Dissociation Behavior of Ionic Liquids in Solvents: 
Thermodynamic Modeling and Molecular Dynamics Simulation

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Ionic liquids (ILs) have gained a lot of attention for niche applications, such as CO₂ capturing, separation solvents, refrigerants, novel electrolytes in batteries and photovoltaic cells, etc. for their negligible vapor pressure. Like all electrolytes, properly accounting for the dissociation chemistry of ionic liquids whether in pure or in solvents is essential in developing accurate thermodynamic models to account for the liquid phase non-ideality as a function of compositions and temperatures. Experimental data show that ionic liquids are partially dissociated [1]. However, in the literature, ionic liquids are often approximated as all molecular form, completely dissociated, or at constant dissociation in solutions for thermodynamic modeling. In this work, we investigate three common ILs, i.e., [emim][EtSO₄], [emim][TFO], and [emim][TFA] in water, ethanol, and methanol. Partial dissociation of ionic liquids is explicitly considered together with the symmetric electrolyte Non-Random Two Liquid (eNRTL) model [2]. The binary interaction parameters are correlated with experimental data on vapor pressure [1,3-5] and dissociation extent [1]. Our new approach accurately correlates all available data, and the model predicts the ionic liquid dissociation phenomena over the entire concentration and temperature ranges. In addition to the thermodynamic modeling, we performed molecular dynamics simulation for these three Ionic Liquids (ILs). The aggregation study in molecular dynamics simulation supports the partial dissociation chemistry used in the thermodynamic modeling.

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