September, 1988] © *1988 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 61, 3087—3091 (1988)*

The Brillouin Scattering of Highly Viscous Liquids-Triacetin and Propylene Glycol Diacetate

Ryuki Hashitani, Hirohito Matsui, Shinobu Koda, and Hiroyasu Nomura*
Department of Chemical Engineering, School of Engineering, Nagoya University,
Chikusa-ku, Nagoya-shi 464

(Received April 9, 1988)

The sound velocities of triacetin and propylene glycol diacetate were measured by means of Brillouin scattering in the temperature range from 200 to 350 K. The velocity dispersions due to the structural relaxation were observed in the gigahertz region. The relaxation behaviors could not be interpreted by the empirical equation proposed by Barlow et al., which holds in megahertz region and also the relaxation curves were located in higher frequency region than those predicted by the Maxwell model. The relaxation curves were well reproduced by single relaxation equation. In the temperature ranges of relaxation region, the temperature dependences of viscosity were expressed by Arrhenius' viscosity equation. The relaxation behaviors can be interpreted in terms of the weak cooperative motions of molecules.

Dynamic properties of liquids have been intuitively understood through observation of the viscous flow of liquids in an ordinary time scale. However, liquids behave as elastic media in a very short time scale, and so a definite time is needed for liquids to flow. The relaxation process is closely related to the collective translational motions and can occur in any liquids. The relaxation is called as viscoelastic and/or structural relaxation. In this sense, the relaxation process should reflect the dynamic nature of the local structure of liquid. In order to observe the relaxation process experimentally, one needs to measure the time- and frequency-dependences of viscosity and/or elastic modulus. The relaxation time in low-viscosity liquids is too short to measure by any experimental techniques available for us now. In this work we used highly viscous liquids or supercooled liquids as samples, because their relaxation times fall on the measurable frequency ranges.

The Brillouin scattering provides the sound velocity and the absorption coefficient of sound wave in the gigahertz region. In our previous papers, the structural relaxations of highly viscous liquids have been investigated by means of Brillouin scattering.[1–3] The relaxation behaviors in the GHz region have been discussed using the reduced variable method proposed by Lamb's school[4] which held very well in the MHz region and we pointed out that the distribution of relaxation times in GHz region was different from those in the MHz region, that is, Maxwellian relaxation curve reproduced our experimental results satisfactorily in the GHz region.

In this paper, the experimental results for two highly viscous liquids, triacetin (hereafter abbreviated as TAT) and propylene glycol diacetate (PGA), will be reported. Comparing with tri-*o*-tolyl phosphate (TOTP) and diisobutyl phthalate (DIBP) investigated before,[1–3] the molar volumes of TAT and PGA are small. In addition, the viscosity of PGA is much lower than that of TAT. The relaxation of PGA will appear in lower temperature region than those of TAT and the others.

Experimental

Samples. Triacetin(TAT), guaranteed grade, and propylene glycol diacetate (PGA), extra grade, were purchased from Kishida Chemical Co., Ltd. and Tokyo Chemical Industry Co., Ltd., respectively. They were purified by distillation under reduced pressure and were poured into scattering cells through a millipore filter with pore size of 0.2 μm.

Measurements. Rayleigh-Brillouin scattering spectra were observed by a pressure-scanning Fabry-Perot interferometer, using a He-Ne laser (NEC, GLG 5800, output 50 mW) as the light source. The detailes of experimental procedures were reported previously.[5] The range of scattering angle used was from 50° to 150°.

Refractive indexes were measured by an Abbe refractometer in the temperature range between 273 to 323 K. The values in the low temperature region were estimated by fitting the high temperature data to the Lorentz-Lorenz equation. The sound velocities at 5 MHz were measured by an ultrasonic interferometer in the temperature ranges from 268 to 318 K for TAT and from 248 to 318 K for PGA. The density and shear viscosity measurements were carried out by a buoyancy balance densitometer and rotational viscometer, respectively. These measurements were made in the temperature range from about 245 to 320 K for TAT and from 220 to 270 K for PGA.

Results

The sound velocity can be calculated from the Brillouin shift, Δf, which is the difference in the peak frequency between Rayleigh and Brillouin lines and is equal to the frequency of the sound wave, by following relation;

$$V=\frac{\lambda_\mathrm{i}\ \Delta f}{2\,n\,\sin\,(\theta/2)} \tag{1}$$

where λ_i is the wavelength of the incident light beam (632.8 nm). n is the refractive index of the sample, and θ is the scattering angle. The frequency dependences of sound velocity are shown in Fig. 1. The velocity dispersions are observed in the GHz region at 278, 298,

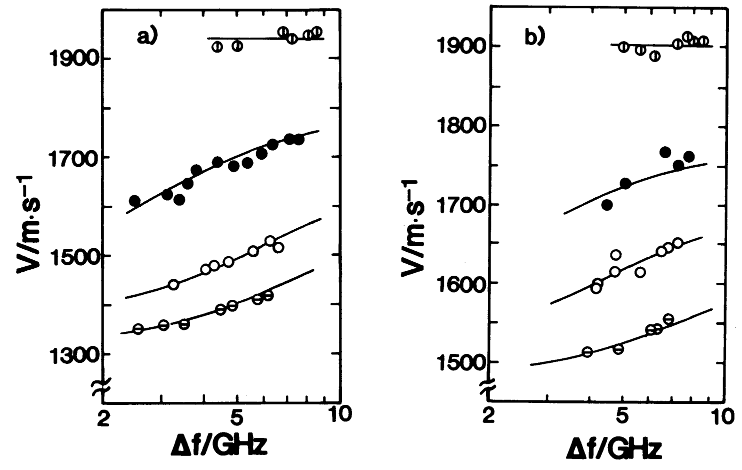

Fig. 1. Frequency dependence of sound velocity.
a) TAT; ⦶: 253 K, ●: 278 K, ○: 298 K, ⊖: 313 K.
b) PGA; ⦶: 218 K, ●: 233 K, ○: 243 K, ⊖: 253 K.

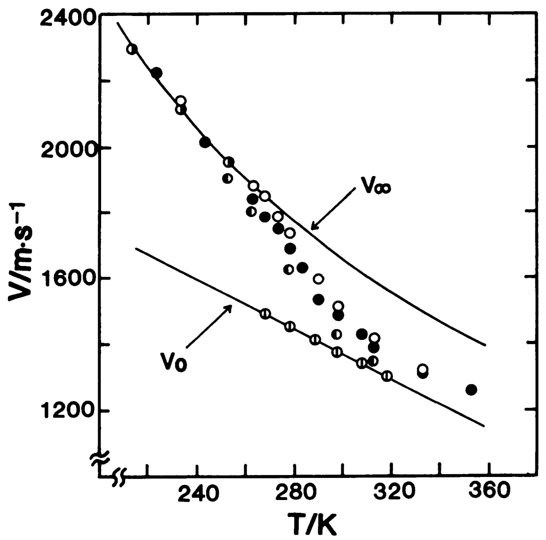

Fig. 2. Temperature dependence of sound velocity of TAT. Brillouin scattering; ◐: θ=50°, ●: θ=90°, ○: θ=100°, ◑: θ=150°. Ultrasonic interferometer (5 MHz); ⦶.

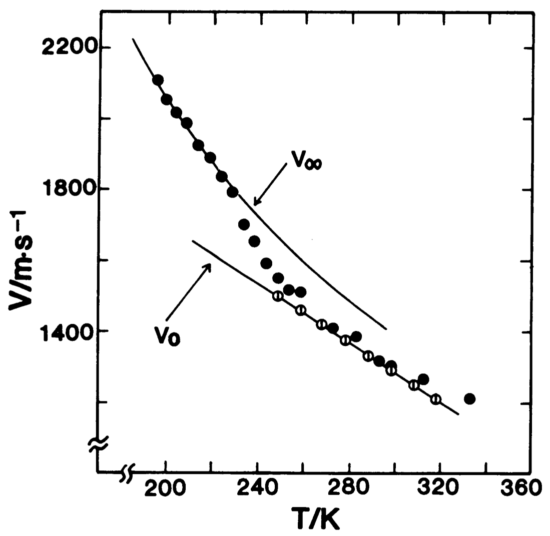

Fig. 3. Temperature dependence of sound velocity of PGA. Brillouin scattering (θ=90°); ●. Ultrasonic interferometer (5 MHz); ⦶.

and 313 K for TAT. In the case of PGA, the sound velocity dispersions appear in the lower temperature region than for TAT. Figures 2 and 3 show the temperature dependence of sound velocity for the TAT and PGA, respectively. The temperature dependence for TAT changes around at 250 K and for PGA around at 220 K. Besides, the velocities of TAT at 253 K and those of PGA at 218 K are independent of the frequency, as shown in Fig. 1. Therefore, the velocities of TAT below ca. 250 K and those of PGA below ca. 220 K may be considered to be the high-frequency limiting values. It has been assumed in our previous paper that the high-frequency limiting velocity, V_∞, has the following temperature dependence:

$$V_\infty = \frac{a}{T} + b \qquad (2)$$

where T is the absolute temperature and a and b are fitting parameters; a=4.80×10^5 m·s^{-1}·K, b=57 m·s^{-1} for the TAT and a=3.97×10^5 m·s^{-1}·K, b=61 m·s^{-1} for the PGA, respectively.

As is seen in Figs. 2 and 3, the relaxation strength, $\varepsilon=(V_\infty^2-V_0^2)/V_\infty^2$, decreases with increasing temperature in the temperature ranges where the sound velocity dispersions were observed (ε=0.34 (273 K)–0.31 (313 K) for TAT and ε=0.24 (233 K)–0.18 (253 K) for PGA). If the sound dispersions were due to the vibrational relaxation, the temperature dependence of the relaxation strength, ε, should increase with increasing temperature. Therefore, the sound velocity dispersions we observed here may be due to structural relaxation, and not to vibrational one.

Discussion

The storage modulus, M', which is the real part of complex longitudinal modulus, M^*, can be calculated from $M'=\rho V^2$ under the assumption of $(\alpha V/\omega)^2 \ll 1$, where α is the absorption coefficient and $\omega = 2\pi\Delta f$. In the reduced variable method proposed by Lamb, reduced modulus, $(M'-M_0)/M_2$, is plotted against reduced frequency, $\omega\eta_s/G_\infty$, where $M_2=M_\infty-M_0=\rho V_\infty^2-\rho V_0^2$, η_s is the shear viscosity, and G_∞ is the high-frequency limit of shear modulus. We have no experimental data for G_∞ of TAT and PGA. For this reason, we adopt $\omega\eta_s/M_2$ instead of $\omega\eta_s/G_\infty$. If G_∞/M_2 is assumed to be independent of temperature, as usually done,[4] the plots of reduced modulus against $\omega\eta_s/G_\infty$ and $\omega\eta_s/M_2$ become the same, although plots as a whole are shifted by an amount of $\log(G_\infty/M_2)$ along the abscissa. Figures 4 and 5 show the reduced plots of M' for TAT and PGA, respectively.

Assuming the B.E.L. (Barlow-Erginsav-Lamb) equation[4] for both complex shear and bulk moduli, one can obtain the following expression for M^*;

$$\frac{M^*-M_0}{M_2} = C\left[1+\frac{1}{i\zeta\omega\tau_s}+2K\left(\frac{1}{i\zeta\omega\tau_s}\right)^{1/2}\right]^{-1} + (1-C)\left[1+\frac{1}{i\omega\tau_s}+2K\left(\frac{1}{i\omega\tau_s}\right)^{1/2}\right]^{-1} \tag{3}$$

and

$$C=\frac{K_\infty-K_0}{M_\infty-M_0}=1-\frac{4}{3}\frac{G_\infty}{M_\infty-M_0}, \quad \tau_s=\frac{\eta_s}{G_\infty}$$

$$\zeta=\frac{\tau_v}{\tau_s}=\frac{\eta_v}{\eta_s}\frac{G_\infty}{K_\infty-K_0}=\frac{3}{4}\frac{\eta_v}{\eta_s}\frac{1-C}{C}$$

where η_v is the bulk viscosity and K is an empirical parameter concerned with the distribution of the relaxation times. The values of K given by means of ultrasonic method were reported to be unity for highly viscous pure liquids. On the other hand, Eq. 3 with $K=0$ corresponds to the Maxwellian model. The solid and broken curves in Figs. 4 and 5 are those calculated from Eq. 3 by putting respectively $K=0$ and $K=1.0$, into the equation and taking account of the shift along the abscissa by $\log(G_\infty/M_2)$ as mentioned above. It has been reported that the value of C lies between 0.35 and 0.5 and that of η_v/η_s, does between 1 and 3.[2,4,6] The differences in C and η_v/η_s in the ranges mentioned above do not affect the relaxation curve largely. We used $C=0.5$ and $\eta_v/\eta_s=3$, in drawing the lines in Figs. 4 and 5.

As is clear in Figs. 4 and 5, the relaxation curves of TAT and PGA obtained from Brillouin scattering are quite different from those calculated from Eq. 3 with $K=1$ (broken lines). At first sight, it may seem that data at the different temperatures are well superimposed on a single curve for each case of TAT and PGA. However, the composed relaxation curves are similar to that calculated by Eq. 3 with $K=0$ (solid curve) and the positions of composed curves in all cases investigated here deviate clearly from the solid curves toward the higher frequency side. The positions and the shapes of curves obtained from Eq. 3 with $K=0$ depend on the choice of the values of C and η_v/η_s. For example in the case of TAT, if we use the values of $C=0.6$ and $\eta_v/\eta_s=0.32$, we can reproduce the composed curve. However, $\eta_v/\eta_s=0.32$ is too small in comparison with the values reported ($\eta_v/\eta_s=1$—3) in literature.[2,4,6] In the case of PGA, the deviation can not be fully interpreted by the variation of C and η_v/η_s. This result indicates that the reduced variable method does not hold well in such wide frequency ranges as covering from MHz to GHz region and that the relaxation

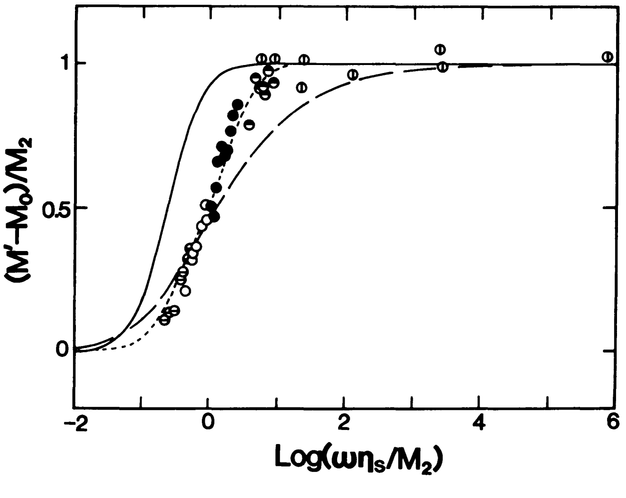

Fig. 4. Plots of $(M'-M_0)/M_2$ against $\log(\omega\eta_s/M_2)$ for TAT. ◓: 263 K, ●: 278 K, ○: 298 K, ⊖: 313 K, ⦶: below 263 K. The dotted curve was calculated by Eq. 3 with $K=0$, $C=0.6$, and $\eta_v/\eta_s=0.32$.

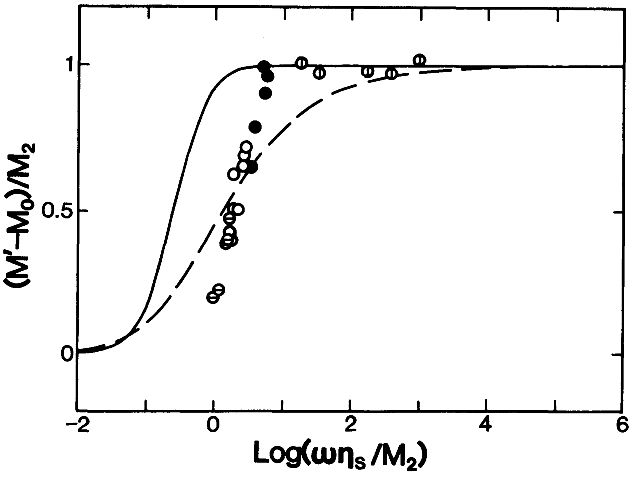

Fig. 5. Plots of $(M'-M_0)/M_2$ against $\log(\omega\eta_s/M_2)$ for PGA. ●: 233 K, ○: 243 K, ⊖: 253 K, ⦶: below 233 K.

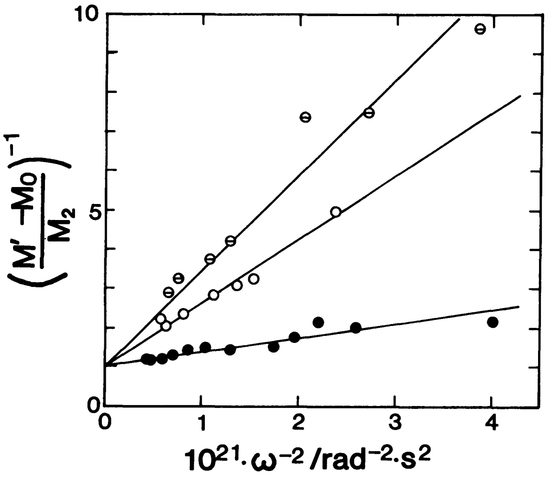

Fig. 6. Plots of $\{(M'-M_0)/M_2\}^{-1}$ against ω^{-2} for TAT. ●: 278 K, ○: 298 K, ⊖: 313 K.

behavior depends explicitly on the temperature in addition to the implicit temperature dependence involved in the reduced frequency. Thus it may be considered that the results obtained from Brillouin scattering reflect the high-temperature behavior, while those from ultrasonic method do the low-temperature one.

The shapes of relaxation curves obtained from Brillouin scattering are close to the Maxwellian model. If the reduced elastic modulus, $(M'-M_0)/M_2$, in the GHz region could be expressed by the following single (Maxwellian) relaxation equation:

$$\frac{M'-M_0}{M_2}=\frac{\omega^2\tau_M{}^2}{1+\omega^2\tau_M{}^2} \tag{4}$$

where τ_M is the relaxation time, the plot of $\{(M'-M_0)/M_2\}^{-1}$ against $1/\omega^2$ should be linear and its slope should be the square of the reciprocal relaxation time, $1/\tau_M$. As an example, Fig. 6 shows this relationship between $\{(M'-M_0)/M_2\}^{-1}$ and $1/\omega^2$ for the case of TAT at each temperature. As may be seen in Fig. 6, linear relationships are obtained within the limits of experimental error. Similar linear relationships are also obtained for the case of PGA at each temperature. If we use the relaxation times thus obtained, the reduced elastic moduli, $(M'-M_0)/M_2$, in the GHz region can be well expressed by a single relaxation equation (Eq. 4) within the frequency and temperature ranges investigated. This is shown in Fig. 7. The relaxation times of TAT obtained are 52, 25, and 20 ps at 278, 298, and 313 K, respectively and for PGA, 57, 33, and 20 ps at 233, 243, and 253 K, respectively.

It has been reported in some papers that single relaxation behavior or similar ones with narrow distribution of relaxation times appear when the temperature dependence of viscosity follows Arrhenius' viscosity equation.[1–3,7–9] At low temperature, where relaxation behavior shows a broad distribution, the temperature dependence of viscosity can be understood in terms of the free volume theory. Litovitz and McDuffie suggest that if liquid viscosity obeys Arrhenius' equation, the cooperative character of molecular motions is weak in comparison with liquids which obey the free volume equation.[10] In the temperature region (278—313 K for TAT, and 233—253 for PGA). where the relaxation could be observed by the Brillouin scattering, the temperature dependence was close to the Arrhenius' equation, while in lower temperature, viscosity increased rapidly with decreasing temperature. Therefore, it is considered that the relaxation behavior investigated here is concerned with the weak cooperative motion of molecules, as well as in the cases of the samples we studied before.[1–3]

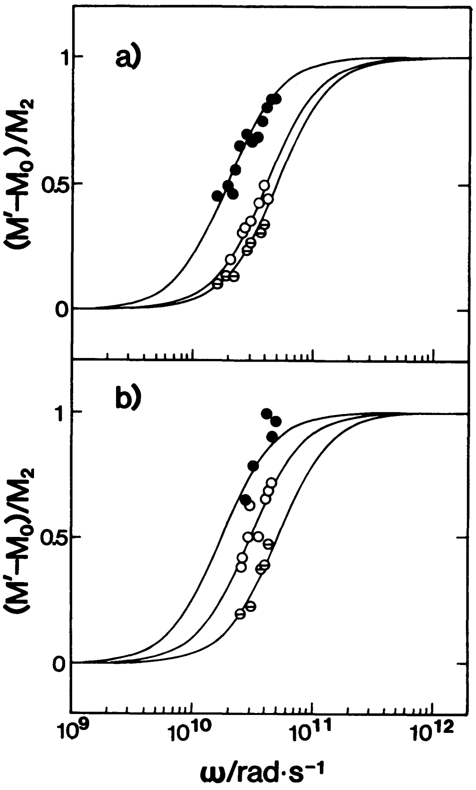

Fig. 7. Plots of $(M'-M_0)/M_2$ against angular frequency ω. a) TAT; ●: 278 K, ○: 298 K, ⊖: 313 K. b) PGA; ●: 233 K, ○: 243 K, ⊖: 253 K. Solid curves were drawn by single relaxation equation (Eq. 4).

References

1) S. Koda, H. Nomura, M. Nakamura, and Y. Miyahara, *Bull. Chem. Soc. Jpn.*, **58**, 1484 (1985).

2) S. Koda, R. Hashitani, and H. Nomura, *Bull. Chem. Soc. Jpn.*, **58**, 3465 (1985).

3) R. Hashitani, S. Koda, and H. Nomura, *Bull. Chem. Soc. Jpn.*, **60**, 2705 (1987).

4) G. Harrison, "The Dynamic Properties of Supercooled Liquids," Academic Press, London (1976).

5) H. Nomura, H. Shimizu, Y. Tanaka, S. Koda, T. Okunishi, S. Kato, and Y. Miyahara, *Bull. Chem. Soc. Jpn.*, **55**, 3899 (1982).

6) A. J. Matheson, "Molecular Acoustics", John Wiley & Sons Ltd., London (1971).

7) J. Tauke, T. A. Litovitz, and P. B. Macedo, *J. Am. Ceram. Soc.*, **51**, 158 (1968).

8) G. J. Gruber and T. A. Litovitz, *J. Chem. Phys.*, **40**, 13 (1964).

9) W. M. Madigosky and R. W. Warfield, *J. Chem. Phys.*, **78**, 1912 (1983).

10) T. A. Litovitz and G. E. McDuffie, Jr., *J. Chem. Phys.*, **39**, 729 (1963).