



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 ([C₄mim][PF₆]) 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 ([C₂mim][EtSO₄]) 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: [C₄mim][PF₆], [C₄mim][Tf₂N] and [C₄mim][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: [Tf₂N][−] > [PF₆][−] > [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)

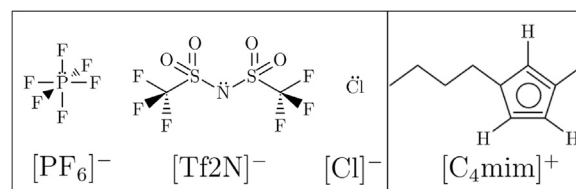


Fig. 1. Anion and cation structures for different ionic liquids studied in this work.

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 [C₄mim][PF₆], 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 “[C₄mim][PF₆]^{±1.0}-Liu2006” and “[C₄mim][PF₆]^{±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 “[C₄mim][PF₆]^{±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 “[C₄mim][PF₆]^{±0.9}-Liu2006”, and “[C₄mim][PF₆]^{±0.8}-Liu2006”, respectively. In addition, the effect of using an AA force field using scaled partial charges for [C₄mim][PF₆] was investigated. Thus, the fifth model is based on the original model by Liu and co-workers [30] and was labeled as “[C₄mim][PF₆]^{±0.8}-Liu2004-AA”. For [C₄mim][Tf₂N] and [C₄mim][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 [C₄mim][PF₆]/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

Table 1

Summary of IL and water models combinations.

Model	Species	Sum of charges	Reference	Water models
[C ₄ mim][PF ₆] ^{±1.0} -Liu2006	[C ₄ mim][PF ₆]	±1.0e	[27]	All
[C ₄ mim][PF ₆] ^{±0.9} -Liu2006	[C ₄ mim][PF ₆]	±0.9e	–	SPC
[C ₄ mim][PF ₆] ^{±0.8} -Liu2006	[C ₄ mim][PF ₆]	±0.8e	–	SPC
[C ₄ mim][PF ₆] ^{±0.8} -Zhong2011	[C ₄ mim][PF ₆]	±0.8e	[28]	SPC
[C ₄ mim][PF ₆] ^{±0.8} -Liu2004-AA	[C ₄ mim][PF ₆]	±0.8e	[30]	SPC
[C ₄ mim][Tf ₂ N] ^{±1.0} -Zhong2011	[C ₄ mim][Tf ₂ N]	±1.0e	–	SPC
[C ₄ mim][Tf ₂ N] ^{±0.8} -Zhong2011	[C ₄ mim][Tf ₂ N]	±0.8e	[28]	SPC
[C ₄ mim][Cl] ^{±1.0} -Liu2010	[C ₄ mim][Cl]	±1.0e	–	SPC
[C ₄ mim][Cl] ^{±0.8} -Liu2010	[C ₄ mim][Cl]	±0.8e	[29]	SPC

Table 2

Summary of water models used in this work.

Model	Oxygen charge	Description	References
TIP5P	–	Five interaction sites	[31]
TIP4P2005	–	Four interaction sites	[32]
SPC	–0.82e	Regular SPC model	[35]
SPC-CCl ₄	–0.77e	Water surrounded by CCl ₄	[23]
SPC-Vac	–0.72e	Water surrounded by vacuum	[23]
SPC-Fw-fixed	–0.82e	Flexible angle, bond fixed	[34]

charges. The second set of charges are those produced by water in a dielectric continuum similar to liquid CCl₄. The dielectric constant of CCl₄ is low when compared to water, but it is similar to the dielectric constant of many ILs [33]. The third set is consistent with water in vacuum. The associated oxygen charges for each of these sets is –0.82e, –0.77e and –0.72e, respectively. Hydrogen charges are half the oxygen values. These models were derived by Kelkar et al. [23] and they showed better agreement with experiments for excess thermodynamic properties with [C₂mim][EtSO₄]. Finally, the fourth water model includes flexibility in the HOH angle, while keeping the bonds fixed. The parameters are taken from the commonly used SPC-Fw water model [34]. This is labeled as SPC-Fw-Fixed. A summary of these models is shown in Table 2.

3. Simulation details

In these studies, the isobaric-isothermal version of the Gibbs ensemble Monte Carlo (NPT-GEMC) method implemented in the code Cassandra [36] was used to compute water absorption isotherms in several ILs. The simulation results were compared to previously published data at 308.15 K for [C₄mim][PF₆] [37], at 353.15 K for [C₄mim][Tf₂N] [38], and 1 bar (different temperatures) for [C₄mim][Cl] [39,40]. The systems consisted of 150 ion pairs for every ionic liquid and 500 water molecules. The initial configurations were generated by inserting ions using a regrowth scheme to avoid overlaps in the initial configurations. Water molecules were first placed in the vapor box and pure IL was inserted into the liquid box. No IL swap moves were allowed during the simulation, as ILs have extraordinarily low vapor pressures. The two boxes were pre-equilibrated by running an NPT simulation at the temperature of interest. The individual systems were then allowed to reach phase equilibrium by using only translation, rotation, regrowth, swap and volume moves with probabilities of 0.45, 0.2, 0.2, 0.1, 0.05, respectively. During this equilibration phase, maximum translation, rotation and volume changes were adjusted to achieve 50% acceptance rates. The number of MC steps required to adequately equilibrate the system depended on the pressure, ranging from 50 × 10⁶ to 300 × 10⁶. Production runs were carried out for 100 × 10⁶ MC steps. A biased insertion scheme was used for improving the swap acceptance rate, with 12 water insertion attempts per swap move. Finally, a fragment-based method was used to sample the internal degrees of freedom of molecules

[36,41]. Uncertainties were estimated by the standard deviations obtained from three independent simulations.

For the pure water VLE calculations, the NVT version of the Gibbs ensemble Monte Carlo (NVT-GEMC) was used. For each of the studied models, a system size of 1000 water molecules was used. Initially, the density of the liquid box was set to be less than that expected for the equilibrium liquid density. For the vapor box, the density was set to be higher. At least 20 × 10⁶ MC steps were conducted for equilibration, followed by another 20 × 10⁶ steps for production. Translation, rotation, volume and swap MC moves were used with probabilities of 0.6, 0.25, 0.05 and 0.1, respectively. No regrowth moves were conducted, as rigid water models were used, except for the angle flexible water model SPC-Fw-Fixed. The same biased insertion scheme described above was used.

For the unlike interactions, the Lorentz-Berthelot combining rules were applied. The geometric mixing rule was also used to test if this influences the results. Most of the simulations used a vapor box cutoff of about 0.4L, where L is the box length, and 12 Å for the liquid phase. For the long range electrostatic interactions, the Ewald sum was used with a number of reciprocal space vectors consistent to achieve a summation accuracy of 10^{–5}.

4. Results and discussion

4.1. VLE of water models

Before computing water absorption isotherms in the ILs, each water model was evaluated for its ability to represent pure water VLE. Fig. 2a shows a comparison between experimental data and the computed phase envelope and Fig. 2b compares simulated vapor pressures against experiment. We verified that our computed values agree with previously published simulation results [42–45] and the data are provided in the Supplementary Material section. The TIP4P2005 model does the best job in matching experimental vapor and liquid densities, whereas the TIP5P model is least accurate in computing the coexistence curve. For the three site water models SPC and SPC-Fw-Fixed, the vapor densities tend to be overestimated, the liquid densities tend to be underestimated and the critical points tend to be underestimated. The inclusion of angle flexibility in the SPC-Fw-Fixed model improves the prediction of the vapor and liquid densities when compared to the regular SPC model, although the results still do not match experimental measurements. Fig. 2b shows the vapor pressure dependence on temperature of all these models. The TIP4P2005 model underestimates the vapor pressure, while TIP5P overestimates it. The SPC and SPC-Fw-Fixed provide the best quantitative agreement with experimental vapor pressure data for pure water. Additionally, it is interesting to note that the predicted enthalpy of vaporization is roughly the same for all these water models. In general, these models were developed for treating liquid water near ambient temperatures, and so it is not surprising that they are unable to accurately reproduce VLE properties. Thus, it is clear from these results that among all of these widely used water models, there is

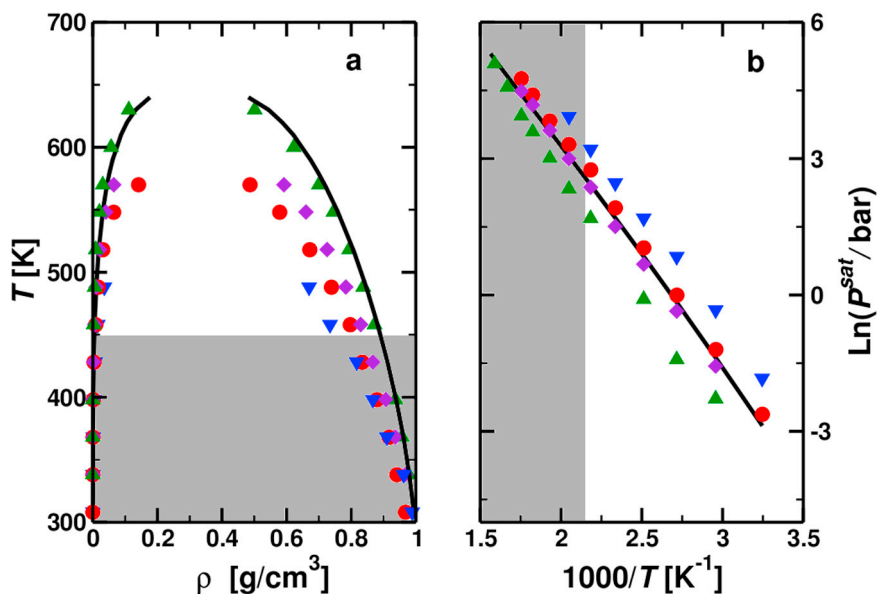


Fig. 2. (a) Temperature-density behavior and (b) vapor pressures of the water models SPC (red circles), SPC-Fw-Fixed (purple diamonds), TIP4P2005 (green up triangles) and TIP5P (blue down triangles). Experiments are displayed as solid black lines. As a reference, shadowed regions indicate the typical temperatures at which IL measurements are conducted (less than 450K). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

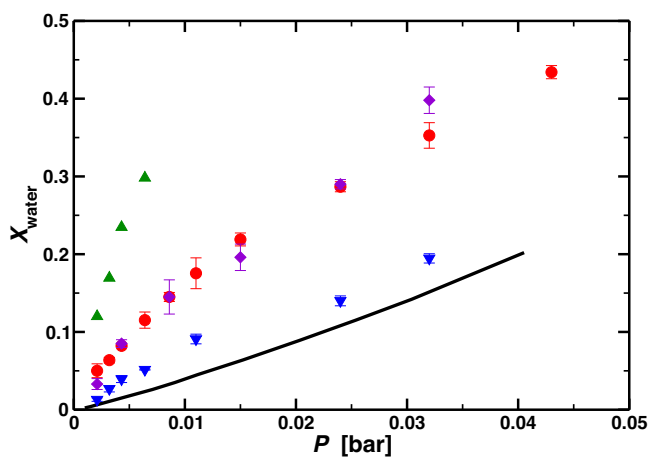


Fig. 3. Isotherms using the model $[C_4\text{mim}][PF_6]^{\pm 1.0}$ -Liu2006 and the water models SPC (red circles), SPC-Fw-Fixed (purple diamonds), TIP4P2005 (green up triangles) and TIP5P (blue down triangles). Pressures are in bar. $T = 308.15$ K. Experiments (solid black line) taken from Anthony et al. [37]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

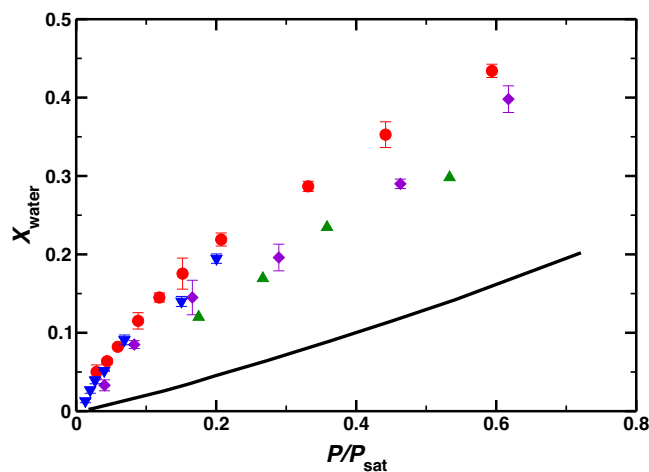


Fig. 4. Isotherms using the model $[C_4\text{mim}][PF_6]^{\pm 1.0}$ -Liu2006 and the water models SPC, SPC-Fw-Fixed, TIP4P2005 and TIP5P. Pressures are normalized by P_{sat} of each water model. Experiments are represented with a black solid line [37]. Other symbols are the same as in Fig. 3.

not one that is clearly superior to the others in terms of modeling both coexistence densities and vapor pressures.

It is therefore unclear which of these models is best suited to compute VLE with ILs. Because of this, we ran simulations with each of these models to investigate their accuracy in these types of calculations.

4.2. Water isotherms in $[C_4\text{mim}][PF_6]^{\pm 1.0}$ -Liu2006

To begin with, water isotherms were calculated for the IL $[C_4\text{mim}][PF_6]$. This IL has an intermediate degree of hydrophobicity relative to the other two ILs under study. The isotherms were computed using the $[C_4\text{mim}][PF_6]^{\pm 1.0}$ -Liu2006 model along with the TIP5P, TIP4P2005, SPC and SPC-Fw-Fixed water models. Fig. 3 shows the computed isotherms at 308.15 K along with experimental data from the literature [37]. All of the simulations yield water

solubilities higher than experiment, with the TIP4P2005 model showing the greatest deviation, followed by the SPC/SPC-Fw-Fixed and finally the TIP5P force field. It is worth mentioning that the predictive ability of the SPC and SPC-Fw-Fixed models is similar, suggesting that at this temperature angle flexibility plays only a minor role in these calculations.

As done by Kelkar and co-workers [23], the vapor pressure of each of the water models at $T = 308.15$ K was used as a scaling factor for the pressure observed in each simulation. This facilitates comparison between the different models, and provides a direct measure of the liquid phase activity coefficients predicted by these force fields. Fig. 4 displays this information. Interestingly, all the models overestimate the experimental solubility, suggesting that the activity coefficient predicted by these models is too low. This means that there is an overestimation of the interactions between water and the IL.

We again note that the water force fields used in these calculations were developed for the simulation of pure liquid water near

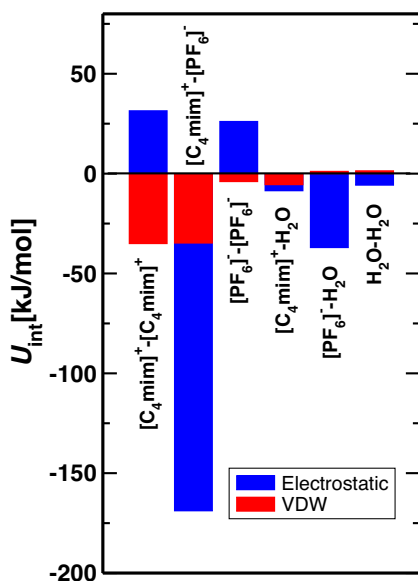


Fig. 5. Intermolecular interaction energies among different species for the system $[C_4mim][PF_6]^{\pm 1.0}$ -Liu2006 and the SPC water model. The red bars represent the VDW interaction energy. The blue bars represent the real part of the total electrostatic energy. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

ambient conditions. Therefore, it is perhaps not unexpected that these water force fields perform poorly when used to predict VLE in an ionic liquid, since the electrostatic environment in water/IL mixtures is considerably different from that present in pure liquid water.

4.3. Interaction energies between SPC and $[C_4mim][PF_6]^{\pm 1.0}$ -Liu2006

In order to assess and modify the dominant interactions between IL and water, VDW and electrostatic interaction energies were computed. A breakdown of all the intermolecular VDW and electrostatic interaction energies between the model $[C_4mim][PF_6]^{\pm 1.0}$ -Liu2006 and the SPC water model are shown in Fig. 5. The depicted energies are averages over pressures in an isotherm, and only the real space portion of the total electrostatic energy is reported. We found that these energies are insensitive to pressure and therefore water concentration. The electrostatic interactions tend to be much larger than the VDW interactions. Not surprisingly, the single largest term is the electrostatic interactions between the cation and the anion. Interestingly, the repulsive electrostatic interactions between cations is almost equally balanced by the attractive VDW interactions. For water, electrostatic interactions with the anion dominate; water–water and water–cation interactions are much weaker. These results suggest that water–anion electrostatics play a dominant role in the solubility. Therefore, force fields that accurately represent the Coulombic interactions between the anion and water should yield better solubility predictions.

4.4. Isotherms using scaled IL force fields

It has been observed that uniform scaling of the IL partial charges can lead to improved agreement between simulations and experimental data for liquid phase calculations [8,46]. The reason behind this is thought to be that charge transfer and polarization of the ionic species can be crudely taken into account by performing this scaling. This scaling factor is usually around 0.8 [20]. To test if

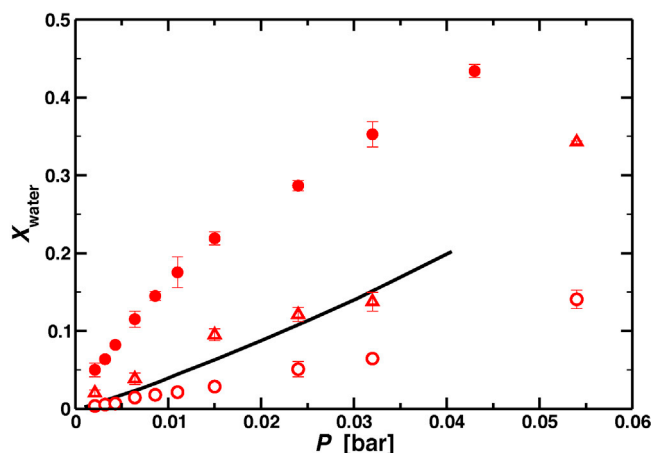


Fig. 6. Isotherms using the reduced charge IL models and SPC water model. Open circle and open triangle represent systems using the scaled charge models $[C_4mim][PF_6]^{\pm 0.8}$ -Liu2006 and $[C_4mim][PF_6]^{\pm 0.9}$ -Liu2006, respectively. As a reference, the system $[C_4mim][PF_6]^{\pm 1.0}$ -Liu2006/SPC is shown using filled circles. Experiments are depicted in black solid line [37].

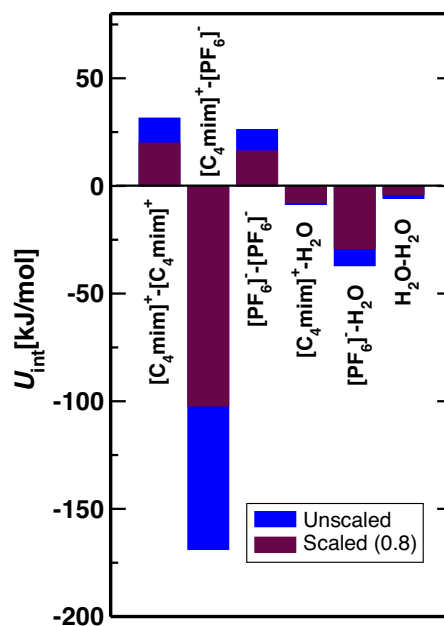


Fig. 7. Coulombic interaction energies of the system $[C_4mim][PF_6]^{\pm 1.0}$ -Liu2006/SPC (blue bars) and $[C_4mim][PF_6]^{\pm 0.8}$ -Liu2006 / SPC (purple bars). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

scaling the charges of the IL improves the IL/water VLE calculations, isotherms using two scaled models, namely $[C_4mim][PF_6]^{\pm 0.8}$ -Liu2006 and $[C_4mim][PF_6]^{\pm 0.9}$ -Liu2006, were computed using the SPC water model. This model was used because it yields vapor pressures in good agreement with experiment, as shown in Section 4.1. The results are displayed in Fig. 6. Clearly, water solubility decreases as the net charge on the IL ions decreases. The model with net charge of $\pm 0.9e$ ($[C_4mim][PF_6]^{\pm 0.9}$ -Liu2006) has the best agreement with experiment, while the model with net charge of $\pm 0.8e$ ($[C_4mim][PF_6]^{\pm 0.8}$ -Liu2006) underestimates the solubilities.

Fig. 7 shows the electrostatic interaction energies of the system $[C_4mim][PF_6]^{\pm 0.8}$ -Liu2006/water SPC and compares those with the system $[C_4mim][PF_6]^{\pm 1.0}$ -Liu2006/water SPC. Due to the charge scaling, the interaction energies between the cation and the anion

Table 3

Summary of computed densities at 308.15 K for [C₄mim][PF₆] with different models. The experimental density is 1.358 g cm⁻³ [47].

Model	Density (this work) [g/mL]	Density (Literature) [g/mL]
[C ₄ mim][PF ₆] ^{±1.0} -Liu2006	1.35 ± 0.01	1.365 (298 K) [27]
[C ₄ mim][PF ₆] ^{±0.8} -Liu2006	1.31 ± 0.01	–
[C ₄ mim][PF ₆] ^{±1.0} -Liu2004-AA	1.33 ± 0.01	1.35 (298 K) and 1.338 (313 K) [30]
[C ₄ mim][PF ₆] ^{±0.8} -Liu2004-AA	1.29 ± 0.02	–

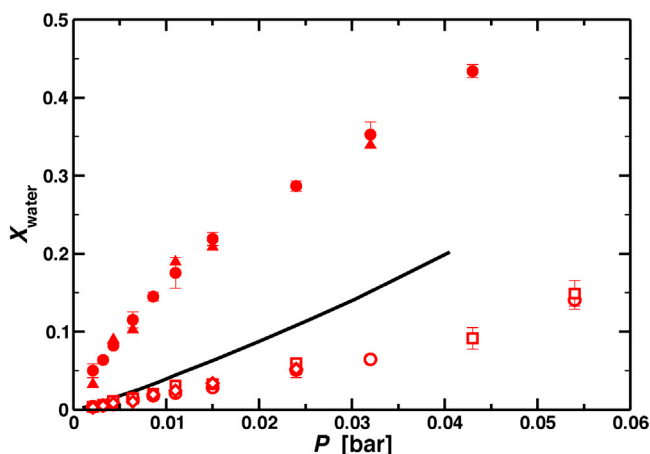


Fig. 8. Isotherms using the different mixing rules or different degrees of atomic resolution. Open circles, open squares and open diamonds represent the models [C₄mim][PF₆]^{±0.8}-Liu2006, [C₄mim][PF₆]^{±0.8}-Zhong2011 and [C₄mim][PF₆]^{±0.8}-Liu2004-AA, respectively. Note that these points are essentially on top of one another. Additionally, up triangles and filled circles represent isotherms using the geometric and Lorentz-Berthelot mixing-rules for the system [C₄mim][PF₆]^{±1.0}-Liu2006/SPC. Experiments are depicted in black solid line [37].

are less attractive when compared to the full charge model interaction energies. The anion–water interactions are similarly reduced. These results suggest that we can adjust the anion–water Coulombic interaction strength so that the experimental isotherms can be reproduced, though obviously this requires knowledge of experimental isotherms and thus it is not an entirely predictive method. The other drawback of scaling the IL charges is that it changes the properties of the pure IL. For example, Table 3 shows that as the net charge on [C₄mim][PF₆] is reduced, the overall density decreases and shows greater difference with experiment. This underestimation of the density upon charge reduction is due to a decrease in cohesive energy, as shown in Fig. 7. Therefore, for consistency, the force field must be refined to take into account this scaling, so that the pure IL properties remain unaltered.

4.5. Mixing rules and atomic resolution

The aforementioned results use united atom force fields along with the standard Lorentz–Berthelot mixing rule to deal with unlike interactions. In order to test whether the mixing rule or the atomic resolution plays a role in the accuracy of the isotherms, the results were recalculated using the geometric mixing rule and using an AA force field. In the case of the geometric mixing rule test, the IL [C₄mim][PF₆]^{±1.0}-Liu2006 model was used. In the case of the tests dealing with all atom force fields, two scaled charge UA models and one scaled charge AA model were used. The results shown in Fig. 8 demonstrate that the influence of mixing rules and atomic resolution is minimal on solubility. The solubility is dominated by the Coulombic interactions between water and the IL.

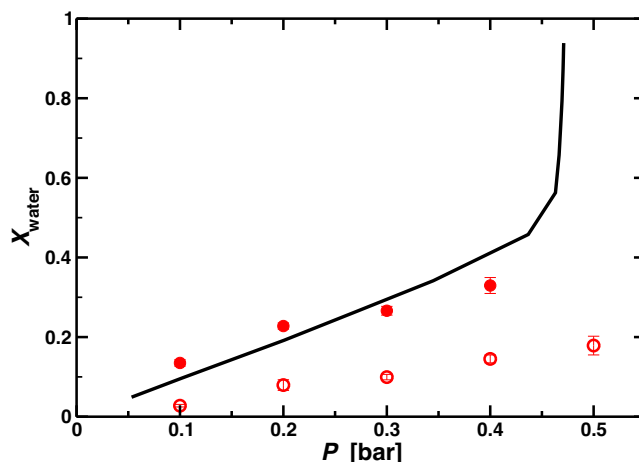


Fig. 9. Isotherms for the systems [C₄mim][Tf₂N]^{±1.0}-Zhong2011 / SPC (filled circles) and [C₄mim][Tf₂N]^{±0.8}-Zhong2011 / SPC (open circles). Experimental results shown as solid black curve [38].

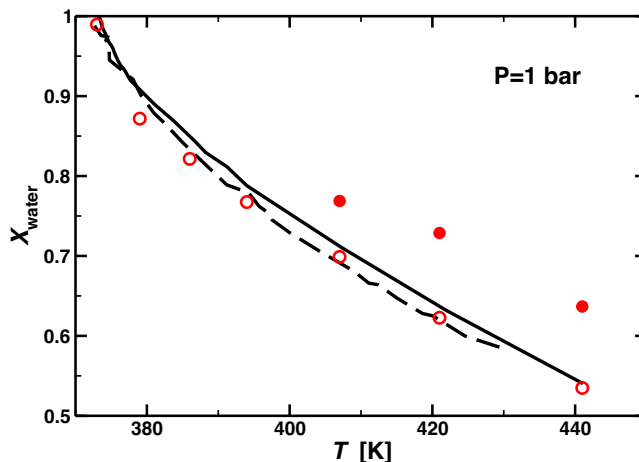


Fig. 10. Isobars for the systems [C₄mim][Cl]^{±1.0}-Liu2010/SPC (filled circles) and [C₄mim][Cl]^{±0.8}-Liu2010 / SPC (open circles). Experimental results shown as a solid and dashed black lines and are taken from two sources [39,40].

4.6. Solubilities in [C₄mim][Tf₂N] and [C₄mim][Cl]

To test whether scaling the IL charges by 0.9 is a general strategy to reproduce experimental water solubilities, further simulations were conducted for two other ionic liquids with different degrees of hydrophobicity. The hydrophobic [C₄mim][Tf₂N] and the relatively hydrophilic [C₄mim][Cl] were selected. The models used for these ILs comprised both scaled and full partial charges. In each of these cases, the SPC model was used. In the case of [C₄mim][Cl], a water isobar was calculated at a pressure of 1 bar because, to the best of our knowledge, there is a lack of isotherm experimental measurements. Results are shown in Figs. 9 and 10. The results for these two substances indicate that the hydrophobic [C₄mim][Tf₂N] water solubilities are best predicted by the full charge IL model, whereas the scaling of 0.8 yields a better prediction for [C₄mim][Cl]. These results suggest that there is no universal scaling factor when computing water solubilities, as the factor depends on the IL under study. Interestingly, the scaling factor of [C₄mim][PF₆] lies in between the one of [C₄mim][Tf₂N] and [C₄mim][Cl]. Similarly, the degree of hydrophobicity of [C₄mim][PF₆] is also between the other two. More studies would be useful to determine if the scaling dependence on the IL hydrophilicity still holds for other ILs.

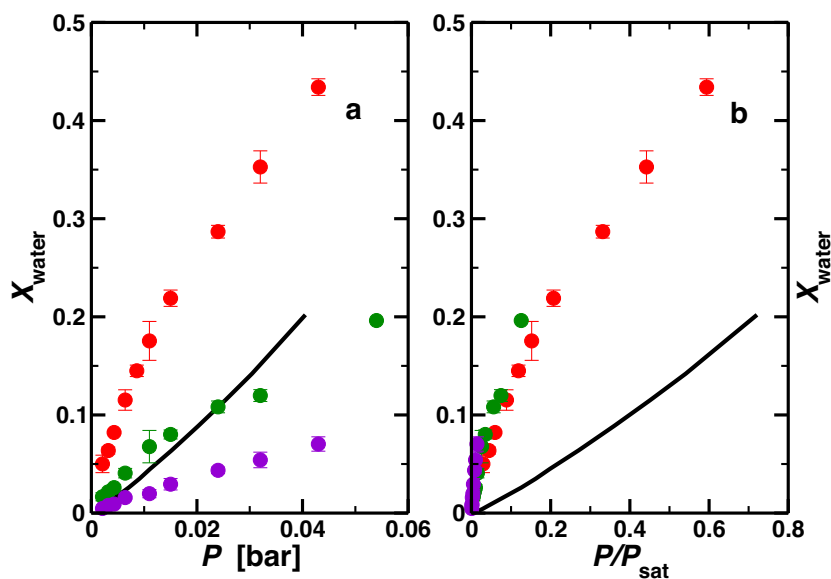


Fig. 11. (a) Isotherms using the IL model $[\text{C}_4\text{mim}][\text{PF}_6]^{\pm 1.0}$ -Liu2006 and the water models SPC (red), SPC- CCl_4 (green) and SPC-Vac (purple). (b) Isotherms plotted as a function of reduced pressures. Experiments are depicted in black solid lines [37]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

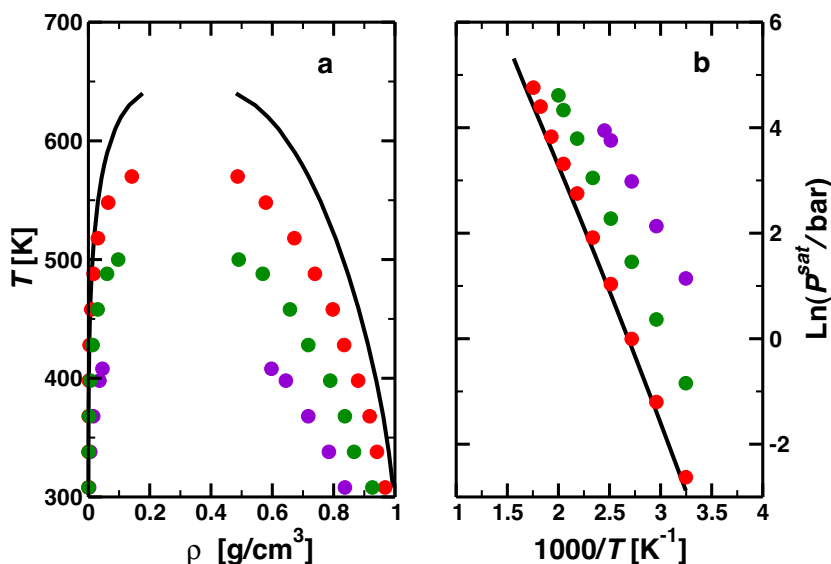


Fig. 12. (a) Temperature-density behavior and (b) vapor pressures of the water models SPC (red), SPC- CCl_4 (green) and SPC-Vac (purple). Experiments are depicted in black solid lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

4.7. Isotherms using scaled water force fields

An alternate way to tune IL/water electrostatic interactions is to scale the partial charges of the water models. Kelkar and Maginn [23] derived modified SPC water models whose charges depend on the dielectric constant that surrounds a single water molecule. In this work, these modified water models are labeled as SPC- CCl_4 and SPC-Vac. More details are provided in Section 2. The isotherms using these water models along with the $[\text{C}_4\text{mim}][\text{PF}_6]^{\pm 1.0}$ -Liu2006 IL model are presented in Fig. 11a. The model SPC- CCl_4 yields the best match to experimental solubility, whereas the model SPC-Vac underestimates it. This result shows that for the system under study, the interaction energy between water and the IL (and hence the water solubility) is best represented when the water partial charges are consistent with a water molecule surrounded by dielectric medium similar to an IL.

The vapor pressure of each of the scaled charge SPC models was calculated and the solubility was plotted as a function of reduced pressure. The results are shown in Fig. 11b. Interestingly, each scaled charge SPC model yields the same solubility at the same reduced pressure, indicating that the activity coefficient is insensitive to the partial charges of water models. The solubilities are higher than experimental data, indicating that the activity coefficient is too small.

The complete VLE of these modified water models is shown in Fig. 12. Fig. 12a shows that the modified water models yield an overestimation of the vapor densities and an underestimation of the liquid densities when compared to experiment. This discrepancy becomes larger as the absolute value of the partial charge on the oxygen decreases. Similarly, Fig. 12b shows that the vapor pressure is overestimated as the absolute partial charge value decreases.

The results presented in this section suggest that having a water model whose partial charges faithfully reflect the surrounding environment is important to reproduce both experimental absorption isotherms for ILs and the pure water phase envelope. Therefore, force fields that involve polarization effects are likely necessary to consistently and robustly simulate water absorption in ILs.

5. Concluding remarks

The focus of this work has been to assess the performance of classical force fields with fixed partial charges when computing water absorption isotherms in ILs. Three ionic liquids with different degrees of hydrophobicity were examined: [C₄mim][PF₆], [C₄mim][Tf₂N] and [C₄mim][Cl]. Several combination of water and IL force fields were used (see Table 1). In the case of IL force fields, partial charges were scaled by factors less than unity, as it has been shown that this is a way to crudely incorporate polarization effects in IL force fields. In the case of water, six different water models were used. Four of them share the SPC geometry (SPC, SPC-Fw-Fixed, SPC-CCl₄ and SPC-Vac), but differ in either the inclusion of angle flexibility or in their partial charges. The other two models explore the influence of adding extra interaction sites to account for lone electron pairs and out-of-plane polarization present in water molecules (TIP4P2005 and TIP5P).

Results suggest that if IL partial charges are scaled and the SPC model is used, the best agreement with experiment in the [C₄mim][PF₆] case is achieved by scaling the partial charges of IL by 0.9. However, this scaling factor is not universal and the optimal value is found to be 0.8 for [C₄mim][Cl] and unnecessary (i.e. 1.0) for [C₄mim][Tf₂N]. On the other hand, if water models are varied while using a full charge IL force field, the best agreement to experiment is found when using a water model whose charges are consistent with a low dielectric environment (SPC-CCl₄), such as that found in ILs. However, the SPC-CCl₄ model does not yield the correct pure water vapor liquid equilibria and underestimates the experimental activity coefficient. The use of different atomic resolution or different mixing rules was shown to have a minimal effect on water solubility for the systems under study.

The results presented suggest that fixed charge force fields can be used to reproduce water isotherms in ionic liquids, however, limitations exist in relation to their predictive power. Scaling charges by means of taking into account the effects of the electrostatic environment is a way to match experimental results, but the scaling factor depends on the nature of the ionic liquid under study and it is not known *a priori*. This suggests that better quality force fields might be useful to achieve quantitative predictions and the inclusion of polarization terms is likely necessary.

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Appendix A. Supplementary Data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.fluid.2015.07.007>

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