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Brillouin Scattering and Ultrasonic Absorption Measurements of Chloroform-Eicosane Mixtures

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An apparatus for the accurate measurement of Brillouin scattering of liquids and solutions was constructed using a multi-pass Fabry-Perot interferometer. The Brillouin scattering spectra of chloroform–eicosane mixtures were obtained at various concentrations. The sound velocity dispersion curves of this system could be expressed by a single relaxation equation. With increasing concentration of eicosane, the relaxation frequency shifted to the higher frequency side, but the relaxation strength was independent of concentration. It is concluded that this relaxation was due to the vibrational-translational energy transfers of chloroform molecules due to the collisions between chloroform and eicosane molecules.

The recent development of laser spectroscopy has opened a way to the study of the dynamical nature of molecules, such as the vibrational and reorientational relaxation times in liquid and dissolved states. The Brillouin scattering method in the only technique so far which can give information of the dynamic nature of a substance in the liquid state in the GHz range. This method has attracted the attention of many investigators.

In a previous paper,[1] we reported that the ultrasonic absorption coefficients of solutions of polycarbonate in chloroform were lower than those of solvent chloroform at all frequencies investigated. The negative value of $\Delta\alpha/f^2$ $(=(\alpha/f^2)_{\text{solution}}-(\alpha/f^2)_{\text{solvent}})$, where α is the ultrasonic absorption coefficient, could be interpreted by the shift of the relaxation frequency of chloroform to a higher frequency.

In order to confirm the above interpretation, the relaxation spectra of chloroform solutions must be determined as a function of concentration of solute in the wide frequency range from MHz to GHz. For this purpose, we constructed an apparatus for the accurate measurement of Brillouin scattering of liquids and solutions, using a multi-pass Fabry-Perot interferometer and measured the sound velocity and attenuation of chloroform solutions in the GHz region. In addition, the ultrasonic absorption coefficients of the same solutions were measured in the MHz region.

Eicosane was chosen as a solute for the following reasons. Eicosane molecule is a linear hydrocarbon containing only twenty methylene groups. One may suppose therefore that the ultrasonic relaxation due to the segmental motion is not observed in the MHz region.[2] Moreover, as the eicosane molecule has no phenyl group which may interact with chloroform molecules, there is no specific interaction between chloroform and eicosane. Therefore, eicosane is a suitable sample in which to investigate the relaxation phenomena of chloroform solutions.

Apparatus and Experimental

Brillouin Scattering Spectrometer. The experimental arrangement of the apparatus is shown in Fig. 1. This is basically the same as used by Stegeman *et al.*[3] and is one of the standard methods for the Brillouin scattering. In the present case, a multi-pass Fabry-Perot interferometer was used. The light source was a helium-neon laser (NEC, GLG 2051) with an output of about 25 mw and it was operated in TEM$_{00}$ mode (λ=632.8 nm). The beam was focused at the center of the scattering cell by a lens (L$_1$) and a total reflection mirror (M$_1$). The scattered light collected by a lens (L$_2$) was collimated and analyzed by a pressure-scanned triple-pass Fabry–Perot interferometer. The fused quartz plates of the interferometer used were 8 cm in diameter and 1.5 cm thick, and each plate has one surface with flatness $\lambda/200$ and more. This surface was dielectrically coated to reflectivity of 97% at λ= 632.8 nm, while the other surface ($\lambda/10$) of the plate had an antireflection coating. The spacers of the interferometer used were 6.04$_0$, 10.03$_1$, and 12.02$_0$ mm long, giving a free spectral range of 24.81$_7$, 14.94$_3$, and 12.47$_1$ GHz, respectively. In operating the interferometer in triple-pass system a pair of total reflection prisms was used. They were arranged with the angle of 120° to each other. All optical parts and instruments were manufactured by Mizojiri Optical Instrument Co., Ltd.

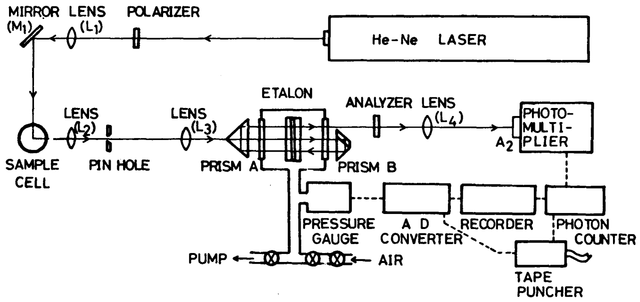

Fig. 1. Block diagram of the experimental set up.

At the beginning of the measurements, the chamber of the interferometer was evacuated with a vacuum pump, then air was introduced into the chamber through a filter, needle valve, and flow controller. The amount of air flow was controlled by a two-step flow control system consisting of two flow control valves (Ohkura Electric Co., Ltd., type CF-221). The pressure in the chamber was detected as a d. c. voltage by means of a piezoelectric pressure gauge (Tokyo Aircraft Instrument Co., Ltd., type TP-310A) and was converted to a digital signal by an AD converter (Takeda Electric. Co., Ltd., type TR-6935). Light incident on the aperture (A$_2$) was detected by a cooled photomultiplier (Hamamatsu TV Co., Ltd., type R-649), amplified by a preamplifier (Hamamatsu TV Co., Ltd., type HTV C-716) and then counted by a photon-counting system (Hamamatsu TV Co., Ltd., type HTV-C 767).

Spectra were recorded on the chart and at the same time punched up as digital data.

The scattering cell, of cylindrical shape (5.0 cm in diameter), was made of pyrex glass. The cell was firmly placed in an aluminium block having a horizontal slit through which to observe the scattered light. The temperature of the block was regulated at 25±0.1 °C by the circulation of water at constant temperature. In our arrangement, the scattering angle was changed from 20° to 160° through the variation of the reflecting angle of the laser beam by the aid of a mirror and a rotating table. The scattering angle could be read with the precision of $\pm 2'$. The sample liquids were introduced into the cell after being passed through the Milliporefilter FG of pore size 0.22 μm.

The refractive index of the samples was measured with a modified differential refractometer manufactured by Shimadzu Instrument Co., Ltd.

Brillouin spectra of chloroform and chloroform-eicosane mixture (at 30.0±0.1 °C) were recorded at various scattering angles in the range from 20° to 160°. At each scattering angle, the interferometer was scanned at least over five free spectral ranges.

Ultrasonic Absorption and Velocity Measurements. Ultrasonic absorption measurements were carried out over the frequency range from 10 to 60 MHz using a standard two crystal r.f. pulse technique with an apparatus described elsewhere.[4] Absorption measurements in the frequency range from 4.5 to 10.5 MHz were carried out using a long measuring cell (effective path length was 20 cm) with a crystal of 3.0 cm in diameter having the fundamental frequency of 1.5 MHz.

The sound velocities were measured with an ultrasonic interferometer working at 4.000 MHz.

Sample. Chloroform used was of spectral grade supplied by Nakarai Chemicals Co., Ltd. and was used without further purification. Eicosane used was also supplied by Nakarai Chemicals Co., Ltd.

Data Analysis of Brillouin Spectra

The observed Brillouin spectrum can be expressed explicitly as a convolution of the true Brillouin spectrum, the instrumental function, and the intensity spectrum of the laser source, as discussed in detail by Leidecker and LaMacchia.[5] However, in our experiment, the latter two response functions were not known exactly, so we have assumed that the observed spectrum, $I(\omega)$, is given by the relation,

$$I(\omega) = \int_{-\infty}^{\infty} I'(\omega-\omega')S(\omega')\mathrm{d}\omega', \tag{1}$$

where $S(\omega)$ represents the total effective response function which involves the laser intensity spectrum and the instrumental broadening function and $I'(\omega)$ is the true Brillouin spectrum. According to the treatment of Stegeman *et al.*,[3] an experimental determination of the convolution of laser and instrumental line profiles was carried out using the light scattered by a white paper. The profile of the diffuse laser was well expressed by a Gaussian function. As the profiles of Brillouin lines of liquids and solutions are expressed by a Lorentzian function, the observed Brillouin spectrum, $I_B(\omega)$, can be written as;

$$I_B(\omega) = \int_{-\infty}^{\infty} \frac{\Gamma_B}{\Gamma_B^2+(\omega'-\omega)^2}\exp\left[-\frac{1}{2}\left(\frac{\omega'}{\sigma_g}\right)^2\right]\mathrm{d}\omega', \tag{2}$$

where Γ_B is the true half-width of Brillouin line, and σ_g the half-width of a Gaussian function which is obtained from the observed profile of the diffuse light.

In order to determine the Brillouin shift accurately, the decomposition of the Rayleigh-Brillouin spectrum was carried out using the non-linear least-mean square method of Fletcher and Powell.[6] The Brillouin frequency shift, $\Delta\omega$, of the scattered light is related to the velocity of sound, V, as follows:[7]

$$\frac{\Delta\omega}{\omega_0} = 2n\left(\frac{V}{c}\right)\sin\left(\frac{\theta}{2}\right), \tag{3}$$

where ω_0 is the frequency of the incident light wave, c the velocity of light, n the refractive index of the liquids and θ the scattering angle. The true half-width of Brillouin line, Γ_B, is obtained by the fitting of Eq. 2 to the observed spectrum. Γ_B is related to the attenuation coefficient of sound by[7]

$$\alpha = \frac{\Gamma_B}{V}. \tag{4}$$

Results

Brillouin Spectra. In Fig. 2 are shown the Brillouin spectra of liquid chloroform recorded at the scattering angles of 87.0° and 88.8° in single and triple-pass systems, respectively. The effective finesse of these systems was about 38—40 in single-pass system and about 59—60 in triple-pass. As seen in Fig. 2, the triple-pass operation gives a much better Brillouin spectrum than that obtained by the single-pass system. In Fig. 3 are shown the Brillouin spectra of liquid chloroform recorded at three scattering angles, 40.0°, 74.7°, and 151.5°. At the largest scattering angle, the Rayleigh and Brillouin components do not overlap. The background scattering of the spectrum extends symmetrically from the central Rayleigh component to the Stokes and anti-Stokes Brillouin components. This fact indicates that there is a significant new component. This new component should be a Mountain line[8] which was found originally in carbon tetrachloride by Stegeman *et al.*[3]

The estimation of the sound velocity and attenuation

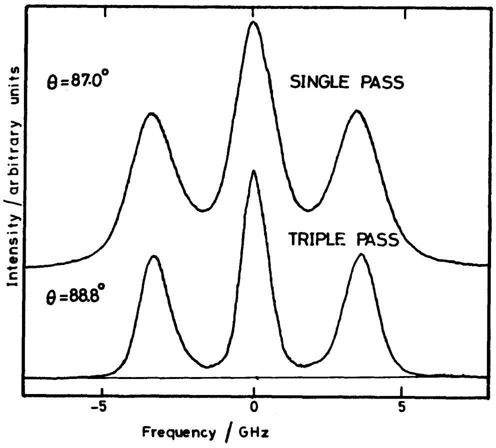

Fig. 2. Brillouin spectra of liquid chloroform recorded at the scattering angles of 87.0° in single-pass and 88.8° in triple-pass systems.

Table 1. Velocity and attenuation in chloroform at 30 °C

Scattering angle θ °	Wave vector 10^{-5} cm^{-1}	Frequency shift $\Delta\omega$ MHz	Sound velocity V m s^{-1}	Line width (obsd) MHz	Line width (correct) MHz	Absorption α/f^2 10^{-15} m s^{-2}
39.98	1.043	1152	979± 8	847±19	202±19	270±27
46.65	1.209	1798	979± 5	870±15	240±15	238±16
54.63	1.401	2123	999± 5	894±25	288±25	114±10
65.10	1.642	2502	1003± 9	862±17	228±17	114±10
74.67	1.851	3076	1011± 2	1002±30	465±30	153±10
81.53	1.993	3300	1016± 9	956±15	387±15	110± 5
88.80	2.130	3442	1021±10	930±12	348±12	96± 4
90.43	2.166	3633	1015± 4	999±45	456±45	107±11
112.92	2.544	3962	1026± 3	1086±92	588±92	115±18
113.57	2.554	3972	1025± 7	979±15	426±15	82± 4
151.53	2.959	4651	1036±10	1064±47	591±47	82± 7

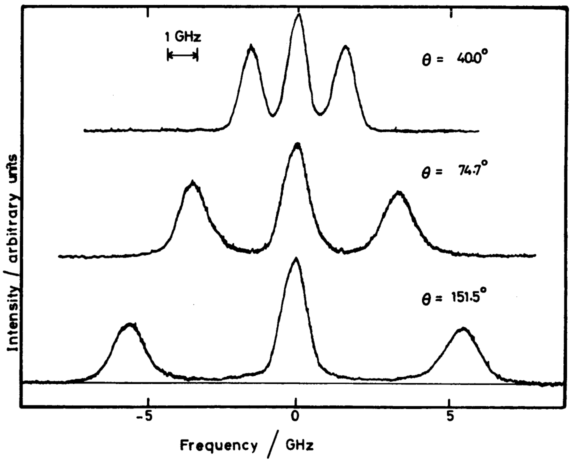

Fig. 3. Brilloiun spectra of liquid chloroform recorded at three scattering angles, 40.0°, 74.7°, and 151.5°.

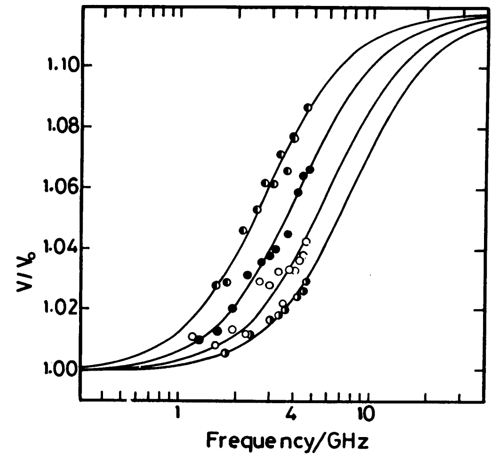

Fig. 4. Sound velocity dispersion curves of chloroform–eicosane mixtures at 30 °C. ◐; pure chloroform, ●; 3.1 wt% of eicosane, ○; 6.8 wt% of eicosane, and ◑; 14.4 wt% of eicosane. The solid lines are the best fit curves for a single relaxation.

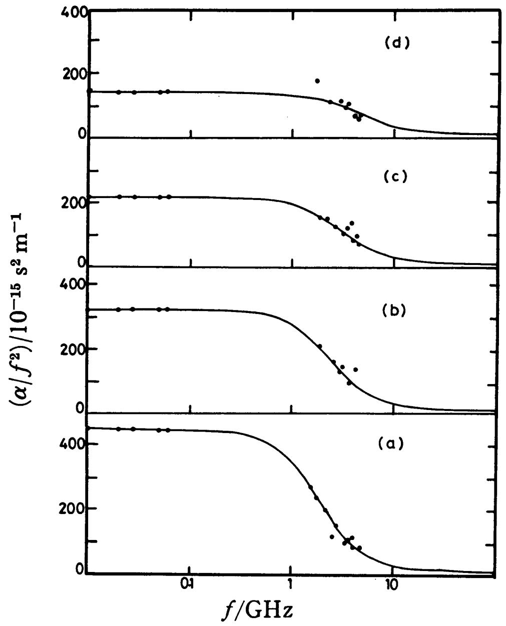

Fig. 5. Sound attenuation of chloroform–eicosane mixtures at 30 °C. The data in GHz region are obtained from the analysis of the Brillouin spectra and the data in MHz region from the ultrasonic absorption measurement. (a): Pure chloroform, (b): 3.1 wt% of eicosane, (c): 6.8 wt% of eicosane, and (d): 14.4 wt% of eicosane. The solid lines are the best fit curves for a single relaxation.

of liquid chloroform and chloroform solutions was carried out from the method indicated in the section of Data Analysis of Brillouin Spectra. As an example, the results for liquid chloroform at 30 °C are summarized in Table 1 together with their experimental errors. The sound velocity and the attenuation of chloroform–eicosane mixtures thus obtained are shown in Figs. 4 and 5. The sound velocity dispersion curve of neat chloroform at 30 °C was in good agreement with that obtained by Takagi *et al.*[9] in the GHz region.

As can be seen in Figs. 4 and 5, the sound velocity dispersion and relaxation curves were observed in the GHz region for all mixtures investigated. Our data in Fig. 4 are analyzed with the following single relaxation formula:

$$\frac{V_0^2}{V^2-V_0^2} = \left(\frac{1}{\varepsilon}-1\right)\left(1+\frac{f_r^2}{f^2}\right), \tag{5}$$

Table 2. Relaxation parameters in chloroform–eicosane mixtures at 30 °C

Concn of eicosane wt%	f_r GHz	V_0 m s^{-1}	V_∞ m s^{-1}	ε
0	3.50	967.7	1081.9	0.2000
3.05	4.33	975.5	1090.6	0.2000
6.85	5.80	986.7	1103.2	0.2000
14.38	8.05	1010.6	1129.9	0.2000

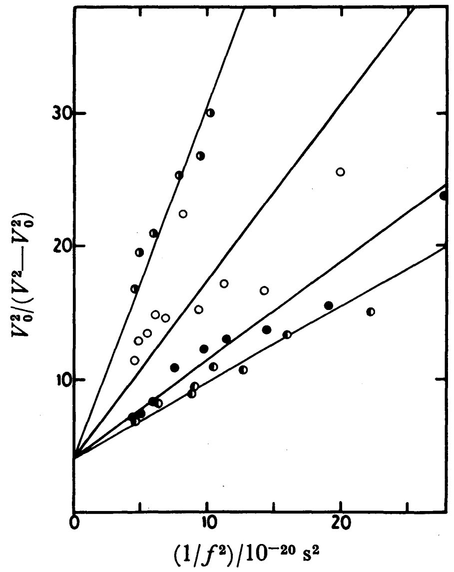

Fig. 6. Relationship between $V_0^2/(V^2-V_0^2)$ and $1/f^2$. The symbols are the same as those in Fig. 4.

$$\varepsilon = \frac{V_\infty^2 - V_0^2}{V_\infty^2},$$

where ε is the relaxation strength and V_0 and V_∞ are sound velocities at low frequency and at high frequency limits, respectively. Figure 6 shows the relation between $V_0^2/(V^2-V_0^2)$ and $1/f^2$ where the values of V_0 are those obtained by the ultrasonic interferometer working at 4 MHz. As shown in Fig. 6, a linear relationship is obtained in every chloroform–eicosane mixture. The relaxation parameters obtained are summarized in Table 2. As shown in Figs. 4 and 5, the experimental data can be well expressed by the single relaxation equation with the relaxation parameters shown in Table 2. The relaxation frequency shifts to the higher frequency side with increasing concentration of eicosane.

Ultrasonic Absorption Spectra. Figure 7 shows the ultrasonic absorption coefficients of chloroform-eicosane mixtures as a function of frequency. As shown in Fig. 7, no relaxation is observed either in chloroform-eicosane mixtures or in neat liquid eicosane over the frequency range investigated. However, the ultrasonic absorption coefficients of chloroform–eicosane mixtures are always smaller than those of neat chloroform at all frequencies investigated. The ultrasonic absorption coefficient, α/f^2, of chloroform–eicosane mixtures decreases rapidly with increasing concentration of eicosane (Fig. 8).

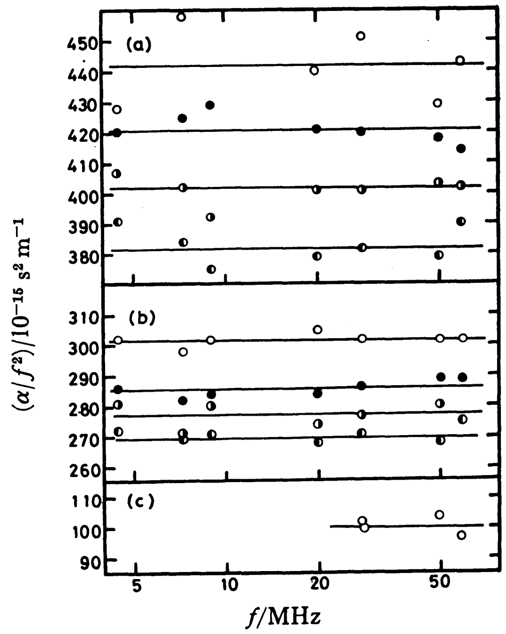

Fig. 7. Ultrasonic absorption coefficients of chloroform–eicosane mixtures.
(a): Pure chloroform, (b): 3.1 wt% of eicosane, and (c): pure eicosane. ◐; 10 °C, ◑: 20 °C, ●: 30 °C, and ○: 40 °C.

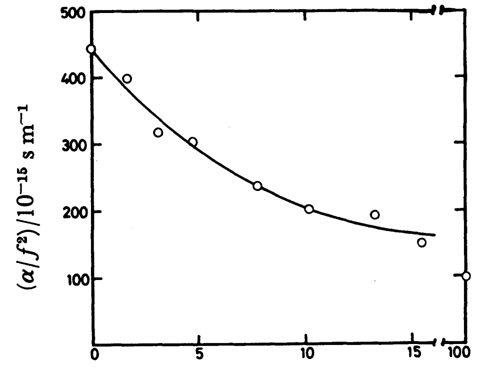

Fig. 8. Concentration dependence of sound absorption coefficients of chloroform–eicosane mixtures at 40 °C and 60 MHz.

Discussion

Recently, Takagi *et al.*[9] found a sound velocity dispersion of chloroform in the frequency range from 3 MHz to 5 GHz and reported that the dispersion reveals two relaxation processes. On the basis of the quantitative analysis of specific heat capacity, they argued that the two relaxation processes of chloroform are ascribable to the vibrational-translational relaxation, that is, the lowest ν_6 (261 cm^{-1}) and the second lowest ν_3 (366 cm^{-1}) foundamental vibrational modes have a common relaxation time, 50 ps, and the group of all above the third mode ν_2 (667 cm^{-1}) has a time of 290 ps.

As is seen in Fig. 4, our data are limited to the GHz region and the two relaxation processes can not be seen. Therefore, we are forced to analyzed our data with a single relaxation process expressed in Eq. 5. The relaxation frequency of neat chloroform obtained in this experiment corresponds to the higher relaxation frequency obtained by Takagi *et al.*[9] but ours is slightly smaller than that obtained by them. This may be due to the lack of data at the low frequency region. However, the relaxation strength obtained ($\varepsilon=0.200$) is in good agreement with the total relaxation strength obtained by Takagi *et al.*[9] ($\varepsilon=0.216$).

As in the case of a gas mixture, if a relaxing liquid, A, such as chloroform, is mixed with a non-relaxing liquid, B, such as eicosane, two collision processes become possible in which vibrational-translational energy transfer may occur:

$$A^* + A \longrightarrow A + A, \tag{6}$$

$$A^* + B \longrightarrow A + B. \tag{7}$$

Since the processes of (6) and (7) will have different collisional efficiencies, a composite relaxation time for A*, should be considered, as given by[10]

$$\frac{1}{\beta} = \frac{1-x}{\beta_{AA}} + \frac{x}{\beta_{AB}}, \beta = \frac{1}{2\pi f_r}, \tag{8}$$

where x is the mole fraction of the component B in the mixture, β_{AA} is characteristic of process (6), and β_{AB} of process (7). This may be represented graphically by a linear plot of relaxation time $1/\beta$ against mole fraction x (Fig. 9). In the chloroform–eicosane system, since the relaxation time of neat chloroform is 4.5×10^{-11} s, it follows that $\beta_{AB}=2.0\times10^{-12}$ s for the relationship shown in Fig. 9. This result indicates that a collisional efficiency between different molecules is larger than that between the same molecules, as reported by Hunter *et al.*[11,12] It is concluded that the observed relaxation of chloroform–eicosane mixture concerns mainly the vibrational-translational relaxation of the solvent chloroform itself, originating from a molecular collision between chloroform and eicosane.

In the MHz region, no ultrasonic relaxation phenomena were observed in either chloroform–eicosane mixtures or in eicosane in the temperature range investigated (see Figs. 5 and 7). As expected, the twenty methylene groups were not sufficient for the local segmental motion to be observed in the MHz frequency range.

As illustrated in Fig. 8, the values of α/f^2 in the MHz region decreased rapidly with increasing concentration of eicosane in the chloroform–eicosane mixture. In this system the value of α/f^2 can be supposed to be the ultrasonic relaxation amplitude, A, because of the very low value of the classical absorption (α/f^2 at high frequency limit), as shown in Fig. 5. The relaxation strength, r, can be given in terms of relaxation frequency, relaxation amplitude, and sound velocity at low frequency limit as shown below:[13]

$$r = Af_r V_0/\pi. \tag{9}$$

Table 2 shows that the concentration dependence of V_0 is very small. Since the relaxation strength remains constant in the concentration range investigated, the increase of the relaxation frequency results in the decrease of the relaxation amplitude. Therefore, it is concluded that the rapid decrease of α/f^2 in the mixture is mainly due to the shift of the relaxation frequency to the higher frequency side under the constant relaxation strength.

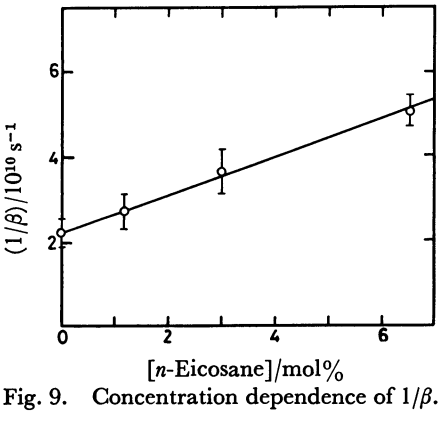

Fig. 9. Concentration dependence of $1/\beta$.

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