RELAXATION IN NITRATE MELTS

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ABSTRACT

We have performed Raman and Brillouin scattering experiments on almost ideal salt melt mixture KNa(NO₃)₂. The Raman spectrum of the breathing mode of NO₃⁻ ion was measured in order to obtain rotational line width. The results were analyzed together with literature data on other nitrate systems. All rotational line widths are compared with inverse relaxation times obtained from shear viscosity (ω→0) measurements (1). It is found that the rotational line width of the NO₃⁻ group is proportional to inverse relaxation time obtained from the static shear viscosity data. Within accuracy of ±15% the proportionality coefficient is the same for all nitrates systems except Ca₂K₃(NO₃)₇. Results of Brillouin measurements were compared with ultrasound measurements in order to estimate the bulk relaxation time. The bulk relaxation time was found in agreement with literature for pure alkali melts. Contrary to the shear relaxation time, it depends strongly on the cation volume.

INTRODUCTION

The shear and bulk viscosities ηₛ, ηᵥ and their relaxation times τₛ, τᵥ are pivotal in the study and understanding of glass transition phenomena. Both ηₛ and ηᵥ are temperature and frequency dependent. The frequency dependence is most pronounced for both viscosities around the frequency ω ≈ 1/τ and temperature dependence for fragile glass systems is most pronounced around T ≈ T₉. Therefore, in order to obtain meaningful information about systems with large viscosity changes, measurements have to be done in wide enough temperature and frequency intervals. Such a wide range study is possible by combining results from Raman and Brillouin spectroscopy, ultrasound and static (low frequency) viscosity measurements.

In the present work we tried to connect results of all these methods. For this first attempt we have chosen alkali nitrates which do not form glasses with one exception.
In order to increase the viscosity changes within the liquid phase, \( \text{KNO}_3-\text{NaN}_3 \) mixture is included. This mixture has low viscosity at high temperature, while in the eutectic point (lowest temperature before crystallization) it has relatively high viscosity about 6 cp. Most physical properties of the components are very similar. Most physical properties of the mixture are also similar i.e. averages of properties of both components. Therefore it is possible to regard this mixture as ideal but with much lower melting point.

**EXPERIMENTAL**

Both salts, \( \text{KNO}_3 \) and \( \text{NaNC}_3 \) (Alpha, Karlsruhe) were mixed 1:1 in a glove-box under argon atmosphere, then slowly heated under vacuum up to 400 °C, filtrated through a quartz filter into a cylindrical ampoule of 2.3 cm diameter and sealed. An optical furnace with resistive heating and with four quartz windows was used in both experiments. The temperature in the furnace was computer controlled with stability and accuracy better than ±0.3 K.

Brillouin spectra were measured at VO and HO polarization in right-angle geometry, with finesse about 50, using a Burleigh RC-110 3-pass Fabry-Perot interferometer, by a procedure essentially as described in (2).

In order to evaluate the damping of the observed hypersound longitudinal waves the Brillouin spectra were fitted as described in (3) including the convolution of theoretical function with experimental apparatus profile that was taken from elastic scattering.

In the Raman experiment the same right angle geometry was used to measure polarized \( \text{VV} \) and depolarized \( \text{HV} \) scattering of the 1050 cm\(^{-1}\) mode for the \( \text{KNO}_3-\text{NaN}_3 \) melt. We used a Jobin-Yvon U-1000 double monochromator with spectral width set to 0.5 cm\(^{-1}\). In Raman and Brillouin experiments we used the 514.5 nm line of an Ar ion laser in multi mode and in single respectively.

The intensity of the isotropic part can be estimated from polarized and depolarized intensity in frequency domain by the following equation:

\[
I_{\text{ISO}}(\omega) = I_{\text{VV}}(\omega) - \frac{4}{3} I_{\text{HV}}(\omega)
\]

[1]

where \( I_{\text{ISO}} \) is the isotropic intensity, \( I_{\text{VV}} \) and \( I_{\text{HV}} \) are polarized and depolarized intensities, respectively and \( \omega \) is the frequency. The value of \( I_{\text{HV}} \) is much smaller than \( I_{\text{VV}} \) value in the 1050 cm\(^{-1}\) line. It allowed us to neglect the contribution of \( I_{\text{HV}} \) value to isotropic intensity in equation [1]. The line width of isotropic intensity become equal under these conditions to the line width of polarized intensity.

The line width of depolarized intensity consists of isotropic and rotational parts. Rotational part can be estimated by deconvolution of depolarized with isotropic intensities (4,5,6). We assume that the shape of intensities \( I_{\text{VV}} \) and \( I_{\text{HV}} \) line is a simple Lorentzian. In this case rotational line widths could be estimated by subtracting the isotropic from the depolarized width instead of deconvolution procedure:

\[
\Gamma_r = \Gamma_{\text{VV}} - \Gamma_{\text{HV}}
\]

[2]
where $\Gamma_r$, $\Gamma_{VH}$, $\Gamma_{VV}$ are line widths of rotational part, depolarized part and polarized part respectively.

To obtain the line widths $\Gamma_{VH}$ and $\Gamma_{VV}$ from the Raman spectra, the 1050 cm$^{-1}$ line was integrated and then divided by the maximum value for both VV and HV polarizations. A coefficient $2/\pi$ was used to transform triangular approximation in to Lorentzian approximation.

The value of rotational line width $\Gamma_r$ was calculated in references (5,6) for molten nitrates NaNO$_3$ and the mixture of LiNO$_3$ with RbNO$_3$ for different concentration and temperatures. The value of rotational line width was calculated in references (4) for NH$_4$NO$_3$, NaNO$_3$ and LiNO$_3$ in water for different concentrations. The values of line widths of $\Gamma_{VH}$ and $\Gamma_{VV}$ were obtained for Ca$_2$K$_3$(NO$_3$)$_7$ from references (7). The $\Gamma_r$ for Ca$_2$K$_3$(NO$_3$)$_7$ and for KNa(NO$_3$)$_2$ was calculated according to eq.[2].

All line widths $\Gamma$ are full widths at half height in Lorentzian approximation, measured in cm$^{-1}$.

**RESULTS AND DISCUSSION**

**Raman Scattering Measurements**

The rotational line width $\Gamma_r$ obtained from Raman scattering measurements in the way described above, may be interpreted as the decay rate of rotation of the NO$_3$ group, yielding the characteristic time $\tau_r$. In earlier investigations (4,8) this characteristic time was connected with static shear viscosity $\eta_s$ in the following way

$$\tau_r = \frac{C}{\eta_s} + \tau_r^o$$

where $\tau_r = 1/(\pi \Gamma_r)$ was derived from the rotational line width and $\tau_r^o$ is the zero viscosity intercept. The slope $C$ may be predicted by a hydrodynamic model. This calculation was performed in (4) to analyze slope C for aqueous nitrate solutions which had different viscosities. The slope C was found 2 ps/cp for NH$_4$NO$_3$ and 1.5 ps/cp for NaNO$_3$ in water.

However, for the LiNO$_3$ solution rotational relaxation time ($\tau_r$) could not be estimated by eq.[3]. It was found (4) that the rotational relaxation time is a non linear function of viscosity in LiNO$_3$ solutions. Slope C was found to be about 1.5(ps/cp) for low viscosity and 1(ps/cp) for high viscosity.

Simple summation of times of decay was used in previous papers (4,8) to describe a relationship between rotational relaxation time and shear viscosity. In the present work we use a different way to connect the rotational line width with static viscosity. We assume that some viscosity independent relaxation process contribution to $\Gamma_r$ has to be taken into account. With this assumption we have to compare between $\Gamma_r$ and inverse relaxation time obtained from shear viscosity, see eq [6] bellow.

Stokes-Einstein ratio establishes a connection between a shear viscosity $\eta_s$ and relaxation time $\tau_s$ for a given temperature $T$

$$\eta_s = k_B \tau_s / V$$

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where $V$ may be interpreted as an effective volume and $k_B$ is the Boltzmann's constant. Below we will compare the inverse relaxation time obtained from the low frequency shear viscosity with rotational line width that correspond to a measurement of viscosity at high frequency. For the inverse relaxation time per unit volume we used the symbol $G$. The unit of volume was chosen $\text{Å}^3$ (the natural volume in molecular scale). Using eq.\([4]\), $G = (\tau_s / V)^{-1}$ was calculated by the following equation:

$$G = 0.46 T / \eta_s$$

[5]

The numerical coefficient in this equation has units ($\text{Å}^3 \text{ cm}^{-1} \text{ cp} / \text{ K}$). We use inverse cm$^{-1}$ scale in order to present $G$ ($\text{Å}^3 \text{ cm}^{-1}$) and $\Gamma_r$ in similar units.

Viscosity and temperature was substituted in eq.\([5]\) for various nitrate melts and solutions in order to calculate $G$. The static shear viscosity data for salt melts were taken from (1). They were extrapolated or interpolated to the temperatures at which $\Gamma_r$ was measured. This was done for every rotational line width ($\Gamma_r$). All $\Gamma_r$ had been calculated from Raman data by one of the methods described above.

In order to test the correlation between $\Gamma_r$ and $G$, $\Gamma_r$ values were plotted against $G$ values calculated by eq.\([5]\) see figures 1, 2 and 3. A clear linear dependence between $\Gamma_r$ and $G$ is found for melts and water solutions.

A regression analysis was used to find the parameters ($\Gamma_\infty, V$) that define linear dependence for different nitrate systems. These parameters are summarized in tables I and II. They were calculated by the following equation:

$$\Gamma_r = \Gamma_\infty + G / V$$

[6]

where $\Gamma_\infty$ is a rotational line width for infinite viscosity, and $V$ is an effective volume.

We found that $\Gamma_r$ depends linearly on $G$ also for $\text{Ca}_2\text{K}_3(\text{NO}_3)_7$ which is a well known glassformer, up to viscosity about 650 cp. The parameters of eq.\([6]\) in this region are $V = 13.8\text{Å}^3$ and $\Gamma_\infty = 0.65 \text{ cm}^{-1}$, see table I. Other systems crystallize already when they have viscosity much lower than 650 cp.

However for $\text{Ca}_2\text{K}_3(\text{NO}_3)_7$ at viscosity larger then 650cp, the difference between $\Gamma_{\text{VH}}$ and $\Gamma_{\text{VV}}$ becomes very small. This circumstance makes an estimation of $\Gamma_r$ by eq.\([2]\) difficult.

We compared relaxation times of $\text{Ca}_2\text{K}_3(\text{NO}_3)_7$ obtained by different methods. In first case we calculated relaxation time ($\tau_{st}$) estimated from shear viscosity up to viscosity 650 cp or down to corresponding temperature 420 K.

$$\tau_{st} = V \eta_s / (k_B T)$$

[7]

where $V = 13.8\text{Å}^3$ from table I. We also calculate relaxation time ($\tau_{sr}$) from rotational line width $\Gamma_r$.

$$\tau_{sr} = 1 / (\pi (\Gamma_r - \Gamma_\infty))$$

[8]
where $\Gamma_{xc}=0.65\text{cm}^{-1}$ from table I. These relaxation times $\tau_{\eta j}$ and $\tau_{\eta f}$ were plotted against inverse temperature together with relaxation times obtained from central line widths from reference (9) see fig. 4.

**Brillouin Scattering Measurements**

Our Brillouin scattering measurements showed that the properties (line width of longitudinal waves and hypersound velocity) of KNa(NO$_3$)$_2$ melt were averages of the properties of the pure components KNO$_3$, NaN$_3$. The relaxation time of bulk viscosity we obtained from our measurements and ultrasound measurements (10) by the method described in (11).

The bulk viscosity was found to be proportional to the cation volume as in pure components (12) see fig. 5.

**CONCLUSIONS**

We found here that shear viscosity is essentially cation independent in all investigated systems of alkali nitrate melts and water solutions. The bulk viscosity depends linearly on the size of cation as was found in (12). In this sense bulk and shear relaxation time of alkali nitrate melts have qualitatively different behavior. We suppose that the shear viscosity depends mainly on rotational properties of the NO$_3$ group.

The correlation between the low frequency shear viscosity and orientation relaxation times described well by the simple ratio eq [4]. The effective volume may be connected with a volume of the (NO$_3$)$^-$ group for alkali nitrate melts and their water solutions.

The relaxation time calculated by our method is in good agreement with relaxation time calculated from width of central line, in the glass forming system Ca$_2$K$_3$(NO$_3$)$_7$.

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| AQUEOUS SOLUTIONS | MELT |
|-------------------|------|
|                   | NH₄  | Li | Na | Na | KNa | Ca₂K₃ |
| V (Å³)            | 25   | 25 | 22 | 25 | 24  | 14    |
| Γ∞                | 0.0  | 1.0| 0.2| 1.5| 1.3 | 0.65  |

Table I. Result of the regression analysis applied on the data plotted in fig. 1 and fig. 2. The slopes $1/V$ are very close for all systems except Ca₂K₃(NO₃)₇.

|          | c(Li) | V (Å³) | Γ∞ |
|----------|-------|--------|----|
| NH₄      | 1.0   | 22     | 1.2|
| Li       | 0.8   | 24     | 3.6|
| Na       | 0.65  | 18     | 2.3|
| Na       | 0.5   | 18     | 2.8|
| KNa      | 0.33  | 20     | 3.5|
| Ca₂K₃    | 0.2   | 21     | 4.7|
|          | 0.0   | 17     | 4.8|

Table II. Result of the regression analysis applied on the data plotted in fig. 3. The slopes are still similar but $Γ∞$ are different for different concentrations.
Fig. 1 Rotational line width $\Gamma_r$ from Raman spectra plotted against $G$ (inverse relaxation time per unit volume) obtained from shear viscosity (eq. [5]) for water solutions of different nitrates from reference (3). All points are measured at temperature $T=302K$. The change in viscosity appears only due to changes in concentration. All solutions show a linear behavior.
Fig. 2 Rotational line width $\Gamma$, from Raman spectra plotted against $G$ (inverse relaxation time per unit volume) obtained from shear viscosity (eq. [5]) for different nitrate melts at different temperatures. (See references (1, 5, 6, 7) and ▲ - our data.)
Fig. 3 Rotational line width $\Gamma_r$ from Raman spectra plotted against $G$ obtained from shear viscosity (eq. [5]) for Li-Rb nitrates for different concentrations of Rb. Linear behavior is followed well, but $\Gamma_\infty$ vary with concentration. (See references (1,6)).
Fig. 4 The relaxation times obtained in different ways, plotted against the inverse temperature for Ca$_2$K$_2$(NO$_3$)$_7$. Relaxation times obtained from shear viscosity data with effective volume from table I; rotational relaxation times obtained from (7), and from central (Rayleigh) line (9) and this work.
Fig. 5 Ratio of bulk to shear viscosities as a function of the cationic volume $V$ for alkali nitrates and silver (10,12). All pure melts are measured at a temperature 40 K above the respective melting points. The KNa(NO$_3$)$_2$ mixture was measured at 140K above its melting point.