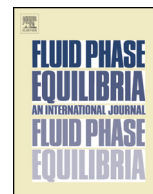




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Monte Carlo simulations of water solubility in ionic liquids: A force field assessment

Eliseo Marin-Rimoldi^a, Jindal K. Shah^b, Edward J. Maginn^{a,*}^a Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, IN, USA^b School of Chemical Engineering, Oklahoma State University, Stillwater, OK, USA

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ABSTRACT

Gibbs ensemble Monte Carlo simulations were used to calculate absorption isotherms of water in three imidazolium-based ionic liquids (ILs) with different degrees of hydrophobicity: 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([C₄mim][PF₆]), 1-*n*-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([C₄mim][Tf₂N]) and 1-*n*-butyl-3-methylimidazolium chloride ([C₄mim][Cl]). An evaluation of several water models and various IL force fields was conducted. The selected water models are the TIP5P, TIP4P2005 and a collection of three site models based on the SPC geometry but with different sets of fixed partial charges. These partial charges are consistent with water surrounded by different electrostatic environments, and crudely account for polarizability. In the case of the IL force fields, net partial charges of $\pm 1.0e$ were used. In addition, scaled charges of $\pm 0.9e$ and $\pm 0.8e$ were used to account for polarization and charge transfer. It is found that most water models tested with the full charge [C₄mim][PF₆] and [C₄mim][Cl] force field overestimate the solubility, but the agreement is reasonably good with [C₄mim][Tf₂N]. Attempts at improving the results by either scaling the charges on the IL or on water were made, but no combination was able to reproduce experimental phase behavior satisfactorily. The main conclusion of the study is that, to consistently model water absorption in ILs, force fields that include effects such as polarization are likely necessary.

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1. Introduction

Ionic liquids (ILs) have emerged as interesting materials that can be used in a wide range of applications [1]. Their properties can be tuned by means of modifying the constituent ions or by varying the concentration of other species present in the system. Many experimental and computational studies have pointed to the fact that ILs are hygroscopic and that the presence of water can have a dramatic effect on IL properties such as density, viscosity, diffusivity and surface tension [2–7]. Therefore, a fundamental understanding of the microscopic interactions between water and ILs is of paramount importance.

Classical molecular dynamics (MD) and Monte Carlo (MC) simulations have played an important role in elucidating the microscopic solution behavior of IL/water mixtures [8]. In order to perform these simulations, force fields that adequately represent the intra- and intermolecular interactions are required. The accuracy of the information obtained from these simulations depends

heavily on the quality of the force field parameters. Due to the ionic nature of ILs, the force field parameters related to electrostatic interactions are of particular importance and have been the subject of much work. In this respect, polarizable force fields offer the possibility to simulate the redistribution of the electron density of a molecule due to the presence of external electric fields [9]. In the IL community, several polarizable force fields have been developed [10–14]. It has been shown that the dynamics of ILs simulated with polarizable force fields is accelerated when compared to the dynamics obtained with non-polarizable IL force fields [15–17]. Often, the polarizable force fields give better agreement with experimental observations. The drawbacks of polarizable force fields are that they require more computation time than fixed charge force fields, and their development is a challenging task.

The usual approach to model electrostatics is to use fixed partial charge models. The charges are derived from quantum mechanical calculations to reproduce the electrostatic field generated by a molecule. It has been observed that charge transfer and polarization might play an important role for ILs [18,19]. As a result, the total effective ion partial charge derived from *ab-initio* calculations has been found to be less than unity, often around $\pm 0.8e$. Using net ion charges less than $\pm 1.0e$ has been shown to improve agreement with

* Corresponding author.

E-mail address: ed@nd.edu (E.J. Maginn).

experimental results for some dynamical and interfacial properties [20]. In this regard, two studies conducted by Chaumont et al. and Chevrot et al. [21,22] on the interfacial behavior of the system 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ($[\text{C}_4\text{mim}][\text{PF}_6]$) and water are of particular relevance to the present work. In these studies, the authors showed that there is no interface formation using the TIP3P water model and an IL model with charges of $\pm 1.0e$. However, they observed an interface if all partial charges were scaled by 0.9. In another study, the authors further explored the influence of force fields on interface creation in this system. They used the SPC/E and TIP5P water models along with the full and scaled charge IL model. When using the full charge model, they found that an interface could be obtained regardless of the water model, although the concentrations were overestimated compared to experimental measurements. If a scaled charge IL model was used, a better match could be achieved.

A related study was conducted by Kelkar et al. [23]. They used a set of water models based on the SPC geometry whose partial charges were consistent with different electrostatic environments to study the behavior of the mixture 1-ethyl-3-methylimidazolium ethylsulfate ($[\text{C}_2\text{mim}][\text{EtSO}_4]$) and water. Using an IL force field in which overall partial charges were $\pm 1.0e$, they found that the excess volume and enthalpy results were better matched to experiments with the “least polarized” water model. They pointed out the importance of polarization in water/IL systems and suggested that the use of polarizable models would likely improve the predictions of the simulations.

The studies mentioned deal with systems in the liquid phase. Despite its importance in process design, simulation studies involving vapor–liquid equilibrium (VLE) are rather scarce compared to liquid simulations. One of the reasons for this is the long equilibration times required by MD techniques if two bulk phases with an explicit interface are involved [24]. Monte Carlo (MC) techniques offer the possibility to naturally study VLE by designing algorithms that sample the correct probability distribution of ensembles related to phase equilibria. For example, Panagiotopoulos [25] developed the Gibbs ensemble Monte Carlo technique to study the phase equilibria of pure substances and mixtures. This method involves the use of two boxes that represent the bulk vapor and liquid phases. No explicit interface is required. We are aware of only one previous study in which MC was used to compute a water absorption isotherm in an IL [26]. These authors carried out simulations in the osmotic ensemble using an unscaled charge IL force field along with a flexible version of the SPC water model. They were able to reproduce the experimental isotherm at 298 K and they matched the concentration at which complete miscibility is observed experimentally.

In the present work, Gibbs ensemble Monte Carlo (GEMC) simulations were used to compute water isotherms in three different ILs: $[\text{C}_4\text{mim}][\text{PF}_6]$, $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ and $[\text{C}_4\text{mim}][\text{Cl}]$. These ILs were chosen since their interaction strength with water might vary significantly, as reflected in the decrease of hydrophobicity with respect to the anion as: $[\text{Tf}_2\text{N}]^- > [\text{PF}_6]^- > [\text{Cl}]^-$. An evaluation of the accuracy of classical force fields in the calculation of these isotherms is conducted by assessing the effect of scaling either the ionic liquid partial charges or the water partial charges. In addition, calculations using different mixing rules and a different degree of atomic resolution were carried out. It is found that to consistently predict water isotherms in ILs, force fields that include polarization effects for both IL and water are likely necessary.

2. Force fields

For the ILs, a standard classical force field was used to represent the angle bending, dihedral rotation, van der Waals (VDW)

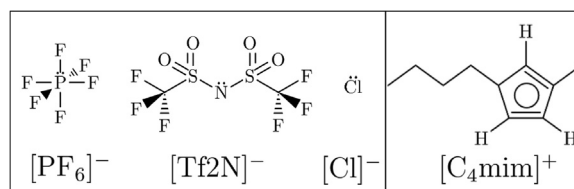


Fig. 1. Anion and cation structures for different ionic liquids studied in this work.

and Coulombic interactions. The bond lengths were held constant. The aromatic ring in the imidazolium cation was kept rigid. The force field functional form is the following:

$$U = \sum_{\text{angles}} K_{\theta}(\theta - \theta_0)^2 + \sum_{\text{dihed}} K_{\chi}[1 + \cos(n\chi + \delta)] + \sum_{i < j} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \sum_{i < j} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (1)$$

The molecular structures of the ILs are displayed in Fig. 1. For most of the simulations, united atom (UA) models were chosen. The parameters of these force fields can be found in the literature [27–30]. These force fields were modified by scaling their partial charges. The scaling factor was such that the total charge adds up to either $\pm 1.0e$ (“full”), $\pm 0.9e$ or $\pm 0.8e$.

For the case of $[\text{C}_4\text{mim}][\text{PF}_6]$, five different models were used. The first four are UA models, while the fifth one is an all-atom (AA) force field. The first two UA models are available in the literature [27,28] and are labeled as “ $[\text{C}_4\text{mim}][\text{PF}_6]^{\pm 1.0}$ -Liu2006” and “ $[\text{C}_4\text{mim}][\text{PF}_6]^{\pm 0.8}$ -Zhong2011”, indicating the scaling factor and original source. The parameters in these models were derived under the constraint of a total ionic charge of $\pm 1.0e$ and $\pm 0.8e$, respectively. Using the model “ $[\text{C}_4\text{mim}][\text{PF}_6]^{\pm 1.0}$ -Liu2006” as a base, two other models were derived by uniformly scaling the charges by 0.9 and 0.8. These are labeled as “ $[\text{C}_4\text{mim}][\text{PF}_6]^{\pm 0.9}$ -Liu2006”, and “ $[\text{C}_4\text{mim}][\text{PF}_6]^{\pm 0.8}$ -Liu2006”, respectively. In addition, the effect of using an AA force field using scaled partial charges for $[\text{C}_4\text{mim}][\text{PF}_6]$ was investigated. Thus, the fifth model is based on the original model by Liu and co-workers [30] and was labeled as “ $[\text{C}_4\text{mim}][\text{PF}_6]^{\pm 0.8}$ -Liu2004-AA”. For $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ and $[\text{C}_4\text{mim}][\text{Cl}]$, UA models with ion total charges of $\pm 0.8e$ or $\pm 1.0e$ were investigated. The same naming convention was used for these models. A summary of all the combinations of IL force fields is displayed in Table 1.

Regarding water in $[\text{C}_4\text{mim}][\text{PF}_6]$ /water mixtures, the popular TIP5P and TIP4P2005 force fields as well as several models based on the SPC geometry were used. In all of these models, the bond lengths were kept fixed. The TIP5P and TIP4P2005 force fields [31,32] include five and four interaction sites, respectively. In the case of TIP5P, the partial charges are located on the two hydrogens and on two virtual sites representing lone pairs. There is one Lennard-Jones interaction site located on the oxygen atom. Regarding the TIP4P2005 model, four interaction sites are used, three of which have partial charges located on two hydrogens and a dummy site located at the bisector between the HOH angle. Similar to the TIP5P model, a Lennard-Jones site is located on the oxygen atom. Finally, the SPC model has three interaction sites located on the atomic centers and uses a Lennard-Jones potential to describe the oxygen van der Waals interactions. Fixed-point charges are assigned to each atom site. Four variations using this SPC geometry were tested. The difference among the first three are the partial charges, which are consistent with those that would reproduce the electrostatic potential of water immersed in different dielectric environments. In these three models, the first set of charges are the standard SPC

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