Anomalous Viscosity Trend for Mixtures of Tetra-Alkyl-Phosphonium Ionic Liquids and Glycerol

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One way to modify the physical properties of ionic liquids (ILs) is to add common organic solvents. While these solvents are frequently chosen for their low viscosities, here we investigate the effect of adding a solvent with a relatively high viscosity – glycerol (~1000 cP, 1 Pa·s, at room temperature). Specifically, we measured the viscosity of mixtures of glycerol with several tetra-alkyl-phosphonium-based ILs that contain Aprotic Heterocyclic Anions (AHAs) at temperatures from 10-80 ℃. We have developed AHA ILs for use in post-combustion CO_2 capture applications. As glycerol is a highly viscous organic solvent, we expected to observe a continuous increase in viscosity with increasing glycerol mole fraction. The data reported in this work, however, demonstrates a range of glycerol mole fractions in which the mixture viscosity decreases with the addition of glycerol. This region is not well represented by commonly employed viscosity mixing rules such as those proposed by Hind, Grunberg and Nissan, or Katti and Chaudhri. With further addition of glycerol, the viscosity increases towards the value of pure glycerol. We explore several possible causes for this unusual phenomenon including the impact of hydrogen bonding and potential inverse micellization caused by the long alkyl-chains of the phosphonium cations. Furthermore, we characterize the effects of alkyl-chain lengths, as well as AHA charge localization on the observed viscosity trends.