Brillouin Scattering of Supercooled Liquids. II.   Diisobutyl Phthalate

Shinobu Koda, Ryuki Hashitani, and Hiroyasu Nomura*
Department of Chemical Engineering, School of Engineering, Nagoya University, Chikusa-ku, Nagoya 464
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The Brillouin scattering spectra of diisobutyl phthalate were measured over a wide range of temperatures. The sound velocity dispersion was observed in the GHz region in a temperature range between 240 and 340 K. We concluded that the sound dispersion of the sample was attributed to the structural relaxation of a supercooled liquid. The relaxation curve of the longitudinal modulus was obtained by a superposition method and could be analyzed using a generalized B.E.L. model with a parameter of $K=0.3$—0.5. The viscoelastic relaxation in the GHz region was found to have a narrower distribution of relaxation times than in the MHz region.

It is well known that molecules in a liquid state are in an ordered structure at local and very short separations. However, at the greater separations, this ordered structure becomes indistinct. Therefore, when a mechanical force is suddenly applied to liquids, they at first respond elastically, just as if they were solid bodies, but relax as viscoelastic bodies. In order to better understand local structures of liquids and solutions regarding molecular interaction forces, it is very important to know the relaxation mechanism of liquids and solutions under such external forces as mechanical and electrical. However, it has been roughly estimated that the structural relaxation times of ordinary liquids are of an order of 10^{-13} s. Because of their low viscosities, we can not measure the relaxation times directly by means of relaxation spectroscopy. In order to study the dynamic properties of liquids, supercooled liquids are suitable materials, since such liquids have a large viscosity coefficient and their characteristic relaxation times are so long that they fall within measurable frequency ranges. Our final goal is to determine the dynamic properties of liquids and solutions. Supercooled materials will present useful information.

Most investigations regarding the dynamic properties of supercooled liquids were carried out in the megahertz regions and relaxation curves were obtained by superimposing data at different temperatures on the basis of a reduced procedure. The Brillouin scattering method is also a very useful technique for studying the viscoelastic properties of liquids. It provides information about the dynamic properties of liquids in the GHz range. Scattering is due to local thermal density fluctuations in the liquid phase.

In our previous paper,[1] the sound velocities of tri-*o*-tolyl phosphate in the GHz region were measured using the Brillouin scattering method with wide scattering angles and temperature ranges. The relaxation curves of the obtained longitudinal modulus were expressed by the B. E. L. model. However, the *K* parameter, which involves a distribution of the relaxation times, was somewhat different from those obtained in the MHz region.

In this paper, we report on the experimental results of Brillouin scattering in diisobutyl phthalate for a wide range of temperatures. The molecular dimension and

symmetry of diisobutyl phthalate are quite different from those of tri-*o*-tolyl phosphate which was previously investigated. Viscoelastic relaxation, obtained from sound dispersion curves in the GHz region, are discussed on the basis of a generalized B. E. L. equation for bulk and shear moduli and is compared with the results from the MHz region.[2] The temperature dependence of the *K* parameter in the generalized B. E. L. equation is also discussed.

Experimental

Diisobutyl phthalate, guaranteed grade, was obtained from Nakarai Chemicals Co., Ltd. The sample was distilled under reduced pressure at 4 mmHg[†], and poured into a scattering cell by filtration using a millipore filter with a pore size of 1.0 µm.

The Rayleigh-Brillouin spectra were obtained with a pressure-scanning Fabry-Perot interferometer, using a He-Ne laser (NEC., GLG 5800, output 50 mW). Detailed descriptions of the apparatus and experimental procedures are given in previous papers.[1,3] Measurements were performed over a temperature range between 197 and 348 K for various scattering angles (30 to 150°). The accuracy of the sound velocity was within ±1.0%.

Velocities at 5 MHz were measured using an ultrasonic interferometer over a temperature range between 273 and 333 K. Ultrasonic absorption coefficients were also measured at a frequency of 5 MHz by the usual pulse method. The refractive indexes of the samples were measured using an Abbe refractometer between 258 and 318 K. Values at the lower and higher temperatures were estimated by extrapolating the temperature dependences of the velocity and the refractive index.

Results

Figure 1 shows the typical Rayleigh-Brillouin spectra of diisobutyl phthalate at a constant scattering angle, $\theta=90°$, as a function of temperature. The sound velocity, V, can be calculated from the values of the Brillouin frequency shift, $\Delta\omega$, and the scattering angle, θ, by the following relation;

$$V = \left(\frac{\Delta\omega}{\omega_0}\right)\frac{c}{2n\sin(\theta/2)},\tag{1}$$
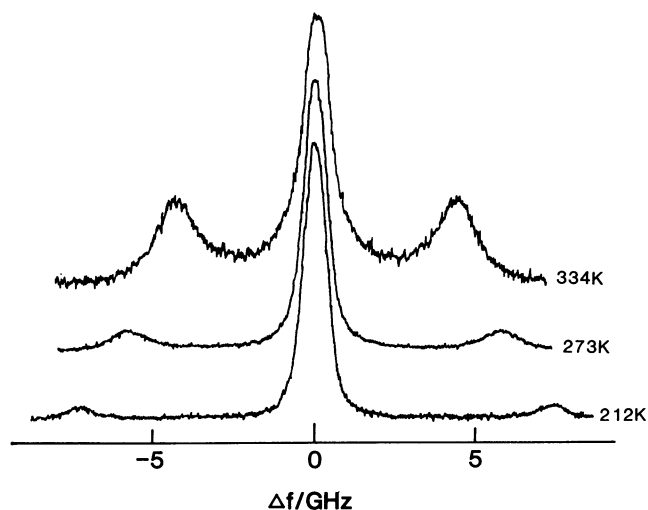
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† 1 mmHg=133.322 Pa.
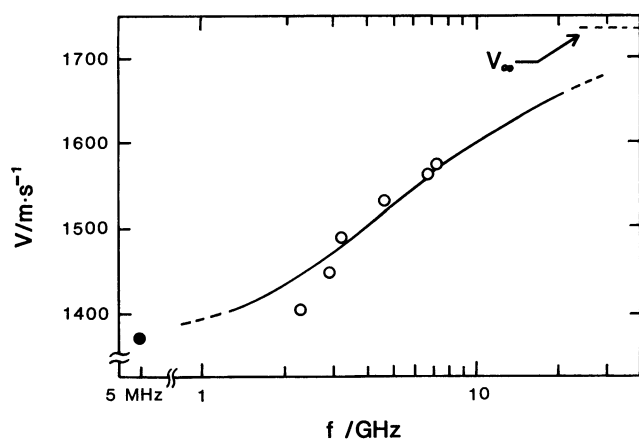
Fig. 1.   Representative Brillouin spectra. (θ=90°).

Fig. 2.   Frequency dependence of the sound velocity at 298 K.
(O); Brillouin scattering method, (●) ; ultrasonic data (5 MHz).

Fig. 3.   Temperature dependence of the sound velocity.
(O); θ=90°, (□); θ=130°, (⬭); θ=140°, (△); θ=145°, (⊡); θ=150°, (●); ultrasonic data (5 MHz).

Fig. 4.   Temperature dependence of the relaxation strength, ε.

where ω_0 is the frequency of the incident light, c the velocity of light, and n the refractive index of the sample.

Figure 2 shows a plot of the sound velocities against the frequencies at 298 K. The sound velocity dispersion was observed in the GHz region. The temperature dependence of the sound velocities, which were obtained at various scattering angles, is shown in Fig. 3. As can be seen, a clear sound velocity dispersion was obtained in the mid temperature range. In the low temperature region, below 238 K, although velocities were measured for various scattering angles, these velocities were independent of the scattering angles, that is, were independent of the frequencies. These velocities can be considered as those at the high frequency limit for various temperatures. The temperature dependence of the velocities at the high frequency limit, V_∞, can be represented by the following equation by analogy with the temperature dependence of the shear modulus.[2]
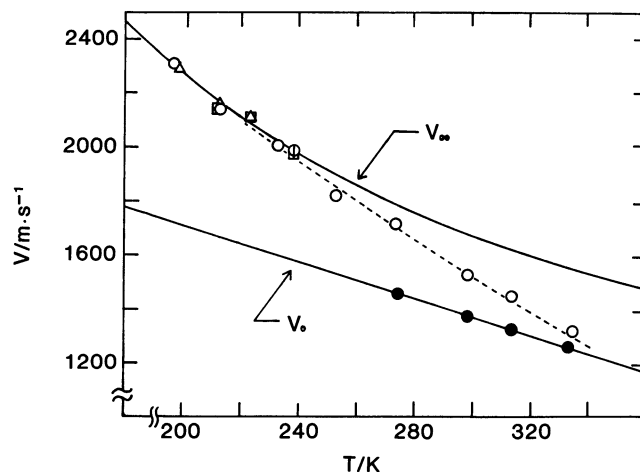
$$V_\infty = \frac{a}{T(\mathrm{K})} + b. \qquad (2)$$

The numerical values of a and b are 3.59×10^5 m s⁻¹·K and 479 m s⁻¹, respectively. Those were determined by a curve fitting method, using data from the lower temperature regions. For the low frequency limit of the sound velocity, V_0, values measured by an ultrasonic interferometer operating at 5 MHz were employed. The temperature dependence of V_0 can be expressed as $V_0 = -3.43\ T(\mathrm{K})+2400$.[2]

Discussion

Generally, the origin of sound velocity dispersion in the GHz region is mainly ascribed to the following two relaxation processes. One is vibrational relaxation, which is due to an energy transfer from vibrational modes of a molecule to translational motion. The other is a viscoelastic relaxation, that is, structural relaxation.
The temperature dependence of the relaxation

strength, $\varepsilon=(V_\infty^2-V_0^2)/V_\infty^2$, is shown in Fig. 4. As can be seen, ε decreases with increasing temperature. If the velocity dispersion were due to vibrational relaxation, ε would increase with increasing temperature.[4] It might be, therefore, concluded that the observed sound velocity dispersion is not mainly due to vibrational relaxation, but to the viscoelastic relaxation. This is also true for tri-o-tolyl phosphate in the GHz region. This conclusion can be supported by taking into consideration the fact that observed value of $\varepsilon=0.331$ (at 298 K) is one order of magnitude larger than $\varepsilon=0.0315$ (at 298 K) estimated using the Planck-Einstein relation with frequencies of the vibrational modes.

At this stage, shear modulus data in the GHz region are not available by any method. Thus, longitudinal data cannot be divided into that related to the bulk and shear modulus, respectively, through the relation $M^*=K^*+4/3\,G^*$ (where K^* and G^* refer to the bulk and shear modulus respectively, and the superscript* refers to the complex modulus). Therefore, our data analysis was constrained to only longitudinal data, that is, M' (hereafter the real and imaginary parts of the complex are distinguished by $'$ and $''$, respectively).

The storage modulus, which is the real part of the complex longitudinal modulus M^*, can be estimated by $M'=\rho V^2$, where ρ is the density. According to a data analysis which was proposed by Lamb's school, a reduced plot of $(M'-M_0)/(M_\infty-M_0)$ against $\omega\eta_s/G_\infty$ was carried out and is shown in Fig. 5, where ω is the angular frequency ($\omega=2\pi f$). η_s/G_∞ ($=\tau_s$) corresponds to the relaxation time of the Maxwell element for a single relaxation, where η_s is the shear viscosity and G_∞ is the complex shear modulus at the high frequency limit. The temperature dependences of the viscosity and the density of the sample investigated here can be found in the literature.[5] The values of G_∞ at each temperature that were used were determined at an ultrasonic frequency at low temperatures.[5] As can be seen in Fig. 5, a master curve has been found in spite of the wide temperature and frequency ranges within the experimental error.

Assuming the generalized B. E. L. equation for K^* and G^*,[2] respectively, the expression for M^* is given as

$$\frac{M^*-M_0}{M_\infty-M_0} = C\left[1+\frac{1}{i\zeta\omega\tau_s}+2K\left(\frac{1}{i\zeta\omega\tau_s}\right)^{1/2}\right]^{-1}$$
$$+ (1-C)\left[1+\frac{1}{i\omega\tau_s}+2K\left(\frac{1}{i\omega\tau_s}\right)^{1/2}\right]^{-1}$$
$$C = \frac{K_\infty-K_0}{M_\infty-M_0} = 1-\frac{4}{3}\frac{G_\infty}{M_\infty-M_0}$$
$$\zeta = \frac{\tau_v}{\tau_s} = \frac{\eta_v}{\eta_s}\frac{G_\infty}{M_\infty-M_0} = \frac{3}{4}\frac{\eta_v}{\eta_s}(1-C), \quad (3)$$

where K is an adjustable parameter for the broadness of the relaxation region. The K parameter is assumed to be the same for both shear and bulk relaxation processes.[2]
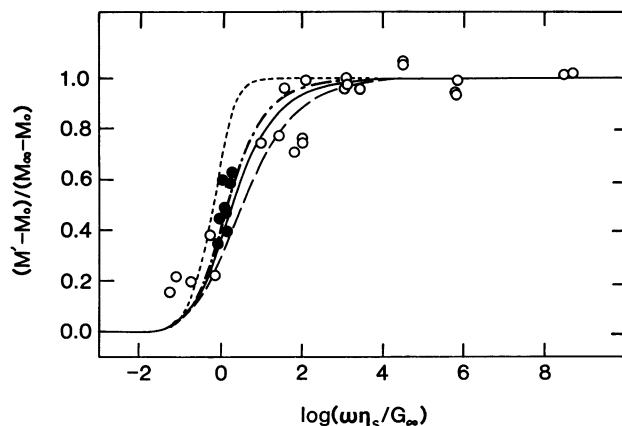

Fig. 5. Values of the normarized longitudinal modulus, $(M'-M_0)/(M_\infty-M_0)$ plotted as a function of $\log(\omega\eta_s/G_\infty)$.
(------); $K=0$, (—·—·-); $K=0.3$, (———); $K=0.5$, (— — —); $K=1.0$.
(●): Data at 25℃.

The value of C was estimated from data regarding the temperature dependence of the relaxation strength (Fig. 4) and G_∞'s which are also found in the literature.[5] C has a constant value of 0.35 in the low temperature range (from 197 to 300 K) but at higher temperatures, C increases slightly ($C=0.40$ at 320 K). The values of ζ can be estimated from data regarding η_v/η_s, which can be determined by measurements of the ultrasonic absorption coefficient at the low frequency limit, using the following equation.[2]

$$\lim_{\omega\to 0}\frac{\alpha}{\omega^2} = \frac{1}{2\rho v_0^3}(\eta_v + 4/3\,\eta_s). \quad (4)$$

The obtained value of η_v/η_s is 2.64.

Calculated curves of $(M'-M_0)/(M_\infty-M_0)$ are drawn in Fig. 5 for $K=0$, 0.3, 0.5, and 1.0, by lines using Eq. 3 with the observed values of C and ζ. The curve with $K=0$ corresponds to that of the Maxwell model for a single relaxation. The curve with $K=1.0$ corresponds to the original B. E. L. equation and is in good agreement with those obtained in the MHz region for many supercooled liquids (as reported by Barlow et al.).[6-11] As can be seen in Fig. 5, the curve for $K=1.0$ is considerably broader than that obtained experimentally. The curve for $K=0.3$ and/or 0.5 reproduces the experimental values within experimental error. In the higher temperature region, that is, in the low frequency region, a deviation from the B. E. L. model was appeared. This deviation may be due to the rotational molecular motion of molecules in the liquid.

Previously,[1] we suggest that the relaxation curves of the longitudinal modulus for tri-o-tolyl phosphate in the GHz region could be reproduced by the B. E. L. model with a parameter of $K=0.5$. Therefore, both results for tri-o-tolyl phosphate and diisobutyl phthalate indicate the same tendency; that is, the longitudinal modulus obtained from the measure-

ments in the GHz region at various temperatures can be apparently composed with a master curve using the B. E. L. method, like that for the MHz region. However, the K parameter obtained from data in the GHz region was somewhat different from that in the MHz region. If the superposition procedure were to hold completely, the values of K which were obtained from data in the GHz and MHz regions should coincide with each other.

The solid circles in Fig. 5 represent the data obtained at a constant temperature of 298 K as a function of the frequency. According to the superposition procedure, these data for the GHz region at log $(\omega\eta_s/G_\infty) \simeq 0$ correspond to that around a frequency of 50 MHz at about 250 K. The data in the MHz region should correspond to the spectrum for $K=1.0$. On the other hand, as shown in Fig. 5, the data in the GHz region at 298 K do not coincide with the spectrum for $K=1.0$ and the data in the GHz region give a narrower relaxation spectrum than the spectrum for $K=1.0$. This fact clearly suggests that the distribution of the relaxation times at 298 K is different from that at 250 K.

At this stage, we would like to limit ourselves to pointing out that the distribution of the relaxation times of the longitudinal modulus of supercooled liquids may depend on the temperature. In order to confirm this fact more clearly, measurements over a frequency range between 300 and 700 MHz are needed. Work along this line is in progress and will be reported elsewhere.

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