Description of Interactions within Ionic Liquids using Ab Intio, DFT-D, and Semiempirical Methods

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There has recently been a wave of interest in the new chemistry and physics of room temperature ionic liquids (IL's) at solid interfaces because of the large number of applications of ILs in electrodeposition, sensing, coating, surface catalysis, and electrochemical energy storage.[1] In all these applications the interfacial structure of IL's is of crucial importance, which has stimulated a large and ever increasing number of theoretical and experimental studies of IL interface properties. Computational chemistry modeling can give a great deal of insight into the physical and chemical properties of liquids, solutions, and liquid/surface boundaries, however, the modeling method must be chosen carefully if it is to accurately represent the systems of interest. Generally speaking, IL cations contain a charged core and an aliphatic tail, while the anion is relatively bulky (at least as large as BF_4^-). IL's have a number of interesting properties that are largely attributable to the amphiphilic nature of IL cations. Long-range ordering has been observed to occur in some IL's within a particular temperature/pressure range,[2,3] numerous reports indicate that IL's form ordered layers near surface boundaries,[4-6] and the solubilities of small-molecule gases are substantially higher in some IL's than in most molecular liquids.[6]

Here we describe studies aimed at understanding the interactions occurring within imidazolium-based ionic liquids and between solvent/solute molecules in ionic liquid solutions. Ionic liquids are generally composed of large cations and anions, and inspection of electrostatic potentials of these species reveals that their charge distributions can be extremely inhomogenous; that is to say that although the potential on an IL cation, for example, is positive everywhere, there are regions of greater and lesser positive potential. One of main goals of our studies is to characterize the strength of cation/anion interactions as a function of relative orientation. We are interested in interaction strengths within the liquid environment, thus it is necessary to use implicit solvation methods to account for solvation effects.

The main questions we seek to address are:
1. Which DFT-D and semiempirical methods are most appropriate for the description of interactions in ionic liquids? Also, is it necessary to modify these methods to give a proper description of these systems. Here CCSD(T)/CBS results are used for comparison.
2. How does the interaction energy vary as a function of the relative orientation of cations/anions/solutes?
3. How sensitive are IL interaction energies to implicit solvation parameters?

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