

Relaxation and shear viscosity in mixed ionic melts

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A linear dependence was found between the reorientational linewidth for alkali nitrate melts, obtained by Raman measurements, and the ratio of temperature divided by shear viscosity. An interpretation of this result in the framework of the Stokes-Einstein-Debye (SED) model leads to a volume for the NO_3 anion which is very close to a literature value. Using this volume, a relaxation time could be derived from static shear viscosity over a wide temperature range, for the well-known glass forming substance $\text{Ca}_2\text{K}_3(\text{NO}_3)_7$. The calculated relaxation time compares favorably with relaxation times obtained by other methods. This agreement supports the validity of a simple SED model over a wide frequency range.

INTRODUCTION

Liquid salt melts and their mixtures attract the attention of researchers not only because of possible applications but also as good model objects for investigation of basic problems.¹ While alkali halides are the simplest binary melts with strong interaction, alkali nitrates differ only in one, but rather important, respect: the fact that the NO_3 anions are nonspherical introduces additional degrees of freedom, which then may be used as a "spectroscopic detector"² in ionic melts. A wide frequency range study, combining results from Raman and Brillouin spectroscopy,³⁻⁸ ultrasound,⁹ and static¹ viscosity measurements, may reveal common features of nitrates. We have performed Raman-scattering measurements in the mixed melt $\text{Na}_{0.5}\text{K}_{0.5}\text{NO}_3$ since it provides a rather wide range of viscosity from its melting point ($T_m = 485$ K) up to the limit of its stability (700 K), being nearly ideal in the sense that all its known macroscopic properties are additive.

Before we describe the experiment let us make a few introductory remarks on relaxation time and viscosity. A spectral linewidth Γ is, in case of homogeneous broadening, defined by a relaxation process characterized by its relaxation time τ , $\Gamma = 1/\tau$. In particular, depolarized Raman scattering from the ~ 1050 cm^{-1} vibrational mode (A_1) of the NO_3 anion has a contribution Γ_R to the linewidth which is caused by the reorientational relaxation time of the NO_3 ion.^{3,4} The Stokes-Einstein-Debye (SED) relation establishes a connection between the shear viscosity η_s of a medium and the relaxation time τ_s for the reorientation of a particle immersed in it:

$$\tau_s = V\eta_s/k_B T, \quad (1)$$

where V is an effective volume of the particle. Although, generally speaking, Eq. (1) has been derived for a macroscopic particle, there are many examples in statistical mechanics where microscopic objects have been successfully considered this way.^{10,11}

Since shear viscosity data are available for some alkali nitrate melts,^{1,12,13} let us see how the reorientational broadening Γ_R , taken from Refs. 4-7, depends on the corresponding—SED—time τ_s . Figure 1 presents the data of Ref. 5 for Γ_R (in cm^{-1}) which determines the microscopic relaxation time, as a function of the macroscopic coordinate T/η_s [T in K, η_s in centipoise (cp)], for molten NaNO_3 . As could be expected, the resulting graph may be rather well represented by a linear expression:

$$\Gamma_R = \Gamma_O + BT/\eta_s. \quad (2)$$

The occurrence of another term (Γ_O) besides the one following from Eq. (1), proportional to T/η_s implies that there are (at least) two different types (Γ_O and BT/η_s) of elementary relaxation processes which are statistically independent. In this case the rates, e.g., inverse times, should be summed rather than the relaxation times themselves. Thus from Fig. 1

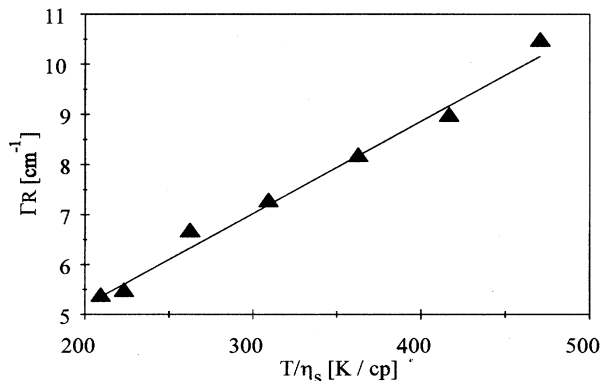


FIG. 1. Reorientational linewidth Γ_R , derived from ~ 1050 cm^{-1} Raman line of the NO_3 ion, as described in text, versus T/η_s for NaNO_3 melt. The straight line is a linear regression through the experimental points. The resulting effective volume from Eq. (2) is 25 \AA^3 , and $\Gamma_O = 1.5 \text{ cm}^{-1}$. Viscosity is taken from Ref. 1, Γ_R from Ref. 5.

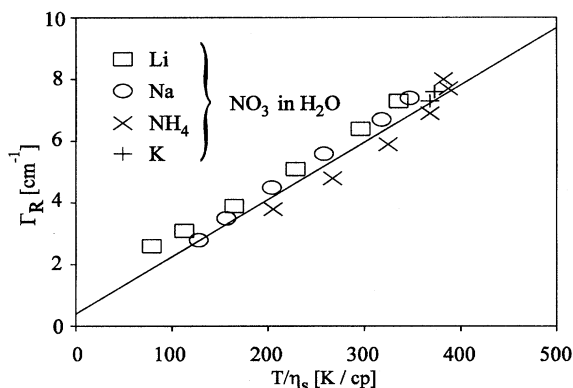


FIG. 2. Reorientational linewidth Γ_R versus T/η_s , from Ref. 4, for concentrated water solutions of alkali nitrates, at constant temperature $T=303$ K. The straight line is drawn according to Eq. (2) with $V=24.8 \text{ \AA}^3$ and $\Gamma_O=0.5 \text{ cm}^{-1}$.

one clearly sees that the reorientational broadening depends in a rather simple way on the macroscopic shear viscosity of the medium.

Let us go further on. Figure 2 presents the data from Ref. 4 on the broadening of the same line, again as Γ_R versus T/η_s . Here for alkali nitrate salts dissolved in water, all taken at the same temperature, the change in viscosity is caused by changes in concentration. Again, the dependence is surprisingly well described by the linear equation (2) with the same slope. Having noted this meaningful linearity one may use formula (1) to derive from this slope B , an effective volume of the particle the relaxation process of which is observed:

$$V(\text{\AA}^3) = 0.46B^{-1}. \quad (3)$$

(The numerical coefficient 0.46 results from the units used.) Indeed, the slope B varies insignificantly from solution to solution in Fig. 2, and remains roughly the same for both, the melt (Fig. 1) and the solutions. The slopes from both figures correspond closely to the same volume $V=25 \text{ \AA}^3$. This experimentally obtained volume compares very favorably with the value of rigid volume V for the NO_3 ion from Ref. 14, $V=24.8 \text{ \AA}^3$.

To the contrary, the initial broadenings Γ_O are different for different environments (see also Ref. 3). The consistency between V obtained from a salt melt and from aqueous solutions suggests that the broadening of the 1050 cm^{-1} line of the Raman spectrum of alkali nitrates (and the corresponding relaxation time) is defined basically by the property of the anion alone. Having in mind that the NO_3 anion is non-spherical (this means it has internal degrees of freedom) and simultaneously is the largest unit in those liquids, it seems interesting to check the observed phenomenon over a wider range of viscosity for different nitrate systems.

EXPERIMENTAL PROCEDURE

Extended measurements of Γ_R were performed on $\text{Na}_{0.5}\text{K}_{0.5}\text{NO}_3$ melt from its melting point up to 700 K. The physical properties of the components, NaNO_3 ($T_m=580$ K),

KNO_3 ($T_m=607$ K) are rather similar, and the phase diagram of the mixture shows the lowest melting point around equimolecular composition.¹ The sample was mixed from the pure (99.99 %) components (Alpha, Karlsruhe) in a glove box under Ar atmosphere. Then it was slowly heated (60 h) under vacuum up to $T=620$ K and carefully filtrated under argon pressure through a $1\text{--}2 \mu\text{m}$ quartz filter directly into a cylindrical quartz cell of about 2.5 cm diameter, then sealed off. Analogous measurements of the width of the central line were also performed for $\text{Ca}_2\text{K}_3(\text{NO}_3)_7$, called for short CKN, in order to extend the temperature range obtained in Ref. 8. The sample was prepared in the same fashion as $\text{Na}_{0.5}\text{K}_{0.5}\text{NO}_3$, which is very similar to the technique described in Ref. 15.

Temperature was measured by a standard chromel-alumel thermocouple placed under the bottom of the quartz ampoule. A furnace with resistive heating and four quartz windows was used in all experiments. The temperature of the furnace was computer controlled with stability and accuracy not worse than ± 0.3 K. The right angle scattering geometry was used to measure polarized (VV) and depolarized (HV) Raman scattering of the 1050 cm^{-1} mode typical for all the nitrates. We used the 514.5 nm line of an Ar-ion laser, and a Jobin-Yvon U-1000 double monochromator. The spectral width of the monochromator was set to 0.4 cm^{-1} for the low-frequency range (central line of CKN) and 0.75 cm^{-1} for the high- (1050 cm^{-1}) frequency mode. The intensity of the isotropic part of the scattering, I_{ISO} , can be obtained from the polarized and depolarized intensity by

$$I_{\text{ISO}}(\omega) = I_{VV}(\omega) - 4/3 I_{HV}(\omega). \quad (4)$$

The value of I_{HV} is much smaller than that of I_{VV} in the $\sim 1050 \text{ cm}^{-1}$ line which allowed us to neglect the contribution of I_{HV} value to the isotropic intensity in Eq. (4). The linewidth of the isotropic intensity becomes equal under these conditions to the width of the VV line after correcting for apparatus resolution.

The linewidth of the depolarized intensity (HV) contains the apparatus, the isotropic, and the anisotropic, i.e., reorientational parts. We assume here that the shapes of both I_{VV} and I_{HV} lines can be represented by simple Lorentzians. Thus the reorientational linewidth is obtained by subtracting the VV (i.e., the apparatus plus the isotropic) from the HV (depolarized) width avoiding a deconvolution procedure:

$$\Gamma_R = \Gamma_{\text{Aniso}} \cong \Gamma_{HV} - \Gamma_{VV}. \quad (5)$$

To obtain the linewidths Γ_{HV} and Γ_{VV} , the line was integrated and then divided by the maximum value, for both VV and HV polarizations. A coefficient $2/\pi$ was used to transform the underlying approximation of a "triangular shape" into the Lorentzian approximation.

RESULTS AND INTERPRETATION

Figure 3 presents our experimental results for Γ_R of $\text{Na}_{0.5}\text{K}_{0.5}\text{NO}_3$ melt obtained from the Raman spectra, together with the data of Refs. 5 and 7 for other nitrates. The viscosity data η_s for the Na-K- NO_3 mixture are available

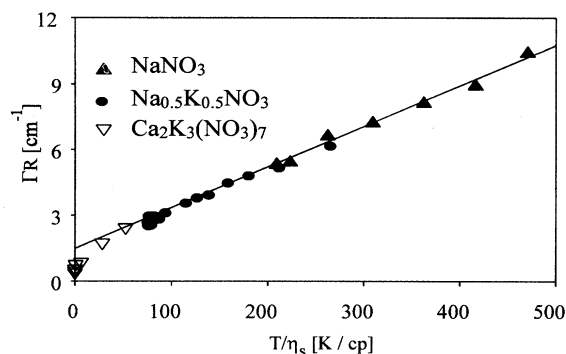


FIG. 3. Reorientational linewidth Γ_R , versus T/η_s for NaNO_3 (Γ_R from Ref. 5, η_s from Ref. 1); $\text{Ca}_2\text{K}_3(\text{NO}_3)_7$, (Γ_R from Ref. 7, η_s from Refs. 1,12,13); $\text{K}_{0.5}\text{Na}_{0.5}\text{NO}_3$ (Γ_R from this work, η_s from Ref. 1). The straight line is drawn as in Fig. 2 with $V=24.8 \text{ \AA}^3$, and $\Gamma_O=1.5 \text{ cm}^{-1}$.

from Ref. 1. The graph (Fig. 3) expands the range of Fig. 1 by a factor of about 2. It includes also a glass forming nitrate melt CKN. One can see that the extended graph is still linear. The mixed $\text{Na}_{0.5}\text{K}_{0.5}\text{NO}_3$ is the only melt which provides a sufficiently wide range of viscosity to cover the gap between the "normal" melts like (NaNO_3) and the glass former CKN.

The slope defining the inverse volume of the common anion remains still unchanged. However, at the lower left corner of the graph (extremely large viscosity) the expected deviation from linearity for CKN takes place. Figure 3 bridges the two kinds of behavior: glass forming behavior as in CKN and the regular behavior demonstrated by all (as far as we know) other nitrate melts (see Figs. 1 and 2). For normal melts (and for CKN at low viscosity) the mechanism of relaxation appears to be determined by shear viscosity and may be understood on the basis of the SED relation.

Figure 4 shows the same dependence for data from Ref. 6 on LiNO_3 , RbNO_3 and their mixtures. Again, the slopes are in qualitative agreement with the other nitrate data. Thus one can conclude that the NO_3 anion mainly determines the τ_s

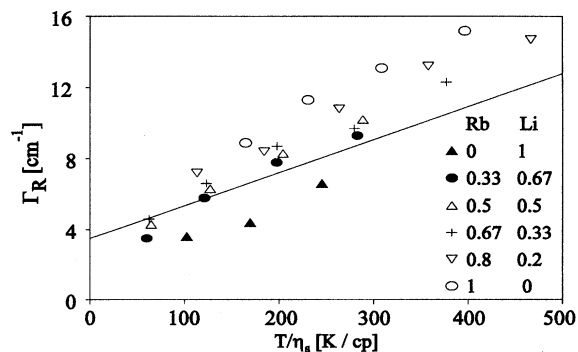


FIG. 4. Reorientational linewidth Γ_R from Ref. 6 versus T/η_s from Ref. 1, for $\text{Li}_{1-x}\text{Rb}_x\text{NO}_3$. The line is drawn as in Fig. 2 for $V=24.8 \text{ \AA}^3$ and $\Gamma_O \approx 4 \text{ cm}^{-1}$.

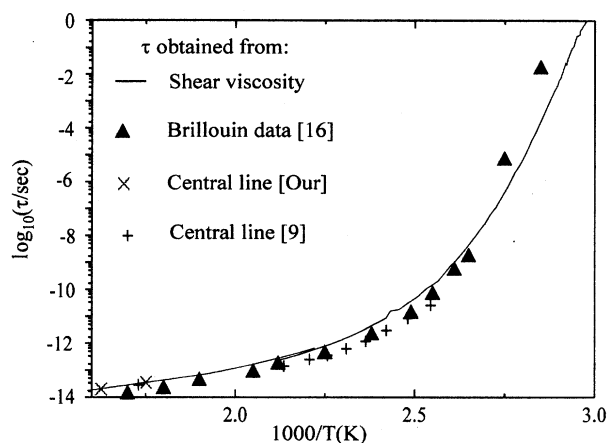


FIG. 5. Temperature dependence of relaxation time τ for $\text{Ca}_2\text{K}_3(\text{NO}_3)_7$ melt. Results from Ref. 16 are multiplied by a factor of 2π . The curve is from Eq. (1) using the volume $V=24.8 \text{ \AA}^3$ and shear viscosity from Refs. 1,12,13.

and η_s values, while the cations are playing only a secondary role. As follows from Refs. 9 and 16, the cations seem to determine the bulk viscosity.

We conclude from graphs (see Figs. 2, 3, and 4) that show the alkali ions (Li,Na,K) in both, melts and water solutions, probably influence only the Γ_O values. Thus one can see that the SED relation (1) is valid quantitatively in a wide interval of varying viscosity, independent of the mechanism of its variation (temperature or dilution). This also suggests that cationic atomic transport and ionic conductivity in these liquids are basically determined by their shear relaxation times. The presence of nonzero Γ_O manifests the existence of other alternative mechanisms of relaxation which might be independently involved in determining the linewidth.

Since the graph of Fig. 3 includes both usual liquids and a glass former, one may calculate the relaxation time for CKN, from its shear viscosity data. Figure 5 presents the resulting curve [Eq. (1)] for this relaxation time (τ) using $V=24.8 \text{ \AA}^3$ together with a few sets of experimental points from Refs. 8, 16, and 17. The graph shows that for about six (or even eight) orders of magnitude of time where data exist, Eq. (1) still provides reliable figures for the slow relaxation. This curve agrees with the experimental points from different methods. It may be worthwhile noting that Fig. 5 includes the region where mode-coupling theory is usually applied.⁸ A deviation from (1) is to be expected for the very high viscosity limit which approaches the already glassy state region. To understand this deviation one will have to include the actual frequency dependence of the viscosity in formula (1).

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