

Heat Transport Properties of Ionic Liquids with Compressed and Supercritical Fluids

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1. Introduction

The molecular flexibility of ionic liquids allows for their potential utilization in a variety of engineering applications, such as reaction media, separations, pre- and post-combustion CO₂ capture^{1, 2}, lubrication, absorption refrigeration³, etc. Many of the aforementioned engineering applications involve biphasic systems of ionic liquids and compressed gases. To properly characterize and design such systems, thermodynamic phase equilibrium data as well as transport property data is needed. Little transport property data, especially heat transport properties, for biphasic ionic liquid and compressed or supercritical gas systems exist in the literature. Here, the liquid thermal conductivity and viscosity are investigated for various imidazolium ionic liquids and compressed and supercritical carbon dioxide, and more polar hydrofluorocarbon gases, such as difluoromethane (R-32, T_c=78°C), 1,1,1,2-tetrafluoroethane (R-134a, T_c=101°C), and pentafluoroethane (R-125, T_c=66°C) to 125 °C and 200 bar.

2. Materials and Methods

A transient hot-wire technique was used to measure the thermal conductivity of pure ILs as well as biphasic systems of ILs/gases at equilibrium. We have previously described the methodology^{81, 82, 90, 91} and an overview will be provided here. A Flucon Fluid Control GmbH thermal conductivity probe and an in-house built high-pressure equilibrium cell are utilized. The gas is introduced using a high-pressure syringe pump. The mixture is stirred using a stir bar and a stir plate placed on a heavy bench to reduce vibration-induced convective effects. Ample time is given such that all convective effects induced through stirring are dissipated. The heating bath circulator is turned off prior to taking measurements as well to minimize possible convective forces.

3. Results and discussion

The liquid phase viscosity was measured for several ionic liquids. The systems investigated systems have shown a significant decrease in viscosity even with just a slight increase in dissolved gas composition. Figure 1 illustrates the viscosity of the IL [HMIm][Tf₂N] with CO₂ at various temperatures and pressures.⁴ The viscosity and thermal conductivity data is initially measured at a given temperature and pressure. Previously-measured Vapor-Liquid Equilibrium (VLE) data is then used to estimate the liquid composition. The behavior seen in Figure 1 is similar for CO₂ with N-n-alkyl-N-methyl pyrrolidinium ILs.⁵ We have recently measured the viscosity of ILs with HFC gases R-134a⁶, R-32, and R-125. With all dissolved gases and ILs, the viscosity of the liquid phase significantly decreases. We attribute this behavior as a “diluent” effect of dissolving lower viscosity species. This dramatic decrease in viscosity increases the diffusivity and mass transfer properties of the liquid phase.⁶ Thus, the mixture of the IL with the compressed gas will have better momentum

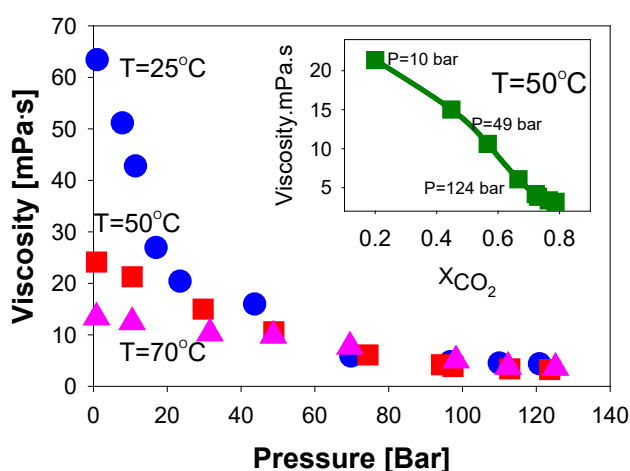


Figure 1. Viscosity of [HMIm][Tf₂N] with dissolved CO₂.⁴

properties of the liquid phase.⁶ Thus, the mixture of the IL with the compressed gas will have better momentum

and mass transport properties than the pure IL itself. ILs coupled with supercritical fluids will have viscosity and diffusivity similar to traditional organic solvents at ambient conditions.

While dramatic changes were shown in the viscosity of the ILs with dissolved gases, the thermal conductivity of the liquid changes relatively little. For CO₂/IL systems, the thermal conductivity of the system is generally dominated by that of the pure ionic liquid across a large composition. Initially, there is a slight decrease in the thermal conductivity with CO₂ composition (Figure 2).⁷ However, eventually the thermal conductivity increases. We have measured the pressure on thermal conductivity of pure IL to 200 bar and have observed a general increase with pressure. Thus, for the CO₂/IL mixture, a diluent effect is observed at lower compositions (pressures) and hydrostatic effects at higher compositions (pressures). The HFC gases have a much higher composition in the IL phase versus CO₂; some are even miscible at their vapor pressures and/or have mixture critical points (L=L or V=L) unlike with CO₂. With the HFCs, only a slight diluent effect is observed, i.e. decrease in thermal conductivity with composition, even to high compositions, e.g. ~80% mole HFC. However, at very high loadings (90+%), the thermal conductivity eventually decreases significantly to approach the value of the saturated liquid HFC. The qualitative behavior of thermal conductivity seems more dependent on the relative polarity of the dissolved component.

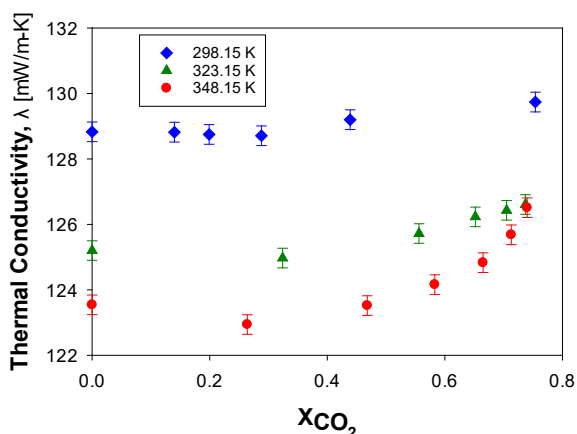


Figure 2. Thermal Conductivity of [HMIm][Tf₂N] with CO₂.⁷

4. Conclusions

The presence of any dissolved gas or supercritical fluid significantly decreases the viscosity of ionic liquids. This decrease will result in increased mass transfer properties in the mixture versus the pure IL. However, for thermal transport, the dissolved compressed gas or supercritical fluid only slightly decreases the thermal conductivity of the liquid phase. Only large amounts (90+%) of more polar hydrofluorocarbon gases can significantly decrease the thermal conductivity. However, in the IL/CO₂ systems especially in the supercritical regime of pure CO₂, the thermal conductivity actually increases due to the dominance of hydrostatic effects. The observed behavior for all systems investigated indicates that simple composition-based mixing rules for thermal transport properties based upon pure component properties would not be appropriate.

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