THERMAL ANALYSIS OF 1-ETHYL-3-METHYLMIDAZOLIUM TETRAFLUOROBORATE MOLTEN SALT

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1-Ethyl-3-methylimidazolium tetrafluoroborate (EtMeImBF4) is a room temperature ionic liquid that is not highly reactive with moisture. The melting point, thermal stability, and heat capacity of this material were determined. The melting point was determined by differential scanning calorimetry to be 4.5° ± 0.4 C (onset) or 11.8° ± 0.2° C (peak). The material is thermally stable to approximately 300° C as determined by thermal gravimetric analysis. The heat capacity as a function of temperature was determined by modulated differential scanning calorimetry.

INTRODUCTION

Ionic liquids with the 1-ethyl-3-methylimidazolium cation were first reported in chloroaluminate systems, where the organic chloride was mixed with aluminum chloride to produce a binary molten salt with melting temperatures generally below room temperature (1). The chloroaluminates have the disadvantage of being reactive with water, requiring the exclusion of ambient atmosphere. More recently, similar molten salts that do not react chemically with moisture were prepared and characterized (2). One such salt, the 1-ethyl-3-methylimidazolium tetrafluoroborate (EtMeImBF4), is the subject of this report.

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\text{EtMeImBF}_4
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Carlin and Fuller have further characterized this relatively simple single component molten salt, with the use as a battery electrolyte in mind (2,3).
EXPERIMENTAL

Materials

Dr. Joan Fuller provided the 1-ethyl-3-methylimidazolium tetrafluoroborate. It was a slightly viscous clear colorless liquid.

Melting Temperature

The melting temperature was determined by recording the heat rate change during the endotherm associated with melting of a sample cooled to dry ice temperature. This was done on a TA Instruments model DSC-2910 differential scanning calorimeter. The sample was prepared by weighing approximately 15 mg into an aluminum pan, and then the pan was hermetically sealed with a crimping tool. A dry ice/acetone slurry cooled the calorimeter cell. For most melting point determinations the sample was cooled as rapidly as possible to -60°C, then a linear temperature ramp of 5°C/min was applied to a maximum of 30°C. The DSC cell was purged continuously with dry nitrogen. The endotherm was analyzed with the TA Instruments DSC Standard Analysis Program version 4.0. The peak temperature is the temperature at which maximum negative heat flow occurs during the endothermic melting transition. The onset temperature is defined as the temperature at which two tangent lines intersect from the initial 12.5% of the endotherm and the last 12.5% of the transition to the maximum heat flow. An integration of the endotherm provides the heat of fusion in J/g.

Thermal Stability

The thermal stability was determined by simultaneous thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) on a TA Instruments model SDT-2960. The experiments were run on approximately 50 mg samples contained in 40 μL platinum pans. Scanning TGA was done by equilibrating the sample at 50°C, then increasing the temperature linearly to 700°C at 20°C/min. Isothermal TGA was done by equilibrating the sample at 100°C, jumping to the desired temperature at maximum heat rate, then maintaining the sample at the temperature for 30 min. Temperature equilibrium was achieved in about 5 min after the start of the jump.

Heat Capacity

The heat capacity (C_p) of 1-ethyl-3-methylimidazolium tetrafluoroborate was measured by modulated differential scanning calorimetry on the TA Instruments DSC-2910 calorimeter using their Modulated DSC Option control software and the Modulated DSC Data Analysis Program version 1.1. We modified the calibration procedure to obtain accurate heat capacity calibration over the wide temperature range of interest. This was done by collecting heat capacity data for a sapphire calibration disk continuously over the same temperature range, exporting the data to a Microcal Origin data file, and fitting the
Cₚ vs temperature data to a polynomial function. This function was used to correct the Cₚ vs temperature data collected on the experimental sample.

RESULTS AND DISCUSSION

Melting Temperature

Figure 1 is an example of a melting temperature determination of 1-ethyl-3-methylimidazolium tetrafluoroborate by DSC. It shows the onset temperature determined by the intersection of a tangent to the final 12.5% of the heat flow rise and the baseline. This gives slightly different values for the onset compared to the method described in the Experimental section. Multiple determinations of melting onset temperature, peak temperature of the endotherm, and heat of fusion are listed in Table I.

Table I. Melting Temperature and heat of Fusion

| Expt. # | Onset Temp °C | Peak Temp °C | Heat of Fusion J/g |
|---------|---------------|--------------|--------------------|
| 1       | 5.27          | 12.15        | 115                |
| 2       | 4.64          | 11.66        | 111                |
| 3       | 4.17          | 11.72        | 110                |
| 4       | 4.03          | 11.81        | 110                |
| Average | 4.53          | 11.78        | 111                |
| ±std dev| ±0.5          | ±0.2         | ±3                 |

Supercooling is an important feature of this material, and complicates the calorimetry. Many DSC experiments showed no melting endotherm at all, due to the failure of the sample to crystallize. We found that the sample could be reliably crystallized by cooling as rapidly as possible (ballistic cooling) to -60° C in the DSC cell. Slow cooling invariably resulted in supercooling. This means that the ionic liquid may be used as an electrolyte substantially below its melting point.

Thermal Stability

The simultaneous TGA/DTA of 1-ethyl-3-methylimidazolium tetrafluoroborate is shown in Figure 2. Decomposition occurs as a single transition with 100% weight loss. The TGA shows a decomposition onset temperature of 443° C and an inflection point in the transition of 494° C. The DTA data largely confirms this, with the endotherm onset at 434° C and a peak temperature of 497° C.

Measurable decomposition does occur at temperatures substantially below the onset temperatures listed above. Isothermal DTA experiments were performed at temperatures below the TGA transition and are shown in Figure 3. The method is able to
measure decomposition rates less than 1% mass loss per minute. An Arrhenius plot of the initial rate data provides an activation energy of 106 kJ/mol.

The thermal decomposition results taken together with the melting point data show that the material has a broad liquidus range. No vapor pressure measurements have been reported for the 1-ethyl-3-methylimidazolium tetrafluoroborate, but the absence of much weight loss at 300°C indicates little evaporation of BF₃. This was a concern, because Al₂Cl₆ evaporates in acidic chloroaluminates with the same of 1-ethyl-3-methylimidazolium cation.

**Heat Capacity**

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 (4). 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.

Some values of heat capacity for 1-ethyl-3-methylimidazolium tetrafluoroborate are listed in Table II. Those results were obtained from a 17.4 mg sample equilibrated for 5 min at 110°C to ensure a molten state and minimize moisture content, then equilibrated at 0°C. A linear temperature ramp of 2°C/min from 0°C to 150°C was modulated ±1.00°C every 100 sec. Our experience with the molten salt led us to believe that the sample was supercooled at the 0°C start, and lack of an endotherm during the experiment verified this. Corrected heat capacity values were tabulated at 1°C increments, but only some representative values are presented in Table II.

**Table II. Heat Capacities**

| Temperature °C | Heat Capacity J/g/°C | Temperature °C | Heat Capacity J/g/°C |
|----------------|----------------------|----------------|----------------------|
| 10             | 1.22₅                | 80             | 1.30₂                |
| 20             | 1.30₀                | 90             | 1.30₆                |
| 30             | 1.26₀                | 100            | 1.28₁                |
| 40             | 1.28₆                | 110            | 1.28₂                |
| 50             | 1.33₉                | 120            | 1.33₂                |
| 60             | 1.29₀                | 130            | 1.29₆                |

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REFERENCES

1. J. Wilkes and M. Zaworotko, J. Chem. Soc. Chem. Commun., 965 (1992).

2. R. T. Carlin, H. C. De Long, J. Fuller, P. C. Trulove, J. Electrochem. Soc., 141, L73 (1994).

3. J. Fuller, R. T. Carlin, R. A. Osteryoung, J. Electrochem. Soc. 144, 3881 (1997).

4. E. Gmelin, Thermochim. Acta, 304/305, 1 (1997).
Figure 1. Differential scanning calorimetry of EtMeImBF4.

Figure 2. Simultaneous TGA/DTA of EtMeImBF4
Figure 3. Isothermal TGA of EtMeImBF$_4$. Weight loss rates listed are for the linear period after the 5 minute thermal equilibration.