Computer Assisted Data Acquisition and Analyses of Brillouin spectra of ZnCl$_2$ single and ZnCl$_2$-NaCl Binary Melts.

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ABSTRACT

The Brillouin scattering experiment has been carried out with carefully purified samples of ZnCl$_2$ single and ZnCl$_2$-NaCl binary melts. The whole profile of Brillouin spectrum was obtained by the use of a computer assisted data acquisition system. The Brillouin spectra have been analyzed by the viscoelastic theory with the assumption of the single relaxation. The relaxation time and the velocities at limiting low frequency, $V_w$, and high frequency $V^*$ were determined.

INTRODUCTION

Zinc chloride melt is well-known for its unusually high viscosity at temperatures near its melting point. This is due to the presence of the network structure in the melt. However the viscosity of ZnCl$_2$ melt decreases remarkably with an increase in temperature, and also decreases with an addition of basic salts, such as alkali metal halides. These facts suggest that modification of the structure of the melt takes place by the addition of the basic salt, and by the variation in temperature. Sonic spectroscopy is one of the most effective method for the detection of the change in structure, especially for a highly viscous liquid. From the sonic spectroscopy, the relaxation phenomenon can be elucidated.

Zinc chloride single melt has been studied by several investigators by the use of ultrasonic spectroscopy (1-3). The existence of shear and structural relaxation have been recognized in these studies. The Brillouin scattering method(4,5) has been also applied to molten ZnCl$_2$. Soltwisch et al.(5) analyzed the Brillouin spectrum of ZnCl$_2$ melt. However, the Brillouin spectra have only been obtained at the frequency range apart from the central line for ZnCl$_2$ melt.

In the case of highly viscous liquids, the central peak of the Brillouin component becomes significant, and extends to the Brillouin doublet, due to the relaxation as described by Mountain(6). Therefore, it is important to obtain the central component of the spectrum.
as well as the doublet. In the present work, the Brillouin scattering experiment was carried out for ZnCl₂ single melt and ZnCl₂-20%NaCl binary melt. To obtain the whole spectra precisely, the scattering experiment was done on a carefully purified sample by using a computer assisted data acquisition system. The profile obtained were analyzed by the viscoelastic theory with the assumption of the single relaxation. The relaxation time and the velocities at limiting low and high frequencies, were obtained at the temperatures ranging from 550 to 1000 K.

EXPERIMENTAL

Experimental Set Up

The Brillouin scattering experiment was carried out by the use of a He-Ne gas laser. The laser beam was modulated into 225 Hz and focused at the center of a scattering cell placed inside a furnace. The scattering cell was made of fused quartz, and was of 30 mm diameter. The light scattered into the angle θ was focused on a pin hole with a collecting lens, was collimated with a collimating lens and was analyzed by a pressure scanned Fabry-Perot interferometer with a spacer of 7 mm. The profiles were observed by a X-Y recorder, and were also recorded digitally by a personal computer. The measuring time were about 15 minutes per spectrum. The profile was recorded in about 400 points per free spectral range FSR (FSR=21 GHz). The experiment was carried out at the scattering angles of 45°, 90° and 140°.

Sample

In the Brillouin scattering experiment, the inclusion may cause the spikes in the spectrum around the central component. For highly viscous liquids, like ZnCl₂ the intensity of the elastic lines scattered from the inclusions is usually very intense compared to the Brillouin component. A typical profile obtained for the sample with light reflecting inclusion is shown in Fig.1(a). In this case the real Brillouin spectrum was buried under the noise and could not be observed. Therefore, the sample must be carefully purified to remove the inclusions. In this work, the sample was purified in the following manner. The reagent grade salts was loaded into a reaction tube made of quartz, and was dehydrated in Ar flow for 6 hr, then was melted. The dehydrated HCl was bubbled into the melt for 3 hr to remove the residual trace amount of the moisture. Then the melt was filtered through a quartz filter. The filtrate was sealed under vacuum into a quartz container to which the optical cell had been connected by a glass blowing technique. The purified sample in the container was transferred into the optical cell by distillation. Then, the sample was sealed into the cell, and was provided to the Brillouin scattering measurement. By the use of a well purified sample, the whole spectrum shown in Fig.1(b) was obtained.
RESULTS AND DISCUSSION

Profiles obtained at different temperatures are compared in Fig.2. The shape of the spectrum changes remarkably with the variation in temperature. At the higher temperature (e.g., 933K) the spectrum has a typical shape of a normal liquid, which consists of a central Rayleigh line and a Brillouin doublet. At the middle temperature region (e.g., 773K), the Brillouin peaks become very broad, and overlapped with the central peak. At the lower temperature (e.g., 623K), the central peak increase its intensity, furthermore, there observed a continuous component between the central line and Brillouin doublet, although the separation between the central peak and Brillouin doublet apparently becomes clear. At the lower temperature, the central peak consists of the weak Rayleigh component, clearly observed in the profiles at 933K, and a strong component due to the relaxation to adiabatic pressure fluctuation.

The viscoelastic theory (7) gives the spectral distribution function \( \sigma(k,\omega) \) as follows.

\[
\sigma(k,\omega) = (1 - \frac{1}{\gamma}) \frac{2(\lambda k^2/\rho_0 C_p)}{(\lambda k^2/\rho_0 C_p)^2 + \omega^2} + \frac{2M_0}{\gamma} \left( \frac{\eta(\omega) + \eta_0}{\rho_0 \omega^2/k^2 - M(\omega)} \right) + \frac{\eta(\omega) + \eta_0}{\rho_0 \omega^2/k^2 - M(\omega)}
\]

where \( k \) is the shift in wave vector, \( \omega \) is the shift in angular frequency of the scattered light, \( \lambda \) is the thermal conductivity, \( \rho_0 \) is the density, \( C_p \) is the heat capacity at constant pressure, \( M(\omega) \) is the longitudinal storage modulus, \( M_0 \) is the low-frequency storage modulus, \( \eta(\omega) \) is the longitudinal viscosity and \( \eta_0 \) is the nonrelaxing part of the viscosity. The first term in eq.(1) represents the Rayleigh line which is caused by the entropy fluctuation at constant pressure. The second term represents the Brillouin component caused by adiabatic pressure fluctuation.

In most case of liquid, in which the modulation due to dispersion in sound wave propagation is not strong, the Brillouin component in Eq.(1), can be separated approximately into three Lorentzians, which are the Brillouin-doublet and the Mountain line(6). Therefore, the Brillouin spectrum can usually be analysed not by using full spectral shape, but rather its decomposition in the Lorentzian lines. This is the way of analysis taken generally at studies on normal liquids. In this case, the details of the profile of the central peak are not necessarily required for the analysis, if the Brillouin doublet are observed precisely. However, approximated analysis becomes rather poor if the modulation is so strong as in the case of present study. We have therefore, tried to analyse the whole spectrum of the Brillouin scattering.

For single relaxation behavior, following relations hold,
\[ \eta(\omega) = \rho_0(V_\infty^2 - V_0^2)\nu/(1 + \omega^2\tau^2) \]  
\[ M(\omega) = \rho_0(V_\infty^2 + V_0^2\omega^2\tau^2)/(1 + \omega^2\tau^2) \]

where \( \tau \) is relaxation time, \( V_0 \) and \( V_\infty \) are velocities at limiting low and high frequencies, respectively.

The Brillouin spectrum has been analyzed by using eqs.1-3. The spectrum obtained corresponds to the dynamical structure factor \( \varphi(k,\omega) \), convoluted with the apparatus profile. The apparatus profile was observed in advance, and is shown in Fig.3. The spectrum was analyzed in the following manner. The theoretical spectrum is computed for a set of initial values of the parameters \( V_0, \ V_\infty, \tau \) and \( \eta_0 \) and then convoluted numerically with the apparatus profile, and compared with the experimental spectrum by a least squares scheme to calculate an improved set of parameters. The parameter fitting is repeated until the squares of the deviation become minimum. For each spectrum, then, a set of parameters \( V_0, \ V_\infty, \tau, \) and \( \eta_0 \) is obtained.

Figure 4 shows the Brillouin spectra of ZnCl\(_2\) at scattering angle of 90° in comparison with the value calculated by best fit of the viscoelastic theory. The circles represent the experimental values, and the lines show the best fit of Eq.(1) with the convolution of the apparatus profile. As shown in Fig.4, eq.1 describes the spectra very well at various temperatures investigated. The spectrum analysis was also done for profiles obtained at other scattering angles, and for ZnCl\(_2\)-20%NaCl binary melt, in the same way.

The temperature dependences of \( V_0 \) and \( V_\infty \) for ZnCl\(_2\) single melt are shown in Fig.5. The circles represent the data obtained at the scattering angle of 90°, and the squares, those of 140°. As shown in this figure, the results obtained at different scattering angles agree very well. The velocities at limiting low frequency \( V_0 \) and high frequency \( V_\infty \) decrease linearly with increasing temperature.

The relaxation time of ZnCl\(_2\) is shown in Fig.6. The value of \( \tau \) decreases rapidly with increasing temperature. At the temperatures near 600K, the relaxation time is in the order of nanosecond (10\(^{-9}\)s), when the temperature increases to 900K, the relaxation time decreases to the order of 10 picosecond (10\(^{-11}\)s). The remarkable variation of relaxation time indicate the structure variation of the melt with temperature change. The structural studies of ZnCl\(_2\) have been done by several researchers (8-10). It has been considered that ZnCl\(_2\) melt consists of polymeric (ZnCl\(_2\))\(_n\) species of various sizes. These species are made up of ZnCl\(_4\) tetrahedra bridged at the corners to give three dimensional networks. With increasing temperature the degree of polymerization lowers. Due to the presence of the large sized polymeric species at the lower temperatures, the response of the melt is very slow. This is the reason for the relaxation time being long at the lower temperatures. The response rate increases with increasing temperature because the degree of depolymerization decreases with increasing temperature. Therefore the relaxation time decreases with increasing temperature.

As has been described, the shape of the Brillouin spectrum of ZnCl\(_2\) melt changes
remarkably with the variation in temperature. The spectral shape mostly depends on the value of the relaxation time. The shape of the Brillouin spectrum changes drastically, if the value of \( \omega \tau \) is nearly equal to unity (2). For the case of molten ZnCl\(_2\), the relaxation time varies more than 1000 times over the temperature range of 1000 to 580K, and the condition, \( \omega \tau = 1 \) stands in the midst of the temperature range. This is the reason for remarkable change observed for the Brillouin spectral shape depending on temperature.

The temperature dependence of \( V_0 \) and \( V_\infty \) for ZnCl\(_2\)-NaCl binary melts is shown in Fig.7. \( V_0 \) and \( V_\infty \) decrease linearly with increasing temperature for each composition. There found about 0.6km.s\(^{-1}\) dispersion in the velocity for ZnCl\(_2\)-20\%NaCl binary melt.

The relaxation time of the binary melts is plotted against temperature in Fig.8. The relaxation time decreases with an addition of NaCl. This effect is remarkable at the lower temperature region. We consider that this is due to the breakage of the network structure in the melt. It seems that sodium chloride acts as a chloride ion donor when it is added to ZnCl\(_2\), and therefore, the addition of NaCl prompts breakage of the network structure in ZnCl\(_2\) and results in the decrease of relaxation time.

CONCLUSION

The Brillouin spectra in ZnCl\(_2\) single and ZnCl\(_2\)-20\%NaCl binary melts were obtained by using a computer assisted data acquisition system. The Brillouin spectra were well described by the viscoelastic theory with the assumption of the single relaxation. The velocities at limiting low frequency, \( V_0 \), and high frequency \( V_\infty \) decrease linearly with increasing temperature. The relaxation time decreases remarkably with an addition of NaCl. It is concluded that both the temperature increase and the addition of NaCl result in the modification of the network structure of ZnCl\(_2\) melt.

REFERENCE

1. H.M.Zhu, Y.Sato, T.Yamamura and T.Ejima, “Proceedings of 11th International Symposium on Molten Salts”, (1990), 152.
2. G.J.Gruber and T.A.Litovitz, J.Chem.Phys., 40(1964).
3. T.Ejima, T.Yoko, M.Saito and Y.Kato, Jpn.Inst. Metals, 43(1979), 929.
4. H.E.G.Knap, J.Chem.Phys., 80(1984), 4788.
5. M.Soltwisch, J.Sukmanowski and D.Quitman, J. Chem. Phys., 86(1987), 3207.
6. R.D.Mountain, J. Res.Natl.Bur.Std., 70A(1966), 207.
7. C.J.Montrose, V.A.Solovyev and T.A.Litovitz, J. Acoust. Soc.Am., 43(1968), 117.
8. J.R.Moyer, J.C.Evans and G.Y.Lo, J. Electrochem. Soc., 113, 158 (1966).
9. M.Itoh, K.Sakai and T.Nakamura, Inorg. Chem., 21, 3552(1982).
10. D.E.Irish and T.F.Young, J.Chem.Phys., 43, 1765(1965).
Fig. 1 Profiles of Brillouin spectrum of ZnCl₂ at 730K, θ=90°. (a) Sample with light reflecting inclusion. (b) refined sample.

Fig. 2 Brillouin spectra of ZnCl₂ at various temperatures, θ=90°.

Fig. 3 Apparatus Profile
Fig. 4 Brillouin spectra of ZnCl₂ for θ=90°, the lines show the best fit of viscoelastic theory.
Fig. 5  Temperature dependence of $V_0$ and $V_\infty$ for ZnCl$_2$ melt.

Fig. 6  Relaxation time of ZnCl$_2$ melt.
Fig. 7 Temperature dependence of $V_0$ and $V_\infty$ for ZnCl$_2$-NaCl binary melts.

Fig. 8 Relaxation time of ZnCl$_2$-NaCl binary melts.