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VISCO-ELASTIC PROPERTIES OF MOLTEN $ZnCl_2$ AND NaCl BINARY SYSTEM

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SYNOPSIS: In order to clarify the viscoelastic properties of $ZnCl_2$-NaCl binary melts, hypersonic velocities have been measured at the temperatures ranging from the liquidus to 1000K over the composition range of 0 to 50 mol%NaCl by means of Brillouin scattering method. Absorption coefficients of ultrasound have been also measured for molten $ZnCl_2$. The hypersonic velocity of $ZnCl_2$ decreases linearly with increasing temperature at high and low temperature regions, but at intermediate temperature region, decreases curvilinearly with increasing temperature, indicating dispersion of sound propagation.

The dispersion behavior has been well described in terms of the single relaxation theory. It was found that the relaxation time of the binary melts decreases steeply with an addition of NaCl due to the depolymerization of the net work structures in the melts.

Key words: ZnCl2, NaCl, melts, visco-elastic properties, vicosity, Brillouin scattering, sonic spectroscopy, structure, associated species

1. Introduction

Among the molten salts, zinc chloride is well known for its unusually high viscosity at temperatures near its melting point. This is due to the presence of the net work structure in the melts. However, the viscosity of zinc chloride decreases remarkably with an increase in temperature, and also with an addition of basic salts, such as alkali metal halides. These facts suggest that the modification of structure of the melt takes place by the increase in temperature or by the addition of the basic salts. The similar temperature and composition dependence of viscosity have been reported[1] for the case of silicate slags. Further more, the structural similarity can be found for silicate slags and molten zinc chlorides, that is to say, the basic units of these liquids are tetragonals , SiO_4^{4-} for the former, and $ZnCl_4^{2-}$ for the latter cases. Because of these similarity, molten zinc chloride can be regarded as a low temperature model of molten slicate slags.

To understand these phenomena mentioned above, the change in structure with the addition of the additives should be elucidated. Sonic spectroscopy is one of the most effective methods to detect the existence of associated species which generally cause the the structural relaxation of sound propagation. The relaxation times of molten salts are usually too short to be measured by a pulse method which has been frequently applied to the molten salts. However, sonic spectroscopy in gigahertzian region becomes possible if a Brillouin scattering method is applied.

In the present study, $ZnCl_2$-NaCl binary melts have been studied by the sonic spectroscopy. Sound velocities in the melts have been measured over the frequency range of 3-8GHz by means of a Brillouin scattering method over the entire composition range and compared with the ultrasonic velocities determined by a pulse method. Absorption of the ultrasound has been also studied by means of the pulse method. The relaxation phenomena have been discussed on the basis of a single relaxation theory. The structural change with an addition of alkali chlorides has been also investigated.

2. Experimental procedures

The hypersonic velocities of molten $ZnCl_2$-NaCl binary melts were measured by a Brillouin scattering method. The experimental arrangement was described in detail in the previous paper[2]. The light source was a He-Ne gas laser operated in single mode at a wave length of 632.8nm. The laser beam was modulated into 225 Hz and focused at the center of the scattering cell placed inside a cylindrical furnace. The scattering cell was made of fused quartz.The light scattered into the angle θ was focused on a pin hole with a collecting lense, was collimated with a lens and was analysed by the Fabry-Perot interferometer. The spectrum of the light scattered by a homogeneous liquid consists of a central Rayleigh line withthe same frequency as that of the incident beam, and a doublet of which the components are shifted symmetrically from the frequency of the incident beam. The latter is induced by the collision of a photon and a phonon in the liquid under thermal equilibrium. The frequency shift $\Delta\nu$ between the Brillouin peaks and the Rayleigh peak can be given as follows:

$$\Delta\nu = 2\nu_i n(V_s/c)\sin\theta \qquad (1)$$

where ν_i is the frequency of the incident light, n ,the refractive index and c,the light speed.The sound velocity V_s can be determined from the frequency shift $\Delta\nu$ and the scattered angle θ. If it is assumed that the sound propagation is an adiabatic process and that the local fluctuation of liquid density due to the sound propagation is small, such thermodynamic values as adiabatic compressibility β_s, isothermal compressibility β_t, constant-volume heat capacity Cv, and internal pressure P_{int} can be derived from the sound velocity.

The moisture absorbed by $ZnCl_2$ would affect the viscoelastic property of the melts by modifying the melt structure as well as by forming hydroxides or oxychlorides. Therefore, the reagent grade $ZnCl_2$ was pretreated to remove the moisture and inclusions which would cause the spikes in the spectrum obtained by the Brillouin scattering experiment.The Reagent grade $ZnCl_2$ was kept in a desiccator with P_2O_5 at 298K for 400 ks.The dried salt was loaded into a reaction tube made of quartz, and was melted. Then,dried HCl was bubbledinto the melt for 20 ks to remove the residual trace amount of moisture. At this stage, there were found dark colored finely dispersed inclusions in the melt.Therefore,the melt was kept under HCl for 40 ks to let the inclusions agglomerate into flakes and then was filtered to remove the inclusions. The filtrate was sealed in vacuo into a quartz container to which a cylindrical optical cell had been connected by a glass blowing technique. The purifed $ZnCl_2$ in the container was transfered in to the optical cell by distillation and was provided to the Brillouin scattering measurement. Sodium chloride was also purified by the bubbling of HCl and mixed with the purified $ZnCl_2$ to prepare the binary salt samples.

3. Rssults and discussion

3.1 Brillouin scattering of molten $ZnCl_2$

The Brillouin scattering measurement of $ZnCl_2$ was done at temperatures of 570 to 720 K and at the scattering angles of 70, 90 and 140°. These scattering angles cover the frequency range of 5 to 10 GHz. The refractive indicies being necessary for the derivation of the sonic velocities from the Brillouin shifts were determined by a minimum deflection angle method. The results of the measurements of the refractive indices has been detailed in the previous paper[3].

The hypersonic velocities for the three different angles were determined from the observed Brillouin shifts by Eq.(1) and are plotted as functions of temperature in Fig.1, where ultrasonic velocities given by Gruber and Litovitz(4),and Yoko et al.[5] are also shown for comparison. Brillouin scatter ing studies on molten zinc chlorides have been also studied by Quitman et al.[6] and Knape[7]. Both results on Brillouin scattering agree well with the present results and will be compared in detail later. As shown in Fig.1, the hypersonic velocities determined at three different angles agree within experimental error both in the low temperature region(570<T<620K) and high temperature region(870K<T). In these temperature regions, the hypersonic velocity increases linearly with increasing temperature and agrees with the ultrasonic velocities as shown in Fig.1. On the contrary, the hypersonic

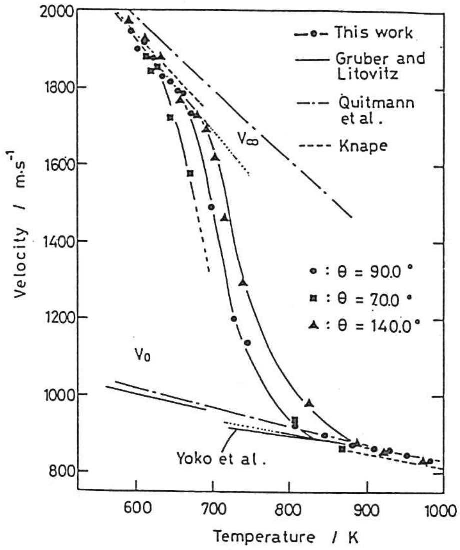

Fig.1 Temperature dependence of sound velocity in molten $ZnCl_2$ determined at various angles.

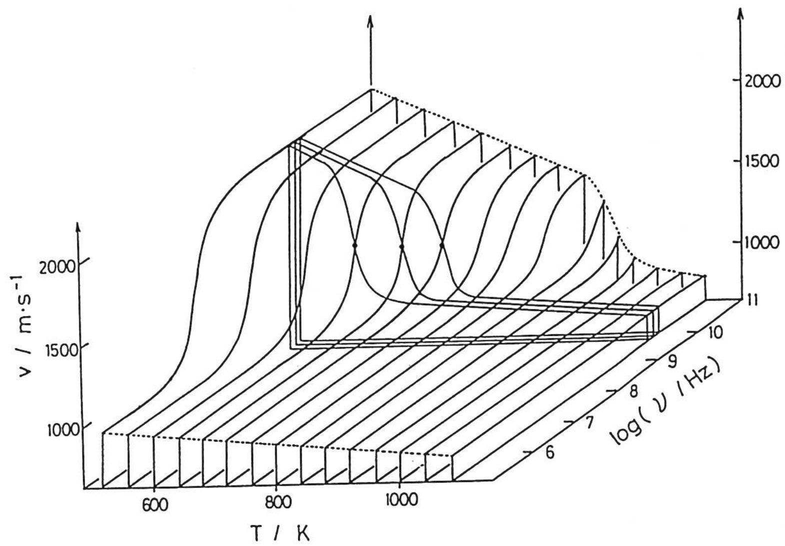

Fig.2 Temperature and frequency dependence of sound velocity for molten $ZnCl_2$.

velocity in the intermediate temperature region depends on the scattering angle, with the velocities measured at a scattering angle of 140° being the highest, and those measured at 70° being the lowest. The scattering angles of 70, 90 and 140° correspond to the frequency ranges of 4.5~5.7, 5.6~7.1 and 6.9~ 9.5 GHz, respectively. Furthermore, the Brillouin lines observed in the intermediate temperature region broaden significantly. These facts all obviously indicate that a dispersion of sound wave propagation occurs in the intermediate temperature region. The widths of the Brillouin lines are so broad that the Rayleigh and Brillouin lines overlap with each other. Therefore, the overlapped waves were resolved by a convolution assuming that wave forms were Lorentzian. Because of this process of waveform resolution the errors involved in the determination of the hypersonic velocity becomes as large as 10% in the intermediate temperature region, while the errorsin the low and high temperature regions are less than about 2.5%. Since it has been found that a dispersion of sound wave occurs in the frequency region observed in molten $ZnCl_2$, a single relaxation theory, which was applied to molten $ZnCl_2$ by Knape[7], has been applied to understand the relaxation behavior observed. The hypersonic velocity determined at temperatures lower than 620 K can be regarded as the velocities of the limiting high frequency since they agree with the ultrasonic ones. On the other hand, the hypersonic velocity determined at the temperatures higher than 870 K can be regarded as the velocity of the limiting low frequency because there is a linear relation between velocity and temperature. On the basis of the single relaxation theory, an equation for the static bulk viscosity, η_B° was derived by Montrose et al [8] as follows:

$$\eta_B^\circ = \rho/(V_\infty^2 - V_o^2)\tau \qquad (2)$$

where τ is the relaxation time and ρ is the density of the medium. Assuming that the values of V and V_o can be extrapolated from the hypersonic velocities obtained in the low and high temperature regions, respectively, the relaxation times were calculated by Eq.(6) from the bulk viscosities determined from the ultrasonic absorption by Yoko et al.[4]. According to the single relaxation theory, the sonic velocity V is given by Eq.(3) as a function of the frequency f.

$$V = V_o^2 + (V^2 - V_o^2)(2\pi f)^2/(1 + (2\pi f)^2\tau^2) \qquad (3)$$

To show the variation of the relaxation behavior with temperature, the sonic velocity is plotted against temperature and frequency in Fig.2. The velocities determined at three different scattering angles are represented by solid lines. As clearly shown in Fig.2, the measurements at the intermediate temperature region was done in the midst of the dispersion.

3.2 HYPERSONIC VELOCITIES OF $ZnCl_2$-NaCl

In order to clarify the effect of the addition of chloride ion doner on the melt structure, the hypersonic velocities were measured at the composition range of 0 - 50 mol% NaCl or KCl. The hypersonic velocities are plotted against temperature for $ZnCl_2$-NaCl in Fig.3. The sonic velocity of 12.5 mol%NaCl decreases steeply upto 650 K, then

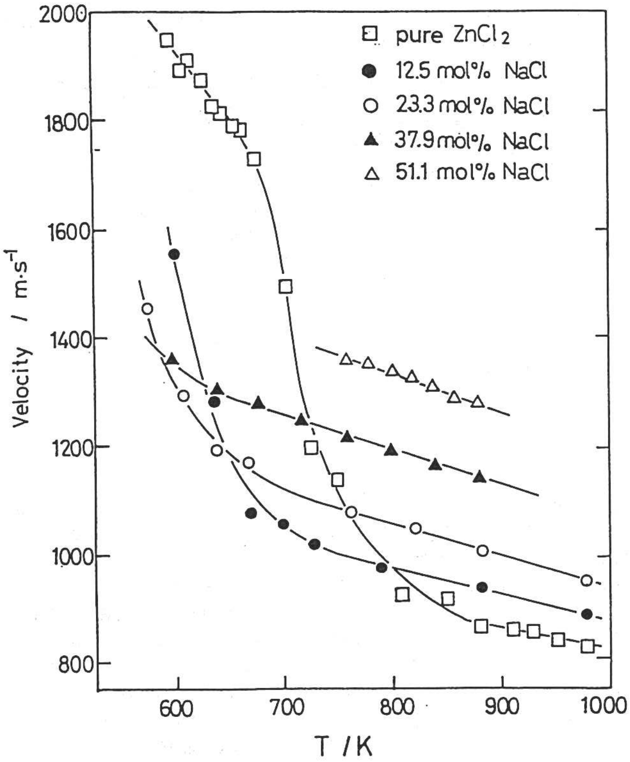

Fig.3 Temperature dependence of sound velocity for $ZnCl_2$-NaCl binary melts.

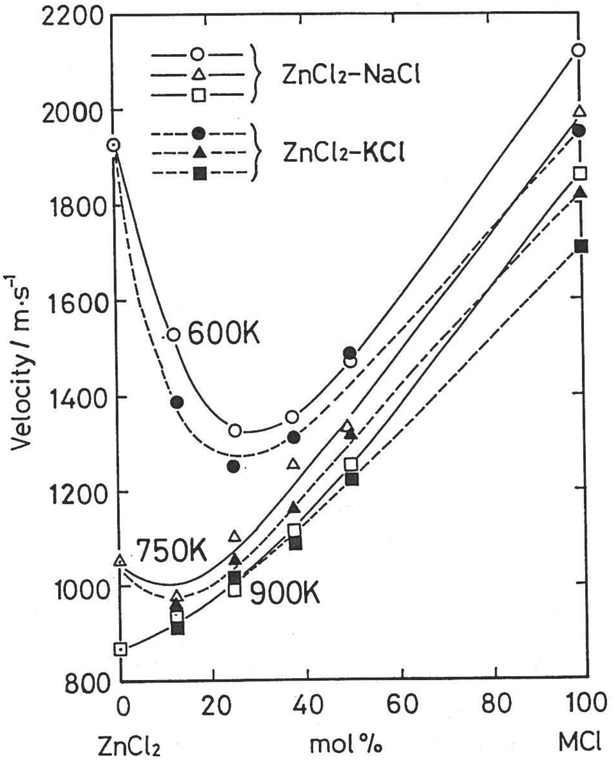

Fig.4 Composition dependence of sound velocity for $ZnCl_2$-NaCl binary melts.

reduces its slope gradually until 780 K and decreases linearly from 800 K with increasing temperature. As the composition of NaCl decreases, the temperature where a transition from the steep curvilinear to the linear occurs decreases. In case of $ZnCl_2$-KCl binary melts, the variation of temperature dependence with composition is similar to that of $ZnCl_2$-NaCl binary melts. As we have seen in the discussion on the relaxation behavior of molten $ZnCl_2$, a curvilinear dependence of the velocity on temperature is associated with the sound wave propagation. In analogy with the case of molten $ZnCl_2$, the curvilinear relation between the velocity and temperature observed for $ZnCl_2$-NaCl binary melts can be attributed to the dispersion of sound wave propagatin.. As obviously shown in Figs.3, the temperature at which the curvilinear relation starts decreases with increasing NaCl composition.

The hypersonic velocities at constant temperatures are plotted against composition in Fig.4. The velocity at 600K, which is 9K above the melting point of $ZnCl_2$, decreases steeply with increasing the composition of NaCl. The hypersonic velocity at 750K also shows a decrease with an addition of NaCl, but its decrement is much slower than that at 600K. The velocity at 900 K increases monotonically with increasing NaCl or KCl composition and does not show any minimum. The sharp decrease observed for hypersonic velocity at 600 K with the addition of NaCl seems to correspond to a dispersion due to the variation of the relaxation frequency with NaCl or KCl composition. Moyer et al.[9] proposed that the addition of alkali chloride to $ZnCl_2$ induces the depolymerization as expressed by the following equation,

$$(ZnCl_2)_n + Cl^- = (ZnCl_2)_{n-m} + (ZnCl_2)_{n-m} + (ZnCl_2)_mCl^- \quad (m<n) \qquad (4)$$

and further addition of the Cl^- donor results in the second process expressed by the following equation.

$$(ZnCl_2)_mCl^- + Cl^- = ZnCl_4^{2-} + (ZnCl_2)_{m-1} \quad (5)$$

Therefore, it is reasonable to consider that the addition of NaCl causes the breakage of the net work structure of $ZnCl_2$ and results in the decrease of the relaxation frequency of the binary melts. On the other hand, the dissociation occurs due to a temperature rise too. As mensioned above, the relaxation frequency of the molten $ZnCl_2$ increases with increasing temperature and exceeds the frequency range, 5-8GHz of the present measurements at about 900 K. Since The relaxation frequency of the binary melts is expected to be more than that of molten $ZnCl_2$ due to the addition of the chloride doner. Therefore, at 900K, the relaxation frequency of the binary melts is more than the frequency range of the present measurements. This accounts for the monotonic dependence of the hypersonic velocity at 900 K on NaCl composition.

4. CONCLUSIONS

Hypersonic velocities of molten $ZnCl_2$ -NaCl have been determined by means of Brillouin scattering method over the composition range of 0-50 mol% NaCl in the temperature range covering about 150 K above the liquidus temperature. The hypersonic velocity of $ZnCl_2$ decreases linearly with increasing temperature at high and low temperature regions, but shows a curvilinear dependence on temperature at intermediate temperature region, where the dispersion of sound propagation is observed.

The visco-elastic behavior observed have been well described in terms of the single relaxation theory. The relaxation time of the binary melts decreases sharply with an addition of NaCl due to the depolymerization of the melt structure.

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