Determination of Thermal Diffusivities, Thermal Conductivities, and Sound Speeds of Room-Temperature Ionic Liquids by the Transient Grating Technique

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We report measurements of thermal diffusivity of several room-temperature ionic liquids (RTILs) using the transient grating method. Measurements are carried out using ionic liquids with small concentrations of an inert dye that is excited by the 532 nm output of a Nd:YAG laser in a grating with a fringe spacings of (92 and 104) μm. The experiments give thermal diffusivities from which thermal conductivities can be determined, sound speeds, and acoustic damping parameters for seven ionic liquids. In this study, we have used combinations of the cation 1-butyl-3-methylimidazolium ([BMMIm]+) with the anions tetrafluoroborate ([BF4]−), hexafluorophosphate ([PF6]−), and bis(trifluoromethylsulfonyl)imide ([Tf2N]−) and combinations of the anion [Tf2N]− with the cations 1-ethyl-3-methylimidazolium ([EMIm]+), 1-pentyl-3-methylimidazolium ([PMIm]+), 1-hexyl-3-methylimidazolium ([HMIm]+), and 1-octyl-3-methylimidazolium ([OMIm]+) to determine the effect of anion and cation on the thermophysical properties of the RTILs. Results obtained indicate that the anion exerts a strong influence not only on the sound speed but also on the thermal diffusivity and acoustic damping of the RTILs. For RTILs with the same cation [BMMIm]+, changing the anion from [BF4]− to either [PF6]− or [Tf2N]− leads to decreases in the sound speed, thermal diffusivity, and thermal conductivity. The size of the cation, however, does not significantly influence the sound speed or the thermal diffusivity of the RTILs.

Introduction

Room-temperature ionic liquids (RTILs) are organic salts that are liquid at room temperature and that have unique chemical and physical properties, including stability on exposure to air and moisture, a high solubility power, and extremely low vapor pressure. Because of these properties, they can serve as a “green” recyclable alternative to the volatile organic compounds that are traditionally used as industrial solvents. In the laboratory, RTILs have successfully been used in a broad spectrum of applications, including replacing traditional organic solvents in organic and inorganic syntheses, solvent extractions, liquid–liquid extractions, electrochemical reactions, and as a medium for enzymatic reactions.1–8

The majority of studies have focused on synthesizing RTILs with new anions and cations and determining their chemical properties. Unfortunately, information on the RTILs including their physical properties and the relationships between structure and physical properties is not widely available despite their superior physical properties, which make them suitable not only as green solvents but also as high-performance fluids for use in a wide range of engineering and materials science applications, such as high-pressure and high-temperature1–8 lubricants. It is probable that industrial applications of RTILs in chemistry, engineering, and material processing are limited because of the paucity of data on their physical properties.

Transient grating method is a noncontact method of probing both photothermal and photoacoustic changes in density9–11 and can be used to determine thermophysical properties of solids, liquids, and gases. The method is based on the formation of a series of nodes and antinodes in the electric field of the laser beams in space generated by intersecting two coherent, pulsed laser beams, referred to as “pump” beams, in a weakly absorbing sample.9–15 Following absorption of the laser radiation, the excited chromophore typically decays on a fast time scale with respect to the laser pulse width depositing the absorbed optical energy in the fluid as heat, giving a sinusoidal temperature rise in the fluid in space and generating counter propagating acoustic waves. The acoustic standing wave acts as a nearly adiabatic energy in the fluid as heat, giving a sinusoidal temperature increase is known as the thermal mode of wave motion.16 Both the acoustic and thermal modes of the wave in the grating have associated density changes; hence, a recording of the intensity of diffraction of a continuous “probe” laser beam directed at the Bragg angle to the grating acts as a monitor of the time evolution of the density variations induced by optical excitation. From a knowledge of the optical fringe spacing in the grating, measurements of the oscillation frequency and decay rate of the acoustic wave can be used to determine the sound speed and damping rate of the acoustic wave, while a measurement of the slow decay of the sinusoidal temperature variation gives the thermal diffusivity of the fluid.12–16

Here we report a study using the transient grating method9–16 directed not only at measurement of the physical properties of RTILs but also toward determining the relationship between the RTIL structure and their thermophysical properties. In the Experimental Section, we describe the experimental apparatus, present data, and give expressions for reduction of the data. The Discussion section points out the correlations in the thermophysical properties of the different RTIL samples studied, elucidating the effects of the different anions or cations on the thermophysical properties of the RTILs.

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Experimental Section

**Instrument and Methods.** The transient grating apparatus used here is similar to that described by previous researchers, except that a relatively long laser pulse and a small crossing angle are used for the pump beams. As shown in Figure 1, the frequency doubled 532 nm; 10 ns output of a Q-switched Nd:YAG laser operated at 10 Hz was used as the pump beam. The 532 nm beam was split into two equal intensity beams by a beam splitter and recombined to produce approximately 100 nm optical fringes in a 1.0 cm x 1.0 cm x 4.5 cm glass cuvette.

A continuous, 4 mW, 633 nm He–Ne laser beam was directed at the Bragg angle, \( \theta_B \), to the grating where \( \theta_B \) satisfies

\[
\sin \theta_B = \frac{\lambda_{\text{probe}}}{2\Lambda}
\]  

(1)

where \( \Lambda \) is the fringe spacing of the grating and \( \lambda_{\text{probe}} \) is the wavelength of the probe beam. A side-on photomultiplier (Hamamatsu, Inc. model R928) whose output was fed to an inverting operational amplifier (Burr-Brown Inc., model OPA686) was used to detect the first-order diffracted beam. The photomultiplier was equipped with a narrow band interference filter to block scattered radiation from the pump laser. Signals from the photomultiplier were averaged with a 1.5 GHz bandwidth (Agilent, Inc., model 545845) digitizing oscilloscope.

The pump laser beam could be attenuated with a half wave plate and Glan Taylor polarizer to give pulse energies of the order of 10 mJ pulses at the front surface of the cuvette. In experiments with [BMIm]+[PF\(_6\)]\(^-\), laser pulse energies were on the order of 33 mJ. (See Table 1 for structures of the RTILs used in this study.) Experiments were carried out over a range of pulse energies to determine if the recorded waveforms were affected by laser pulse energy. Because the RTIL samples are transparent at 532 nm, an absorbing dye tris(1,10-phenanthroline) iron(II) sulfate known as ferroin was added to each sample.

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**Figure 1.** Schematic diagram of the transient grating system.

**Table 1.** List of Room Temperature Ionic Liquids Used in This Study

<table>
<thead>
<tr>
<th>Structure</th>
<th>RTIL Name</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Structure 1" /></td>
<td>1-ethyl-3-methylimidazolium Tf₂N⁺ or [EMIm]⁺ [Tf₂N]⁻</td>
</tr>
<tr>
<td><img src="image2" alt="Structure 2" /></td>
<td>1-butyl-3-methylimidazolium Tf₂N⁺ or [BMIm]⁺ [Tf₂N]⁻</td>
</tr>
<tr>
<td><img src="image3" alt="Structure 3" /></td>
<td>1-butyl-3-methylimidazolium BF₄⁻ or [BMIm]⁺ [BF₄]⁻</td>
</tr>
<tr>
<td><img src="image4" alt="Structure 4" /></td>
<td>1-butyl-3-methylimidazolium PF₆⁻ or [BMIm]⁺ [PF₆]⁻</td>
</tr>
<tr>
<td><img src="image5" alt="Structure 5" /></td>
<td>1-pentyl-3-methylimidazolium Tf₂N⁺ or [PMIm]⁺ [Tf₂N]⁻</td>
</tr>
<tr>
<td><img src="image6" alt="Structure 6" /></td>
<td>1-hexyl-3-methylimidazolium Tf₂N⁺ or [HMIm]⁺ [Tf₂N]⁻</td>
</tr>
<tr>
<td><img src="image7" alt="Structure 7" /></td>
<td>1-octyl-3-methylimidazolium Tf₂N⁺ or [OMIm]⁺ [Tf₂N]⁻</td>
</tr>
</tbody>
</table>
Specifically, 1.0 mL of 0.025 mol L\(^{-1}\) aqueous ferroin solution was added to 2 mL of each RTIL sample. A control experiment was carried out with [BMIm][BF\(_4\)]\(^-\), which has a small absorbance so that a transient grating experiment could be done without the addition of a dye. The results of the experiment agreed, within the experimental error, with a measurement on the same RTIL containing the 1.0 mL ferroin dye solution used with the other RTILs.

Experiments were conducted first to determine the fringe spacing, performed by using a solution of CoCl\(_2\) in methanol whose sound speed is well-documented.\(^{1,7}\) The acoustic wavelength \(\Lambda\) (related to the wavenumber \(K\) through \(K = 2\pi/\Lambda\)) for two different angles of intersection of the pump beams was found to be 104 \(\mu\)m and 92 \(\mu\)m. Data for each RTIL sample was taken several times using different laser fluences; data were taken at the two different angles of intersection of the pump beams as well. All experiments were done at 0.1 MPa and 296.85 K.

**Chemicals.** 1-Methylimidazole (mole fraction purity of 99%), 1-chloro-octane (mole fraction purity of 99%), 1-chloro-pentane (mole fraction purity of 99%), 1-chloro-octane (mole fraction purity of 99%), acetonitrile (mole fraction purity of 99%), ethyl acetate (mole fraction purity of 99%), lithium trifluoromethane sulfonimide (LiTf\(_2\)N) (mole fraction purity of 99.95%), and hexafluorophosphoric acid with a mass fraction 99.95% were purchased from Sigma-Aldrich. The NMR characteristics of these RTILs were obtained from previous research.\(^{6,18,24}\) Purity of the ionic liquids obtained was verified by their mass and the isobaric heat capacity, respectively, of the fluid. The first and second terms in eq 2 describe the temperature dependence of the thermal and acoustic modes of wave motion, respectively. Since the decays of the acoustic and thermal modes were not visible on the long time scale used for recording the thermal mode, hence, the acoustic mode contribution to the signal on a short time scale is approximated as:

\[
\delta = \frac{\alpha E_0}{C_p} \left[ -e^{-K\alpha t} + e^{-K\alpha t} \cos(cKt) \right]
\]

where the damping parameter \(\alpha\) and the viscous and heat conduction lengths \(l_v^\prime\) and \(h_b\), respectively, are given by:

\[
l_v^\prime = \frac{\eta + 4\mu}{\rho c} \quad l_b = \frac{2}{c}
\]

The values of \(\alpha\), \(c\), \(\gamma\), \(\eta\), \(\mu\), and \(\rho\) are the thermal diffusivity, sound speed, heat capacity ratio, bulk viscosity coefficient, shear viscosity coefficient, and density of the fluid, respectively. \(E_0\), \(\alpha\), \(\beta\), and \(C_p\) are the energy fluence of the laser beam, the optical absorption coefficient, the volume expansion coefficient, and the isobaric heat capacity, respectively, of the fluid. The first and second terms in eq 2 describe the time dependences of the thermal and acoustic modes of wave motion, respectively. Since the decay of the acoustic and thermal modes are not visible on the long time scale used for recording the thermal mode, hence, the diffraction light intensity recorded by the photomultiplier, represented by \(N_t\) and \(F_t\) for the two different modes, were fitted separately with the following two expressions:

\[
N_t(t) = \left( F - A + \frac{e^{-E(t+C)}}{B} \cos \left( \frac{2\pi(t+C)}{B} \right) \right)^2 + D_1
\]

\[
F_t(t) = \left( -G e^{-E(t+C)} \right)^2 + D_2
\]

where the quantities denoted by capital letters are adjustable parameters used in the least-squares fitting procedure. In the data fitting, the thermal mode contribution to the signal on a short time scale is approximated as \(-1\) in eq 4, as its decay is negligible on a short time scale. Figures 2 and 3 show an experimental waveform for the ionic liquid [BMIm][BF\(_4\)]\(^-\) and their least-squares fits using eq 4.

To ensure the accuracy of the technique and the reliability of the fitting model, calibration experiments were performed...
Table 2. Experimental Thermal Diffusivities (α), Sounds Speeds (c), and Damping Parameters (σ) of Ionic Liquids Compared with Literature Sound Speeds and Viscosities

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>10⁻² α (m²/s)</th>
<th>c (m/s)</th>
<th>ρc²/α (m/s²)</th>
<th>10⁻⁴ σ (m²/s)</th>
<th>η (mPa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[EMIm][BF₄]⁻</td>
<td>0.86 ± 0.01</td>
<td>1564 ± 8</td>
<td>1570 ± 3</td>
<td>3.7 ± 0.4</td>
<td>298</td>
</tr>
<tr>
<td>[BMIm][PF₆]⁻</td>
<td>0.75 ± 0.02</td>
<td>1441 ± 4</td>
<td>1433 ± 3</td>
<td>4.2 ± 0.4</td>
<td>298</td>
</tr>
<tr>
<td>[BMIm][Tf₂N]⁻</td>
<td>0.60 ± 0.01</td>
<td>1227 ± 6</td>
<td>1238 ± 6</td>
<td>2.4 ± 0.6</td>
<td>293.15</td>
</tr>
<tr>
<td>[EMIm][Tf₂N]⁻</td>
<td>0.601 ± 0.004</td>
<td>1234 ± 4</td>
<td>2.6 ± 0.7</td>
<td>2.6 ± 0.7</td>
<td>31</td>
</tr>
<tr>
<td>[PMIm][Tf₂N]⁻</td>
<td>0.58 ± 0.02</td>
<td>1227 ± 2</td>
<td>3.0 ± 0.8</td>
<td>2.3 ± 0.3</td>
<td>3.1 ± 0.7</td>
</tr>
<tr>
<td>[HMIm][Tf₂N]⁻</td>
<td>0.606 ± 0.009</td>
<td>1232 ± 11</td>
<td>1227 ± 2</td>
<td>2.3 ± 0.3</td>
<td>3.1 ± 0.7</td>
</tr>
<tr>
<td>[OMIm][Tf₂N]⁻</td>
<td>0.61 ± 0.01</td>
<td>1232 ± 5</td>
<td>1227 ± 2</td>
<td>2.3 ± 0.3</td>
<td>3.1 ± 0.7</td>
</tr>
</tbody>
</table>

α The literature values were taken from ref 26. b The literature values were taken from ref 27. c The literature values were taken from ref 2. d The literature values were taken from ref 28.

using CoCl₂ in methanol (with an absorbance less than 0.3 cm⁻¹) as a standard. It was found that the thermal diffusivity of methanol determined by the transient grating method was found to be (1.00 ± 0.03)·10⁻⁷ m²/s⁻¹ and is in excellent agreement with ref 17. In measurements on the RTILs, data were taken at grating fringe spacings of 104 µm and 92 µm (i.e., with wavenumbers of 6.0·10¹⁴ m⁻¹ and 6.8·10¹⁴ m⁻¹, respectively). The data for each chemical species listed in Table 2 are averages from experiments taken with different laser energy fluences and fringe spacings.

The discrepancies in thermal diffusivities and sound speeds of the RTILs had no dependence on changes in either laser energy fluorescence or fringe length. Typically, the percent relative standard deviation of the experiments for each RTIL in determining the thermal diffusivity is better than ± 4 % and in determining the sound speed is better than ± 0.5 %. The standard deviations of the data are reported in Table 2. Some of the uncertainties and conditions of the reference values were not found in the literature.

![Figure 2](image1.png)

**Figure 2.** Photomultiplier signal vs time for an experiment with [BMIm][BF₄]⁻ showing the acoustic mode of wave motion. The solid trace is the experimental signal and the circles are the model fit using eq 4.

![Figure 3](image2.png)

**Figure 3.** Photomultiplier signal vs time for an experiment with [BMIm][BF₄]⁻ showing the thermal mode of wave motion. The ratio of the standard deviation of the fit to the least squares value of the thermal diffusivity is 0.01.

**Results and Discussion**

The results listed in Table 2 show that the properties of the anion of the RTILs have a strong effect on the sound speed; specifically, changing the anion from [BF₄]⁻ to either [PF₆]⁻ or [Tf₂N]⁻ leads to a decrease in the sound speeds, from (1564 ± 8) m/s⁻¹ for [BMIm][BF₄]⁻ to (1441 ± 4) m/s⁻¹ for [BMIm][PF₆]⁻ and to (1227 ± 6) m/s⁻¹ for [BMIm][Tf₂N]⁻. A change of the cation in these species, on the other hand, does not show a significant effect on the sound speed of the RTILs: the sound speed of the RTILs with C₅MIm cations (i.e., [EMIm][Tf₂N]⁻ (1240 ± 4) m/s⁻¹) is similar to that for RTILs with C₆MIm cations ([BMIm][Tf₂N]⁻ (1227 ± 6) m/s⁻¹), C₇MIm cations ([PMIm][Tf₂N]⁻ (1227 ± 2) m/s⁻¹), C₈MIm cations ([HMIm][Tf₂N]⁻ (1232 ± 11) m/s⁻¹), and C₉MIm cations ([OMIm][Tf₂N]⁻ (1232 ± 5) m/s⁻¹). Generally, it would be expected that an increase in size of the cation by lengthening the alkyl chain would increase the viscosity and hence the damping of the acoustic mode.²² Although, the use of the damping constant appears to be an effective indicator for measuring large viscosity changes, it does not appear to discern between small changes in viscosity. More experiments with different RTILs are required for an accurate assessment. It is noteworthy that the sound speeds reported here for [BMIm][BF₄]⁻ and [BMIm][PF₆]⁻ agree to within ± 8 m/s⁻¹ with the results determined by other workers²⁶ using an acoustic microcell operating at 0.5 MHz.

As can be seen by inspection of Figure 4, the damping constant for [BMIm][PF₆]⁻ is similar to that of [BMIm][BF₄]⁻ but is approximately double that of [BMIm][Tf₂N]⁻. As Table 2 shows, the character of the anion of the RTIL has a strong effect on the damping parameter σ, while that of the cation exerts no significant effect—a trend that parallels the relative influence of the anion and cation on the sound speed, as noted above. Since σ is a decay parameter that includes energy losses primarily due to viscosity with typically only a small contribution from heat conduction, the data suggest that for identical
viscosities for [BMIm]+[BF4]− and shear viscosities through Figure 5.

The thermal diffusivities of several RTILs were calculated, and the results listed in Table 3.

In summary, we have reported values for the sound speed, acoustic damping, and thermal diffusivities of several RTILs. The relative ease of determining these parameters, the small error found in the resulting data fits, and the agreement of some of the extracted parameters with conventional methods reconfirms the value of the transient grating method for determining thermophysical parameters of fluids.

Supporting Information Available:
The complete H1 NMR spectra of the seven RTILs reported in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited
(19) Luo, H.; Dai, S.; Bonnesen, P. V.; Buchanan, A. C., III; Holbrey, J. D.; Bridges, N. J.; Rogers, R. D. Extraction of cesium ions from

<table>
<thead>
<tr>
<th>ionic liquid</th>
<th>ρ(MPa)</th>
<th>T(K)</th>
<th>C(κ/(J·kg⁻¹·K⁻¹))</th>
<th>λ(W·m⁻¹·K⁻¹)</th>
<th>λac(Γ/(W·m⁻¹·K⁻¹))</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BMIm]+[BF4]−</td>
<td>0.1</td>
<td>298.15</td>
<td>1205.0 ± 0.2</td>
<td>1613 ± 81</td>
<td>0.162 ± 0.006</td>
</tr>
<tr>
<td></td>
<td>295.4</td>
<td>1205 ± 2</td>
<td>1555 ± 58</td>
<td>0.186 ± 0.001</td>
<td></td>
</tr>
<tr>
<td>[BMIm]+[PF6]−</td>
<td>0.1</td>
<td>293.15</td>
<td>1201.8</td>
<td>1614</td>
<td></td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>1363</td>
<td>1438 ± 72</td>
<td>0.109 ± 0.005</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1399 ± 62</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[BMIm]+[Tf2N]−</td>
<td>0.1</td>
<td>298.15</td>
<td>1437.04</td>
<td>1293</td>
<td>0.108 ± 0.004</td>
</tr>
<tr>
<td></td>
<td>295</td>
<td>1429</td>
<td>1279 ± 46</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>296.4</td>
<td>1438.6 ± 0.3</td>
<td>1291</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[EMIm]+[Tf2N]−</td>
<td>0.1</td>
<td>298.15</td>
<td>1520</td>
<td>1340 ± 52</td>
<td>0.120 ± 0.005</td>
</tr>
<tr>
<td></td>
<td>296.0</td>
<td>1521 ± 2</td>
<td>1291</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a The thermal conductivities presented by this work were calculated from the averages of the literature heat capacities and literature densities. b The literature values were taken from ref 26. c The literature values were taken from ref 27. d The literature values were taken from ref 28. e The literature values were taken from ref 29.

Figure 5. Photomultiplier signal vs time for three RTILs. The signal for all three traces is scaled to unity at time = 0. The thermal diffusivities of the RTILs can be seen to decrease with the size of the anion.

Table 3. Experimentally Determined Thermal Conductivities (λ) of [BMIm]+[BF4]−, [BMIm]+[PF6]−, [BMIm]+[Tf2N]−, and [EMIm]+[Tf2N]− from Previously Reported Values of Density (ρ) and Specific Heat Capacity (C)


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