The New Non-Polarizable Force Field Model of Imidazolium-Based Ionic Liquids

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Room temperature ionic liquids (ILs) have attracted much attention over the past few years. The most promising areas of their application, amongst many, are lithium batteries, supercapacitors, lubricants, actuators, sensors, reaction media, and hypergolic propellants. Their excellent thermal and electrochemical stability, negligible vapor pressure, dissolution in many solvents, and low flammability are the most exciting properties of these modern alternative materials. Molecular dynamics (MD) simulations have become a common practice to reliably probe the effects of various cation/anion tandems on the structure and dynamic properties of the ILs.

Many polarizable [Borodin, 2009] and non-polarizable [Liu et al., 2004; Canongia Lopes et al., 2008] force fields (FFs) have already been developed in order to perform extensive simulations of ILs by means of the classical MD and Monte Carlo techniques. While their structure and thermodynamics properties are well reproduced in almost every simulation, the main problem of all the non-polarizable FFs remains in the substantial (up to one order of magnitude) underestimation of the self-diffusion coefficients and specific electrical conductivity, and a considerable overestimation of the shear viscosity. These deviations are usually explained by the total neglect of electronic polarization effects in the classical MD simulations. The new polarizable FFs allow us to overcome this problem, although the usage of such techniques is much more time-consuming. Besides, for some classes of ILs, some inexplicable divergence with experimental data (up to 50%) is still observed [Borodin, 2009].

The primary goal of our work is to develop a procedure to account for ILs polarization effects in the framework of the classical MD. Through this work, we illustrate its successful operation on two imidazolium-based ILs, 1-methyl-3-ethylimidazolium tetrafluoroborate [EMIM][BF₄] and 1-methyl-3-buthylimidazolium tetrafluoroborate [BMIM][BF₄]. The initial electrostatic charges on all the cation and anion interaction sites were reduced according to the charge distributions derived from the Car-Parrinello MD simulations of the bulk ILs. The charges were obtained from electrostatic potential fit by using 10 uniformly spaced system configurations and then averaged. The obtained charge distributions together with Lennard-Jones (12, 6) parameters from AMBER force field excellently reproduced the experimental properties of both the [EMIM][BF₄] and [BMIM][BF₄] systems for self-diffusion, electrical conductivity, and shear viscosity over a wide temperature range (from 298 K up to 400 K). Being successful with the imidazolium-based ILs, we believe that the proposed procedure should become useful for other classes of ILs and similar compounds where the polarizability effects play a key role.