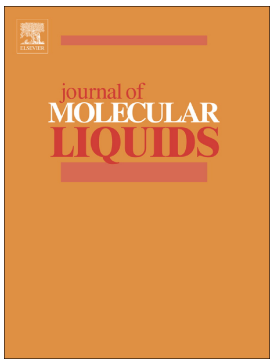

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Thermodynamic Properties of the 1-Butyl-3-Methylimidazolium Mesilate Ionic Liquid [C_4mim][OMs] in Condensed Phase, using Molecular Simulations

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This work presents a molecular dynamics simulation study of the vapor-liquid equilibrium curve for the 1-butyl-3-methylimidazolium mesilate ionic liquid [C_4mim][OMs] along with other thermodynamic properties in condensed phase, such as: densities, surface tension, heats of vaporization, constant pressure heat capacities, and the dielectric constant. The latter were obtained using molecular simulation calculations employing a new non-polarizable classical force field developed in this work, for this ionic liquid experimental thermodynamic properties as well as calculated properties by molecular simulations are very scarce in the literature.

The development of the force field for the [C_4mim][OMs] ionic liquid involved first the parameterization of all-atom non-polarizable force fields for two well-studied imidazolium ionic liquids [C_4mim][BF_4], in order to validate first against existing experimental and calculated thermodynamic properties using molecular simulations. Even though many transferable force fields for ionic liquids have been developed in the past years, some of these force fields predict extremely well structural properties such as densities and radial distribution functions etc., while other force fields fail to predict accurately heats of vaporization, condensed phases properties such as dielectric constant and transport properties such as viscosity, diffusivity, and vice versa.

The force fields developed in this work are centered on the OPLS functional, and were parameterized using a simple and robust methodology focused mainly in electrostatic charges determination and in the refinement of the most representative dihedral angles. The calculation of the electrostatic charges follows the methodology proposed by Salas *et al.* (J. Chem. Theory Compute. 2015, 11, 683−693) involving the inclusion of polarization effects in quantum mechanical calculations in order to represent implicitly the solvent by employing the experimental or calculated dielectric constant in conjunction with a restrain electrostatic potential fitted to an ionic liquid dimer, to account for the inclusion of solvation coordination effects.

The dihedral angles were parameterized simultaneously from the energetic differences in molecular conformations between *ab-initio* calculations and the energies obtained with the classic force field. The force field validation for the ionic liquids 1-butyl-3-methylimidazolium Tetrafluoroborate, [C_4mim][BF_4], and 1-butyl-3-metilimidazolium Hexafluorophosphate [C_4mim][PF_6], gave good agreement for the properties calculated compared with experimental and literature results.

Our motivation for this work focused mostly in force field development for specific individual ionic liquids capable of reproducing thermodynamic properties in condensed phase, such as density, heats of vaporization, surface