Liquid-Liquid Equilibrium Between Ionic Liquids with Aprotic Heterocyclic Anions (AHAS) and Water

Gabriela Avelar Bonilla [S], Oscar Morales-Collazo and Joan Brennecke [C]
McKetta Department of Chemical Engineering, University of Texas at Austin, Austin, TX, U.S.A.
jfb@che.utexas.edu

Water is a crucial impurity in many different applications using ionic liquids (ILs), because most processes do not take place in dry conditions and ILs are notoriously hygroscopic. In addition, different IL physical properties, such as viscosity, density, conductivity, surface tension, and polarity, can be affected by the presence of water even in hydrophobic ionic liquids (i.e., ILs that are not completely miscible with water)[1, 2]. Moreover, the presence of water can also modify reaction rates, equilibrium constants, selectivity, and reaction mechanisms for applications ranging from separation processes[3] to electrochemical applications[4] and CO_2 capture[5]. Therefore, it is important to develop a deeper understanding of the liquid phase behavior between water and ILs and probe the effect of the cation size and anion nature on ionic liquids hydrophobicity. The hydrophobic-hydrophilic character of aprotic heterocyclic anion (AHA) ionic liquids, which we have developed for post-combustion CO_2 capture, was studied by Karl Fischer titration to measure the water content in the IL-rich phase in equilibrium with a water-rich phase at room temperature. The effect of the tetra-alkyl-phosphonium cation on hydrophobicity was investigated by increasing the alkyl chain length to increase hydrophobicity. The effect of the anion on hydrophobicity was studied by pairing the tetra-alkyl-phosphonium cation with different AHAs and by adding different substituents on the anion. The anion nature, basicity, and electron withdrawing effect of different substituents proved to have a significant impact on the IL's hydrophobicity. Changes in the alkyl chain length of the cation and the nature of the anion produce changes in the solubility of water in the ILs of up to an order of magnitude.

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