Ternary Liquid-Liquid Equilibrium Measurement and Modeling of Imidazolium and Pyridinium Ionic Liquids

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The liquid-liquid equilibrium (LLE) of multicomponent systems involving ionic liquids (ILs) is important in evaluating ILs as solvents to replace traditional liquid extraction solvents. Here, we present experimentally determined phase diagrams of ternary systems of ILs with water and alcohols, with direct analysis of the equilibrium phases performed by HPLC. Our experimental goals are to develop ternary diagrams for various IL-water-alcohol systems, in order to find general trends. Tunability of the cation and anion are exploited to design ILs for specific separations.

In addition, we present modeling of the binary and ternary LLE using both the conventional (non-electrolyte) Nonrandom Two Liquid (NRTL) Equation and an electrolyte model that takes into account dissociation in the water or alcohol-rich phase. Modeling LLE is comprised of two problems: parameter estimation and phase equilibrium. Our goal is to attempt to "predict" the ternary phase behavior solely from binary liquid-liquid equilibrium data. Therefore, binary interaction parameters in the models are estimated from the binary data. Many models can have multiple sets of parameters that satisfy the equifugacity requirement. In order to choose the set of parameters that gives the most physically reasonable values, one must be able to find all the parameter solutions. We do this with computational methods based on interval analysis that guarantee that all solutions are found. The actual calculation of phase equilibrium requires the alternation between phase stability and phase split calculations. Once again, we use interval analysis to guarantee the correct solution. Our modeling goals are to determine model parameters for IL/alcohol and IL/water binary systems, and to predict the phase behavior for IL-water-alcohol systems using an interval Newton method combined with generalized bisection (IN/GB) as a tool. We can then evaluate different excess Gibbs free energy models based on their ability to model LLE systems that contain ILs.