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Bulk and Surface Properties of Polar Liquids and Ionic Liquids by Classical and *Ab initio* Molecular Dynamics Simulation

By

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Supervised by

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March 2012

In The Name of God

The compassionate, the merciful

IN THE NAME OF GOD

Declaration

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IN THE NAME OF GOD

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BY

AMIN REZA ZOLGHADR

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Dedication

To all my respected teachers and professors who have been inspiring me throughout these years.

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Abstract

Bulk and Surface Properties of Polar Liquids and Ionic Liquids by Classical and *Ab initio* Molecular Dynamics Simulation

By

Amin Reza Zolghadr

The influence of alkyl chain length on bulk and surface properties of the polar liquids and ionic liquids (ILs) has been studied through molecular dynamics simulation. Also, we present a detailed calculation of atomic charges of ionic liquids with 1-butyl-3-methylimidozoilum cation and tetrafluoroborate or hexafluorophosphate anions. The results are organized in three parts.

In the first part, MD simulations were performed to investigate the liquid/vapor interfacial structure of neat polar liquids. Large-scale ensembles of liquid pyridine and its alkyl derivatives, 4-methylpyridine and 4-ethylpyridine, were simulated by

classical molecular dynamics at 298 K. For the liquid system of low polarity, the surface density profile of the atoms meet exactly at the middle of interfacial region, and atoms of hydrophobic nature can be hardly discriminated from hydrophilic ones in either vapor or liquid sides. For a liquid system of high polarity, the surface density profiles of atoms with different natures are highly discriminated all over the interfacial region, and as the polarity increases, a dense region of atomic density is clearly developed in the subsurface region. The recognized bivariate method was also used to study the molecular orientational distribution, quantitatively. Orientational analysis of the three liquid systems with different polarities indicates that the pyridine ring plane in the outmost surface tends to be vertical. Its tendency in the innermost interfacial region is parallel. The orientational states available to 4-ethylpyridine and pyridine are discriminated by predicting the possibility of a bisector-wise tumbling for the ring plane in pyridine and a side-wise tumbling in 4-ethylpyridine. The orientational distribution maps explain the trend of experimental surface tension and surface entropy. As the dipole moment of these liquids increases with the alkyl chain length, the surface structural profile changes from a regular definite one to a surface of complex atomic structure involving a dense phase near the interface. The development of dense region in alkyl derivatives is the result of segregation of molecules due to the alkyl group, which is captured and discriminated by simulation even when the length of a short alkyl chain is increased by one carbon atom.

In the second part, bulk and surface properties of the 1-alkyl-3-methyl-imidazolium iodides, [$C_n$mim]I (n=4, butyl; 6, hexyl; 8, octyl), were simulated by classical

molecular dynamics simulation using all atom non-polarizable force field. The structure of ionic liquids were optimized by density functional theory and atomic charges obtained by CHELPG method. Reducing partial atomic charges (by 20% for simulation of density and surface tension, and by 10% for viscosity) found to improve the accuracy, while a non-polarizable force field was applied. Additionally, the simulation ensembles approach the equilibrium faster when the charge reduction is applied. By these refined force field parameters, simulated surface tensions are quite in agreement with the experiments in the range of 298-370 K. Simulation of temperature dependent surface tension of [C_4mim]I well beyond room temperature (up to 700 K) permits prediction of the critical temperature in agreement with that predicted from experimental surface tension data. Simulated densities in the range of 298-450 K for the three ionic liquids are within 0.8% of the experimental data. Structural properties for [C_4mim]I were found to be in agreement with the results of Car-Parrinello molecular dynamics simulation we performed, which indicates a rather well-structured cation-anion interaction and occurs essentially through the imidazolium ring cation. Diffusion coefficient changes with alkyl chain length in the order of [C_8mim]I > [C_6mim]I > [C_4mim]I for the cation and the anion, which demonstrates the glass-transition temperature of [C_4mim]I could be more distant than the two other ionic liquids. Formation of a dense domain in subsurface region is quite evident, and progressively becomes denser as the alkyl chain length increases. Bivariate orientational analysis was used to determine the average orientation of molecule in the surface, subsurface, and bulk regions. Dynamic bisector-wise and side-wise movement of the imodazolium ring cation in the surface region can be

deduced from the bivariate maps. Atom-atom density profile and bivariate analysis indicate that the imidazolium cation takes a spoon like configuration in the surface region and the tilt of alkyl group is a function of length of alkyl chain exposing as linear as possible to the vapor phase.

In the last part, the *ab initio* molecular dynamics simulation have been performed for pure [C_4mim]PF_6 and [C_4mim]BF_4 and also their mixtures with water in order to shed light on the hydrophobicity and hydrophilicity of these ionic liquids from electronic point of view. We first analyze DFT results on isolated ion pairs with various methods of assigning partial charges to the atomic centers. In a second run, we analyze the trajectory of a 40 ps long Car-Parrinello MD run under bulk conditions. The influence of water on partial atomic charges of ionic liquids constituting atoms has been discussed extensively. We observed that the interaction of anions with water have pronounce effect on the extent of the miscibility of ILs.

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