ULTRASONIC AND HYPersonic SPECTROSCOPY OF ALKALI 
NITRATE SINGLE AND BINARY MELTS 
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ABSTRACT 

Sound propagation in the molten alkali nitrate single salts, LiNO₃, NaNO₃, 
RbNO₃ and CsNO₃ and the binary melts, NaNO₃-LiNO₃, -RbNO₃ and -CsNO₃, 
have been studied over the frequency range of 5-25 MHz and 3-8 GHz by means 
of pulse and Brillouin scattering methods, respectively. A dispersion of sound 
propagation is observed at the frequency between ultra- and hyper-sound 
region for KN03, RbNO3 and CsNO3. The thermodynamic properties derived 
from the sound velocity are approximately additive for the binary melts 
investigated. The bulk viscosity, \( \eta_b \) was derived from the 
absorption coefficient determined. The value of \( d \eta_b /dT \) is negative and 
temperature dependence of \( \eta_b / \eta_s \) is insignificant for the molten 
alkali nitrate single salts. The bulk viscosity of the binary melt 
decreases rapidly with the addition of the component having smaller bulk 
viscosity in pure salt. 

INTRODUCTION 

Molten alkali nitrate mixtures have been considered as one of the 
most promising candidates for a heat storage medium at high temperatures 
because of its wide temperature range of chemical stability. However, the 
structure of molten alkali nitrate is not as simple as a typical ionic 
melt such as an alkali halide because of the existence of associated 
species. Sonic spectroscopy is one of the most effective methods of 
detecting the existence of associated species which cause the structural 
relaxation in sound propagation. In the present study, sound velocities in 
the molten alkali nitrate single salts, LiNO₃, NaNO₃, KNO₃, RbNO₃ and 
CsNO₃ and binary salts, NaNO₃-LiNO₃, NaNO₃-RbNO₃, NaNO₃-CsNO₃ have 
been measured over the frequency ranges of 5-25 MHz and 3-8 GHz by means 
of pulse and Brillouin scattering methods, respectively. Ultrasonic and 
hypersonic velocities measured are compared with each other to elucidate 
the relaxation process of sound propagation in the melts. Ultrasonic 
absorption coefficients have been measured to determine the bulk 
viscosities for the binary melts. Relaxation times have been derived from the 
hypersonic and ultrasonic velocities and bulk viscosity on the basis of 
a relaxation theory with a single relaxation time. Thermodynamic 
properties such as adiabatic compressibility, constant pressure heat 
capacity, isothermal compressibility and internal pressure were obtained.
EXPERIMENTAL

ULTRASONIC SPECTROSCOPY

The propagation velocity of ultrasound in molten alkali nitrate has been measured by the use of a pulse method. Details of the pulse method was described elsewhere. The sound pulses piezoelectrically generated by a X-cut quartz crystal are introduced into the melts through a lower conduction rod made of fused quartz. The sound pulses propagated through the melt are received by an upper conduction rod made of fused quartz and is transduced into electrical signals by a quartz crystal attached to the end of the upper conduction rod. The sound velocity and absorption coefficient are determined from the measured delay time and the amplitude change accompanying the displacement of the spacing between the upper and lower conduction rods. The measurement was carried out over the temperatures ranging from the melting point of the salt to about 150K above it. The maximum of the error is estimated to be less than 0.2% for the sound velocity and 3% for the absorption coefficient determination.

BRILLOUIN SCATTERING METHOD

As predicted by Brillouin, the light scattered by a homogeneous liquid consists of a central Rayleigh line with the same frequency as that of a exciting light, and a doublet of which the components are shifted in frequency symmetrically from the frequency of the exciting light. 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 peak is expressed as follows:

\[
\Delta \nu = \pm 2 \nu \cdot n \left( \frac{V_s}{c} \right) \sin \theta
\]

where \( \nu \) is the frequency of the exciting light, \( n \) is the refractive index of the liquid, \( V_s \) and \( c \) are the velocities of sound wave and light respectively, and \( \theta \) is the scattering angle. The frequency shift is also equal to the frequency of sound wave which induces the light scattering. The sound velocity can be obtained from the frequency shift and the scattering angle.

A schematic diagram of the experimental apparatus used for the measurement of Brillouin scattering is shown in Fig.1. The system is composed of a light source, a high temperature cell, and a Fabry-Perot interferometer. The light from the He-Ne gas laser is modulated to 225Hz by the use of an optical chopper. The modulated light is then focused upon the cell placed in an electric furnace. The light scattered at an angle of \( \theta \) is focused on a pin hole with a collecting lens and is collimated with a lens. The light passed through the interferometer is focussed and is changed into electrical signals with a photomultiplier. Reagent grade alkali nitrate is dried at 393K for 24 h in vacuo, melted in argon atmosphere and filtered through a sintered Pyrex glass disk to remove small suspended inclusions. The filtrate is poured into a cylindrical cell made of Pyrex glass and the cell is sealed under vacuo.
RESULTS AND DISCUSSION

SOUND VELOCITY AND ABSORPTION OF ALKALI NITRATE SINGLE SALTS

Frequency shifts of Brillouin peaks for molten alkali nitrates were measured over the temperature range of their melting points to 820K at scattering angles of 45, 90 and 135 deg. The velocity of hypervelocity was determined from the observed frequency shifts in the sound frequency ranges of 7-8 GHz for LiNO$_3$, 2-7 GHz for NaNO$_3$, and 3-8 GHz for CsNO$_3$. In these frequency ranges sound velocity appears to be independent of frequency.

Ultrasonic velocities were measured in the frequency range of 5-25 MHz for LiNO$_3$, NaNO$_3$, and KNO$_3$, and 5-15 MHz for RbNO$_3$ and CsNO$_3$. The ultrasonic velocity does not exhibit frequency dependence for these salts.

The ultrasonic and hypersonic velocities obtained were plotted against temperature and are shown in Fig. 2. It can be seen from Fig. 2 that both ultrasonic and hypersonic velocities monotonously decrease with increasing temperature. However, in case of ultrasonic velocity a curve linear relation is found for all the single salts investigated. As shown in Fig. 2 both ultrasonic and hypersonic velocities decrease with increasing cation-size except for LiNO$_3$. When the hypersonic and ultrasonic velocities are compared with each other for each alkali nitrate, both velocities agree well within the limit of the experimental error for molten LiNO$_3$ and NaNO$_3$. On the contrary, the difference between hypersonic and ultrasonic velocities clearly exceeds the limit of the experimental error for KNO$_3$, RbNO$_3$ and CsNO$_3$. The observed dispersion of the sound propagation indicates that the relaxation frequency of KNO$_3$, RbNO$_3$, and CsNO$_3$ are more than the highest of the ultrasonic measurement and less than the lowest frequency of the Brillouin scattering measurement. The relaxation frequencies of LiNO$_3$ and NaNO$_3$ are more than the highest frequency of the Brillouin scattering measurement. Relaxation behavior of the single salt will be examined in detail later in this section.

The absorption coefficient, $\alpha$ of the ultrasound was determined over the frequency range of 5-25 MHz for molten alkali nitrate single salts. The ratio of the absorption coefficient to the square of the frequency, $f$, are plotted against temperature and shown in Fig. 3. The value of $\alpha/f^2$ decreases monotonously with increasing temperature. The bulk viscosity was determined from the absorption coefficient measured by the use of the following equation,

$$\eta_s = 4\eta_s (\alpha_{o}\alpha_s - 1)/3$$

(2)

where $\eta_s$ is the shear viscosity, $\alpha_o$ is the observed absorption coefficient and $\alpha_s$ is the absorption coefficient due to shear viscosity expressed by Eq. (3).

$$\alpha_s = 8\pi^2 f^2\eta_s / 3\rho v^2$$

(3)
where \( f \) is the frequency, \( \rho \), the density, \( v \), the velocity of ultrasound.

As shown in Fig. 4, showing the temperature dependence of the bulk viscosity, the bulk viscosity decreases with increasing temperature and cation-size for alkali nitrates. Figure 5 shows the temperature dependence of the ratio of \( \eta / \eta_{\infty} \). The values of \( \eta / \eta_{\infty} \) are approximately constant with temperature change for LiNO\(_3\) and NaNO\(_3\). Even in maximum case of KNO\(_3\) the change of the value is less than 15% with the temperature change of 150 K. As the origin of the bulk viscosity in the molten alkali nitrates, thermal relaxation and structural relaxation are possible. The former arises from the slow interchange of energy between the external and internal degrees of freedom and is typical for nonassociated liquids. On the other hand, the latter is the case for the associated liquids which has structural order due to strong intermolecular bonding. According to the classification of Higgs and Litovitz\(^{22}\) in the associated liquid \( d\eta /dT \) is negative, and \( \eta_{\infty} / \eta \) is approximately constant with temperature and rarely has a value above 5. As described above, negative \( d\eta/\eta \) and constancy of \( \eta / \eta_{\infty} \) with temperature observed in this study suggest that the bulk viscosity of the alkali nitrates originates in the structural relaxation and the molten alkali nitrates appears to be an associated liquid. However, it should be noted that the values of \( \eta_{\infty} / \eta \) of KNO\(_3\), RbNO\(_3\), and CsNO\(_3\) exceed by far 3.5 which is the maximum for the hydrogen bonded associated liquids. This fact suggests that the long range coulombic interaction among the constituent ions in the molten alkali nitrates causes the structural relaxation more than the hydrogen bond does.

Since the dispersion of sound propagation was observed in the alkali nitrates, detailed consideration has been given to the relaxation behavior under the assumption that relaxation with a single relaxation time, which has been successfully applied to some molten salts by Knape and Torell\(^{23}\) can also be applied to the present results. On the assumption that relaxation has a single relaxation time \( \tau \), an equation for a static bulk viscosity \( \eta_{\infty} \) has been derived by Montrose et al.\(^{24}\).

\[
\eta_{\infty} = \rho \left( \frac{v_{\infty}^2}{v_p^2} \right) \tau
\]

where \( \rho \) is the density of the medium, \( v_{\infty} \) and \( v_p \) are sound velocities at the limiting high and low frequencies respectively. The relaxation time was calculated from the ultrasonic velocity for \( v_{\infty} \), the ultrasonic bulk viscosity for \( \eta_{\infty} \) and hypersonic velocity for \( v_p \). The relaxation times determined at 700 K are listed in Table I. The relaxation time increases with increasing cation-size in accord with the behavior of bulk viscosity with cation-size.

### SOUND VELOCITY AND ABSORPTION IN ALKALI NITRATE BINARY MELTS

Sound velocity of NaNO\(_3\), LiNO\(_3\), RbNO\(_3\), and CsNO\(_3\) binary melts have been measured over the frequency range of 5–25 MHz by means of the pulse method. Figure 6 shows the composition dependence of the adiabatic compressibility at 650 K and 600 K for NaNO\(_3\), RbNO\(_3\) binary melts. In Fig. 6, thin solid line represents the adiabatic compressibility calculated on the...
basis of the volume additivity. The observed compressibility deviates positively from the additive line. But the extent of the deviation is as small as 2% even at the maximum. The composition dependence of such thermodynamic properties as isothermal compressibility, constant pressure heat capacity and internal pressure have been examined, and it has been found that these thermodynamic properties of the alkali nitrate mixtures do not deviate much from the values calculated on the basis of the additive rule.

On the contrary to the thermodynamic properties, the bulk viscosities of NaN03, -LiNO3, -RbNO3, and -CsNO3 binary melts deviate from the linear additivity as clearly shown in Fig. 7 showing the relation between the bulk viscosity and composition. As shown in Fig. 7, the bulk viscosities of NaN03, -CsNO3, and NaN03, -RbNO3 binary melts decrease rapidly with increasing NaN03 content up to 20 mol% NaN03. Further addition of NaN03 decreases the bulk viscosity slightly. As for NaN03, -LiNO3 binary melts, bulk viscosity decreases monotonously with increasing LiNO3 content. Since the difference between the bulk viscosities of NaN03 and LiNO3 is small, a change in the bulk viscosity with composition is slight. However, the same composition dependence of the bulk viscosity as that of NaN03, -RbNO3, and NaN03, -CsNO3, can be seen, i.e., the bulk viscosity of the binary melt decreases rapidly to approach that of the pure additive on addition of a component which has smaller bulk viscosity in pure melt. The observed behavior of the composition dependence of the bulk viscosity may be explained in terms of relaxation time in the following manner. The relaxation of the sound propagation in the binary melts seems to be structural one in analogy with the relaxation process of the pure component melts. The relaxation time of the binary melts may be controlled by the motion of the constituent having shorter relaxation time in pure component melt because the relaxation time is related to the time in which rearrangement of the constituent particles occur upon the passage of sound wave. Therefore, the viscosity of the binary melts decreases rapidly with the addition of the component having smaller bulk viscosity in the pure melt and approach the value of the pure melt of the additive.

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Fig. 1 Experimental arrangement for Brillouin scattering measurement.

Figure 2 Temperature Dependence of Ultrasonic and Hypersonic Velocities for Molten Alkali Nitrate Single Salts.
Figure 3 Temperature Dependence of Absorption in Molten Alkali Nitrate Single Salts.

Figure 4 Temperature Dependence of Bulk Viscosity for Molten Alkali Nitrate Single Salts.
Figure 5 Temperature Dependence of $\eta / \eta_s$ for Molten Alkali Nitrate Single Salts.

Figure 6 Composition Dependence of Adiabatic Compressibility for NaNO$_3$--RbNO$_3$ binary melts.
Figure 7 Composition Dependence of Bulk Viscosity for NaNO₃-MNO₃ (M:Li, Rb, Cs) Binary Melts.

Table 1 Relaxation Time of Alkali Nitrate at 700 K

| Salt   | Relaxation Time/10⁻⁹s |
|--------|-----------------------|
| KNO₃   | 0.045                 |
| RbNO₃  | 0.085                 |
| CsNO₃  | 0.23                  |