IONIC LIQUIDS AS THERMAL FLUIDS

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ABSTRACT

The general properties of ionic liquids match many of the physical and chemical properties required of liquids used as heat transfer fluids. The properties of the ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF₄]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) that are relevant to their use as thermal fluids were measured or compiled from the literature. The properties where the ionic liquids compare favorably with established fluids are heat storage capacity, vapor pressure, liquidus range, boiling point, and freezing point. They compare unfavorably in cost. They compare roughly equally in viscosity, thermal stability, and thermal conductivity. Comparison data are still lacking for flammability, toxicity, thermal expansion, volume change at melting and freezing, surface tension, maximum film temperature, and critical point quantities.

INTRODUCTION

"Thermal fluids" is a general term that includes the important class of materials used for heat transfer and short-term heat storage. Examples of materials presently in commercial use are the Dowtherm® family of glycol based liquids, the silicone oil based SYLTHERM®, and the Therminol® diphenyl oxide/biphenyl fluids. Historically, the most common high temperature heat transfer fluid is steam. The applications range from refrigeration systems at the low temperature end, to solar energy collection and storage at high temperatures. The focus of this report is on liquids usable as heat transfer fluids used 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.

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 two ionic liquids with 1) the properties of Therminol® VP-1 (1), and 2) specifications proposed for new fluids contained in a request for proposal from the National Renewable Energy Laboratory (2). 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 (3). 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 1990’s...”, 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 reference 2 are summarized in Table 1.

Table 1. Heat Transfer Fluid Requirements

| Requirement                             | Specification     |
|-----------------------------------------|-------------------|
| Storage density                         | >1.9 MJ/m³        |
| Freezing point                          | ≤0°C              |
| High temperature stability              | ≥430°C            |
| Cost goal                               | ≤$15/kWh          |
| Required quantity for a solar plant     | 460,000 m³        |
| Vapor pressure                          | <1 atm            |
| Materials compatibility                 | Carbon and stainless steel |
| Viscosity                               | Similar to Therminol® VP-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 it is included as a comparison material in the NREL requirements, it is useful to list some of the many physical properties reported for the commercial fluid. See reference 3 for more properties. It is interesting to note that thermal conductivity and surface wetting are properties not specified for the fluids.

At present we know of no ionic liquid that has had 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 two 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. The ionic liquids considered are 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF₄]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]). The information reported here is sufficient to make a preliminary judgment of the efficacy of some ionic liquids as thermal fluids.
Table 2. Therminol® VP-1 Properties

| Property                                      | Value                  |
|-----------------------------------------------|------------------------|
| 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/m³             |
| Volume contraction upon freezing              | 6.27%                  |
| Specific resistance at 20°C                   | 6.4 x 10¹¹             |
| 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              |

EXPERIMENTAL

Materials and Equipment

1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) was prepared by metathesis reactions of 1-butyl-3-methylimidazolium chloride (4) ([BMIM]Cl) with AgBF₄ (5) or NaBF₄ (6). The AgBF₄ was purchased from Janssen Chimica (#19.709.18); the NaBF₄ was purchased from ACROS (#192125000). The [EMIM][BF₄] used in this study was prepared from AgBF₄ (5). The ionic liquids were screened for purity by IR and NMR spectroscopy.

Ag and Na contamination in ([BMIM][BF₄]) was determined on a Varian Vista-Pro CCD Simultaneous ICP-OES. Water content analysis of the various ionic liquids was performed by Karl Fischer titration on a Mettler-Toledo DL38. Chloride analysis was accomplished by two methods: argentometric titration and detection with a chloride ion selective electrode. Thermal gravimetric analyses were run on a TA Instruments SDT 2960, and differential scanning calorimetry and modulated differential scanning calorimetry was performed on a TA instruments DSC 2910.

Thermal Analysis

Thermal gravimetric analysis (TGA) was calibrated from room temperature to 800°C at 10°C/min. using indium and aluminum. TGA was run on ([BMIM][BF₄]) samples (~40mg) in triplicate. Differential scanning calorimetry (DSC) was calibrated using mercury, water, and indium at 5°C/min. Sapphire (Al₂O₃) was used to establish the heat capacity constant needed for the modulated DSC (MDSC).
Chloride Determination

Samples (approx. 1 gram) of ([BMIM][BF₄]) were dissolved in 18 MΩ water and diluted to 50 mL. The argentometric titration was performed by titrating 10.00 mL aliquots (or 20 mL in one case) of samples with a AgNO₃ solution standardized against a 0.01415 M NaCl solution using AgCrO₄ indicator. The chloride ion selective electrode analyses used a 10-250 ppm calibration curve. The calibration curve was linear (R² = 0.9972) but the slope was not Nernstian.

Added Chloride Experiment

[BMIM]Cl was added to [BMIM][BF₄] to make the final composition 10 mol% Cl.

Added Water Experiment

The ionic liquids were exposed to a 100% relative humidity atmosphere in the following manner. Two to three grams 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 hours to come to equilibrium before any measurements were taken, though it was noted that the mass of the ionic liquid solutions could reach constant mass in as little as 4 hours time. Ionic liquids were constantly stored in this manner and samples from them taken 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.

Thermal Conductivity

The thermal conductivity cell was constructed by spot welding tantalum wire (99.9%, Alfa Aesar) to silver leads. One lead was bent 90° at one end, both leads were inserted into glass tubes and sealed with epoxy, and the glass tubes were cemented together with the tantalum wire taut. The exposed tantalum wire measured 2.53 cm by 0.052mm. 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 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 (EG&G Instruments Corp.) was used to remotely operate the M273A and record the data. A constant current was applied for 1 or 2 seconds and voltage was recorded at 25 ms intervals. The voltage was converted to resistance from which the temperature was determined using the resistivity-temperature curve for tantalum and the wire dimensions. Thermal conductivity was calculated from the temperature-time data by equation 2 in the Results and Discussion section.

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RESULTS AND DISCUSSION

We chose the [EMIM][BF₄] and [BMIM][BF₄] ionic liquids, because both 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, and the BMIM salt is hydrophobic.

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

Table 3. Summary of Ionic Liquid Properties

| Property                               | [EMIM][BF₄] | [BMIM][BF₄] |
|----------------------------------------|-------------|-------------|
| Density at 60°C                        | 1.2187 g cm⁻³ | 1.1811 g cm⁻³ |
| Freezing point                         | 4°C         | -88°C (Tg) |
| Thermal decomposition onset            | 434°C       | 424°C       |
| Heat capacity at 100°C                 | 1.281 J g⁻¹ °C⁻¹ | 1.627 J g⁻¹ °C⁻¹ |
| Heat of fusion                         | 109.9 J g⁻¹  | —           |
| Heat storage density, sensible         | 152.4 MJ m⁻³ | 187.2 MJ m⁻³ |
| Heat storage density, latent           | 137.9 MJ m⁻³ | —           |
| Vapor pressure                         | <<1 atm     | <<1 atm     |
| Thermal conductivity at 298 K          | 0.200 W m⁻¹ K⁻¹ | 0.186 W m⁻¹ K⁻¹ |
| Cost, at 100°C for ΔT=100°C            | 30,870 USD (kW h)⁻¹ | 19,430 USD (kW h)⁻¹ |

Freezing Point

The value for the freezing point of [EMIM][BF₄] was from our earlier work (7). The [BMIM][BF₄] salt does not freeze, but instead is a glass at low temperature. The glass transition temperature (Tg) was observed by differential scanning calorimetry, and was quite reproducible at -88.3° ±1.2° C. That value averages samples prepared from both AgBF₄ and NaBF₄, and is roughly in agreement with the value reported by Holbrey & Seddon (8).

The freezing point specification of 0° C in Table 1 is very nearly met by [EMIM][BF₄], and the glassy nature of [BMIM][BF₄] make freezing not an issue for that ionic liquid.

Thermal Stability

Thermal stability was measured by thermal gravimetric analysis, and we report the onset temperature in Table 3. The [EMIM][BF₄] value was previously reported (7).
The [BMIM][BF₄] values are again very reproducible at 424.3° ± 3.4° C. The value in Table 3 is an average from samples prepared from both AgBF₄ and NaBF₄, and both of those with or without chloride purposefully added as a possible contaminant.

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. This is shown in the TGA-DTA thermogram in Figure 1. Clearly, there is some decomposition occurring at temperatures lower than the onset temperature. A clearer indicator of thermal stability is seen in the isothermal gravimetric analyses shown in Figure 2. Some decomposition is evident at 350° C. Table 4 lists the rates of weight loss at various temperatures below and above the onset temperature.

**Table 4. Thermal Decomposition Rates**

| Temperature, °C | [EMIM][BF₄] Rate (mass %/min) | [BMIM][BF₄] Rate (mass %/min) |
|----------------|-------------------------------|-------------------------------|
| 250            | 0.0130                        | 0.0228                        |
| 300            | 0.0260                        | 0.0398                        |
| 350            | 0.4699                        | 0.240                         |
| 400            | 1.637                         | 1.507                         |
| 450            | 7.193                         | 8.333                         |

The “high temperature stability” specification for heat transfer fluids apparently is met by the two 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 4 can be used to decide if the ionic liquids are thermally stable enough.

**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 (9). 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.

The temperature dependent values of the heat capacity of [EMIM][BF₄] were reported earlier (7). Table 3 shows the values at 100° C for this liquid and [BMIM][BF₄]. The heat capacity of [BMIM][BF₄] 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 Equation 1.

\[
C_p = -6.139 \times 10^{-6}T^2 + 3.228 \times 10^{-3}T + 1.366 \quad (1)
\]

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

**Heat of Fusion**

No heat of fusion is available for [BMIM][BF\(_4\)], since it has no melting/freezing phase change. The value for [EMIM][BF\(_4\)] is from our earlier work (7). The heat of fusion will be used to calculate latent heat storage density below.

**Sensible Heat Storage Density**

The capacity of the ionic liquids for storing heat is a crucial quantity for solar energy collection. For sensible heat storage, it 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 (3). The values of 152.4 MJ m\(^{-3}\) and 187.2 MJ m\(^{-3}\) for [EMIM][BF\(_4\)] and [BMIM][BF\(_4\)] respectively are much larger then the 1.9 MJ m\(^{-3}\) minimum specified in Table 1.

The goal of 1.9 MJ m\(^{-3}\) seems rather conservative. We did not find a published heat capacity of the commercial Therminol VP-1, however we estimated the storage density from the heat capacity of solid biphenyl (a principal component of Therminol VP-1). The sensible heat storage density estimates at 104 MJ m\(^{-3}\); a value also substantially above the requirement, but less than the ionic liquids. The Therminol is a vapor at the high temperatures seen in the solar collectors, and the much lower heat capacity and density of vapors would result in much lower sensible heat storage.

**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.

**Thermal Conductivity**

The thermal conductivity of a fluid is an obviously important quantity for heat transfer applications. We chose to use the transient hot wire method for several reasons; 1) 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, 2) it appeared to be a very simple method. We were correct about 1), but not 2). 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 Equation 2,

$$\Delta T = \left( \frac{q}{4\pi A} \right) \ln t + \left( \frac{q}{4\pi A} \right) \ln \left( \frac{4\kappa}{a^2 C} \right)$$

(2)

where $\lambda$ is thermal conductivity in W m$^{-1}$ K$^{-1}$, $\kappa$ is thermal diffusivity in m$^2$ s$^{-1}$, $q$ is the heat generation per unit length of wire in watts per meter (W m$^{-1}$), $a$ is radius of wire in m, $C = \exp \gamma = 1.781$ ($\gamma$ is Euler's constant), $t$ is time after start of heating in s. The heat $q$ is calculated from $q = \frac{i^2}{L} R$, where $i$ is the current in amperes, $R$ is the resistance in ohms, and $L$ is the wire length in meters. $\Delta T$ is calculated from the known temperature dependence of the resistivity of the wire. The experiment is complete in about one second, so fast data acquisition is necessary.

Thermal conductivities of the two ionic liquids plotted as a function of temperature are in Figure 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 5.

| Ionic Liquid | $a$ (W m$^{-1}$ K$^{-2}$) | $b$ (W m$^{-1}$ K$^{-1}$) |
|--------------|--------------------------|---------------------------|
| [EMIM][BF$_4$] | -1.22E-4 | 0.238 |
| [BMIM][BF$_4$] | -6.20E-5 | 0.204 |

$\lambda$ is thermal conductivity in W m$^{-1}$ K$^{-1}$, $T$ is absolute temperature.

The figure also shows the temperature dependence of thermal conductivity for the two reference standards water and toluene (10). The interesting question is: do ionic liquids behave more like water or more like toluene? The answer is clearly toluene.

Cost

Ionic liquids do not even remotely come close to the cost goal of $15 \text{ kW}_{1}^{-1} \text{ h}^{-1}$. To reach that goal the cost of the ionic liquids would have to approach that of Evian bottled water ($17.05 \text{ kW}_{1}^{-1} \text{ h}^{-1}$). However, the high cost of the ionic liquids listed in Table 3 is not as bad as it appears. The cost is based on small quantity (1000 mL) purchases from a specialty chemical supplier (11). If the ionic liquids were produced in the volumes needed for solar power plants, the cost would be much lower. Also, the cost is expressed as USD per amount of sensible heat stored over a 100° C temperature range. The ionic liquids can store heat over a temperature range up to 400° C, thus reducing the cost of the fluid by up to 4-times.

Effect of Contaminants

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 (12) and alkali metal ions (13) 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 (14). 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.

Silver ion, sodium ion, chloride, and water were analyzed in the ionic liquids. Table 6 is a compilation of the results.

| Ionic Liquid          | Water (%w/w) | Metal (%w/w) as Ag or Na | Chloride (%w/w) |
|-----------------------|--------------|--------------------------|-----------------|
| [EMIM][BF₄] from AgBF₄ | 0.065±0.006  | -                        | -               |
| [BMIM][BF₄] from AgBF₄ | 0.08±0.015   | 11.5±0.014               | 0.159           |
| [BMM][BF₄] from NaBF₄ | 0.13±0.025   | 1273.9±2.7               | 0.131           |

The levels of all contaminants are relatively low, except for the sodium in the [BMIM][BF₄] synthesized using NaBF₄. The thermal stability studies were done on samples of [BMIM][BF₄] prepared from both, and the results were not affected by the presence (or absence) of metal ions. We examined further the effect of these 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. Results of these experiments will be presented in a subsequent symposium. One surprising finding was that the [BMIM][BF₄] ionic liquid can absorb moisture from a humid atmosphere nearly as well as the [EMIM][BF₄].

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. Cost and availability will be important future issues.

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REFERENCES

1. “Product Information, Therminol VP-1 Vapor Phase/Liquid Phase Heat Transfer Fluid,” Solutia Inc. Web site, http://www.therminol.com. April 2002.
2. Thermal Storage for Solar Thermal Parabolic Trough Electric Power Systems,” National Renewable Energy Laboratory, Request for Proposal Number RCQ-0-30910, March 27, 2000.
3. Survey of Thermal Storage for Parabolic Trough Power Plants, Pilkington Solar International, report submitted to the National Renewable Energy Laboratory, May 10, 2000.
4. J. S. Wilkes, J. A. Levisky, R. A. Wilson, and C. L. Hussey, Inorg. Chem., 21, 1263 (1982).
5. J. S. Wilkes and M. J. Zaworotko, J Chem. Soc, Chem Commun, 965 (1992).
6. J. D. Holbrey and K. R. Seddon, J. Chem Soc, Dalton Trans., 2133 (1999).
7. M. L. Mutch and J. S. Wilkes, in Molten Salts XI, P. C. Trulove, H. C. De Long, G. R. Stafford, S. Deki, PV 98-11, p. 254, The Electrochemical Society Proceedings Series, Pennington, NJ (1998).
8. J. D. Holbrey and K. R. Seddon, J. Chem. Soc., Dalton Trans., 2133 (1999).
9. E. Gmelin, Thermochim. Acta, 304/305, 1 (1997).
10. M. J. Assael, C.A. Nieto de Castro, H.M. Roder, W.A. Wakeham in Measurement of the Transport Properties of Fluids, Vol III, W.A. Wakeham, A. Nagashima, J.V. Sengers, eds., Blackwell Scientific Publications, London (1991).
11. Solvent Innovation Gmbh, Alarichstraße 14-16, 50679 Köln, Germany.
12. Armand A. Fannin, Jr., Danilo A. Floreani, Lowell A. King, J. Stephen Landers, Bernard J. Piersma, Daniel J. Stech, Robert L. Vaughn, John S. Wilkes and John L. Williams, J. Phys. Chem., 88, 2614 (1984).
13. Anselmo M. Elias and John S. Wilkes, J. Chemical and Engineering Data, 39, 79 (1994).
14. K. R. Seddon, A. Stark and M.-J. Torres, Pure Appl. Chem., 72, 2275 (2000).
Figure 1. Thermal gravimetric analysis of [BMIM][BF$_4$]

Figure 2. Isothermal gravimetric analysis [BMIM][BF$_4$]
Figure 3. Thermal conductivities ($\lambda$) of ionic liquids compared to the reference standards water and toluene.