The effect of regioisomerism on the thermal and physical properties of ionic liquids


Methods

Synthesis - The ionic liquid isomers reported in this publication were synthesized previously by this group with the synthetic method and supporting characterization data presented in full.¹

For the purposes of this study viscosity, conductivity and density measurements were taken under dry conditions obtained through drying at 100 °C under vacuum overnight. The water contents of samples equilibrated in air for 48 hours were measured as (1) 2790 ppm, (2) 3030 ppm using Karl-Fisher titration. These values were found to be lower than HMIM Tf₂N (4680 ppm) under the same conditions.

Viscosity - Viscosity measurements were carried out over a temperature range of 20-50 °C on a Rheosense Inc. µVisc equipped with a temperature control unit.

Density - Densities of ionic liquids were measured over a temperature range of 20-30 °C ±0.1 °C on a Micromeritic Accupyc II 1340 helium pycnometer. All density measurements were performed in 10 cycles and the average recorded.

Electrochemistry – Cyclic voltammetry was performed using a Solartron SI1287 potentiostat (Solartron Analytical, Hampshire, UK) controlled by Corr-Plot (Scribner Associates, Southern Pines, NC, USA). For electrochemical impedance spectroscopy a 1252A frequency analyzer (Solartron Analytical, Hampshire, UK) was added and controlled by Z-Plot (Scribner Associates, Southern Pines, NC, USA).

Electrochemical Impedance Spectroscopy (EIS) - EIS was carried out using a custom built electrochemical cell utilizing two 1.6 mm diameter platinum electrodes (BASI) placed in a face on configuration into a PTFE tube with a separation of 2mm. The samples were injected into the inter-electrode space and the entire assembly was placed into a thermostatic oven for the duration of the experiment. The temperature was allowed to equilibrate for 20 minutes at each new temperature before measurements were taken in increments of 5 °C between 20 and 50 °C. Samples were pretreated by holding at OCP for 2 minutes before EIS was carried out on each sample using 10, 20 and 50mV perturbations sequentially over a frequency range of 0.1-100,000 Hz. Each set of measurements was repeated 3 times. The cell constant was found by calibration with a 1413 µS/cm conductivity standard solution over the appropriate temperature range.

Differential Scanning Calorimetry (DSC) - The heat capacity for each regioisomer was measured using a Quasi-isothermal method. The reported heat capacity value was calculated by averaging the last 5 minutes of the reversing heat capacity signal at each temperature. DSC scans were also conducted on regioisomers (1) and (2) with a heating and cooling rate of 10 °C/minute over a temperature range of -100 °C to 50 °C. The DSC was calibrated using the sharp melting of an indium metal standard.
Figure 1. DSC graph of regioisomer (1) 10 °C/minute heating and cooling rate. (a) first heat, (b) second heat, (c) third heat, (d) first cool, and (e) second cool.

There is no obvious melting peak in Figure 1 for the DSC run of regioisomer 1 this is due to the relatively high heating and cooling rate of 10°C/min. The sample does not have time to crystallize and therefore, there is no melting peak. For Figure 2 the regioisomer does cold crystallize, but the average heating rate is only 0.5°C/min. This gives the sample enough time to cold crystallize, and therefore a melting peak is observed. Please note that observing a melting peak does not necessarily mean a crystalline sample.
Figure 2: MDSC of regio isomer (1) with an average heating rate of 0.5°C/min. (a) reversing heat flow signal, (b) total heat flow signal, and (c) nonreversing heat flow signal
Figure 3: DSC graph of regio isomer (2) 10 °C/min heating and cooling rate. (a) first heat, (b) second heat, (c) third heat, (d) first cool, and (e) second cool.

The second and third heating cycle and the two cooling cycles for sample (2) seen in Figure 3 are very similar, with nearly identical $T_g$ and final melting points. The cold crystallization and crystal perfection peaks are difficult to interpret therefore, a MDSC scan was run with a slow heating rate of 0.5°C/min, which can be seen in Figure 4. The change in peaks is due to thermal history associated with these samples.
Figure 4: MDSC of regio isomer (2) with an average heating rate of 0.5 °C/min. (a) reversing heat flow signal, (b) total heat flow signal, and (c) nonreversing heat flow signal.

It should be noted that melting peaks are not usually seen in the non-reversing signal. Additionally even at a very slow heating rate of 0.5 °C/min there were only 2-3 modulations at half height and not the recommended 4-5 modulation cycles for the melting peak in sample (1). The 4-5 modulation cycles at half height is recommend for good results with no artifacts in the signals when running a MDSC experiment.²
Figure 5. Cyclic voltammograms showing the electrochemical windows of (1) and (2) for a 0.1 M solution in MeCN at a 1.6 mm diameter platinum disc working electrode, platinum mesh counter electrode and silver wire reference electrode and a scan rate of 10 mVs⁻¹.