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The Brillouin Scattering of Highly Viscous Mixtures

Ryuki HASHITANI, Shinobu KODA, and Hiroyasu NOMURA*
Department of Chemical Engineering, School of Engineering, Nagoya University, Chikusa-ku, Nagoya 464
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The sound velocities of mixtures of tri-*o*-tolyl phosphate and diisobutyl phthalate were measured by means of the Brillouin scattering method in the temperature range from 214 to 333 K. The velocity dispersion was observed in the mixtures at temperatures from 273 to 323 K in the gigahertz region. The velocity dispersion was attributed to the structural relaxation, as in the case of pure highly viscous liquids. The reduced variable method proposed by Lamb et al. could not be applied to the storage moduli over wide frequency and temperature ranges. The relaxation curves of the reduced storage modulus obtained at room temperature, where the viscosity obeyed the Arrhenius equation, were well expressed by a single relaxation equation. The structural relaxation mechanism of the highly viscous liquids investigated here is related to the weak cooperative motions of molecules in the liquid state. The activation energy, ΔE_τ, obtained from the temperature dependences of the relaxation times was about a third of those estimated from the Arrhenius plots of the shear viscosities of the mixtures.

Generally, liquids cannot support shear stress, no matter how small it may be. They yield or flow in response to the applied shear stress. However, on a short time scale, liquids can show elastic properties. Therefore, in the liquid state relaxations exist which are related to the collective motion of molecules. Such relaxations are called viscoelastic and/or structural relaxations. In order to study the dynamical aspects of the local structure in liquids and solutions, information on the mechanism of structural relaxation is highly desirable. Highly viscous liquids, such as glycerol and 1,3-butanediol, are suitable for the investigation of these relaxations, since they have long relaxation times as a result of their high viscosities at low temperatures and their relaxation times can be easily determined by experiments.

Such highly viscous liquids, which have no definite freezing point, are called "supercooled liquids." The viscoelastic and/or structural relaxations of supercooled liquids have been extensively investigated by means of ultrasonic methods, and the studies have been summarized.[1)] In the studies by Lamb's school, the relaxation curves were obtained by superimposing the data at different temperatures on the basis of a reduced variable method. i.e., the frequency-temperature superposition method, applied to the elastic modulus, since measurable ultrasonic frequencies were limited to a narrow range. Besides, in the experiments on ultrasonic methods, measurements were made only at low temperatures, since, at room temperature, the relaxation times are too short to be measured in the megahertz region. In view of this situation, direct measurements of relaxation behavior in higher temperature ranges are indispensable to elucidate the structural relaxation mechanism of highly viscous liquids in detail.

The Brillouin scattering method is also very useful for investigating the structural relaxation of highly viscous liquids. The Brillouin spectra which arise from the local thermal density fluctuation provide information about the dynamic properties of liquids in the GHz region.

Previously, we investigated the relaxation behavior of two pure highly viscous liquids, tri-*o*-tolyl phosphate[2)] and diisobutyl phthalate,[3)] by means of Brillouin scattering method. Assuming that the reduced variable method can be applied to the data obtained from Brillouin scattering, as well as those from the ultrasonic method, the master curves obtained were analyzed by means of the generalized B.E.L. (Barlow, Erginsav, and Lamb) model.[1)] The values of the parameter K in the generalized B.E.L. equation were found to be around 0.3—0.5, within the limits of experimental error, although, in ultrasonic studies, the K's of these materials have been found to be nearly unity.[1)] Besides, the data on the master curves deviated systematically from the curves calculated by the B.E.L. model, even if experimental errors were taken into account. These results suggested that a reduced variable method might be invalid for the superposition of elastic moduli over such wide frequencies as from MHz to GHz regions. However, the differences in K values obtained by the two methods were not so large that we could not conclude clearly whether or not the reduced variable method was useful.

In order to ascertain the validity of the reduced variable method for analyzing the data in the GHz region, and in order to discuss the relaxation mechanism in detail, careful experiments are required.

Large deviations in the parameter K from unity were observed by Barlow et al.[4)] for several binary mixtures of supercooled liquids in their ultrasonic studies. The values of the parameter K have varied widely, from about 0.2 to about 2.0, depending on the mole fraction of the components of the binary mixtures. Besides, these composition dependences of the parameter K have been expressed by a universal curve, independent of the species of the supercooled liquids.

In this paper, the structural relaxation of binary mixtures of diisobutyl phthalate and tri-*o*-tolyl phosphate are investigated by means of the Brillouin scattering method. The compositions of the binary mixtures were chosen as 0.20 mole fraction and 0.78 mole fraction of diisobutyl phthalate. In these compositions, the parameter K takes the minimum and maximum values. The spectra were observed over wide frequency ranges at various temperatures, especially in the relaxation regions. The dependences of the relaxation behavior on the temperature and/or the frequency are discussed by comparing the data in the GHz region with those in the MHz region. The structural relaxation mechanism of highly viscous liquids in the higher-temperature range is also discussed.

Experimental

The diisobutyl phthalate (DIBP), which was of a guaranteed grade, was obtained from the Nakarai Chemicals Co., Ltd., while a practical grade of tri-*o*-tolyl phosphate(TOTP) was obtained from Eastman Organic Chemicals. They were distilled under reduced pressure. Mixtures with composition of 0.78 and 0.20 mole fraction of DIBP were prepared. For pure DIBP, some measurements were carried out in addition to those previously reported.,[3] The sample liquids were poured into the scattering cells through a millipore filter with a pore size of 1.0 μm.

The Rayleigh-Brillouin spectra were obtained by the use of a pressure-scanning Fabry-Perot interferometer, using a He-Ne laser (NEC, GLG 5800, output 50 mW). Measurements were done over the temperature range from 214 to 331 K (0.78 DIBP mole fraction) and from 223 to 333 K (0.20 DIBP mole fraction). At 263, 273, 298, and 323 K, spectra were obtained over scattering angles from 40 to 145°. The experimental procedures were described in detail previously.[2,5]

The sound velocity and density were measured by means of an ultrasonic interferometer operating at 5 MHz and by means of the buoyancy balance method respectively. The viscosity measurements were carried out using a rotational viscometer, which was calibrated using standard sample liquids with known viscosities. The refractive indexes were measured by the use of an Abbe refractometer, manufactured by the Erma Optical Co., Ltd. All measurements were carried out within the temperature range from about 260 to 340 K. The values needed for the data analysis at the lower temperature were estimated by means of the extrapolation method.

Results

Typical Rayleigh-Brillouin scattering spectra of the 0.78 DIBP mole fraction mixture are shown in Fig. 1 at a constant scattering angle (θ=90°) as a function of the temperature. The sound velocity, V, can be calculated from the Brillouin shift, Δf, and the scattering angle, θ, by the use of the following relation;

$$V=\frac{\lambda_i\ \Delta f}{2n\sin(\theta/2)} \tag{1}$$

where λ_i is the wavelength of the incident light, and n, the refractive index of the sample.

Figure 2 shows the frequency dependence of the sound velocities of the samples obtained. The data measured at 273, 298, and 323 K all show clear sound velocity dispersions. These velocity dispersions can be attributed to the structural relaxation, much as in the

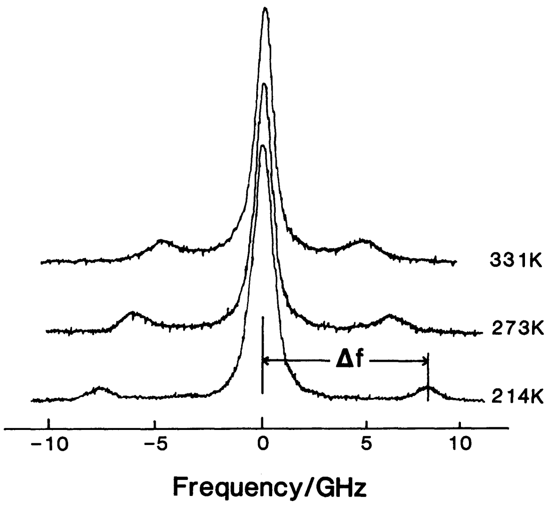

Fig. 1. Representative Rayleigh-Brillouin spectra of 0.78 mole fraction mixture at the scattering angle at 90°.

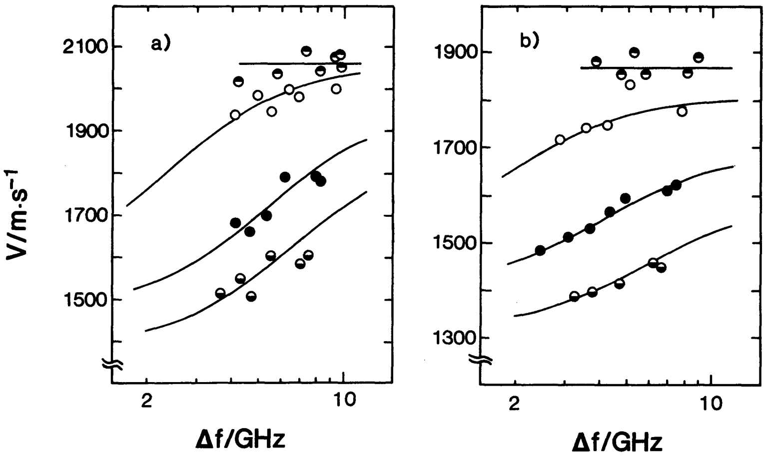

Fig. 2. Frequency dependence of sound velocities. a) 0.2 DIBP mole fraction, b) 0.78 DIBP mole fraction. ◓: −10°C, ○: 0°C, ●: 25°C, ◒: 50°C.

cases of pure DIBP[3)] and TOTP.[2)] The temperature dependences of the sound velocity obtained from the Brillouin scattering spectra at the scattering angle of 90° are shown in Figs. 3 and 4. In those figures, the temperature dependences of the sound velocities are different in the lower and higher temperature ranges. The sound velocities in the higher temperature region belong to those in the relaxation range, as is shown in Fig. 2. Besides, the sound velocities for the 0.20 DIBP mole fraction and 0.78 DIBP mole fraction mixtures below 260 K were almost independent of the frequencies investigated, as is shown in Fig. 2. Therefore, we can consider that the sound velocities below 260 K shown in Figs. 3 and 4 correspond to the velocities of the high-frequency limit. These limiting values were fitted to the following Doolittle type equation;

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

where T is the absolute temperature. The following values were obtained for the fitting parameters: a=4.00×10^5 (m s^{-1} K^{-1}), b=339 (m s^{-1}) for the 0.78 DIBP mole fraction and a=3.59×10^5 (m s^{-1} K^{-1}), b=739 (m s^{-1}) for the 0.20 DIBP mole fraction.

The sound velocities measured at 5 MHz by means of an ultrasonic interferometer were used as the low-frequency limiting sound velocities, as is usually done. The temperature dependences of these data were reproduced by the following linear relations;

V_0=−3.410×T+2420 for the 0.20 DIBP mole fraction (3)

and;

V_0=−3.573×T+2538 for the 0.78 DIBP mole fraction. (4)

In order to discuss the viscoelastic behavior of highly viscous liquids, the storage modulus, M', which is the real part of the complex longitudinal modulus, M^* (=$M'+iM''$), was calculated by the use of $M'=\rho V^2$ assuming that $(\alpha V/\omega)^2 \ll 1$, where ρ is the density and α is the absorption coefficient of the sound wave in a sample.

Discussion

The Validity of the Reduced Variable Method. First, we will discuss the value of making a composed relaxation curve, a master curve, by means of the reduced variable method for structural relaxation, as was proposed by Lamb's school. According to the reduced variable method, proposed by Lamb, a reduced elastic modulus, $(M'-M_0)/(M_\infty-M_0)$, should be plotted against $\omega\eta_s/G_\infty$, where ω is the angular frequency ($\omega=2\pi f$) and where G_∞ is the shear modulus at the high frequency limit. In our mixed systems, no values of G_∞ were found at any temperature in any literature. For this reason, we used the parameter $\omega\eta_s/M_2$ ($M_2=M_\infty-M_0$) instead of $\omega\eta_s/G_\infty$. According to Litovitz and Davis,[6)] the relation $(1/M_2)(\partial M_2/\partial T)=(1/G_\infty)(\partial G_\infty/\partial T)$ holds over a wide temperature range and the quantity G_∞/M_2 is independent of the temperature.

Therefore, a reduced plot of $(M'-M_0)/(M_\infty-M_0)$ against $\omega\eta_s/M_2$ should provide the same distribution of relaxation times as those obtained by plotting the reduced modulus against $\omega\eta_s/G_\infty$. The master curves obtained are shown in Figs. 5 and 6 for the 0.20 DIBP mole fraction mixture and 0.78 DIBP mole fraction mixture, respectively.

Assuming the generalized B.E.L. equation for complex shear and bulk moduli,[1,4)] the expression for complex longitudinal modulus can be given as follows;

$$\frac{M^*-M_0}{M_\infty-M_0} = C\left[1+\left(\frac{1}{i\zeta\omega\tau_s}\right)+2K\left(\frac{1}{i\zeta\omega\tau_s}\right)^{1/2}\right]^{-1} + (1-C)\left[1+\left(\frac{1}{i\omega\tau_s}\right)+2K\left(\frac{1}{i\omega\tau_s}\right)^{1/2}\right]^{-1} \qquad (5)$$

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_s and η_v are the shear and bulk viscosities and where K is an adjustable parameter which represents a measure of the distribution of the relaxation times. As has been mentioned previously, the estimation of the parameters, C and ζ, of our experimental systems is impossible, since the data on G_∞ are lacking. However, the values of C and ζ exert little effect on the shape of the relaxation curve calculated from Eq. 5. The broken lines in Figs. 5 and 6 are those calculated using Eq. 5 with the same values of C=0.35, and ζ=2.64 as were used for pure DIBP. The values of K

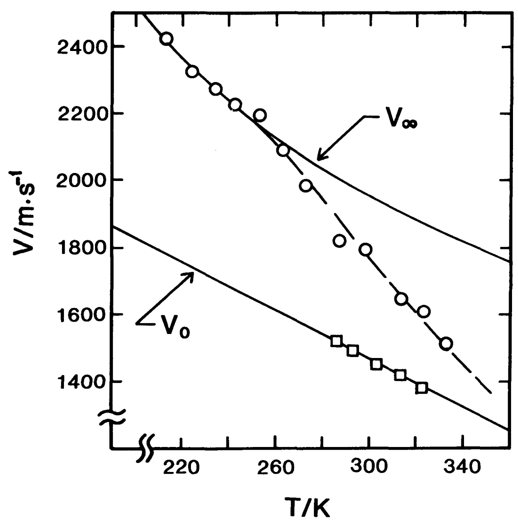

Fig. 3. Temperature dependence of sound velocities for 0.2 DIBP mole fraction. ○: Brillouin scattering (scattering angle at 90°), □: ultrasonic interferometer (5 MHz).

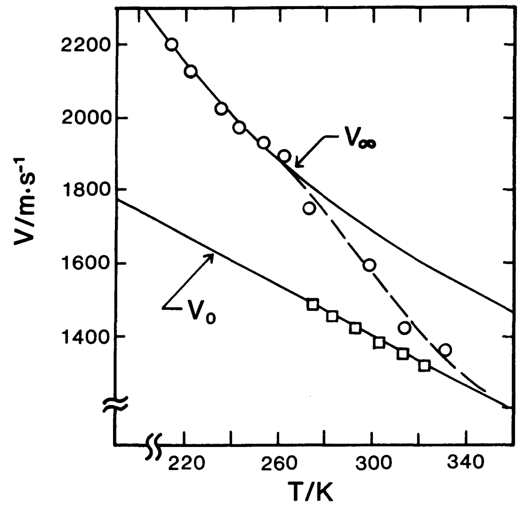

Fig. 4. Temperature dependence of sound velocities for 0.78 DIBP mole fraction. ○: Brillouin scattering (scattering angle at 90°), □: ultrasonic interferometer (5 MHz).

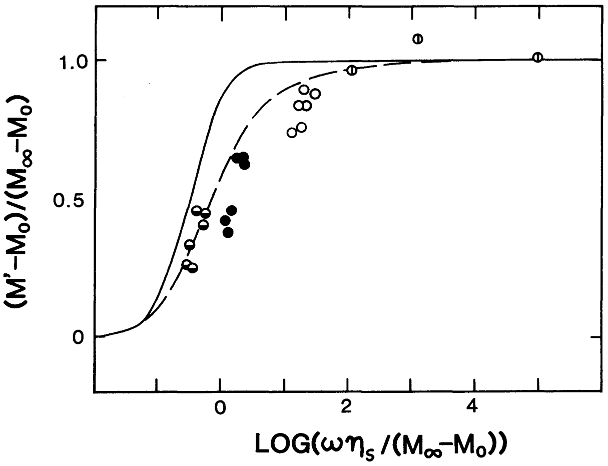

Fig. 5. Plots of $(M'-M_0)/(M_\infty-M_0)$ against log $(\omega\eta_s/(M_\infty-M_0))$ for 0.2 DIBP mole fraction. The solid and broken lines were drawn by the generalized B.E.L. Eq. 5 with K=0 and K=0.28, respectively. ○: 0 °C, ●: 25 °C, ◒: 50 °C, ⦶: others.

used in Figs. 5 and 6 were 0.28 and 1.8 respectively; they were determined by experiments in the ultrasonic region.[4] The solid lines in Figs. 5 and 6 correspond to the Maxwell equation with K=0 in Eq. 5.

As is shown clearly in Figs. 5 and 6, the data obtained in the GHz region do not agree with the broken lines in either case. This indicates that the reduced variable method fails in the superposition of elastic moduli over such a wide frequency range as from the MHz to the GHz region. Besides, the data in the GHz region deviate systematically from the curve calculated using Eq. 5. Consequently, we can not draw a master relaxation curve for both systems. Moreover, the data at each constant temperature form a group which seems to be parallel to a Maxwellian relaxation curve.

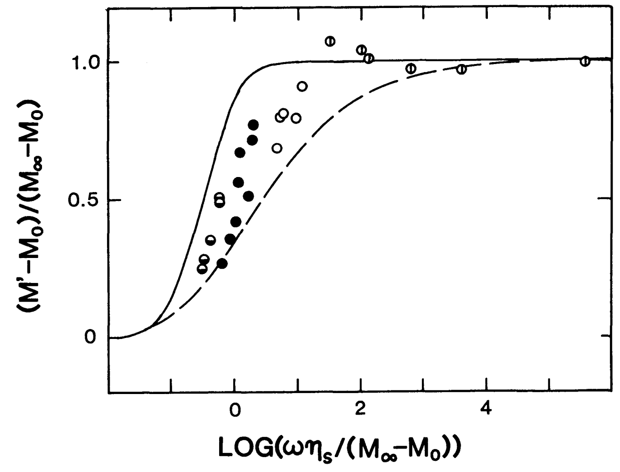

Fig. 6. Plots of $(M'-M_0)/(M_\infty-M_0)$ against log $(\omega\eta_s/(M_\infty-M_0))$ for 0.78 DIBP mole fraction. The solid and broken lines were drawn by the generalized B.E.L. Eq. 5 with K=0 and K=1.8, respectively. ○: 0 °C, ●: 25 °C, ◒: 50 °C, ⦶: others.

As is shown in Fig. 6, the data corresponding to $(M'-M_0)/(M_\infty-M_0)=0.5$, can be measured at 298 K with an angular frequency, $\omega=2.5\times10^{10}$ (rad s^{-1}), that is, $f=\omega/2\pi=3.99$ (GHz). In order to obtain the same plot based on the ultrasonic method working at f=50 (MHz), and considering the temperature dependence of V_0, V_∞, η_s, and ρ, the temperature must be controlled at about 242 K. Brillouin scattering provides information about the relaxation behavior at room temperature, while the ultrasonic methods provide information in the low temperature region.

Therefore, we can clearly conclude that the reduced variable method for the relation between $(M'-M_0)/(M_\infty-M_0)$ and $\omega\eta_s/M_2$ may hold for the behavior at low temperatures, but that it breaks down at room temperature.

Relaxation Spectrum Obtained by Brillouin Scattering. Apart from the generalized B.E.L. model and the reduced variable method, we would like to examine Figs 5 and 6 carefully. As has been mentioned previously, we can recognize in Figs. 5 and 6 that the data at the same temperature are located on the line parallel to the Maxwellian curve in both cases. If the reduced elastic modulus, $(M'-M_0)/(M_\infty-M_0)$, in the GHz region could be expressed by the following single relaxation equation;

$$\frac{M'-M_0}{M_\infty-M_0}=\frac{\omega^2\tau^2}{1+\omega^2\tau^2} \tag{6}$$

where τ is the relaxation time, the plot of $((M'-M_0)/(M_\infty-M_0))^{-1}$ against $1/\omega^2$ should be linear and its slope should show the square of the reciprocal relaxation time, $1/\tau^2$. As an example, Fig. 7 shows this relationship between $((M'-M_0)/(M_\infty-M_0))^{-1}$ and $1/\omega^2$ for the case of 0.78 DIBP mole fraction at each temperature. As may be seen in Fig. 7, linear relationships are obtained within the limits of experimental error. Sim-

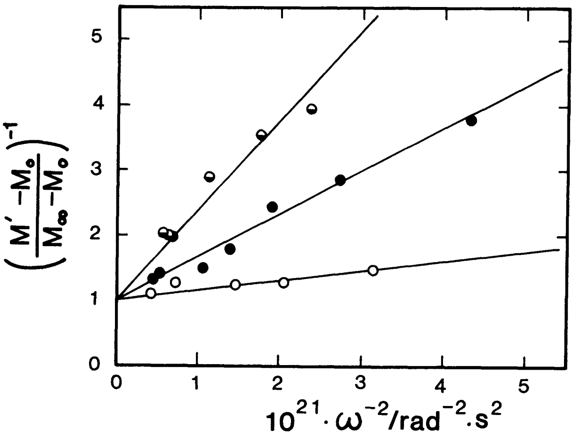

Fig. 7. Plots of $((M'-M_0)/(M_\infty-M_0))^{-1}$ against $1/\omega^2$ for 0.78 DIBP mole fraction.
○: 0 °C, ●: 25 °C, ◒: 50 °C.

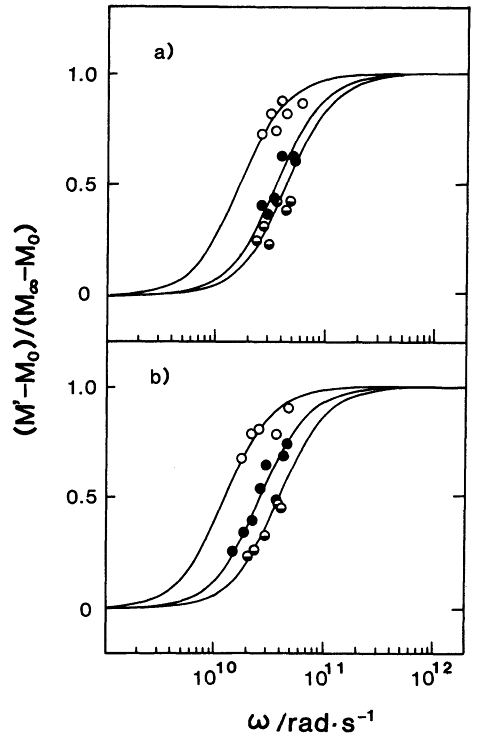

Fig. 8. Plots of $(M'-M_0)/(M_\infty-M_0)$ against angular frequency ω. a): 0.2 DIBP mole fraction, b): 0.78 DIBP mole fraction. ○: 0 °C, ●: 25 °C, ◒: 50 °C. Solid lines were drawn by single relaxation Eq. 6.

ilar linear relationships are also obtained for the case of the 0.2 mole fraction at each temperature. Using the relaxation times thus obtained, the reduced elastic moduli, $(M'-M_0)/(M_\infty-M_0)$, in the GHz region can be well expressed by a single relaxation equation (Eq. 6) within the measured frequency and temperature ranges, as is shown in Fig. 8.

Previously, we also analyzed the Brillouin scattering data of pure DIBP[3] and TOTP[2] by the use of the generalized B.E.L. equation, on the basis of the reduced variable method. However, as has been mentioned above, the elastic moduli measured over a wide frequency range and at several constant temperatures suggested that the reduced variable method might be invalid for analyzing the Brillouin scattering data. Therefore, the previous experimental data for the pure systems of DIBP and TOTP were re-analyzed using a single relaxation equation by means of the method described above. Figure 9 shows plots of $(M'-M_0)/(M_\infty-M_0)$ against the observed Brillouin frequency. A single relaxation process can reproduce very well the experimental results at any temperature of our experiments. Thus, it is confirmed that the viscoelastic behavior of highly viscous liquids at higher temperatures, (that is, around room temperature) can be expressed well by a single relaxation process.

Similar single relaxation behavior in viscoelastic and/or structural relaxations have previously been reported. Tauke, Litovitz, and Macedo[7] reported that the B_2O_3 in the liquid state behaves as a simple Maxwellian liquid in the temperature ranges where its viscosity obeys the Arrhenius viscosity equation, while the liquid of B_2O_3 showed relaxation processes with a wide distribution of relaxation times in the temperature ranges where its viscosity is expressed in terms of the free volume type, namely, the Doolittle-type equation. For the molten zinc chloride, a single relaxation time was also observed for the absorption of the longitudinal wave in the frequency range from 5 to 95 MHz at temperature ranges from 582 to 673 °C.[8] Madigosky and Warfield,[9] who carried out ultrasonic relaxation

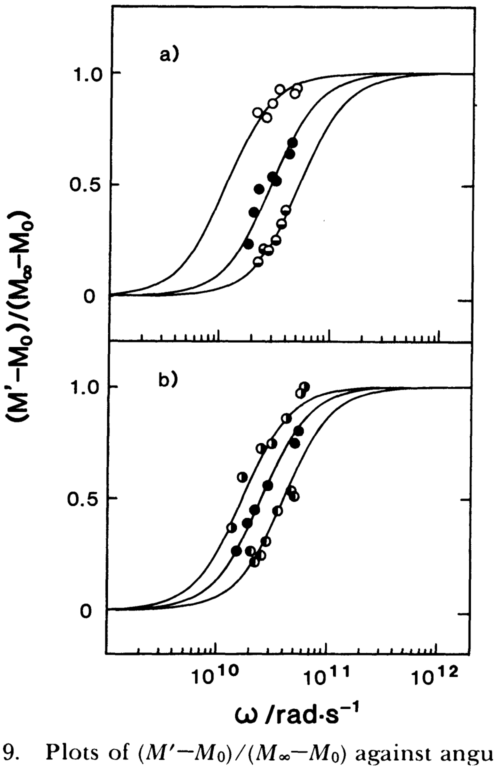

Fig. 9. Plots of $(M'-M_0)/(M_\infty-M_0)$ against angular frequency ω. a): Pure DIBP, b): pure TOTP.
○: 0 °C, ◑: 10 °C, ●: 25 °C, ◐: 40 °C, ◒: 50 °C.
Solid lines were drawn by single relaxation Eq. 6.

measurements in the frequency range from 5.5 to 200 MHz, concluded that the mixture of water and dimethyl sulfoxide (DMSO) shows structural relaxation behavior at temperatures below −55 °C. This relaxation behavior can also be expressed by a single relaxation equation, while the viscosities of these mixtures can be fitted well by Arrhenius equation in the temperature ranges investigated. In these papers, it was suggested that single relaxation behavior is observed if the viscosity obeys the Arrhenius viscosity equation.

Figure 10 shows the temperature dependence of the viscosities of the 0.20 and 0.78 DIBP mole fraction mixtures. As may be seen in Fig. 10, in the high temperature region the relationship between ln η and $1/RT$ is almost linear for the liquid mixtures involved here. This also indicates that, in the temperature range where the temperature dependence of the viscosity is expressed by the Arrhenius equation, the relaxation spectrum of the elastic modulus of liquids shows a single relaxation.

Litovitz and McDuffie[10] considered that, in a liquid obeying a free volume type equation for viscosity, a molecule moves in a manner cooperative with the surrounding ones, while in a liquid obeying Arrhenius viscosity equation, the motions of molecules have a non-cooperative character. They proposed that the distribution of the relaxation time arises from the cooperative motions of molecules. From this point of view, the relaxation behavior of the reduced elastic moduli of highly viscous liquids obtained from Brillouin scattering are considered to be related to the weak cooperative motions of molecules.

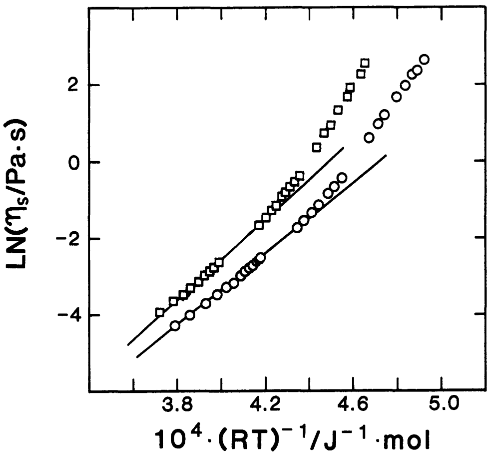

Fig. 10. Plots of ln η_s against $1/RT$. □: 0.2 DIBP mole fraction, ○: 0.78 DIBP mole fraction. The lines were drawn by fitting the data in the higher temperature region to linear relation between ln η_s against $1/RT$.

The relaxation times of pure TOTP, the 0.20 DIBP mole fraction, the 0.78 DIBP mole fraction, and pure DIBP at various temperatures, and the activation energies obtained from the linear plot of ln τ against $1/RT$, are summarized in Table 1. In view of the experimental errors, it is difficult to discuss the concentration dependence of ΔE_τ. The activation energy for viscosity, ΔE_η, obtained from the slope in Fig. 10 is also listed in Table 1. The values of ΔE_τ are about a third those of ΔE_η. Also, the concentration dependence of ΔE_η can not be found clearly.

The composition of a mixture should affect the cooperative motions of molecules very much because of the large differences in their molecular size and in their intermolecular interaction. As for the low-temperature behavior which corresponds to that of the free volume type liquids, the relaxation curves (broken lines in Figs. 5 and 6) depend largely on the composition of the mixture. The values of the parameter K in the generalized B.E.L. equation vary largely, from 1.8 for the 0.78 DIBP mole fraction to 0.28 for the 0.2 DIBP mole fraction.[4] On the contrary, in the case of high-temperature behavior obtained from the Brillouin scattering investigated here, all the relaxation curves can be reproduced well by the use of the single relaxation equation. This fact also confirms that the cooperative character involved is weak in this relaxation mechanism.

Very recently, Oh et al.[11] have reported the experimental results on the Rayleigh-Brillouin spectra of bis(2-ethylhexyl)sebacate (hereafter abbreviated as DOS) and tetracosane at temperatures higher than their

Table 1. Relaxation Times at Various Temperatures and Activation Energies

Temperature	DIBP	0.78 DIBP mole fraction	0.20 DIBP mole fraction	TOTP
K	ps	ps	ps	ps
273	88.0	81.7	62.8	
283				58.7
293				56.1
298	34.6	38.9	29.1	32.5
303				30.2
313				24.8
323	19.0	26.9	23.6	
ΔE_τ (kJ mol^{-1})	22.5±1.3	14.5±2.6	16.3±1.6	23.5±3.7
ΔE_η (kJ mol^{-1})	50.2[a]	46.6	48.3	60.3[b]

a) Ref. 13. b) Ref. 14.

melting points. They analyzed the temperature dependences of the Brillouin spectra, using the generalized hydrodynamic theory proposed by Lin and Wang,[12] and concluded that these spectra were attributable to the single relaxation of the longitudinal stress modulus. The relaxation times estimated by them are 49 and 67 ps at 325 K, while the activation energies are 16.1 and 12.7 kJ mol^{-1} for DOS and tetracosane respectively. Their experimental results are in close agreement with ours. They have pointed out that this relaxation is related to the structural relaxation of liquids, but they did not present any detailed relaxation picture.

Conclusion

According to the experimental results obtained in this investigation, the following conclusions can be drawn. 1) The reduced variable method proposed by Lamb et al. does not hold over the wide temperature and frequency ranges. 2) The relaxation spectra of the elastic moduli of highly viscous liquids and mixtures at higher temperature and in the GHz region can be well expressed by a single relaxation equation. 3) In the temperature range where the single relaxation spectrum is obtained, the viscosity of liquids and mixtures can be expressed by the Arrhenius equation. 4) The activation energies obtained by the relation between $\ln \tau$ and $1/RT$ were a third of those obtained from the Arrhenius plot of viscosity. These facts indicate that this structural relaxation mechanism is related to the weak cooperative motions and the elementary dynamic properties of liquids.

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