Atomistic Simulation of Pyridinium- and Triazolium-Based Ionic Liquids

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Knowledge of the thermophysical properties of ionic liquids is critical to their application in industrial processes. Ionic liquids can be made from a wide range of cation classes, including those based on imidazolium, pyrrolidinium, ammonium, phosphonium, triazolium, tetrazolium, guanidinium, and pyridinium. The immense number of ionic liquids that could be made by combining these different cations with a host of potential anions has stimulated work directed at understanding the link between the structure and chemical composition of ionic liquids, and their resulting dynamic and thermophysical properties. Without such understanding, the search for ionic liquids with optimal properties for a given application is a daunting task. Here we report the first atomistic level simulations performed on ionic liquids made from pyridinium and imidazolium cations. We have developed intermolecular potential functions (forcefields) for three ionic liquids containing alkyl-pyridinium cations paired with the bis(trifluoromethanesulfonyl)imide anion, as well as six ionic liquids containing various triazolium cations paired with nitrate and perchlorate anions. The forcefields were developed using a combination of ab initio calculations and literature data. Classical molecular dynamics simulations were then used to compute volumetric, thermal, and dynamic properties of these ionic liquids as functions of temperature and pressure. We find that heat capacities, crystal structures, and volumetric properties are all captured well by the simulations. We find evidence of glass-like dynamics for some ionic liquids at lower temperatures, making determinations of self-diffusivities difficult. The calculations shed light on the structural features that are important in determining the properties of these liquids, and also show that quantitative properties can be reliably obtained from atomistic simulations of ionic liquids.