

Cyclic Sulfonium Ionic Liquids with Dramatically Varying Transport Properties

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One of the attractive features of ionic liquids (ILs) is the ability to vary their thermophysical and transport properties by the choice of cation, anion and substituents. Nonetheless, some general trends have emerged. Particularly, in the search for low viscosity, high conductivity ILs for electrochemical applications, most researchers point to ILs with bis(trifluoromethylsulfonyl)imide ([Tf2N]), bis(fluorosulfonyl)imide ([FSA]) and dicyanamide ([DCA]) anions as good candidates. Lower viscosity ILs generally have higher conductivities. These trends do not hold for a series of cyclic sulfonium ILs that we have synthesized and characterized in our laboratory. Specifically, we have investigated the properties of three ILs with the same cyclic sulfonium cation paired with the [Tf2N] anion, as well as two aprotic heterocyclic anions. All three ILs have attractively low viscosities. In fact, the viscosity of one of the AHA ILs is only 13.5 cP at 25°C. However, the conductivities of the three ILs vary by three orders of magnitude. The conductivity of the [Tf2N] IL at 25°C is 2.56 mS/cm, which is consistent with its low viscosity. By contrast, the conductivities of the two AHA ILs are low, with one of them being just 0.0045 mS/cm at 25°C. Due to both a lower viscosity and lower conductivity, the two AHA ILs deviate significant from the ideal line on the Walden plot, which implies strong cation-anion association. The CO₂ solubility in all three ILs is relatively low, consistent with physical dissolution, even though the two AHA anions readily react with CO₂ at low partial pressures of CO₂ when paired with tetra-alkylphosphonium cations. We will also report densities and ion diffusivities, as measured by PFG-SE NMR Spectroscopy, of this interesting series of new ILs.