure. Since both the viscosity and the reorientational relaxation times of the liquid are also strong functions of pressure, the question arises whether the correlation between η and τ is maintained under conditions of high pressure. This is an important issue, given the fact that molecular interactions are modified in different ways by these two thermodynamical variables. Whereas temperature mainly affects the energy of molecules attempting to surmount potential barriers, pressure changes intermolecular distances and consequently the height of these barriers [9].
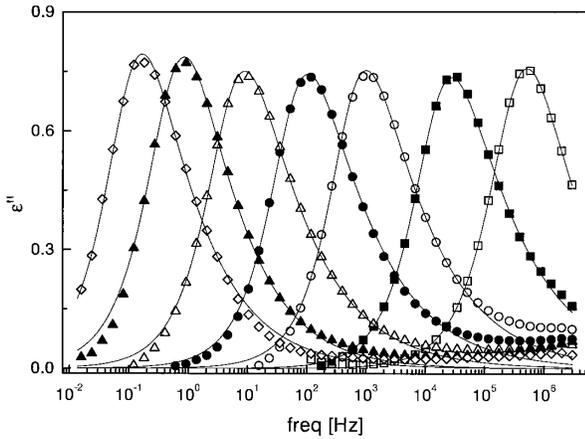
FIG. 1. Dielectric loss versus frequency for DBP at $T = 22.5\,°C$ and $P = 0.65$ ($\square$), 0.863 ($\blacksquare$), 1.075 ($\bigcirc$), 1.188 ($\bullet$), 1.294 ($\triangle$), 1.375 ($\blacktriangle$), and 1.45 ($\diamondsuit$) GPa.
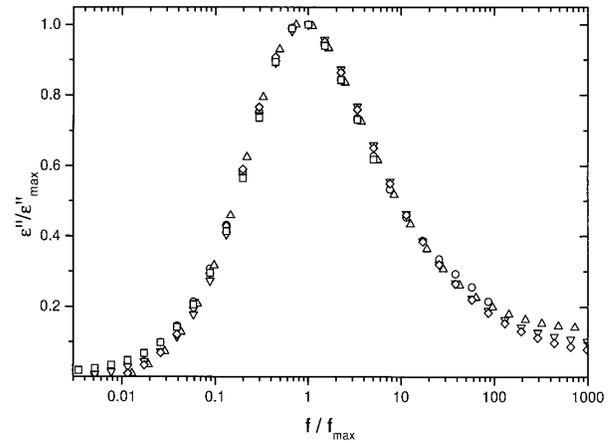

FIG. 2. The spectra of Fig. 1 with the frequencies normalized by frequency of the maximum and the intensities normalized to unity at the peak (symbols as in Fig. 1). The central portion of the peaks superimpose, while there is deviation at higher frequencies due to the contribution of a secondary process. The full width at the half intensities points, indicated by the arrow, is 1.76 decades.

Herein we compare for the first time the viscosity and dielectric relaxation time obtained from isothermal, pressure-dependent measurements on di-n-butylphthalate. The isothermal viscosity data up to 1.4 GPa was reported in Ref. [10]. The experimental challenge was to measure the dielectric relaxation time over the same pressure range. Toward this end, we modified our high pressure apparatus. Briefly, the liquid sample and the two electrodes forming a capacitor were placed in a Teflon bellows mounted in the high pressure chamber. Force was applied to the piston by means of a hydraulic press, to generate hydrostatic pressure within the chamber. Using this technique, pressure of a few GPa could be attained. The dielectric measurements were carried out at $T = 22.5\,°C$ in a frequency range from 10^{-2} to 10^6 Hz, using an Alpha spectrometer (Novocontrol). The sample was 98% pure, as obtained from Aldrich.

In Fig. 1, representative dielectric spectra are shown. The maximum of the dielectric loss moves toward lower frequencies with increasing pressure. The Havriliak-Negami function [11]: $\varepsilon_{HN}^* = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)[1 + (i\omega\tau_{HN})^\alpha]^{-\gamma}$ provided satisfactory fits (solid line) to the α dispersions. At high frequencies, deviation from the fitting function occurs, due to the proximity of a secondary relaxation process [6]. For the Havriliak-Negami shape parameters, we obtain $\alpha = 0.95 \pm 0.02$ and $\gamma = 0.49 \pm 0.03$, independent of pressure; that is, for di-n-butylphthalate, in which the dipole moment is near the center of mass, the shape of the loss peak is virtually unchanged with pressure. This behavior is illustrated in Fig. 2, in which the spectra in Fig. 1 are replotted, after normalizing by the peak maxima and shifting along the frequency axis to superimpose. This conformance to time-pressure superpositioning is consistent with results from temperature dependent measurements at ambient pressure. Olsen and co-workers [12] and Behrens *et al.* [6] found that the respective shapes of the dielectric and

the mechanical loss peaks for DBP do not change with temperature close to T_g; that is, the time-temperature superposition principle is obeyed for the primary relaxation process at low temperatures. Thus, the evolution of the relaxation spectrum reveals analogous behavior under isothermal (high pressure) and isobaric (ambient pressure) conditions.

The dielectric relaxation times determined as the inverse of frequency of the maximum in the loss peak ($\tau = 2\pi_{\max}f$) are plotted versus pressure in Fig. 3. The relaxation times increase dramatically on approaching the glass transition. The strong curvature of the $\log\tau$ dependence on P indicates that the activation volume [$\Delta V =$
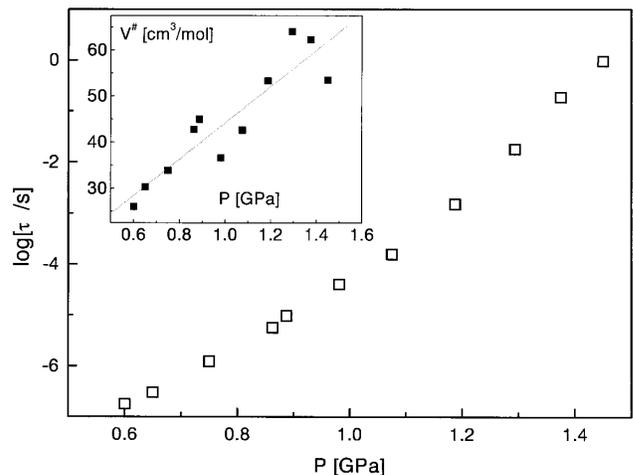

FIG. 3. Pressure dependence of the dielectric relaxation times measured at $T = 22.5\,°C$. The inset shows the activation volume calculated from the slope of the curve.

$RT(d \log\tau/dP)_T]$ is also an increasing function of pressure, as shown in Fig. 3. Since the activation volume is pressure dependent, simple volume activated models for describing the evolution of the relaxation times are inadequate. This same pattern of behavior was observed previously at lower pressures for DBP and related phthalate derivatives, in which a pressure variant of the Vogel-Fulcher equation was used to describe the $\tau(P)$ data [13,14].

The main result of our analysis is presented in Figs. 4 and 5. The viscosity and dielectric relaxation times are compared in Fig. 4. It is evident that both quantities exhibit a very similar pressure dependence. Thus, there is no indication of decoupling between η and τ in the vicinity of the glass transition, consistent with results obtained by cooling experiments at ambient pressure.

The correlation between viscosity and dielectric relaxation time is often examined by analyzing the ratio $\eta/T\tau_{\mathrm{diel}}$. Interpolating the viscosity data [15] (solid line in Fig. 4), this ratio is plotted versus pressure in Fig. 5. The invariance of the ratio over the entire pressure range demonstrates conformance to the ED relation as the liquid is compressed.

The fact that the dipole moment of DBP, which governs the dielectric response, is near the molecular center of mass contributes to the strong correlation of the dielectric relaxation times with the viscosity. However, strict conformance to the ED relation throughout the supercooled regime is more directly a result of the nature of the intermolecular cooperativity in DBP. It has been shown for various glass formers that breakdown of the ED relation, as well as similar phenomena involving decoupling of relaxational and transport properties, are correlated with a broader relaxation function [8,16]. Thus, the breakdown is a manifestation of the strong intermolecu-

lar cooperativity that develops near T_g [8]. The severity of this intermolecular cooperativity is reflected in the fragility or T_g-normalized temperature dependence of the viscosity and relaxation times [17]. Fragility is correlated both with the breadth of the relaxation function and with the rapidity of the increase of this breadth with decreasing scaled temperature T_B/T [18,19]. T_B is the temperature at which the relaxation time crosses over from one Vogel-Fulcher dependence to another [20]. The crossover at T_B is associated with a change in the dynamics from weakly intermolecularly cooperative to moderately or strongly cooperative, dependent on the magnitude of the cooperativity at T_g. While T_B is a function of pressure, for a given material, the relaxation time associated with the change in dynamics is invariant [21,22]. The disparity between the two Vogel-Fulcher dependences also correlates with this intermolecular cooperativity, and how rapidly it changes with T_B/T [23].

In DBP, intermolecular cooperativity is relatively weak even near T_g, as evidenced by its small fragility (= 69 [24]) and narrow loss peak (FWHM < 1.8 decades; see Fig. 2). Thus, as T_g is approached from above, either by cooling or compression, one expects only a modest change in the dynamics. This is exactly what is observed; the dispersion in the dielectric loss is virtually unchanged upon approach to T_g (Fig. 2). Consequently, no decoupling is induced between the viscosity and relaxation times. The same behavior is also observed in experiments in which DBP is cooled to T_g at atmospheric pressure [6,7]: there is no broadening of the relaxation function and no decoupling of the viscosity and relaxation times. Thus, our results herein establish that the intimate connection between intermolecular cooperativity and dynamic properties is maintained whether the supercooled state is attained isothermally by compression of the liquid or by isobaric cooling.
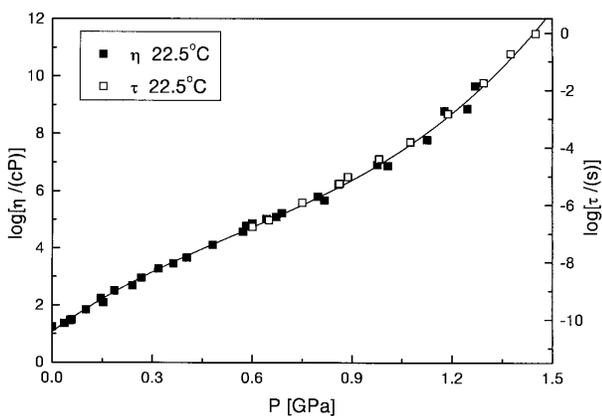

FIG. 4. The dielectric relaxation times (open symbols) and the viscosities (solid symbols, from Ref. [10][10]) for DBP as a function of pressure at $T = 22.5\,°C$. The ordinate scales have the same expanse, demonstrating conformance to the Einstein-Debye relation. The solid line through the data is the best fit of a third-order polynomial.
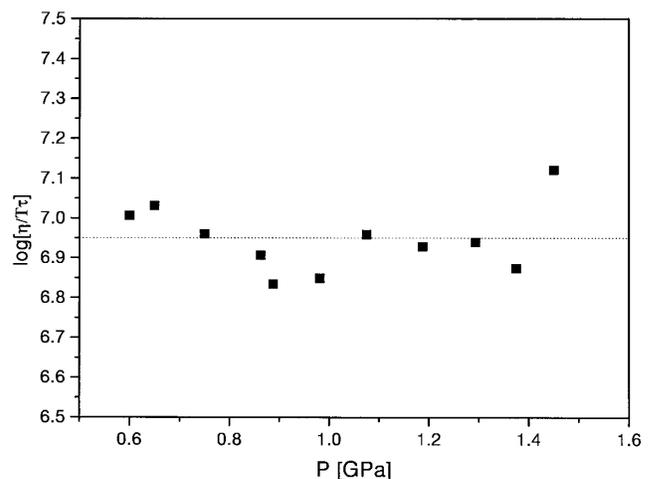

FIG. 5. The ED ratio versus pressure for DBP at $T = 22.5\,°C$. The mean value, $\eta/T\tau_{\mathrm{diel}} = 6.95$, is indicated by the dotted line.

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