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Thermochemistry of ionic liquid heat-transfer fluids☆

Michael E.Van Valkenburg, Robert L. Vaughn, Margaret Williams, John S. Wilkes*

Department of Chemistry, 2355 Fairchild Drive, Suite 2N225, US Air Force Academy, CO 80840-6230, USA

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Abstract

Large-scale solar energy collectors intended for electric power generation require a heat-transfer fluid with a set of properties not fully met by currently available commercial materials. Ionic liquids have thermophysical and chemical properties that may be suitable for heat transfer and short heat term storage in power plants using parabolic trough solar collectors. Ionic liquids are salts that are liquid at or near room temperature. Thermal properties important for heat transfer applications are melting point, boiling point, liquidus range, heat capacity, heat of fusion, vapor pressure, and thermal conductivity. Other properties needed to evaluate the usefulness of ionic liquids are density, viscosity and chemical compatibility with certain metals. Three ionic liquids were chosen for study based on their range of solvent properties. The solvent properties correlate with solubility of water in the ionic liquids. The thermal and chemical properties listed above were measured or compiled from the literature. Contamination of the ionic liquids by impurities such as water, halides, and metal ions often affect physical properties. The ionic liquids were analyzed for those impurities, and the impact of the contamination was evaluated by standard addition. The conclusion is that the ionic liquids have some very favorable thermal properties compared to targets established by the Department of Energy for solar collector applications.

Keywords: Ionic liquid; Heat capacity; Heat transfer; Thermal conductivity; Thermal stability

1. Introduction

Ionic liquids are not a new class of materials, but they do have a set of physical properties that has sparked increased attention in recent years. A commonly accepted practical definition for an ionic liquid is a salt with a melting temperature below the boiling point of water [1]. Most salts identified in the literature as ionic liquids are liquid at room temperature, and often at substantially lower temperatures. One fairly general feature of ionic liquids that is not part of the definition is that most have organic cations and inorganic anions. There are many synonyms used for ionic liquids that complicate a literature search. 'Molten salts' is the most common and most broadly applied term for ionic compounds in the liquid state. Unfortunately the term 'ionic liquids' was also used to mean the same thing long before there was much literature on low melting salts [2,3]. It may seem that the difference between ionic liquids and molten salts is just a matter of degree (literally); however, the practical differences are sufficient to justify a separately identified niche for the salts that are liquid around room temperature. That is, in practice the ionic liquids usually may be handled like ordinary solvents. There are also some fundamental features of ionic liquids, such as strong ion–ion interactions that are not often seen in higher temperature molten salts.

Heat-transfer fluids are found in a large number of industrial and consumer applications. The applications range from refrigeration systems at the low temperature end, to solar energy collection and storage at high temperatures. Probably, the most common heat-transfer fluid is steam, but that will definitely not be the topic of this paper. Examples of liquid and liquid/vapor fluids presently in commercial use are the Dowtherm® family of glycol-based liquids, the sili-

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* Corresponding author. Tel.: +1 719 333 6005; fax: +1 719 333 2947.
E-mail address: john.wilkes@usafa.af.mil (J.S. Wilkes).

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cone oil based SYLTHERM®, and the Therminol® diphenyl oxide/biphenyl fluids. The focus of this report is on liquids usable as heat-transfer fluids from normal ambient temperatures (starting near 0 °C) to very high temperatures seen in solar collectors (>400 °C). In this report, we will describe the properties of some ionic liquids that are relevant to this mid- to high-temperature range, and the effect that common contaminants have on these properties.

A specific application for the ionic liquid heat-transfer fluids is electric power plants using parabolic trough solar collector technology. This so-called solar electric generating system (SEGS) is now in the large-scale demonstration stage in the US and Europe [4]. These plants collect solar energy in a field of parabolic cross-section trough mirrors by circulating a heat-transfer fluid in a pipe at the focus of the parabola, then transferring the heat to an exchanger. Steam is generated in the exchanger, and the rest of the system operates like a conventional electric power plant. Such plants are now operating in the 14–80 MW capacity range.

The values of the specific properties important for heat transfer are difficult to find. In fact we have found no such specific listing for solar collection applications. For the purposes of this study, we will compare properties of three ionic liquids with (1) the properties of Therminol® VP-1 [5], and (2) specifications proposed for new fluids contained in a request for proposal from the National Renewable Energy Laboratory [6]. A systems study of thermal storage media for large parabolic trough solar electric plants compared the materials used in eight plants, but did not identify any as being ideally suited [7]. The report did conclude (among other things) that (1) 'there have been no major bold developments in the field of thermal energy storage systems for trough power plants in the 1990s...' and (2) 'molten salt systems with lower melting points should be explored for trough applications'. If the low melting ionic liquids do qualify as viable thermal fluids for solar collectors, then we believe that they will in fact constitute a '...major bold development in the field of thermal energy storage systems...'.

The target requirements stated by NREL in [6] are summarized in Table 1. The heat storage could be provided by sensible heat, by reversible chemical reactions, or by phase change. Sensible heat storage will depend on the heat capacity and the density of the fluid, while phase change storage depends on the heat of fusion and density. The cost goal unit is a bit unusual, since it is normalized to amount of sensible heat stored. The 't' subscript refers to the temperature range over which the heat is absorbed or evolved, which is often only 100 °C. Since Therminol® VP-1 is a common heat-transfer fluid, and is included as a comparison material in the NREL requirements, it is useful to list in Table 2 some of the many physical properties reported for the commercial fluid. See reference [5] for more properties.

Table 1
Heat-transfer fluid requirements

Storage density	>1.9 MJ/m^3
Freezing point	≤0 °C
High temperature stability	≥430 °C
Cost goal	≤\$15/kW h$_t$
Required quantity for a solar plant	460,000 m^3
Vapor pressure	<1 atm
Materials compatibility	Carbon and stainless steel
Viscosity	Similar to Therminol® VP-1

Table 2
Therminol® VP-1 properties

Crystallizing point	12 °C
Moisture content	300 ppm
Flash point	124 °C
Kinematic viscosity at 40 °C	2.48 cSt
Coefficient of thermal expansion at 200 °C	0.000979/°C
Density	1060 kg/m^3
Volume contraction upon freezing	6.27%
Surface tension in air at 25 °C	36.6 dyn/cm
Specific resistivity at 20 °C	6.4×10^{11}
Heat of fusion	97.3 kJ/kg
Normal boiling point	257 °C
Heat of vaporization	206 kJ/kg
Optimum use range, liquid	12–400 °C
Optimum use range, vapor	260–400 °C
Heat capacity at 100 °C	1.78 J g^{-1} °C^{-1}
Thermal conductivity at 100 °C	0.1276 W m^{-1} K^{-1}

At present we know of no ionic liquid that has all of the relevant properties measured and reported. Some of the properties, such as vapor pressure, are not applicable to the salts. Most properties have not been measured simply because the numbers were not needed. The goal of this study was to measure and compile the properties of at least three representative ionic liquids that would allow us to judge the possibility of use of ionic liquids as heat-transfer fluids. The properties needed are density, heat capacity, freezing–melting temperature, heat of fusion, and thermal decomposition temperature. From the density and the heat capacity or heat of fusion we can calculate the sensible and latent storage density. Also important are the effects of contaminants on the physical properties, so the effects of metal ions, chloride, and water were examined. The ionic liquids considered were 1-methyl-3-ethylimidazolium tetrafluoroborate ([EMIM][BF4]), 1-methyl-3-butylimidazolium tetrafluoroborate ([BMIM][BF4]), and 1,2-dimethyl-3-propylimidazolium bis(trifluorosulfonyl)imide ([DMPI]Im). Those ionic liquids cover a wide range of hydrophobicity. The information reported here is sufficient to make a preliminary judgment of the efficacy of some ionic liquids as thermal fluids.

Ionic liquids are more difficult to purify than volatile organic solvents, and thus are often contaminated with one or more of the starting materials or water (generally absorbed from the atmosphere). We know from our experience with chloroaluminate ionic liquids that chloride [8] and alkali metal ions [9] have dramatic effects on transport properties. More recently Seddon et al. have reported the effects of chloride, water and organic solvents on viscosity and density of a wide variety of air and water stable ionic liquids [10]. It is abundantly clear that physical properties must be measured on pure samples, and that the samples be analyzed for the contaminants mentioned above. Otherwise the values reported for physical properties will be suspect.

2. Experimental

2.1. Materials

1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM] [BF_4]) and 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF4]) were prepared by metathesis reactions of the chloride [11] salt with $AgBF_4$ [12] or $NaBF_4$ [13]. The $AgBF_4$ was purchased from Janssen Chimica (#19.709.18); the $NaBF_4$ was purchased from ACROS (#192125000). The [DMPI]Im was provided by Covalent Associates, Inc.

The ionic liquids were screened qualitatively for purity by IR and NMR spectroscopy. No contamination by the monoalkylimidazole was detected to limit of these methods (about 1%), but water was often detected. Quantitative assays of common contaminates are presented in Section 3. Ag and Na contamination was determined on a Varian Vista-Pro CCD simultaneous inductively coupled plasma atomic emission spectrometer. Water content analysis of the various ionic liquids was performed by Karl Fischer titration on a Mettler-Toledo DL38 automated titrator. Chloride analysis was done by two methods: argentometric titration and detection with a Fisher Accumet^{TM} chloride combination ion selective electrode (ISE). The argentometric titration was performed by titrating 10.00 mL aliquots (or 20 mL in one case) of samples with a $AgNO_3$ solution standardized against a 0.01415 M NaCl solution using $AgCrO_4$ indicator. The chloride ion selective electrode analyses used the standard curve method. The calibration curve was linear ($R^2 = 0.9972$) but the observed slope was −0.0493 versus the expected −0.0592 Nernstian slope.

Water was added to the ionic liquids by exposure to a 100% relative humidity atmosphere. Two to 3 g of each liquid previously stored under a dry nitrogen atmosphere were placed in a 10 mL straight walled crystallizing dish with a small magnetic stir bar. These vessels were then placed inside a larger Petri dish along with a larger crystallizing dish containing deionized water. The apparatus was covered, sealed and the ionic liquid was stirred at a very low rate on a magnetic stir plate. The ionic liquid was given a minimum of 24 h to equilibrate before any measurements were taken. However, it was noted that the mass of the ionic liquid solutions could reach constant mass in as little as 4 h. Ionic liquids were constantly stored in this manner and samples taken from them as needed. Additionally, time was minimized between withdrawal of sample from the saturation apparatus and any respective measurement (especially during TGA analysis) as mass noticeably decreased due to water evaporation in the relatively dry Colorado atmosphere (15–18% RH).

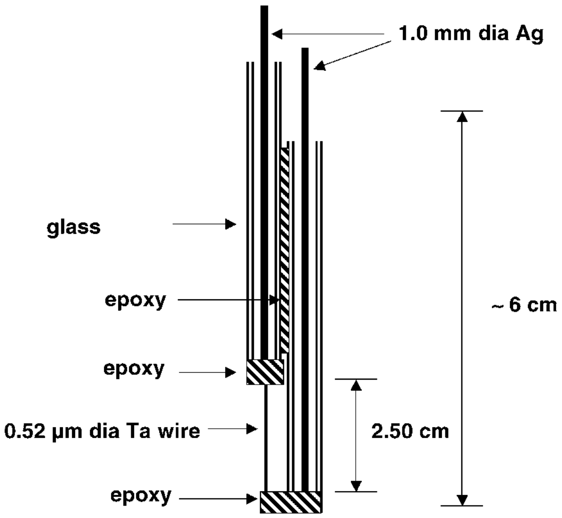

Fig. 1. Thermal conductivity cell.

2.2. Thermal analysis

Thermal gravimetric analyses were run on a TA Instruments SDT 2960, and differential scanning calorimetry (DSC) and modulated differential scanning calorimetry (MDSC) were performed on a TA instruments DSC 2910. The TGA instrument was temperature calibrated from room temperature to 800 °C at 10 °C/min scan rate using indium and aluminum. It was weight calibrated with ceramic standards provided with the instrument. The DSC instrument was calibrated using mercury, water, and indium at 5 °C/min. A sapphire disk (Al_2O_3) was used to establish the heat capacity constant needed for the modulated DSC.

2.3. Thermal conductivity

The thermal conductivity cell shown in Fig. 1 was constructed by spot-welding tantalum wire (99.9%, Alfa Aesar) to silver leads with one lead bent 90° at one end. Both leads were inserted into parallel glass tubes and sealed with epoxy. The glass tubes were then cemented together with the tantalum wire taut. The exposed tantalum wire measured 2.53 cm by 0.052 mm. The cell was placed in a tube containing the liquid to be measured and the complete assembly was immersed in a temperature controlled silicone oil bath. A fast potentiostat/galvanostat (EG&G Princeton Applied Research, Model M273A) was used to supply a constant current and monitor potential as a function of time. A desktop PC running Model 270 Electrochemical Analysis Systems software (EG&G Instruments Corp.) was used to remotely operate the M273A and record the data. A constant current was applied for 1 or 2 s and voltage was recorded at 25 ms intervals. The voltage was converted to resistance, and the temperature was calculated using the resistivity–temperature curve for tantalum and the wire dimensions. Thermal conductivity was calculated from the temperature-time data by Eq. (4) in Section 3. The cell was periodically tested with water and toluene standards to assure ourselves that it was operating correctly. Over a period of 2 months and a temperature range of 298–334 K the average deviation was 0.3%.

2.4. *Density*

Liquid densities were measured with a Mettler-Toledo DE40 density meter with density and temperature accuracy of ±0.0001 g/cm^3 and ±0.05 °C, respectively.

2.5. *Viscosity*

Viscosities were measured with a Cambridge Applied Systems Viscolab 4100 moving piston viscometer that has a specified accuracy of ±1.0%.

3. Results and discussion

We chose the [EMIM][BF$_4$], [BMIM][BF$_4$] and [DMPI]-Im ionic liquids because all are commercially available, or alternatively are easily prepared in two steps from commercially available starting materials. More importantly, these liquids are air and water stable, and we already know some of their properties relevant to their use as thermal fluids. Furthermore, the EMIM salt is generally thought to be hydrophilic, the BMIM salt hydrophobic, while the [DMPI]Im is even more hydrophobic.

3.1. *Summary of thermal properties*

The thermal properties of the ionic liquids are summarized in Table 3, and are discussed in more detail in the sub-sections below.

3.1.1. *Contaminant effects*

Silver ion, sodium ion, chloride, and water were analyzed in the ionic liquids. Table 4 is a compilation of typical concentrations of the expected contaminants in the ionic liquids as prepared. They do vary from sample to sample. The levels of all contaminants are relatively low, except for the sodium in the [BMIM][BF$_4$] synthesized using NaBF$_4$. The thermal stability studies were done on samples of [BMIM][BF$_4$] prepared via Ag and Na synthetic routes and the results were not affected by the presence (or absence) of metal ions. So, we conclude that metal ion impurities will not significantly affect the thermal properties.

We examined further the effect of the other impurities by purposeful addition of chloride or water, since in practical use the fluids could easily become contaminated (particularly by water). We then measured the thermal properties in the presence of substantial contamination. The discussions of the effects are included in the sections below, where each property is discussed separately.

3.1.2. *Melting temperature*

We actually report melting temperatures rather than freezing temperatures. These ionic liquids tend to super-cool, so the freezing temperature is not a reliable number. Once frozen, a sample will show a fairly reproducible melting temperature. The [BMIM][BF$_4$] salt does not freeze, but instead

Table 3
Summary of ionic liquid properties

Property	Ionic liquid		
	[EMIM][BF$_4$]	[BMIM][BF$_4$]	[DMPI]Im
Density at 60 °C (g cm^{-3})	1.2526 ± 0.0001	1.1747 ± 0.0001	1.4205 ± 0.0001
Melting point (°C)	14.42 ± 0.33	−87.38 ± 2.43 (T_g)	11.29 ± 0.01
Thermal decomposition onset (°C)	445.49	423.73 ± 0.34	457.04 ± 0.06
Heat capacity at 100 °C (J g^{-1} K^{-1})	1.28	1.66 ± 0.08	1.20 ± 0.05
Heat of fusion (J g^{-1})	48.2 ± 2.1	–	46.96 ± 5.98
Heat storage density, sensible, $\Delta T = 100$ °C (MJ m^{-3})	160.9	194.9	169.9
Heat storage density, latent[a] (MJ m^{-3})	60.4	–	66.7
Vapor pressure (atm)	≪1	≪1	≪1
Thermal conductivity (298 K) (W m^{-1} K^{-1})	0.200 ± 0.003	0.186 ± 0.001	0.131 ± 0.001
Viscosity (298 K) (cP)	36.07 ± 0.17	119.78 ± 1.28	90.05 ± 0.51

[a] Calculated from liquid density extrapolated to the freezing temperature.

Table 4
Post synthesis contaminant levels in the ionic liquids

Ionic liquid	Water (% w/w)	Metal (ppm) as Ag or Na	Chloride (% w/w)
[EMIM][BF$_4$] from AgBF$_4$	0.065 ± 0.006	1.59	0.113
[BMIM][BF$_4$] from AgBF$_4$	0.08 ± 0.015	11.5 ± 0.014	0.159
[BMIM][BF$_4$] from NaBF$_4$	0.13 ± 0.025	1273.9 ± 2.7	0.131
[DMPI]Im	0.05	–	0.0033

is a glass at low temperature. The glass transition temperature (T_g) was observed by DSC, and was quite reproducible at $-87.4 \pm 2.4\,^{\circ}$C. That value averages samples prepared from both $AgBF_4$ and $NaBF_4$, and is in agreement with the value reported by Holbrey and Seddon [13]. Our melting temperature for the [DMPI]Im was close to that reported by Ngo et al. [14], but misses the goal of 0 °C.

The freezing–melting behavior of the ionic liquids when adventitious water was introduced by equilibration with 100% relative humidity at room temperature are a bit complicated. The [EMIM][BF_4] has two freezing exotherms at −36 and −59 °C. During heating there is a multi-component melting endotherm with a reproducible temperature of −17 °C. The presence of water extends the low temperature limit of the liquidus range substantially, compared to the pure ionic liquid. [BMIM][BF_4] behaves similarly, except that there is only a single set of freezing–melting transitions slightly below 0 °C, which are undoubtedly water with its freezing point depressed. The [DMPI]Im is uninteresting, because so little water is present in the melt.

Gross contamination by chloride was introduced by adding the chloride salt of each of the three cations to the appropriate ions so that the final composition was 10 mol% in chloride. There was little effect on the freezing–melting.

3.1.3. Thermal stability

Thermal stability of the pure ionic liquids was measured by thermal gravimetric analysis, and we report the onset temperature in Table 3. The [BMIM][BF_4] values are an average from samples prepared from both $AgBF_4$ and $NaBF_4$, yet are very reproducible at $424.3^{\circ} \pm 3.4\,^{\circ}$C. The [DMPI]Im is the most thermally stable of the three ionic liquids.

One must be careful in interpreting the onset temperature for thermal decomposition. The thermal analysis software calculates the onset temperature by extrapolating a straight baseline along the temperature axis from a lower temperature region where there is no weight loss, then it creates a straight line through the inflection point of the weight versus temperature data. The intersection of the two lines is defined as the onset point. Clearly, there is some decomposition occurring at temperatures lower than the onset temperature. Kosmulski et al. have recently discussed this issue of reporting ionic liquids thermal stability, and they provide some instructive examples where the true stability is a lower temperature than that provided by a TGA scan [15]. A clearer indicator of thermal stability is isothermal gravimetric analyses. At temperatures of about 350 °C, significant decomposition is evident. Table 5 lists the rates of weight loss at various temperatures below and above the onset temperatures of the studied liquids.

The 'high-temperature stability' specification for heat-transfer fluids apparently is met by the three ionic liquids in question, but it is not clear just what the temperature in Table 1 means. If it is the onset temperature, then the ionic liquids are sufficiently stable. If long-term stability at the highest temperature is needed, then the stability should be stated as maximum weight loss rate at the specified minimum temperature. Data in Table 5 can be used to decide if the ionic liquids are thermally stable enough.

Table 5
Isothermal thermal decomposition rates

Temperature (°C)	Decomposition rate (mass%/min)		
	[EMIM][BF_4]	[BMIM][BF_4]	[DMPI]Im
250	0.0130	0.0228	0.0030
300	0.0260	0.0398	0.0320
350	0.4699	0.240	0.0765
400	1.637	1.507	0.5204
450	7.193	8.333	9.941

Table 6
Effect of water contamination on thermal stability

Ionic liquid	H_2O (wt.%)	TGA onset (°C)	
		Wet	Dry
[EMIM][BF_4]	30.99 ± 0.66	433	445
[BMIM][BF_4]	20.83 ± 0.11	423	424
[DMPI]Im	1.39 ± 0.04	460	457

We anticipated that water contamination of the tetrafluoroborate ionic liquids would decrease the thermal stability of the anion, since $BF_4{}^-$ is thermodynamically unstable towards hydrolysis to boric acid and HF. Table 6 shows this is not true. The wet ionic liquids have a weight loss at about 100 °C due to water evaporation, but the remaining salt decomposes as if it was the pure melt (which it is at that point). Similarly, 10 mol% chloride contamination did not affect the thermal stability (Table 7).

3.1.4. Heat capacity

Heat capacity must be known in order to calculate the sensible heat storage density of the ionic liquids. Modulated differential scanning calorimetry (MDSC, also known as 'AC calorimetry') imposes a time varying heat rate on the linear ramp used in normal DSC. Analysis of the heat flow at temperatures where no enthalpic or glass transitions occur gives the heat capacity directly [16]. Calibration is a little more complicated, but a single experiment on the same sample used for the melting point measurement provides continuous values of heat capacity over any desired temperature range. Table 3 compares the heat capacities for the three ionic liquids at 100 °C.

The temperature dependent values of the heat capacity are best represented by the polynomial fits to the MDSC data. [EMIM][BF_4] heat capacity over the range 0–130 °C is in

Table 7
Effect of 10 mol% chloride contamination on thermal stability

Ionic liquid	TGA onset (°C)	
	Added Cl^-	No added Cl^-
[EMIM][BF_4]	442	445
[BMIM][BF_4]	427	424
[DMPI]Im	457	457

the following equation

$$C_p = -8.810 \times 10^{-6}T^2 + 1.563 \times 10^{-3}T + 1.235 \qquad (1)$$

where C_p is the heat capacity in J g^{-1} K^{-1}, and T is temperature in °C.

The heat capacity of [BMIM][BF$_4$] was determined over the temperature range −50 to 300 °C, and found to have a relatively weak temperature dependence that was fitted to the quadratic in the following equation

$$C_p = -6.139 \times 10^{-6}T^2 + 3.228 \times 10^{-3}T + 1.366 \qquad (2)$$

The heat capacity of [DMPI]Im was determined in a similar manner, but in a temperature range of 50–390 °C and again a weak temperature dependence was observed as shown by the following equation

$$C_p = -8.263 \times 10^{-7}T^2 + 1.468 \times 10^{-3}T + 1.058 \qquad (3)$$

We did not investigate the heat capacities of ionic liquid with purposefully added contaminants.

3.1.5. *Heat of fusion*

The heats of fusion for [EMIM][BF$_4$] and [DMPI]Im shown in Table 3 were calculated from the area included by the DSC melting endotherm. No heat of fusion is available for [BMIM][BF$_4$] since it has no melting/freezing phase change.

The presence of water in the hydrophilic [EMIM][BF$_4$] ionic liquid has a substantial effect on the heat of fusion. A sample containing estimated 30% water had a heat of fusion of 124.6 J/g, which compares to 48.2 J/g for a dry liquid. This is not unexpected, since the heat of fusion of water is about eight times higher than the ionic liquid.

A sample of [EMIM][BF$_4$] with 10 mol% chloride has a slightly lower heat of fusion than the pure ionic liquid (39.5 versus 48.2 J/g.) The heat of fusion of [DMPI]Im with 10 mol% chloride varied in the range 9.2–20.1 J/g. This wide range of values is because the liquid freezes during the heating scan in the DSC, and the melting occurs almost immediately after or in some cases simultaneously with the freezing transition. The freezing of the sample is often incomplete.

3.1.6. *Sensible heat storage density*

The capacity of the ionic liquids for storing heat is a crucial quantity for solar energy collection. Sensible heat storage is easily calculated from the heat capacity, density and the temperature change chosen. For purposes of comparison we chose a very conservative 100 °C temperature change, since that is a value often used in solar applications. The values of 156.1, 192.1 and 176.3 MJ m^{-3} for [EMIM][BF$_4$], [BMIM][BF$_4$] and [DMPI]Im, respectively, are much larger than the 1.9 MJ m^{-3} minimum specified in Table 1. The ionic liquids can easily accommodate temperature changes much greater than 100 °C, so the realistic sensible heat storage could be higher by a factor of 2–3.

3.1.7. *Latent heat storage density*

The [BMIM][BF$_4$] ionic liquid does not undergo a phase change, so no latent heat storage is possible. A substantial amount of heat can be stored in the solid/liquid phase change in the [EMIM][BF$_4$] salt. However, that phase change is at a low temperature (4 °C), which would be inconvenient for high-temperature heat storage applications. However, it could be used for maintaining a temperature near the freezing point of water.

3.1.8. *Thermal conductivity*

The thermal conductivity of a fluid is an obviously important property for heat transfer applications. We chose to use the transient hot-wire method [17] because it is an absolute method, so we knew we were applying the method correctly when our results matched the accepted values for two reference standards. The error introduced by using an un-insulated wire in the ionically conductive ionic liquids is small. This is not unexpected, since the conductivity of the most conductive of the ionic liquids is only 14 mS/cm at 298 K. The impact of the liquid conductivity was tested by measuring the resistance of the cell at time zero with toluene or the ionic liquid surrounding the Ta wire. The resistance in toluene was within 1% of the resistance values measured in experiments with [EMIM][BF$_4$] and [BMIM][BF$_4$] and within 2% of the values measured in [DMPI][Im]. The transient hot-wire method involves the heating of a wire with a constant current, then measurement of the temperature of the wire during the heating. One must know the temperature dependence of the resistivity for the material in the wire. In the experiment one observes the potential, $E(V)$, over time at constant current, i (amperes). From the change in temperature with time, one can calculate the thermal conductivity from the slope of the following equation [18].

$$\Delta T = (q/4\pi\lambda)\ln t + (q/4\pi\lambda)\ln(4\kappa/a^2C) \qquad (4)$$

where λ is thermal conductivity in W m^{-1} K^{-1}, κ the thermal diffusivity in m^2 s^{-1}, q the heat generation per unit length of wire in watts per meter (W m^{-1}), a the radius of wire in m, $C = \exp\gamma = 1.781$ (γ is Euler's constant), and t the time after start of heating in s. The heat q is calculated from $q = i^2R/L$, where i is the current in amperes, R the resistance in ohms and L the wire length in meters. ΔT is calculated from the known temperature dependence of the resisitivity of the wire [19]. The thermal conductivity is determined from the slope of the ΔT versus ln(t) plot, as shown in Fig. 2. The experiment is complete in about 1 s, so fast data acquisition is necessary.

Thermal conductivities of the three ionic liquids, VP-1, and a reference liquid [20] are plotted as a function of temperature in Fig. 3. The error bars are smaller than the plot symbols, so they are not shown. The temperature dependence is very weak for the ionic liquids, and it fits to straight lines having the adjustable parameters listed in Table 8. The interesting question is: do ionic liquids behave more like water or more like toluene? The answer is clearly toluene.

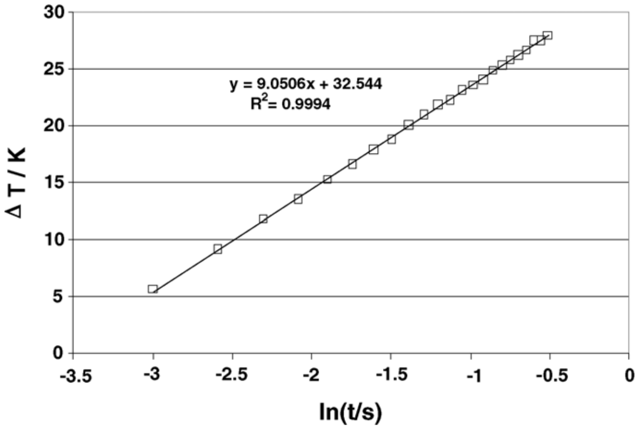

Fig. 2. Linear ΔT vs. ln(t) plot for thermal conductivity determination of [EMIM]BF$_4$.

Table 8
Temperature parameters for thermal conductivity

Ionic liquid	$\lambda = aT + b$[a] (300–390 K)	
	$-a \times 10^5$ (W m^{-1} K^{-2})	b (W m^{-1} K^{-1})
[EMIM][BF$_4$]	12.1 ± 1.5	0.235 ± 0.005
[BMIM][BF$_4$]	6.13 ± 0.11	0.204 ± 0.004
[DMPI]Im	4.61 ± 0.79	0.144 ± 0.004

[a] λ is thermal conductivity in W m^{-1} K^{-1} and T the absolute temperature.

The effect of water contamination on the thermal conductivities was significant, but not as great as expected, based on the large difference between the values for the pure ionic liquid and water. The [EMIM][BF$_4$] and [BMIM][BF$_4$] with 25 wt.% added water are compared with dry samples of the ionic liquids in Table 9. A wet (only 0.2% water) sample of [DMPI]Im was tested, but the thermal conductivity was the same as the dry liquid.

We did not investigate the effect of added chloride on thermal conductivity.

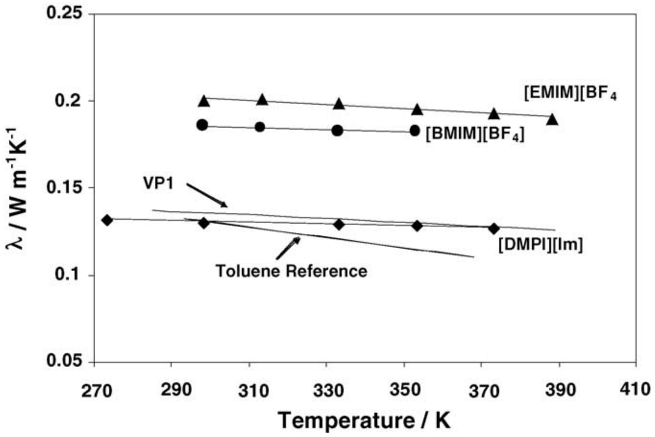

Fig. 3. Temperature dependence of thermal conductivity of three ionic liquids [EMIM][BF$_4$] (▲), [BMIM][BF$_4$] (●), [DMPI]Im (♦).

Table 9
Effect of water contamination on thermal conductivity (λ)

Ionic liquid	λ at 298 K (W m^{-1} K^{-1})	
	25 wt.% H_2O	Dry
[EMIM][BF$_4$]	0.276 ± 0.003	0.200 ± 0.003
[BMIM][BF$_4$]	0.279 ± 0.004	0.186 ± 0.001
[DMPI]Im	0.132 ± 0.002[a]	0.131 ± 0.001

[a] 0.2 wt.% water.

Table 10
Effect of water contamination on density

Ionic liquid	H_2O (wt.%)	Density at 20 °C (g cm^{-3})	
		Wet	Dry
[EMIM][BF$_4$]	8.3	1.2481	1.2829
[BMIM][BF$_4$]	9.6	1.1779	1.2018
[DMPI]Im	0.67	1.4541	1.4584

Table 11
Effect of water contamination on viscosity

Ionic liquid	H_2O (wt.%)	Viscosity at 25 °C (cP)	
		Wet	Dry
[EMIM][BF$_4$]	8.3 ± 0.04	9.21 ± 0.058	36.07 ± 0.17
[BMIM][BF$_4$]	9.6 ± 0.14	15.77 ± 0.05	119.78 ± 1.28
[DMPI]Im	0.67 ± 0.02	70.18 ± 0.34	90.05 ± 0.51

3.1.9. Density

Density is not a thermal property, but is needed to calculate some thermally related quantities, like heat storage capacity. The densities of the [EMIM][BF$_4$] and [BMIM][BF$_4$] [21] ionic liquids are reported in the literature, and the value 1.47 g/cm^3 for [DMPI]Im is on the MSDS from the supplier at an unspecified temperature [22]. We measured them again on our instrument in order to make reliable comparisons with the ionic liquids containing contaminants. Water in the ionic liquids appears to act as a diluent, and thus lowers the density. Table 10 shows this relatively small effect.

3.1.10. Viscosity

Since heat-transfer fluids are generally used in flowing systems, viscosity is an important physical property. Ionic liquids are generally viscous compared to molecular solvents. It appears that water in the ionic liquids affects viscosity much like it affects density. That is, it dilutes the ionic liquid, thus making it less viscous. Table 11 shows that the effect is quite substantial.

4. Conclusions

The thermal properties of the ionic liquids presented here indicate that they are suited for use as heat-transfer fluids. In many ways they are superior to present commercial heat-transfer fluids. They are stable over a wide temperature range, can store substantial heat, and have the advantage of low vapor pressure. Contamination of ionic liquids by water, metal cations, and chloride has variable impact on their physical and thermal properties. Cost and availability will be important future issues.

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