# MOLECULAR DYNAMICS SIMULATIONS OF PROTIC IONIC LIQUIDS

by

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# MOLECULAR DYNAMICS SIMULATIONS OF PROTIC IONIC LIQUIDS

by

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# DISSERTATION

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## MOLECULAR DYNAMICS SIMULATIONS OF PROTIC IONIC LIQUIDS

Amir Taghavi Nasrabadi, PhD The University of Texas at Dallas, 2017

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This dissertation concerns the study of protic ionic liquids (PILs) by means of molecular dynamics (MD) simulations. PILs are a subset of ionic liquids in which cations possess an acidic proton. They have been a focus of intense research in the past decade due to their promising properties. In this dissertation, we first begin with an introduction to PILs, and briefly review their properties and applications in Chapter 1. In Chapter 2, the main features of MD simulations are explained.

Empirical force fields used in simulation studies of ILs have often failed to correctly describe their dynamics and transport properties. Chapter 3 describes how to improve the ability of well-known empirical force fields to describe tertiary ammonium triflate PILs by scaling the atomic partial charges of ions using an optimal scaling factor derived from experimental data. Our results show that this method successfully enhances the dynamics of the simulated PILs and improves the computed transport coefficients without increasing the computational cost.

The degree of proton transfer in PILs, which indicates the percentage of ions formed from the reactant acid and base molecules, is a key quantity. However, the effects of this quantity on PIL properties are still not well-understood. In Chapter 4, we try to understand these effects by simulating a family of alkylammonium acetate PILs over the entire range of the degree of proton transfer. Our results show that properties of PILs change dramatically with varying degree of proton transfer. We also use the data obtained to estimate the degree of proton transfer in experimental PILs by comparison with simulation.

In Chapter 5, we introduce a rigorous thermodynamic approach by which to calculate the degree of proton transfer in PIL media. Our approach is based on a thermodynamic cycle and uses constrained MD simulations to obtain the free energy change associated with the proton transfer reaction. We apply this scheme to trimethylammonium acetate, a tertiary ammonium acetate PIL. Our results show that the proton transfer takes place only partially in this PIL, which is in good agreement with experiment. This approach can effectively be used to predict the degree of proton transfer and associated thermodynamics in PILs with varying degree of proton transfer, which is difficult to assess experimentally.

In Chapter 6, we briefly summarize our findings and elaborate on possible future applications of the computational approaches used in this dissertation.

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### CHAPTER 1

## AN INTRODUCTION TO PROTIC IONIC LIQUIDS

Ionic liquids (ILs) are liquid salts composed entirely of ions, with melting points usually below 100 °C.<sup>12,13</sup> Salts with higher melting points are classified as molten salts. The room temperature ionic liquids (RTILs) are a subset of ILs with melting points close to or below room temperature.<sup>14,15</sup> ILs are usually a combination of a weakly Lewis-acidic cation with a weakly Lewis-basic anion.<sup>16</sup> ILs are mostly often based on large, asymmetric imidazolium cations to which alkyl chains of varying length are attached. A wide selection of organic and inorganic anions can be paired with these cations.

ILs have been the focus of intense research over the past decade due to their unique characteristics, in particular low vapor pressure,<sup>17,18</sup> low flammability,<sup>19</sup> wide liquid temperature range,<sup>14</sup> good thermal<sup>20,21</sup> and chemical stability,<sup>22</sup> and high ionic conductivity.<sup>23</sup> These have made them promising candidates in numerous applications including synthesis and catalysis,<sup>14,24</sup> solar cells,<sup>25,26</sup> sensors,<sup>27,28</sup> batteries,<sup>29,30</sup> gas absorption,<sup>31,32</sup> and biomass processing.<sup>33,34</sup>

ILs can be divided into two major groups: aprotic ionic liquids (AILs) and protic ionic liquids (PILs).<sup>35</sup> This division is based on the proton-donating ability of ILs, which is very similar to the well-established classification of molecular solvents into proton-donating (protic) and nonproton-donating (aprotic) subclasses. The conventional method for synthesis of AILs usually consists of three steps: (1) alkylation of the precursor Lewis base, and formation of its alkyl halide salt, (2) anion exchange, and (3) removal of metal halides.<sup>36</sup> These steps are shown for the synthesis of dialkylimidazolium triflate in Figure 1.1(a). Such ILs have no exchangeable (active) proton.

In contrast, PILs are formed through the transfer of a proton from a Brønsted acid (proton donor) to a Brønsted base (proton acceptor) in a simple neutralization reaction.<sup>37,38</sup> Figure 1.1(b) shows this reaction for a tertiary ammonium triflate PIL. Such proton transfer

(a) Aprotic ionic liquid (AIL)



Trialkylamine Triflic acid Trialkylammonium triflate

Figure 1.1. Typical synthetic routes for (a) aprotic and (b) protic ionic liquids. (a) Synthesis of dialkylimidazolium triflate by an alkylation reaction followed by an anion exchange reaction. (b) Synthesis of a tertiary ammonium triflate by a neutralization reaction between a Brønsted acid (triflic acid) and a Brønsted base (tertiary amine).

results in hydrogen-bond donor and acceptor sites on cations and anions, respectively. The key feature that distinguishes PILs from AILs is the presence of an acidic proton on the cation. A large variety of PILs can be obtained by mixing asymmetric large organic cations with organic or inorganic anions. Figure 1.2 shows a number of ions commonly used in PILs.

The first IL, discovered in 1888, was the PIL hydroxyethylammonium nitrate with melting point of 52-55 °C.<sup>39</sup> The first RTIL, reported in 1914, was the PIL ethylammonium nitrate, with melting point of 12.5 °C.<sup>40</sup> Ethylammonium nitrate is probably the most studied early PIL, primarily due to similar properties with water, such as high cohesive energy density and polarity, and similar micelle formation of surfactants in these media.<sup>41</sup> Nowadays, this field is no longer dominated by a specific PIL, as the simplicity of the proton transfer reaction and a large selection of available precursor acid and base molecules has resulted in an enormous number of PILs with various functionalities and properties.<sup>42</sup>



Figure 1.2. Typical cations used in PILs: (a) Primary ammonium, (b) secondary ammonium, (c) tertiary ammonium, (d) 1-alkylimidazolium, (e) 1,2-dialkylimidazolium, (f) 2-methylpyridinium. Typical anions used in PILs: (g) carboxylates, (h) trifluoromethane-sulfonate (triflate), (i) nitrate, (k) bistriflimide (TFSI).

## 1.1 Degree of Proton Transfer

The proton transfer reaction in PILs is complete if the precursor acid (HA) and/or base (B) is very strong, which results in a fully (purely) ionic system.<sup>37</sup> For example, in Figure 1.1(b), the triffic acid is a very strong acid ( $pK_a^{aq} = -14.7$ ),<sup>43</sup> resulting in a PIL made almost entirely of ions. However, depending on the parent acid/base molecules, this reaction may not lie entirely to the right, resulting in an equilibrium between precursor neutral species and ions:<sup>41,42</sup>

$$HA + B \rightleftharpoons A^{-} + HB^{+} \tag{1.1}$$

The acid-base equilibrium and strong hydrogen bonding in most PILs make the chemistry of these ILs more complex than that of AILs.<sup>1,41</sup>

The extent of the proton transfer reaction (degree of proton transfer from acid to base) is a key quantity, which can influence PILs properties to a great extent.<sup>8</sup> Angell et al.<sup>37</sup> suggested that the degree of proton transfer can be estimated qualitatively based on  $\Delta p K_a^{aq}$ :

$$\Delta p K_a^{aq} = p K_a^{aq} (HB^+) - p K_a^{aq} (HA)$$
(1.2)

and PILs with a large  $\Delta p K_a^{aq}$  (~10) should exhibit complete proton transfer.<sup>37</sup> However, this measure is qualitative and does not reflect the non-aqueous environment in PILs. Furthermore, it has been shown that it may not be applicable to many PILs with comparable  $\Delta p K_a^{aq}$ .<sup>8</sup> A reliable and quantitative standard method by which to determine the degree of proton transfer is highly desirable. Moreover, how and to what extent the degree of proton transfer can affect the properties and behavior of PILs are still key questions in this field.

## 1.2 Properties

Thermal properties, including glass transition, melting point, boiling point, decomposition temperature, and various physicochemal properties such as viscosity and ionic conductivity have been determined for numerous PILs in recent years.<sup>41,42</sup> These properties strongly depend on the structure of the constituent cations and anions. Ion-ion interactions in PILs are known to be a mixture of hydrogen bonding, electrostatic, and dispersion interactions.<sup>1,41</sup> Comprehensive recent studies of the relationship between the structure and properties of PILs shows that our understanding of theses complex liquids is still at a developing stage. An in-depth knowledge of structure/property relationships can help scientists design PILs with desirable properties.

Most PILs are thermally unstable compared to AILs due to the possibility of an acid-base equilibrium shift from the ions back to the neutral acid and base molecules. PILs with low degree of proton transfer can easily distill through their neutral acid/base molecules, and thus their vapor pressure is not negligible.<sup>41</sup> However, experimental observations have shown that PILs can show all of the typical properties of AILs, such as high ionic conductivity and thermal stability, and negligible vapor pressure, if the  $\Delta p K_a^{aq}$  value is sufficiently large.<sup>37,44,45</sup>

The glass transition temperature  $T_{\rm g}$  is a measure of the cohesive energy within a PIL, which is increased by increasing the attractive electrostatic and van der Waals interactions between ions.<sup>46</sup> PILs with low  $T_{\rm g}$  usually show lower viscosity and higher conductivity which is favorable in many industrial applications.<sup>41</sup> This can be achieved by careful selection of cations and anions or their functionalization.<sup>47</sup> Decreasing the size of ions and increasing the asymmetry of ions have been shown to lower  $T_{\rm g}$ .<sup>48</sup> For example, in primary alkylammonium PILs, lower  $T_{\rm g}$  can be achieved with increasing alkyl chain lengths of the anion or cation, and higher  $T_{\rm g}$  is obtained with the substitution of hydroxyl groups onto the cation or anion.<sup>47</sup>

PILs with lower melting points and higher boiling points (or higher decomposition temperatures) have a wider liquid temperature range, and thus more flexibility in their use. Generally, the melting point can be reduced through decreasing the packing efficiency of the ions, which can be achieved by inducing steric hindrance in the liquid structure and reducing Coulomb and hydrogen bonding interactions.<sup>41</sup> For example, imidazolium-based PILs with large anions such as TFSI and bis(perfluoroethylsulfonyl)imide exhibit low melting points because the size of the anions weakens their coordination with cations.<sup>49</sup> However, the factors that control and determine the melting point of ILs are still not well-understood.

A typical PIL either boils or decomposes upon heating, depending on the strength of the acidity/basicity of the precursor molecules.<sup>38</sup> PILs with a high degree of proton transfer will decompose before they can reach their boiling point.<sup>38</sup> Most PILs show decomposition temperatures ( $T_d$ ) between 120 and 360 °C.<sup>41</sup> However, the most thermally stable PILs are those that are obtained from a proton transfer reaction with superacids such as triflate or TFSI.<sup>45,50</sup> For instance, trialkylammonum triflates exhibited  $T_d$  over 340 °C.<sup>50</sup> PILs that are obtained from a super-strong base and a super-strong acid show even higher  $T_d$ . For example, a PIL obtained from 1,8-diazabicyclo-[5,4,0]-undec-7-ene (p $K_a^{aq} = 13.1$ ) with TFSI (p $K_a^{aq} = -10$ ) showed a high  $T_d$  of 431.2 °C.<sup>44</sup>

The viscosity of PILs depends strongly on intermolecular interactions such as van der Waals and hydrogen bonding, and PILs with stronger ion-ion interactions are more viscous.<sup>41</sup> In PILs with alkylammonium cations, the viscosity increases with increasing alkyl chain length which is also a well-known effect in AILs, and has been rationalized based on the increase in the van der Waals interactions between the alkyl chains of cations.<sup>1,41,42</sup> Viscosity is also dependent on the degree of proton transfer, and PILs with a high concentration of neutral species are less viscous than more highly ionic PILs or AILs.<sup>8</sup> For example, 1ethylimidazolium and N, N-dimethyl-N-ethylammonium acetate PILs showed significantly less viscosity than dialkylimidazolium and pyrrolidinium acetate AILs.<sup>51</sup>

Ionic conductivity in PILs depends on various factors, with the mobility of ions (viscosity) and the number of charge carriers playing major roles. Ion association and incomplete proton transfer have been shown to affect the ionic conductivity through reducing the effective number of available diffusing ions.<sup>16,52</sup> Trialkylammonium triflate PILs have shown the highest ionic conductivity among PILs.<sup>50</sup> Recently, allyldimethylammonium triflate was reported as the PIL with the highest ionic conductivity of 88 mS/cm at 170 °C which was higher than its fully alkyl counterpart of dimethylpropylammonium triflate (76 mS/cm).<sup>1</sup>

# 1.3 Applications

The application of PILs has been studied extensively in fields including catalysis,<sup>53,54</sup> fuel cells,<sup>50,55</sup> chromatography,<sup>56</sup> biology,<sup>57,58</sup> and lubricants.<sup>59</sup> The physicochemical properties of PILs including surface tension, viscosity, and ionic conductivity are important factors when considering a specific application. The ultimate goal is to make ILs specifically for the application of interest, better known as "task specific" ILs.<sup>60,61</sup> Such ILs can be achieved through tuning their physicochemical properties by careful selection and functionalization of constituent ions.<sup>62,63</sup>

One of the major areas in which PILs have been studied is organic reactions. The main motivation has been to replace conventional reaction media and catalysts, most of which are volatile organic compounds, with more environmentally friendly ones. In many instances, PILs generally have shown higher selectivity, higher yields, faster reactions, milder conditions, and better re-usability than conventional methods.<sup>41,42</sup> The Diels-Alder reaction,<sup>64</sup> Henry reaction,<sup>65</sup> Fischer esterification,<sup>66</sup> and Beckmann rearrangement<sup>67,68</sup> are just a few of the reactions that have been carried out with PILs.

The potential application of PILs as proton-conducting electrolytes in polymer membrane fuel cells (PEFCs) has sparked interest in recent years.  $^{50,55,69}$  It has been shown that the cost of conventional PEFCs can be considerably reduced, and their performance can be improved greatly by replacing conventional aqueous electrolytes with new anhydrous electrolytes.  $^{50}$  In a study of over 100 different PILs, diethylmethylammonium triflate has been shown to be the best PIL for this purpose due to its low melting point (-6 °C), wide liquid temperature range (decomposition temperature of 360 °C), high ionic conductivity (55 mS/cm at 150 °C), and facile electrode reactions.  $^{69}$ 

Research in synthesis of new PILs, characterizations, properties analysis, and finding new applications is still developing and expanding toward new areas. Greaves and Drummond have extensively reviewed the properties and broad range of applications of PILs.<sup>41,42</sup> In Chapters 3 and 4, the molecular dynamics simulations of ILs and PILs, and the current challenges in this field will be reviewed in detail.

### CHAPTER 2

# AN INTRODUCTION TO MOLECULAR DYNAMICS

Molecular dynamics (MD) is a statistical mechanical method in which the time evolution (trajectory) of a system of interacting particles is obtained under certain thermodynamic conditions. This trajectory is produced by integrating the classical equations of motion for the system. For an atomic system of N particles with coordinates  $r^N = (r_1, r_2, ..., r_N)$ , and potential energy  $U(r^N)$ , this requires the solution of Newton's equations of motion:<sup>70</sup>

$$m_i \frac{d^2 r_i}{dt^2} = f_i = -\frac{\partial}{\partial r_i} U(r^N)$$
(2.1)

This is a system of N coupled second-order non-linear differential equations which does not have an exact solution. A numerical solution can be obtained by using an appropriate numerical time integration algorithm. The trajectory of the system is generated in a 6Ndimensional phase space  $(r^N, p^N)$ , with 3N dimensions giving the particle positions  $(r^N)$ , and 3N dimensions the particle momenta  $(p^N)$ .

The first MD simulation was performed by Alder and Wainwright at Lawrence Livermore National Laboratory.<sup>71</sup> They used simple "hard sphere" models to represent monoatomic liquids. Since then, methodological advances and more powerful computers have made feasible the simulation of complex liquids, such as ILs, among many other systems. Such simulations have greatly assisted the scientific community in better understanding the behavior of liquids at the molecular level.

Since this dissertation has extensively used MD simulations in studying PILs, we will provide a brief review of the main features of this technique. In the following chapters we will give additional specific details about MD simulations of ILs and PILs as appropriate. The principles of MD simulation has been reviewed comprehensively in books by Allen and Tildesley,<sup>70</sup> Haile,<sup>72</sup> Rapaport,<sup>73</sup> and Frenkel and Smit.<sup>74</sup>

# 2.1 Force Field (Potential Energy)

Force evaluation is the most computationally demanding part of a MD simulation. In principle, the forces acting on each atom can be derived by using quantum mechanics (*ab initio*) calculations. Such an approach is called *ab initio* MD simulation or AIMD.<sup>75,76</sup> AIMD is limited to small systems (usually of the order of a few hundred atoms) and time scales of a few hundred picoseconds. Even then the computational cost is still very expensive. This approach is thus not applicable to systems which are significantly larger and/or require much longer simulation times. For instance, the IL simulations described later consist of a few thousands of atoms, and run for tens of nanoseconds.

In practice, simulations of larger systems makes use of empirical force fields.<sup>77</sup> In this scheme, interatomic interactions are approximated by a sum of physically motivated terms which have been parametrized against quantum mechanics calculations or experimental data.<sup>78</sup> In conventional empirical force fields, the molecules are modeled as sets of atoms held together by simple non-breakable bonds. The largest simulations that can be run with such models have on the order of millions of atoms, and simulation times reaching to microseconds.<sup>79,80</sup>

A typical force field describes the potential energy of the system  $U(r^N)$ , and forces can be derived as the gradients of the potential with respect to atomic displacements (Eq. 2.1). Each part of a force field has a functional form which corresponds to a given type of interaction, along with a set of parameters. The parameters are usually derived by *ab initio* calculations, by fitting to experimental data, or by a combination of these two.<sup>81</sup> The force field terms are divided into intramolecular and intermolecular parts which will be discussed shortly.

Nowadays, there are many well-known empirical force fields, such as CHARMM,<sup>82</sup> AM-BER,<sup>83</sup> and OPLS.<sup>84</sup> As we will see in the Introduction of Chapter 3, there are force fields modified and developed specifically for simulating ILs. For brevity we only explain here

the Optimized Potential for Liquid Simulations-All Atom (OPLS-AA) force field that is exclusively used in this study.

### 2.1.1 OPLS-AA Force Field

OPLS-AA was originally developed to simulate molecular liquids, and has the functional form:

$$U = \sum_{bonds} K_b (r_b - r_{0,b})^2 + \sum_{angles} K_a (\theta_a - \theta_{0,a})^2$$
  
+ 
$$\sum_{dihedrals} \sum_{m=1}^3 \frac{V_{m,d}}{2} \Big[ 1 + (-1)^{m+1} \cos(m\psi_d) \Big]$$
  
+ 
$$\sum_i \sum_{j \neq i} \left\{ 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \right\}$$
  
+ 
$$\sum_i \sum_{j \neq i} \left\{ \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} \right\}$$
 (2.2)

In OPLS-AA, the intramolecular part of the potential energy is expressed in the first three terms as harmonic bond-stretching, harmonic angle-bending, and a Fourier series for dihedral interactions, respectively. The intermolecular contributions to the total potential energy include the pairwise additive 12-6 Lennard-Jones (LJ) potential for van der Waals interactions and Coulomb terms for electrostatic interactions (the two last terms). Figure 2.1 shows these terms in a simplified fashion for molecular models.

The first term in Eq. 2.2 is bond-stretching, which is represented with a simple harmonic function that controls the length of covalent bonds.  $K_b$ ,  $r_b$ , and  $r_{0,b}$  are the force constant, instantaneous bond length, and equilibrium bond length, respectively;  $K_b$  and  $r_{0,b}$  are parameters that differ for each type of bond. Angle-bending is represented by a harmonic potential (the second term) which controls the angle of three atoms bonded consecutively.  $K_a$ ,  $\theta_a$ , and  $\theta_{0,a}$  are the force constant, instantaneous bond angle, and equilibrium bond angle, respectively;  $K_a$  and  $\theta_{0,a}$  are parameters that differ depending on the atoms making the angle.



Figure 2.1. Schematic representation of bonded and non-bonded interactions for molecular models.

Dihedral (torsional) interactions are the most important part of the intramolecular terms as they play a major role in determining the local structure of a molecule. The dihedral potential is represented by a cosine function (the third term in Eq. 2.2) which is periodic through a 360° rotation.  $V_{m,d}$  (three parameters),  $\psi_d$ , and m are the force constant, instantaneous dihedral angle, and the multiplicity for the dihedral angle term, respectively;  $V_{m,d}$ is parametrized for each type of dihedral term.

Van der Waals interactions are represented with the 12-6 Lennard-Jones (LJ) potential. Van der Waals interactions are weak interactions that act between two atoms in close proximity. The LJ potential has attractive and repulsive components. Repulsion arises from the overlap of the electron orbitals of interacting atoms at short distances which (approximately) varies as  $r^{-12}$ . Attraction originates from the induced dipole-induced dipole interactions between induced dipoles of atoms that varies as  $r^{-6}$  at longer distances.  $\epsilon_{ij}$  is the depth of the well of the potential between atoms i and j;  $\sigma_{ij}$  is the point at which the LJ potential becomes zero, and  $r_{ij}$  is the distance between the atoms of i and j.

In most force fields (and in OPLS-AA) the LJ parameters are given individually as  $\epsilon_i$  and  $\sigma_i$  for each atom type. However, there are combining rules to derive the cross interaction LJ parameters. The Lorentz-Berthelot mixing rules  $\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}}$  and  $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$ , are often used to obtain the cross interaction LJ parameters between different atom types.

The final term in Eq. 2.2 represents the electrostatic interactions. The usual practice in empirical force fields is to assign "partial charges" to atomic sites and use Coulomb's law to calculate the electrostatic interactions.  $q_i$  and  $q_j$  are the point partial charges on atoms *i* and *j*, respectively;  $\epsilon_0$  is the vacuum permittivity. Atomic partial charges are usually determined by charge calculation methods such as CHELPG,<sup>85</sup> and RESP<sup>86</sup> in which atomic charges are fitted so as to reproduce the molecular electrostatic potentials derived from high level *ab initio* calculations.

Intermolecular interactions, including LJ and Coulomb potentials, act between any pair of atoms belonging to different molecules but they can also act between atoms from the same molecule. In OPLS-AA, the intermolecular interactions between two directly bonded atoms (1-2), and two atoms separated by two consecutive bonds (1-3) are excluded. For the interactions between two atoms separated by three consecutive bonds (1-4) a scaling factor of 0.5 is applied. This is mainly done to avoid numerical problems as the potential energy can become too repulsive or attractive under such circumstances. Interactions between atoms separated by more than three consecutive bonds are modeled at full strength.

#### 2.2 Periodic Boundary Conditions

If one simulates a system of N particles with no boundary conditions, it will correspond to a simulation of a droplet in vacuum which is not desired in many cases. The boundary of the simulation box should always be tailored to the problem of interest. When bulk



Figure 2.2. Illustration of periodic boundary conditions in 2D for the simulation of diethylmethylammonium triflate PIL. This shows a selected triflate ion in the primitive simulation cell surrounded with 8 image cells in faded colors. The circle shows the cutoff distance around the triflate within which LJ interactions are calculated between the triflate and other molecules.

properties are of interest, one needs to approximate a macroscopic (near-infinite) system at low computational cost. Periodic boundary conditions (PBC)<sup>70</sup> are the solution to this, in which an infinite number of image cells are replicated around the primitive simulation cell, shown in Figure 2.2. If a particle leaves the simulation box, an "image" particle will enter the box from the opposite side. Such treatment preserves the original number of particles Nthroughout the simulation. The main disadvantage of this approach is that it can induce some artificial periodicity in the simulated system. This might not be a problem when simulating a crystal but in the case of a liquid it can have unwanted effects. To overcome this, the simulation cell should be sufficiently large that these effects are minimized.

#### 2.3 Potential Truncation

Most often the short-ranged potential terms (LJ) decay quickly at distances much smaller than the simulation box length (L) which makes the full computation of these forces unnecessary. The common approach to compute these interactions more efficiently is to simply truncate them at a given cutoff distance  $(R_c)$  from each atom. That is, only particles separated by a distance smaller than  $R_c$  are included in potential calculations:

$$U_{trunc}(r) = \begin{cases} U(r), \ r \le R_c \\ 0, \ r > R_c \end{cases}$$
(2.3)

 $R_c$  must be large enough so the potential is truncated safely at a point beyond which the potential can be considered negligible. In molecular systems  $R_c$  is usually taken at 9-15 Å. However, the contribution of the excluded potentials to the total energy is not negligible since the number of interacting atoms increases significantly with distance. This can be handled approximately by adding "tail correction" terms to compensate the missing interactions.<sup>70</sup>

Unlike the LJ potential, long-ranged electrostatic interactions do not decay quickly with distance. Electrostatic interactions require special treatments for which a number of methods have been developed. "Ewald summation" is probably the most commonly used method in calculating the electrostatic interactions in periodic systems.<sup>87</sup> In this method, the summation of Coulomb energies in real space is replaced with an equivalent summation in Fourier space. The electrostatic interaction is divided into two parts: a short-range contribution and a long-range contribution. The short-range contribution is calculated in real space, and

truncated (usually at the same cutoff used for the LJ term). The long-range contribution is calculated using a Fourier transform. Improved alternative methods known as "particlemesh" methods<sup>87</sup> have been developed such as Particle-Particle Particle-Mesh (PPPM)<sup>88</sup> which increases the accuracy and efficiency in calculating Coulomb interactions.

## 2.4 Integrator and Time Step

As mentioned earlier, Eq. 2.1 must be solved numerically by an appropriate integrator to generate the trajectory of the system. The integrator is based on finite difference methods and works by taking small steps known as time steps  $(\Delta t)$ :<sup>70,74</sup>

$$r_i(t_0) \to r_i(t_0 + \Delta t) \to r_i(t_0 + 2\Delta t) \to \cdots r_i(t_0 + n\Delta t)$$
 (2.4)

By iterating the integrator, the positions and velocities over a long series of time steps (the trajectory) is generated.

The Verlet integrator<sup>89</sup> is probably the most-used integration algorithm in the history of MD simulations. In its basic form it is:

$$r_i(t + \Delta t) = -r_i(t - \Delta t) + 2r_i(t) + a_i(t)\Delta t^2 + O(\Delta t^4)$$
(2.5)

In this scheme, the particle position for the next time step is obtained from its positions at the current and previous time steps, and the current acceleration a. The error in this algorithm is the order of  $O(\Delta t^4)$ . The velocities are not used in the integration but can be simply derived:

$$v_i(t) = \frac{1}{2\Delta t} \left[ r_i(t + \Delta t) - r_i(t - \Delta t) \right]$$
(2.6)

There are equivalent variants of this algorithm including "leap-frog" and "velocity-Verlet".<sup>70,74</sup> In general, these algorithms are simple, stable, efficient and show excellent energy conservation. The size of the time step is an important factor in the accuracy of a simulation. In general, a smaller time step will increase the numerical accuracy of the integration algorithm but it will also increase the computational effort needed to simulate for a certain time by increasing the required number of time steps. Too-large time steps may cause large fluctuations or drift in the energy of the system which are highly undesirable. The choice of time step is usually a compromise between these two considerations.

A more efficient way to simulate flexible molecules is to use "multiple time step" integrators such as the reverse reference system propagator algorithm (RESPA)<sup>90</sup> used in this dissertation. In this algorithm, the different degrees of freedom can be evaluated at different levels of frequency. High frequency (fast) motions such as bonding terms can be updated more frequently (at smaller time steps), while slower motions can be evaluated less frequently (at larger time steps). The force values associated with the less frequent motions are used until the next update (the largest time step), and physical quantities are calculated at updates of the largest time step.

In molecular systems, the time step should be small enough to correctly represent the motions with the highest frequency. For example, in a typical molecular simulation, the C-H bond-stretching terms are usually the fastest motions; these can be safely simulated using time step of 0.5-1 fs. However, bond-stretching terms are often kept fixed with a rigid approximation in MD simulations<sup>91,92</sup> which allows the use of larger time steps.

#### 2.5 Thermodynamic Ensembles

The integration of Eq. 2.1 for a system with N particles, and PBCs will generate a trajectory in which the number of particles (N), the volume of the simulation cell (V), and the total energy of the system (E) remain constant. This corresponds to running a MD simulation in a microcanonical or NVE ensemble. However, in NVE simulations the temperature or pressure of the system cannot be defined in advance. Simulations at fixed known temperature or pressure are more interesting because they more closely represent the conditions comparable with real experiment. Here we explain the two ensembles used in this dissertation.

**Canonical Ensemble** (*NVT*): In this ensemble the number of particles (*N*), the volume of the simulation cell (*V*), and the temperature of the system (*T*) are kept constant. At constant *T*, the total energy fluctuates and so modified equations of motion must be used, known as "thermostat".<sup>70</sup> Generally, a thermostat works by coupling the system to a heat bath through the total kinetic energy. The coupling procedure is done differently in different common thermostats such as those due to Berendsen,<sup>93</sup> Anderson<sup>94</sup> and Nosé-Hoover.<sup>95,96</sup> The Nosé-Hoover thermostat is a rigorous thermostat which samples the canonical ensemble correctly and induces minimum perturbation to the dynamics of system.

**Isobaric-Isothermal Ensemble** (NPT): In this ensemble the number of particles (N), the pressure of the system (P), and the temperature of the system (T) are kept constant. Similar to the thermostat used in NVT ensemble, the pressure of the system is controlled by the use of a barostat. A barostat acts by scaling the system volume such that the average pressure converges to the target pressure. In simulating liquids, the volume change is usually done isotropically in which all three dimensions of the simulation box change uniformly; however, other modes are also possible. In practice, fluctuations in the pressure are usually much larger than fluctuations in temperature, and the barostat is often applied less frequently than the the thermostat in use.

# CHAPTER 3

# STRUCTURAL AND TRANSPORT PROPERTIES OF TERTIARY AMMONIUM TRIFLATE IONIC LIQUIDS: A MOLECULAR DYNAMICS STUDY<sup>1</sup>

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#### Abstract

Ammonium-based protic ionic liquids (PILs) have shown promising physicochemical properties as proton conductors in polymer membrane fuel cells. In this work molecular dynamics simulations are used to study the structural, dynamic, and transport properties of a series of tertiary ammonium triflate PILs. Nonpolarizable all-atom force fields were used, including two different models for the triflate anion. Previous simulation studies of these PILs have yielded poor results for transport properties due to unrealistically slow dynamics. To improve performance, polarization and charge-transfer effects were approximately accounted for by scaling all atomic partial charges by a uniform factor,  $\gamma$ . The optimum scaling factor  $\gamma = 0.69$  was determined by comparing simulation results with available experimental data and found to be transferable between different ammonium cations and insensitive to both the temperature and choice of experimental data used for comparison. Simulations performed using optimized charge scaling showed that the transport properties significantly improved over previous studies. Both the self-diffusion coefficients and viscosity were in good agreement with experiment over the whole range of systems and temperatures studied. Simulated PIL densities were also in good agreement with experiment, although the thermal expansivity was underestimated. Structural analysis revealed a strong directionality in interionic interactions. Triflate anions preferentially approach the ammonium cation so as to form strong hydrogen bonds between sulfonate oxygen atoms and the acidic ammonium hydrogen. The ionic conductivity was somewhat underestimated, especially at lower temperatures. Analysis of conductivity data suggests that there is significant correlated motion of oppositely charged ions in these PILs, especially at short times. These results overall indicate that the transport properties of this class of PILs are accurately modeled by these force fields if charge scaling is used and properly calibrated against selected experimental data.

## 3.1 Introduction

Ionic liquids (ILs) are molten salts with melting points below 100 °C, negligible vapor pressure, low flammability, high ionic conductivity, and good thermal stability.<sup>14</sup> ILs can be divided into two large subsets: protic ionic liquids (PILs) and aprotic ionic liquids (AILs). PILs are obtained through proton transfer from a Brønsted acid to a Brønsted base;<sup>37</sup> if the acid and base are sufficiently strong this transfer will be essentially complete, resulting in a purely ionic system.<sup>8</sup> The key feature that separates PILs from AILs is the presence of an active proton, which can form a hydrogen bond or be transferred to other species in the solution. Greaves and Drummond<sup>41,42</sup> published comprehensive reviews on structure-property relationships and the various applications of PILs in organic and inorganic syntheses, chromatography, biological applications, nonaqueous electrolytes, polymer membrane fuel cells, and other areas.

Molecular simulation is a powerful method by which to study the structural, thermodynamic, and transport properties of ILs and other liquids. Simulations, in particular molecular dynamics (MD), can provide us with a better picture at the molecular level of ILs and insight into the relationship between their molecular structure and dynamic properties. Numerous classical (empirical) force fields have been developed for ILs;<sup>97</sup> however, most of them cover only a small subset of ILs.<sup>98,99</sup> The majority of these force fields are nonpolarizable, pairwiseadditive models, which have been developed by modification of well-established force fields, such as OPLS,<sup>84</sup> AMBER<sup>83</sup> and CHARMM.<sup>82</sup> Such force fields represent electrostatic interactions through assignment of partial point charges to each atom; the assignments are commonly made through fitting of the corresponding electrostatic potential field to electronic structure calculations on isolated ions in vacuum.<sup>100</sup> Perhaps the most widely used IL force field is that developed by Lopes and Pádua,<sup>100</sup> an all-atom force field based on OPLS which includes a wide variety of cations and anions. Most nonpolarizable force fields fail to adequately reproduce the dynamic properties of ILs because of the total neglect of electronic polarization and charge-transfer effects.<sup>97</sup> Ab *initio* calculations on ILs have shown that there can be significant electronic charge transfer between IL cations and anions.<sup>101,102,103</sup> Nonpolarizable force field simulations with integer molecular charges of  $\pm 1e$  generally produce diffusion coefficients of both cations and anions that are much lower than experimental values. The corresponding ionic conductivities are badly underestimated, and the viscosities are overestimated.<sup>104,105,106,107</sup> These studies have clearly shown that the charge distributions obtained by gas-phase *ab initio* calculations on isolated ions do not produce realistic dynamics in simulation of ILs.

Polarizable force fields generally give better agreement between experimental and simulated transport properties.<sup>108,109</sup> For example, Yan et al.<sup>108</sup> developed a polarizable model for 1-ethyl-3-methylimidazolium nitrate and compared it with the nonpolarizable version. Comparisons of shear viscosity and diffusion constants showed that the effects of polarizability are significant and the polarizable model results are in better agreement with the experimental values. Diffusion constants obtained with polarizable models were roughly three times larger than those obtained with nonpolarizable models; the viscosity was likewise reduced from 6.8 to 4.7 cP, close to the experimental result of 4.42 cP at 400 K. Unfortunately, the inclusion of polarizability in molecular simulations is computationally expensive, which is undesirable in IL studies which generally require very long simulation times.<sup>97</sup>

An inexpensive way to approximately account for polarizability and charge-transfer effects in classical force fields is through charge scaling.<sup>97,110</sup> In this approach, the charges of ions are scaled down from  $\pm 1e$  to  $\pm \gamma e$  through multiplying the atomic partial charges by a scaling factor,  $\gamma$ . This corresponds to a uniform, non-fluctuating transfer of  $(1 - \gamma)e$  of charge from anion to cation, and no change in the relative distribution of charge in each species. This simple scaling of the atomic charges mimics the average effect of polarization and charge transfer in ILs without additional complication of the force field and has
been shown to substantially improve agreement with experiments.<sup>111,112,113,114,115</sup> Sprenger et al.<sup>115</sup> used a charge-scaling factor of 0.8 in simulations of a set of 19 ILs and obtained good agreement for self-diffusivity and shear viscosity with experimental data across a wide range of cation and anion types. Maginn et al.<sup>114</sup> carried out MD simulations on nine ILs using both unit charges and charges scaled by a factor of 0.8. Generally, the force field with scaled charges gave better agreement with experimental results.

Comparisons with quantum mechanical calculations provide some justification for the charge-scaling approach. Youngs and Hardacre<sup>110</sup> studied the systematic effect of scaling partial charges on the structure, dynamics, and energetics of the 1,3-dimethylimidazolium chloride IL. They concluded that the use of  $\pm 1e$  charges overestimated the intermolecular attractions between ions, resulting in overstructuring and slow dynamics, while scaling atomic charges by a factor of 0.6-0.7 provided excellent agreement with *ab initio* MD results. Chaban et al.<sup>102</sup> used density functional theory calculations to obtain optimal  $\gamma$  values of 0.80 and 0.84 for 1-ethyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium tetrafluoroborate ILs, respectively. Their total ionic charges are considerably lower than those in the original force field, developed by Liu et al.,<sup>98</sup> and resulted in better agreement with experimental data. Zhong et al.<sup>101</sup> used electronic structure calculations on isolated ion pairs to estimate suitable charge-scaling factors for a family of seven 1-alkyl-3-methylimidazolium ILs. They obtained values of 0.64-0.75 and then used 0.8 in subsequent MD simulations. This work gave a good description of the self-diffusion coefficients and shear viscosities of the ILs, with results comparable to experiment.

Ammonium-based triflate PILs have shown promising electrochemical and physicochemical characteristics as ionic-conducting electrolytes in electrochemical systems and as proton conducting electrolytes in polymer membrane fuel cells and hence they have received considerable attention in recent years.<sup>50,55,69</sup> Only a few simulation studies of these PILs have been performed to date.<sup>5,6,116</sup> These have generally shown unrealistic dynamics and poor



Figure 3.1. Chemical structure of the ions used in this work.

estimation of the transport properties. Most recently, Sunda et al.<sup>5</sup> performed simulations of trialkylammonium triflate PILs using a charge-scaling factor of 0.78 but substantially underestimated the self-diffusion coefficients and ionic conductivity as compared with experimental data. Simulation models with more realistic dynamics are thus quite desirable for this class of PILs.

In this work, we studied a series of PILs consisting of a trialkylammonium cation and a triffuoromethanesulfonate (triffate) [TfO] anion. Four tertiary ammonium PILs with varying alkyl chains were considered: N,N-dimethyl-N-propylammonium [N113], N,N-diethyl-N-methylammonium [N122], N,N-diethyl-N-propylammonium [N223], and N,N-dipropyl-N-methylammonium [N133]. The chemical structures of these PILs are shown in Figure 3.1. Because triffuoromethanesulfonic acid is an exceptionally strong acid, it is generally assumed that proton transfer in these PILs is essentially complete; our simulations therefore included only proton-transferred cations and anions, with no neutral species present. Particular focus was placed on the accurate reproduction of experimental self-diffusivity, ionic conductivity, and viscosity by careful choice of the charge-scaling factor used. To achieve this, a fitting procedure was employed to derive the optimal charge-scaling factor on the basis of comparison with the comprehensive experimental data of Yasuda et al.<sup>1</sup> We observed that the choice of  $\gamma$  strongly affects the dynamics and transport properties and that with the optimum value obtained these simulations showed substantial improvement over previous studies,<sup>5,6</sup> with results in generally good agreement with experimental data.<sup>1,4</sup>

## 3.2 Computational Methods

## 3.2.1 Force Field

In this work, we used one model for the trialkylammonium cations and two different models for the triflate anion. The ammonium model and one of the triflate models were taken from the systematic all-atom force field of Lopes and Pádua,<sup>117</sup> using the recent version of the parameters available from the Pádua group website.<sup>118</sup> The second triflate model studied is that developed by Sunda and Venkatnathan.<sup>119</sup> All of these models have been developed in the framework of the Optimized Potential for Liquid Simulations-All Atom (OPLS-AA) force field<sup>84</sup> and hence are mutually compatible. In OPLS-AA, the intramolecular part of the potential energy is expressed in terms of harmonic bond stretching, angle bending, and a Fourier series for dihedral interactions. The intermolecular part includes the pairwise additive 12-6 Lennard-Jones (LJ) potential for van der Waals interactions and Coulomb terms for electrostatic interactions. The two triflate models have similar (though not identical) LJ parameters, differing mainly in the partial charges and intramolecular parameters. Electrostatic interactions in the Lopes and Pádua force field were originally obtained by generating electron densities at the MP2/cc-pVTZ(-f) level and fitting using the CHELPG procedure.<sup>85</sup> For the triflate model developed by Sunda and Venkatnathan, electrostatic interactions were similarly obtained by fitting electron densities from MP2/6-31G calculation using the CHELP method.<sup>120</sup> The complete sets of partial charges and other parameters are given in Appendix A. In describing the simulations below, we refer to the combination of the Lopes and Pádua triflate model with ammonium as "TM1" and the Sunda and Venkatnathan triflate model with ammonium as "TM2".

# 3.2.2 Simulation Details

MD simulations were performed using the LAMMPS package<sup>121</sup> over the temperature range of 20-170 °C and at atmospheric pressure (0.1 MPa). The simulations were conducted in cubic boxes with periodic boundary conditions in all directions. A total number of 256 ion pairs were used in production simulations. Simulations with 64-512 ion pairs were used to determine the influence of finite-system size effects before choosing this system size which will be discussed in Section 3.2.5.

Standard Lorentz-Berthelot mixing rules, that is,  $\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}}$  and  $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$ , were used to obtain the "cross" interaction LJ parameters between different atom types. Nonbonded interactions were calculated between atoms in different ions or in the same ion separated by more than three bonds. A scaling factor of 0.5 is applied to the nonbonded interactions between atoms separated by three consecutive bonds (1-4 interactions).<sup>84</sup> A cutoff distance of 12 Å was used for both the LJ and the real part of the Coulomb pairwise interactions. The particle-particle particle-mesh (PPPM) solver<sup>88</sup> was employed to compute long-range electrostatic interactions with a precision of  $10^{-5}$  beyond the cutoff distance. Long-range LJ tail corrections were added to the energy and pressure of the system. As explained previously, in order to approximately account for the anion-to-cation charge transfer and polarization effects, the total charge on cations and anions were scaled down uniformly from unity to fractional charges using a charge-scaling factor,  $\gamma$ , the determination of which is described in Section 3.3.1.

Careful equilibration is needed in IL simulations.<sup>101,113</sup> We used PACKMOL<sup>122</sup> to set up the initial configurations. These were first relaxed by conjugate gradient energy minimization and then annealed by heating the system from 303 K to 700 K and cooling to the target temperature over 2 ns. Annealing was done in the isobaric-isothermal (*NPT*) ensemble. The resultant configuration was then used as the input in an *NPT* equilibration run of 10 ns duration, in which the density information was recorded during the last 4 ns.

Production runs were performed in the canonical (NVT) ensemble. To obtain better statistics, we carried out 30 independent NVT runs for each system at each temperature considered. To initialize these, the final configuration obtained from the NPT equilibrium run was first resized to match the average density obtained at that temperature. Thirty copies were then made with particle velocities independently resampled from the Maxwell-Boltzmann distribution. These were run for a further 4 ns of equilibration and was followed by 10 ns of simulation over which data were collected.

### 3.2.3 Integrator and Time Step

To reduce computational cost, we used the reverse reference system propagator algorithm (RESPA),<sup>90</sup> a multiple time step method. We first established RESPA parameters for comparison with the velocity Verlet integrator. Microcanonical (NVE) simulation runs of 10 ps were performed on [N112][TfO] (256 ion pairs), starting from an equilibrated configuration. Three different NVE simulations were performed, using the velocity Verlet algorithm with time steps of 1.0 (Verlet/1 fs) and 2.0 fs (Verlet/2 fs), and RESPA with a time step of 5 fs (RESPA/5 fs). In RESPA, the nonbonded interactions beyond the cutoff distance were integrated with a time step of 5 fs. The nonbonded interactions within the cutoff distance were evaluated every 2.5 fs. Dihedral interactions were updated every 1.25 fs, and the bonding and angle-bending terms were evaluated every 0.625 fs.

All bonds containing hydrogen were constrained using the SHAKE algorithm,  $^{92}$  with a tolerance of  $10^{-4}$  and maximum iteration of 20. The Nosé-Hoover thermostat  $^{95,123}$  and barostat were used to keep the temperature and pressure constant with damping factors of 0.5 and 1.0 ps, respectively.

Figure 3.2 shows the time evolution of the total energy of the simulations. Both RESPA/5 fs and Verlet/1 fs show excellent energy conservation, whereas Verlet/2 fs shows large fluctuations. Standard deviations of 1.96 and 2.09 kJ/mol were obtained for the total energy of simulations of Verlet/1 fs and RESPA/5 fs, respectively, corresponding to less than 0.03% of the total energy, with no detectable drift. A standard deviation of 8.59 kJ/mol was obtained for Verlet/2 fs. Moreover, self-diffusion coefficients, viscosity and ionic conductivity values



Figure 3.2. Total-energy fluctuation in *NVE* simulations of [N112][TfO] using Verlet and RESPA integrators.

Table 3.1. Transport coefficients from simulations of [N112][TfO] at 120 °C using Verlet and RESPA integrators.

Property	Verlet $(1 \text{ fs})$	Respa $(5 \text{ fs})$
Ionic conductivity(mS/cm)	$4.48 {\pm} 0.26$	$4.52 {\pm} 0.26$
Shear viscosity (mPa s)	$5.04{\pm}0.36$	$5.16 {\pm} 0.47$
Cation self-diffusion coefficient $(10^{-6} \text{ cm}^2/\text{s})$	$4.11 {\pm} 0.04$	$4.10 {\pm} 0.04$
Anion self-diffusion coefficient $(10^{-6} \text{ cm}^2/\text{s})$	$3.08 {\pm} 0.03$	$3.09 {\pm} 0.03$

obtained from RESPA/5 fs and Verlet/1 fs were in good agreement, shown in Table 3.1. Most importantly, we observed a  $\sim 2.5 \times$  speedup for RESPA/5 fs over Verlet/1 fs.

# 3.2.4 Transport Coefficients

The Green-Kubo relations<sup>70,72,74,124</sup> were used for the calculation of transport coefficients from the running time integrals of the corresponding autocorrelation functions. In computing time correlation functions, we used multiple-time origin averaging to improve the statistics.<sup>74</sup> The statistical uncertainties (error bars) reported for each quantity are  $\pm \frac{2\sigma}{\sqrt{n}}$ , where  $\sigma$  is the standard deviation of the values obtained from each of the n = 30 runs. Transport coefficients obtained from test simulations in the *NVT* and *NVE* ensembles agreed well. Overall, the transport coefficients were calculated at eight temperatures (30, 50, 70, 90, 110, 130, 150 and 170 °C) for [N122][TfO] and at three temperatures (50, 90 and 130 °C) for [N113][TfO], [N223][TfO], and [N133][TfO].

The self-diffusion coefficients were calculated from the mean-square-displacement (MSD) of the center of mass of each ion using the Einstein relation:<sup>70</sup>

$$D = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} \left\langle [r_i(t) - r_i(0)]^2 \right\rangle$$
(3.1)

where the quantity in  $\langle ... \rangle$  is ensemble-averaged MSD of the center of mass of ion *i* over time interval *t*. For these calculations, the locations,  $r_i(t)$ , were stored every 1.0 ps for each independent run. The slope (time derivative) was measured for each run by linear regression of MSD data between 3 and 8 ns, and these slopes were then averaged over the 30 independent runs.

The self-diffusion coefficients were also calculated from the equivalent Green-Kubo relation,<sup>70,124</sup> using the time integral of the velocity autocorrelation function (VACF):

$$D = \frac{1}{3N} \int_0^\infty \sum_{i=1}^N \left\langle v_i(t) \cdot v_i(0) \right\rangle dt \tag{3.2}$$

The brackets represent the average over all time origins,  $v_i$  represents the velocity of the center of mass of ion i, N is the total number of ions, and t is the delay time of the correlation function. Summing over all ions and including all three components of the velocity improves the statistics.<sup>72</sup> Velocity data were stored every 20 fs for each independent run, and the self-diffusion coefficients were calculated from the VACF integrated to 100 ps.

The ionic conductivity,  $\sigma_{GK}$ , was calculated through the Green-Kubo relation,<sup>124</sup> using the time integral of the electric current autocorrelation function (ECACF):

$$\sigma_{GK} = \frac{1}{3k_B T V} \int_0^\infty \left\langle j(t) \cdot j(0) \right\rangle dt \tag{3.3}$$

where V is the volume of the system, T is the temperature,  $k_B$  is the Boltzmann constant, and j(t) is the electric current:

$$j(t) = \sum_{i=1}^{N} q_i v_i(t)$$
(3.4)

where  $q_i$  and  $v_i(t)$  represent the charge and center-of-mass velocity of ion *i*, respectively. Velocity data were recorded every 20 fs from 30 NVT independent runs. For each independent run, the integral was calculated to 100 ps.

The shear viscosity,  $\eta$ , was calculated from the time integral of the pressure tensor autocorrelation function (PTACF) using the following Green-Kubo relation:<sup>125,126,127</sup>

$$\eta = \frac{V}{10k_BT} \int_0^\infty \sum_{\alpha\beta} \left\langle P_{\alpha\beta}(t) \cdot P_{\alpha\beta}(0) \right\rangle dt \tag{3.5}$$

The brackets represent the average over all time origins.  $P_{\alpha\beta}$  is the  $\alpha\beta$  element of the pressure tensor, which is calculated via the following expression:<sup>70</sup>

$$P_{\alpha\beta} = \frac{1}{V} \left[ \sum_{j} m_{j} v_{\alpha j} v_{\beta j} + \frac{1}{2} \sum_{i \neq j} r_{\alpha i j} f_{\beta i j} \right]$$
(3.6)

where  $m_j$  is the mass of atom j,  $v_j$  is the velocity of atom j, and  $r_{ij}$  and  $f_{ij}$  represent the distance and the force acting between atoms i and j, respectively. The sum of the autocorrelation of six independent terms of the pressure tensor,  $2P_{xy}$ ,  $2P_{yz}$ ,  $2P_{zx}$ ,  $\frac{4}{3}[P_{xx} - \frac{1}{3}(P_{xx} + P_{yy} + P_{zz})]$ ,  $\frac{4}{3}[P_{yy} - \frac{1}{3}(P_{xx} + P_{yy} + P_{zz})]$ , and  $\frac{4}{3}[P_{zz} - \frac{1}{3}(P_{xx} + P_{yy} + P_{zz})]$  were used, which results in the factor of 10 in the denominator of Eq. 3.5. The use of all components of the pressure tensor has been found to provide more accurate statistics than using only the off-diagonal components.<sup>127,128</sup> The six independent components of the pressure tensor were recorded every 10 fs in each independent run, and the PTACF integrals were computed to 1 ns.



Figure 3.3. Effect of system size on (a) density (b) self-diffusion coefficients (c) ionic conductivity and (d) shear viscosity of [N112][TfO] system at 120 °C and 0.1 MPa.

#### 3.2.5 System Size Effects

We performed a series of simulations of the [N112][TfO] PIL, varying the number of ion pairs. The objective of this study is to determine the smallest system size that can be used to determine structural and transport properties without inducing systematic errors due to the use of periodic boundary conditions. System size between 64 and 512 ion pairs were considered, at the temperature and pressure of 120 °C and 0.1 MPa. Charge scaling was used, with  $\gamma = 0.78$ . Other details regarding the simulations and calculation of properties are the same as explained earlier. Figure 3.3 shows how density, self-diffusion coefficients, ionic conductivity and shear viscosity vary with the number of ion pairs. The density shows a small dependence on system size, with very small simulation cells yielding systematically high densities. Self-diffusivities measured in small simulation cells are likewise systematically low. In both cases these systematic deviations disappear once a system size of 256 ions pairs is reached. The ionic conductivity and viscosity results were insufficiently precise to establish any systematic dependence on system size. Based on these observations, we selected 256 ion pairs as appropriate for production calculations. This system size has also been used for simulation of PILs by other workers.<sup>5,6</sup>

### **3.3** Results and Discussion

# 3.3.1 Charge-Scaling Factor Determination

As discussed earlier, scaling the partial charges of ions by a uniform factor is an effective way to represent charge-transfer effects at reduced computational cost. This method has been shown to enhance the dynamics and improve the transport coefficients of simulated systems<sup>110,113</sup> and give better agreement with experiments.<sup>114,115,129</sup> However, determination of the charge-scaling factor to use is not straightforward.<sup>101,102</sup>

In this work we take an empirical approach to determining the optimal  $\gamma$  value. For a single system [N122][TfO] as simulated with model TM1, simulations were carried out with  $\gamma = 0.60, 0.65, 0.70, 0.75,$  and 0.80, and the density and the transport coefficients were calculated in each. The variation of each quantity with  $\gamma$  was fit to a quadratic function, and the optimum  $\gamma$  was then obtained by interpolation at the experimental value. As prior studies have generally used  $\gamma = 0.8$  or below, this was the largest  $\gamma$  considered here. The experimental data of Yasuda et al.<sup>1</sup> were used for these interpolations.

Figure 3.4 shows the density, self-diffusivity, ionic conductivity, and viscosity of simulated [N122][TfO] at 30 °C as functions of  $\gamma$ , along with the corresponding quadratic fits



Figure 3.4. Plots of (a) density  $\rho$ , (b) self-diffusion coefficient D, (c) ionic conductivity  $\sigma$ , and (d) shear viscosity  $\eta$  as a function of charge-scaling factor  $\gamma$  for [N122][TfO] at 30 °C. For density and self-diffusivity the uncertainties are smaller than the symbols used. Experimental data (expt. value) are taken from Yasuda et al.<sup>1</sup>

and experimental values. Similar calculations were also performed at temperatures of 90 and 130 °C, shown in Figure 3.5. The density of the simulated system decreases with decreasing  $\gamma$  (that is, with increasing amount of charge transferred), which is a consequence of weaker electrostatic interactions. The diffusion coefficients and ionic conductivity increase significantly with decreasing  $\gamma$ , while viscosity shows a dramatic decrease.

The optimum  $\gamma$  values for each quantity, for which the interpolation exactly matches the corresponding experimental value, are shown in Table 3.2. Experimental density data were only available near 30 °C, so only a single  $\gamma$  value is given for this quantity. All



Figure 3.5. Plots of (a,b) self-diffusion coefficient D, (c,d) ionic conductivity  $\sigma$ , and (e,f) shear viscosity  $\eta$  as a function of charge-scaling factor  $\gamma$  for [N122][TfO] at 90 and 130 °C. For self-diffusivity the uncertainties are smaller than the symbols used. Experimental data are taken from Yasuda et al.<sup>1</sup>

Table 3.2. Optimum charge-scaling factors derived for density  $(\gamma_{\rho})$ , cation and anion self-diffusion coefficients  $(\gamma_{D^+}, \gamma_{D^-})$ , ionic conductivity  $(\gamma_{\sigma})$ , and shear viscosity  $(\gamma_{\eta})$  for [N122][TfO] at different temperatures.

$T (^{\circ}C)$	$\gamma_{ ho}$	$\gamma_{D^+}$	$\gamma_{D^-}$	$\gamma_{\sigma}$	$\gamma_{\eta}$
30	0.67	0.69	0.70	0.66	0.69
90	-	0.69	0.69	0.62	0.70
130	-	0.69	0.66	0.63	0.69

of the  $\gamma$  values fall in the range 0.62–0.70, and, if the high-temperature values for ionic conductivity are excluded, they all fall in the range 0.66–0.70, which is fairly narrow. We note in this regard that the statistical uncertainties on ionic conductivity are by far the highest of any quantity measured, although this does not entirely explain the lower (on average)  $\gamma$  values corresponding to this quantity. Nonetheless, the reasonable agreement between the  $\gamma$  values derived from different experimental quantities and the near-independence of  $\gamma$ with temperature suggests that uniform charge scaling is a physically sensible way to handle charge-transfer and polarization effects in these PILs.

To proceed, we chose an optimum overall  $\gamma$  by averaging the  $\gamma$  values derived from selfdiffusivity and viscosity. A  $\gamma$  value of 0.69 was thus used in all production simulations of these PILs (incorporation of  $\gamma = 0.67$  from the density measurement does not change this result to two significant figures.) It is important to note that, although this value represents a consensus fit to selected experimental data on [N122][TfO], no experimental results on the other PILs simulated below were used in its derivation.

#### 3.3.2 Density and Liquid Structure

The computed densities for both models of [N122][TfO], [N113][TfO], [N223][TfO], and [N133][TfO] are shown in Figure 3.6, along with available experimental data.<sup>1</sup> As expected, the densities of the PILs decrease with increasing temperature. TM2 simulations give systematically higher densities than TM1 over the whole temperature range studied. Deviations



Figure 3.6. Density vs temperature. Experimental data are from Yasuda et al.<sup>1</sup> Uncertainties in simulation results are smaller than the symbols used.

between simulated and experimental densities are less than 1.0% and 1.6% for TM1 and TM2, respectively, between 20 and 40 °C.

As temperature increases, the deviation between experiment and simulation becomes larger; simulations do not perfectly capture the trends in experimental densities. In order to show this, thermal expansion coefficients,  $\alpha_p = -\frac{1}{\rho} (\frac{\partial \rho}{\partial T})_p$ , were calculated. For [N122][TfO], thermal expansion coefficients of  $7.87 \times 10^{-4}$  K<sup>-1</sup> and  $1.17 \times 10^{-3}$  K<sup>-1</sup> were obtained from simulated (TM1) and experimental data at 40 °C, respectively; the expansivity of this PIL is thus underestimated by about 30% by the simulation model. A similar underestimation of the thermal expansivity was also observed for [N113][TfO], [N223][TfO], and [N133][TfO],

Table 3.3. Thermal expansion coefficients for TM1, TM2, and experimental data at 40  $^{\circ}$ C. Units are K<sup>-1</sup>.

	[N122][TfO]	[N113][TfO]	[N223][TfO]	[N133][TfO]
$\alpha_p(\text{TM1})$	$7.87 \times 10^{-4}$	$7.58\times10^{-4}$	$8.29 \times 10^{-4}$	$8.49 \times 10^{-4}$
$\alpha_p(\text{TM2})$	$8.11 \times 10^{-4}$	$8.17  imes 10^{-4}$	$7.57  imes 10^{-4}$	$7.78  imes 10^{-4}$
$\alpha_p(\text{expt.})$	$1.17 \times 10^{-3}$	$1.18 \times 10^{-3}$	$1.19 \times 10^{-3}$	$1.23 \times 10^{-3}$

independent of the model (TM1 or TM2) used as shown in Table 3.3. In all cases, then, simulated densities would be higher than the experimental value at high temperatures. We also observed (using data from the  $\gamma$ -calibration study) that changing  $\gamma$  had virtually no effect on the thermal expansion coefficients. The developers of the TM1 force field<sup>100</sup> likewise found their simulated imidazolium triflate and bistriflylimide densities also to be higher than the experimental ones and suggested that fine-tuning the LJ parameters might improve agreement on this quantity. It is important to note, however, that that study did not employ charge scaling, which here is shown to substantially reduce PIL densities.

The experimental density of the PILs follows the order [N133][TfO] < [N223][TfO] < [N113][TfO] < [N122][TfO]. Simulations reproduced this trend well at all temperatures. Increasing the alkyl chain lengths on the cation leads to lower density, similar to the behavior of other ILs previously reported.<sup>41,101,111</sup>

The structures of simulated PILs were analyzed by calculating center-of-mass and atomic radial distribution functions (RDFs) and spatial distribution functions (SDFs). Figure 3.7 shows the cation-cation, anion-anion, and cation-anion center-of-mass RDFs at 50 °C. All of the center-of-mass RDFs show oscillatory behavior up to 20 Å, which includes three solvation shells. This is an indication of the long-range spatial correlations between ions, which is typical of ILs.<sup>6,130</sup> The cation-anion RDFs show the strongest first peak, which indicates highly favorable cation-anion associations due to strong attractive electrostatic interactions. Integration of the cation-anion RDFs up to the position of the first minimum leads to coordination numbers of 7.3, 7.2, 7.1 and 7.0 for [N113][TfO], [N122][TfO], [N223][TfO], and



Figure 3.7. Center-of-mass RDFs at 50 °C.  $\frac{L}{2} > 20.0$  Å.

[N133][TfO], respectively. This corresponds to a slight reduction in the degree of liquid ordering as the alkyl chain lengths are increased.

In the cation-anion RDFs, the first peak is clearly bifurcated for [N122][TfO] and [N223][TfO], while for [N113][TfO] and [N133][TfO], the first peak is sharp with a small shoulder at larger separation; these findings suggest that there are two preferred positions or orientations at nearest approach. The first peak in the cation-cation RDFs is well defined and sharper than that in the anion-anion RDFs. The first peak in the anion-anion RDFs is broad with a bi-furcated shape. The oscillations in the cation-cation and anion-anion RDFs are out of phase

with those in the cation-anion RDFs, which is due to charge ordering,<sup>130</sup> in which ions are surrounded by their corresponding counterions.

A better picture of the distribution of anions around cations in the first solvation shell is obtained from the SDFs, shown in Figure 3.8. SDFs give the probability of finding a particle at a certain position in space around a fixed reference particle and thus provide additional orientational information that is not present in RDFs.<sup>2</sup> In general, the SDFs reveal that there are two major regions where anions are most likely to be found around a given cation. The first corresponds to an approach from the top direction (along the N-H vector), driven by the strong hydrogen-bond interactions between the acidic proton (ammonium) and the oxygen atoms in the sulfonate group (triflate). These can be seen as separate lobes above [N122] and [N223] in Figure 3.8.

The second region is facing the bulky and hydrophobic alkyl chains. The distribution of anions vary between cations because of the different spatial configurations of the alkyl chains; the anions tend to position themselves in the empty spaces between the chains. Of the two preferred anion positions, the first (hydrogen bond to the acidic proton) is of higher probability, as determined by mapping SDFs at higher isosurface values (not shown). Such preference has been recently shown by *ab initio* methods,<sup>131</sup> where triflate anions located at the N-H site of the [N122] cation were more stable than anions located on the opposite side of the cation.

Figure 3.9 shows selected site-site (atomic) partial RDFs of the simulated PILs at 50 °C. The most obvious feature in these data is the sharp first peak between the acidic hydrogen of the cation and the oxygen atoms of the sulfonate group of anion at roughly 2 Å. This implies strong hydrogen bonding between these two groups. The first peak between the acidic hydrogen and the sulfur atom is located near 3 Å. The first peaks between the acidic proton and fluorine and carbon atoms of the anion are much weaker and located at larger distances. It seems clear that the acidic hydrogen prefers interaction with anion oxygen atoms over



Figure 3.8. SDFs of triflate anions around a reference cation at 50 °C. Isosurface values correspond to 2.5 times the bulk density. SDFs were calculated with TRAVIS<sup>2</sup> and visualized in VMD.<sup>3</sup>

fluorine atoms, in agreement with previous studies.<sup>5,6,116</sup> This preference originates from the partial negative charge on the oxygen atoms being larger than that on the fluorine atoms, and confirms the strong directionality of the interaction of cation and anion in the simulated PILs.

## 3.3.3 Translational Dynamics

The dynamics of the simulated systems were characterized by calculating self-diffusion coefficients, as described in Section 3.2. Normalized VACFs of each component of the simulated PILs are shown in Figure 3.10. These show behavior typical of ILs; they decay quickly and reach a plateau within a few picoseconds.



Figure 3.9. Atomic RDFs at 50 °C. H represents the acidic proton attached to the ammonium nitrogen; C, S, O and F correspond to carbon, sulfur, oxygen and fluorine atoms in the triflate anion.

The cation VACF decays more quickly than the anion VACF for all systems, reaching the zero line at roughly 0.14 ps for both [N122] and [N113], 0.15 ps for [N223], and 0.17 ps for [N133]. The anion VACF decays more slowly, reaching zero at roughly 0.25 ps in all cases. The position of the first zero represents the average collision time for each ion. In these PILs the cations are all lighter than the triflate anion and so their first collision times are shorter; the lighter cations also randomize their velocities faster because of the greater number of collisions.

The cation VACFs show very small oscillations, known as "rattling", because of the "cage" effect.<sup>104,130</sup> This happens when the lighter cation is temporarily trapped inside a



Figure 3.10. Normalized VACFs of cations (solid lines) and anions (dashed lines) from TM1 simulations at 50 °C.

relatively long-lived cage formed by heavier (triflate) counterions. These oscillations are not as large as those reported for other ILs,<sup>104,105</sup> where there is a larger mass difference between counterions. The cationic rattling is most noticeable in [N122][TfO] and [N113][TfO], which have the largest difference in mass between cation and anion.

Figure 3.11 depicts the averaged MSD plots of the center of mass of ions for each PIL over the course of 10 ns simulation at 50° C. Figure 3.12 shows the self-diffusion coefficients of [N122][TfO] and [N113][TfO] as functions of temperature for two models and their comparison with experimental data and previous MD studies. For clarity, only the self-diffusion coefficients derived from MSD data are shown. The self-diffusion coefficients increase with increasing temperature. For [N122][TfO], the cation self-diffusion coefficients show excellent agreement with the experimental data over the whole temperature range. The anion self-



Figure 3.11. MSD plots at 50 °C (TM1 model).

diffusion coefficients are in excellent agreement with experimental data except at the highest temperatures (110 and 130 °C), where simulation results are systematically low. At all temperatures, the self-diffusion coefficients obtained for [N122][TfO] show significant improvement over previous MD studies.<sup>5,6</sup> The simulated self-diffusion coefficients of [N113][TfO] also agree well with experiment, although like the [N122][TfO] values they are slightly too low at the highest temperature studied; in both cases, this may be a consequence of too high a density in the simulated PILs, as discussed above. In these data TM1 appears to give slightly higher diffusion constants than TM2, which is again consistent with the overestimation of density by the TM2 model.



Figure 3.12. Cation and anion self-diffusion coefficients of [N122][TfO] and [N113][TfO] vs temperature. Experimental data: Yasuda et al.;<sup>1</sup> Lebga-Nebane et al.<sup>4</sup> Prior simulations: Sunda et al.;<sup>5</sup> Chang et al.<sup>6</sup> Statistical uncertainties are smaller than the symbols used.

The calculated self-diffusion coefficients of [N133][TfO] and [N223][TfO] are given in Table 3.4; no experimental data on these PILs are available for comparison. In general, self-diffusion coefficients obtained from VACFs are slightly larger than those obtained from MSD; this discrepancy is consistent with findings from previous studies of ILs.<sup>112,113,132</sup> The Einstein and Green-Kubo methods are theoretically equivalent but exhibit different systematic dependences on simulation time and system size, which can result in slightly different answers.

			TM1		TM2	
PIL	$T(^{\circ}C)$		VACF	MSD	VACF	MSD
[N133][TfO]	50	cation	0.56(2)	0.49(1)	0.52(2)	0.44(1)
		anion	0.51(2)	0.41(1)	0.49(2)	0.36(1)
	90	cation	1.60(4)	1.54(4)	1.59(3)	1.51(4)
		anion	1.48(4)	1.43(4)	1.48(4)	1.35(4)
	130	cation	3.62(6)	3.67(7)	3.54(8)	3.58(8)
		anion	3.47(6)	3.53(8)	3.33(7)	3.35(8)
[N223][TfO]	50	cation	0.53(2)	0.46(2)	0.55(2)	0.42(2)
		anion	0.49(2)	0.41(1)	0.50(1)	0.35(1)
	90	cation	1.57(4)	1.55(3)	1.58(4)	1.42(3)
		anion	1.52(4)	1.43(4)	1.42(4)	1.30(2)
	130	cation	3.52(6)	3.47(9)	3.53(6)	3.42(7)
		anion	3.42(7)	3.45(8)	3.25(6)	3.11(8)

Table 3.4. Self-diffusion coefficients of [N133][TfO] and [N223][TfO]. Units are  $(10^{-6} \text{ cm}^2/\text{s})$ . Uncertainties in the last digit are given in parentheses.

Consistent with results in Figure 3.12, TM1 yields slightly higher diffusivities than TM2; this difference is more pronounced for MSD-derived diffusivities than VACF-derived ones. As expected from the difference in molecular masses, these cations shows higher self-diffusivity than the anion.<sup>6,112,113</sup>

Comparing all four PILs, these simulations predict the trend in diffusivities [N223][TfO] < [N133][TfO] < [N122][TfO] < [N113][TfO] for almost all temperatures. This captures the experimental result <math>[N122][TfO] < [N113][TfO]. Interestingly, cations with the same molecular masses show slightly different diffusivities. [N122] and [N113] have the same molecular mass, but the latter has a slightly higher diffusivity; [N223] and [N133] have the same molecular mass, but the latter has higher diffusivity. It may be that the presence of longer alkyl chains promotes faster diffusion, although the effect may also be due to small differences in density; [N133][TfO] and [N113][TfO] are less dense than [N122][TfO] and [N223][TfO], respectively.

# 3.3.4 Ionic Conductivity

Ionic conductivity is a measure of the ability of a solvent or solute to transport charge and is significant in the application of PILs as electrolytes. The computed ionic conductivities are shown in Figure 3.13 and compared with experiments and previous simulation studies. In both simulations and experiments, the ionic conductivity increases with increasing temperature, which is a direct result of faster ion diffusion at higher temperatures. The ionic conductivities are generally underestimated by both models, except for that of [N122][TfO] at high temperatures. Averaged over the temperature range studied, these simulations underestimate the conductivities of [N122][TfO], [N113][TfO], [N223][TfO], and [N133][TfO] by approximately 25, 35, 25, and 35%, respectively. This is consistent with the results from the  $\gamma$ -calibration (Table 3.2), in which lower values of  $\gamma$  were required to match experimental ionic conductivities than were needed for other quantities. Nevertheless, these results are still a substantial improvement over previous MD studies.<sup>5,6</sup>

The experimental ionic conductivities are ordered as follows: [N223][TfO] < [N133][TfO] < [N122][TfO] < [N113][TfO]. Simulations more or less reproduced this trend at high temperatures. The ionic conductivity depends strongly on the mobility of ions, and PILs with higher diffusivity should exhibit higher conductivity. The large statistical uncertainty in simulation results makes comparison of the two triflate models difficult, but TM1 generally gives higher ionic conductivities and better agreement with experiment than TM2.

Because of strong electrostatic interactions, ions of opposite charges associate to form short-lived neutral clusters, which do not effectively transport charge.<sup>104,112,130</sup> The ECACF,



Figure 3.13. Ionic conductivity v<br/>s temperature. Experimental data: Yasuda et al.;  $^1$ Leb<br/>gane et al. $^4$  MD simulations data: Sunda et al.;<br/>  $^5$  Chang et al. $^6$ 

J(t), can be written as the sum of self-terms Z(t) and cross terms J(t) - Z(t):

$$J(t) = \langle j(t) \cdot j(0) \rangle = \sum_{i}^{N} \sum_{j}^{N} \langle q_{i}q_{j}v_{i}(t) \cdot v_{j}(0) \rangle$$
  
$$= \sum_{i}^{N} \langle q_{i}^{2}v_{i}(t) \cdot v_{i}(0) \rangle + \sum_{i}^{N} \sum_{j \neq i}^{N} \langle q_{i}q_{j}v_{i}(t) \cdot v_{j}(0) \rangle$$
  
$$= Z(t) + (J(t) - Z(t))$$
  
(3.7)

The self term, Z(t), is the total VACF, proportional to the average of the cation and anion VACFs (Figure 3.10). The cross term represents the deviation from ideal Nernst-Einstein



Figure 3.14. Normalized ECACF, J(t), self-term, Z(t), and cross correlation term, J(t) - Z(t), for [N122][TfO] at 50 °C.

(NE) behavior.<sup>124</sup> If the cross term is negligible, then the ionic conductivity is entirely due to self-diffusivity, and the NE equation applies:<sup>124</sup>

$$\sigma_{NE} = \frac{N_{pair}}{Vk_B T} (q_+^2 D_+ + q_-^2 D_-)$$
(3.8)

where  $N_{pair}$  is the number of ion pairs. The cross term, J(t) - Z(t), is a measure of correlated motion. The ratio of actual to NE conductivity,  $Y = \sigma_{GK}/\sigma_{NE}$ , is known as the "ionicity",<sup>8,112,133</sup> which is interpreted as the fraction of ions that contribute to the ionic conductivity. When Y = 1, the cross term in Eq. 3.7 is zero; cations and anions move independently so their motion fully contributes to the ionic conductivity. When Y = 0, the ionic motion is totally correlated such that oppositely charged ions move together, which contributes to mass transport but not charge transport.<sup>104,130</sup> Ionicities calculated for the PILs (50–130 °C) are in the ranges of 0.58–0.87, 0.61–0.67, 0.41–0.77, and 0.62–1.0 for [N122][TfO], [N113][TfO], [N133][TfO], and [N223][TfO], respectively, with Y generally decreasing with increasing temperature. These values imply that correlated ion motion is a significant factor affecting charge transport in these PILs. The correlated motions of cations and anions and their contribution to the ionic conductivity can be better understood by considering the time dependence of the self-term, Z(t), and cross term, J(t) - Z(t), as shown in Figure 3.14. The cross term is negative for times up to around 0.3 ps, indicating positively correlated motion of oppositely charged ions. Such ion clustering appears to be short-lived, however. At longer times, the cross correlation term becomes positive, indicating negatively correlated motion of oppositely charged ions, and very nearly cancels the self-term.

## 3.3.5 Shear Viscosity

Figure 3.15 compares the simulated PIL viscosities with experimental results. Viscosity decreases with increasing temperature. The computed viscosities of [N122][TfO] and [N113][TfO] are in excellent agreement with the experimental data of Yasuda et al.;<sup>1</sup> measurements by Lebga-Nebane et al.<sup>4</sup> are somewhat lower. For [N223][TfO] and [N133][TfO], the viscosity is overestimated by simulation at 50 °C but is in good agreement with experiment at higher temperatures; in general, the deviation between simulation and experiment decreases with increasing temperature. The two triflate models give very similar viscosities over the temperature range studied, with TM1 viscosities slightly higher than those of TM2.

Both experimental and simulated shear viscosities follow the trend [N113][TfO] < [N122][TfO] < [N123][TfO] < [N223][TfO], which is the reverse of the trends displayed by self-diffusivity and ionic conductivity. Viscosity depends on the strength of interionic interactions, including electrostatic forces, van der Waals interactions, and hydrogen bonding. Previous work has shown that increasing the length of alkyl chains in ILs increases the viscosity due to stronger van der Waals interactions, which is consistent with the behavior of these PILs.<sup>41,101,132</sup>



Figure 3.15. Arrhenius plots of shear viscosity. Experimental data: Yasuda et al.;<sup>1</sup> Lebga-Nebane et al.<sup>4</sup>

# 3.4 Conclusions

MD simulations were used to study the structural and transport properties of a family of ammonium-based protic ILs. These PILs consist of the triflate anion and tertiary ammonium cations with different alkyl chains. Two different models for triflate, TM1<sup>117</sup> and TM2,<sup>119</sup> were evaluated. In order to include polarizability and charge-transfer effects, ionic charges were scaled by a uniform factor  $\gamma$ . We derived the optimum  $\gamma$  values for this family of PILs by fitting several properties as functions of  $\gamma$  and interpolating to match experimental data of Yasuda et al.<sup>1</sup> Importantly, this could be done using data from only a single PIL; the chosen  $\gamma$  value of 0.69 was found to be effectively transferable between different tertiary ammonium cations. Selection of  $\gamma$  in this way could be made based on any of several choices of experimental data (or temperature), but in practice the different options were all shown to yield similar values, with the exception of ionic conductivity. This is significant both because it suggests a reasonable physical basis for the charge-scaling approximation and because it removes some arbitrariness from the choice of which experimental data to use to calibrate  $\gamma$ . Although smaller than the popular choice of 0.80, the value of 0.69 is nonetheless well within the range of previously-used charge-scaling factors and, importantly, is comparable with scaling factors and estimates of the amount of charge transfer obtained by some previous studies using electronic structure methods.<sup>101,102,103</sup>

Simulations using scaled charges showed significant improvement in transport coefficients over the previous simulations,<sup>5,6</sup> resulting in better agreement with experiment<sup>1,4</sup> for all quantities considered. This was true for both the [N122][TfO] PIL used for determination of the optimal charge-scaling factor and for the other tertiary ammonium triflates studied.

Simulated densities showed good agreement with experiments, with better results obtained from TM1. However, both models underestimated thermal expansivities. This behavior was found to be independent of the  $\gamma$  value used, suggesting that this effect is not due to charge transfer in the PILs but instead is a feature of the underlying force field. Structural analysis revealed that there is a strong directionality of the interionic interactions, where triflate anions preferred to approach the cations with sulfur atoms coordinating the acidic ammonium proton.

Computed self-diffusion coefficients showed excellent agreement with experiment, with cations diffusing faster than anions in all cases. Self-diffusion coefficients obtained from VACF data tended to be slightly higher than those obtained from MSD. The ionic conductivity was underestimated in most cases, although reasonable agreement was obtained at high temperatures, and TM1 simulations gave higher ionic conductivities than TM2 simulations. This underestimation is consistent with the results from the  $\gamma$ -calibration study, in which lower values of  $\gamma$  were required to match the experimental ionic conductivities than were required to match other quantities, and suggests that quantitative treatment of ionic conductivity may require further modification of the force fields used; this quantity, in particular is likely to be sensitive to ionic charge fluctuations due to polarizability (which are neglected here.) Comparison with the Nernst-Einstein predictions suggests that there is a considerable degree of correlated motion in these PILs, which reduces ionic conductivity. Finally, simulated shear viscosities were in generally good agreement with experimental data, especially at higher temperatures.

In summary, we have demonstrated that selection of the optimal charge-scaling factor for a series of PILs can be accomplished by interpolating simulated data at varying  $\gamma$  so as to match experimental results; that the value thus obtained is reasonably independent of the choice of measurement (diffusion constant, viscosity, etc.) and temperature used; and that the results can be effectively transferred between PILs of closely related structure, in this case several tertiary ammonium cations paired with triflate anions. Good performance on multiple transport quantities over a wide range of temperature is obtained in each case. Of the quantities considered, the density and diffusion constants are the most rapidly and accurately obtained by simulation and may therefore be preferable for use in  $\gamma$ -calibration. In future work, we shall consider the transferability of charge-scaling factors between PILs containing different anions and among a larger range of cations.

### **CHAPTER 4**

# ACID AND BASE NEUTRAL SPECIES IN PROTIC IONIC LIQUIDS: EFFECTS ON STRUCTURE AND TRANSPORT PROPERTIES

## 4.1 Introduction

Protic ionic liquids (PILs) are a subset of ILs in which cations and anions are produced by proton transfer from a Brønsted acid (HA) to a Brønsted base (B):<sup>37</sup>

$$HA + B \rightleftharpoons A^{-} + HB^{+} \tag{4.1}$$

The equilibrium state of the proton transfer reaction depends on the parent acid and base. If the precursor acid (base) is very strong, the equilibrium will lie heavily to the right, leading to an IL composed almost entirely of ions. However, in PILs consisting of weak acids and bases, the reaction may not proceed to completion, resulting in an equilibrium solution of ions and neutral species.<sup>8,134</sup> For example, Doi et al.<sup>135</sup> determined that in the equimolar solution of *N*-methylimidazole with acetic acid, the proton transfer reaction hardly occurs, and neutral molecular species predominate in solution. They suggested that it might be better call such liquids "pseudo-ionic liquids" rather than ionic liquids. MacFarlane and Seddon have suggested that a PIL should be considered "purely ionic" if the proton transfer reaction is 99% complete.<sup>136</sup>

There is no standard method for assessing the degree of proton transfer in PILs, but attempts have been made to characterize this feature. Early on, Yoshizawa et al.<sup>37</sup> introduced the  $\Delta p K_a^{aq}$  measure as an estimate for the degree of proton transfer in PILs, which for Eq. 4.1 is defined:

$$\Delta p K_a^{aq} = p K_a^{aq} (HB^+) - p K_a^{aq} (HA)$$
(4.2)

The larger the value of  $\Delta p K_a^{aq}$  is, the stronger is the proton transfer reaction. Based on their experiments, they suggested that  $\Delta p K_a^{aq} > 10$  is required for a PIL to be considered fully ionic. However, simple equilibrium calculations<sup>134</sup> showed that  $\Delta p K_a^{aq} = 4$  results in 99% proton transfer in aqueous solutions. This implies that the non-aqueous environment in the PIL has a strong effect on the proton transfer, and that the degree of proton transfer strongly depends on the solution environment. Further studies also questioned the validity of  $\Delta p K_a^{aq}$  for determining the degree of proton transfer simply based on dilute aqueous  $p K_a^{aq}$  values as will be discussed shortly. This suggests that a better measure for predicting the degree of proton transfer in PILs is required, which could take into account the solvent effects in PILs media.

Stoimenovski et al.<sup>8</sup> studied the extent of proton transfer in alkylammonium acetate PILs using a probe indicator acid (phenol red) and Walden plot analysis. Their findings, though qualitative, were significant. First, they showed that PILs with similar  $\Delta p K_a^{aq}$  (~ 6) could nonetheless exhibit different degrees of proton transfer, i.e., primary ammoniums had nearly complete proton transfer, while tertiary ammoniums had little proton transfer. Second, primary ammonium PILs with  $\Delta p K_a^{aq}$  (~ 6), lower than the limit proposed by Yoshizawa et al.,<sup>37</sup> exhibited the behavior of a pure ionic liquid. This study raised concerns on the applicability of  $\Delta p K_a^{aq}$  as a reliable estimator for determining the degree of proton transfer in PILs.

Davidowski et al.<sup>137</sup> studied the proton transfer reactions between diethylmethylamine and acids of varying strengths to examine the degree of proton transfer in these PILs. The strengths of acids were determined by the gas phase proton affinities of acids which were calculated by  $\Delta H$  of the protonation of the anions,  $A^-(g) + H^+(g) \rightarrow AH(g)$ . The lower the proton affinity the stronger is the acid. Good correlations were observed between the <sup>1</sup>H chemical shift of the proton on the ammonium cation and the gas phase proton affinities; the lower the proton affinity, the larger the degree of proton transfer. Moreover, the proton chemical shifts showed much better correlations with gas phase proton affinities than with  $\Delta p K_a{}^{aq}$ . This suggests that the gas phase proton affinity is a better predictor of the extent of proton transfer than the  $\Delta p K_a{}^{aq}$  predictor, although still only qualitative. A few studies have attempted to quantify the degree of proton transfer in PILs. Kanzaki et al.<sup>138</sup> studied the extent of proton transfer in PILs consisting of *N*-methylimidazole with acids of varying strengths by means of potentiometric and calorimetric titrations. They observed that in the presence of strong acids such as bis(trifluoromethanesulfonyl)amide and trifluoromethanesulfonic acid, the proton transfer is complete. However, only about 50% proton transfer was estimated from acetic acid (which is a weak acid) to *N*-methylimidazole.

Most recently Shen et al.<sup>139</sup> used total reflection Fourier transform infrared spectroscopy and nuclear magnetic resonance to determine that in N-propylammonium acetate PIL the degree of proton transfer is 93%. This quantitative finding agrees with the qualitative observations of Stoimenovski et al.<sup>8</sup> as mentioned above.

Molecular dynamics (MD) is a powerful technique by which to study liquids under various conditions, including those which may not be experimentally realizable. MD simulations have been used extensively in the study of structure, thermodynamic and transport properties of ILs.<sup>101,112,113,114,115</sup> These simulations have significantly assisted the scientific community to better understand the behavior of these complex liquids. The majority of MD studies have focused on imidazolium based AILs,<sup>102,112,140,141</sup> though MD studies of PILs have also appeared in the literature.<sup>116,142,143,144</sup> In Chapter 3, we studied the structural and transport properties of a family of tertiary ammonium triflate PILs by MD simulations.<sup>143</sup> Our results indicated that a more realistic dynamics with great improvement in transport coefficients can be achieved by applying an optimum uniform scaling (reduction) of atomic partial charges.

To date, no MD study has been performed to address the degree of proton transfer in PILs. This is partly because the popular force fields developed for IL simulations are non-reactive and so cannot be employed to directly simulate the proton transfer reaction in PILs. Furthermore, even if simulations were possible with reactive force fields,<sup>145</sup> the proton transfer reaction itself may be too slow to reach equilibrium given current limitations on the time-scale and size of MD simulations. However, we should note here that the proton transfer reaction itself has been studied using quantum mechanical calculations. For instance, Sun et al.<sup>146</sup> studied proton transfer reaction and its mechanism in three acetate-based PILs. However, this type of study is limited only to a single transfer event which involves only an ion pair and a molecular pair, and cannot determine the equilibrium state of the PIL as a whole.

Here we take a different approach, in which a PIL is simulated at a series of different degrees of proton transfer. Each simulation corresponds to a fixed degree of proton transfer at which PIL properties can be calculated. The degree of proton transfer is controlled by changing the numbers (ratios) of the neutral molecules and ions in the PIL medium. Depending on the extent of the proton transfer simulated, the simulations may contain neutral species, ions, or a mixture of both. Such simulations can give an insight into how the behavior of a PIL will change with varying degree of proton transfer.

We consider two primary ammonium PILs, N-propylammonium and N-butylammonium acetate, and one tertiary ammonium PIL, N,N-dimethylbutylammonium acetate. The amine molecules are N-propylamine [N3], N-butylamine [N4], and N,N-dimethylbutylamine [N114]. The corresponding ammonium ions are N-propylammonium [N3H<sup>+</sup>], N-butylammonium [N4H<sup>+</sup>], and N,N-dimethylbutylammonium [N114H<sup>+</sup>], respectively. The common acid is acetic acid [AcH], which in dissociated form is acetate [Ac<sup>-</sup>]. The chemical structures of these molecules are shown in Figure 4.1. For simplicity, the notations [N3][Ac], [N4][Ac] and [N114][Ac] were chosen to represent N-propylammonium acetate, N-butylammonium acetate, and N,N-dimethylbutylammonium acetate PILs, respectively, at all degrees of proton transfer studied.

MD studies of acetate-based PILs are scarce. Chandran et al.<sup>147</sup> studied the structure and dynamics of tetramethylguanidinium acetate PIL by MD simulations. Strong interactions between the amino group of guanidinium with the acetate anion caused higher cohesive energy density, stronger ion packing, and lower translational and rotational ion mobilities



Figure 4.1. Chemical structures of the molecules and with their abbreviated names.

than in AILs studied. Most recently, Reddy and Malik<sup>144</sup> studied the structure, dynamics and thermophysical properties of five alkylammonium carboxylate PILs, including ethylammonium acetate, and assessed the effects of alkyl chains on both cations and anions on these properties.

Simulations were carried out for each PIL over the full range of proton transfer from zero to 100%, and properties including structure, density, self-diffusion coefficients, viscosity and ionic conductivity measured. Such calculations allowed us to study the systematic effect of the extent of proton transfer on PILs properties, which is not well-understood. Moreover, by applying an interpolation procedure using simulation and experimental data, we were able to estimate the degree of proton transfer in experimental systems. Our results show a clear distinction between primary ammonium and tertiary ammonium PILs, with the former showing complete proton transfer and the latter showing very little proton transfer. This finding is in good agreement with qualitative and quantitative experimental observations.

### 4.2 Computational Methods

Models developed within the OPLS-AA force field<sup>84</sup> were used in this work. The potential parameters developed by Jorgensen et al.<sup>84</sup> were used for the primary ammonium ions,

and the tertiary ammonium ions were modeled with the Lopes and Pádua force field.<sup>117</sup> The neutral amine molecules were modeled with parameters developed by Rizzo and Jorgensen.<sup>148</sup> Acetic acid and the acetate anion were modeled with parameters from Kamath et al.<sup>149</sup> and Chandran et al.,<sup>147</sup> respectively. The acetic acid and acetate force field parameters are given in Appendix B.

Many recent IL simulations have made use of charge scaling.<sup>102,112,113,143</sup> Within this scheme, the partial charges of ions are scaled uniformly from  $\pm 1e$  to  $\pm \gamma e$  by multiplying all the atomic partial charges by a scaling factor  $\gamma$ . The objective of this scaling is to approximately account for polarization and charge-transfer effects without increasing computational cost.<sup>110</sup> Charge scaling has been shown to result in much better estimation of transport properties such as self-diffusion coefficients, viscosity and ionic conductivity.<sup>101,102,112,113,114,115</sup> In Chapter 3, we showed that an optimum charge-scaling factor of 0.69 gave excellent selfdiffusion coefficients and much better results for the viscosity and ionic conductivity of tertiary ammonium triflate PILs than did previous MD studies.

The optimal value of  $\gamma$  depends on the type of the ions in the IL. Following previous MD studies of ILs containing ammonium and acetate ions<sup>101,115</sup>  $\gamma = 0.8$  was used here. Charge scaling was only applied to ions, independent of the degree of proton transfer. This approach has been previously employed in MD simulations of imidazolium based ILs with acetonitrile (neutral) molecules, in which only the partial charges of ions were scaled, and the scaling factor used was independent of the concentrations of the ions and neutrals.<sup>150</sup>

As discussed above, simulations were conducted at different degrees of proton transfer for [N3][Ac], [N4][Ac] and [N114][Ac] PILs. The degree of proton transfer for Eq. 4.1 is simply represented by  $\chi$ :

$$\chi = \frac{N_{\rm ion}}{N_{\rm total}} \tag{4.3}$$

 $N_{\text{ion}}$  is the number of ions, and  $N_{\text{total}}$  is the total number of molecules. Each PIL was simulated at  $\chi = 0, 0.125, 0.25, 0.375, 0.50, 0.625, 0.75, 0.875$  and 1.0.  $\chi = 0$  corresponds
		realized of molecules				
$\chi$	%Proton Transfer	Amine	Acetic Acid	Ammonium	Acetate	
0	0	256	256	0	0	
0.125	12.5	224	224	32	32	
0.25	25.0	192	192	64	64	
0.375	37.5	160	160	96	96	
0.50	50.0	128	128	128	128	
0.625	62.5	96	96	160	160	
0.75	75.0	64	64	192	192	
0.875	87.5	32	32	224	224	
1.0	100.0	0	0	256	256	

Table 4.1. Specifications of each PIL simulated at different  $\chi$ . Number of molecules

to zero proton transfer, a fully neutral non-ionic liquid containing only amine and acetic acid molecules;  $\chi = 1.0$  corresponds to 100% proton transfer, a fully ionic liquid composed entirely of ions. Any  $\chi$  between these two limits implies a liquid mixture containing both ions and neutral molecules. System specifications including  $\chi$ , corresponding proton transfer percentages, and respective numbers of neutrals and ions associated with each  $\chi$  are given in Table 4.1.

MD simulations were performed at 30 °C and 1.0 bar using the LAMMPS package.<sup>121</sup> A system size of  $N_{\text{total}} = 512$  was used throughout, in cubic boxes with periodic boundary conditions in all directions. Standard Lorentz-Berthelot mixing rules were used to derive the cross interaction LJ parameters between different atom types. A cutoff distance of 12 Å was used for both the LJ and the real part of the Coulomb pairwise interactions. The particle-particle particle-mesh (PPPM) solver<sup>88</sup> was employed to handle long-range electrostatic interactions with a precision of  $10^{-5}$  beyond the cutoff distance. Long-range LJ tail corrections were added to the energy and pressure of the system.

The reverse reference system propagator algorithm (RESPA),<sup>90</sup> a multiple time step integrator, was used to integrate the equations of motion. Nonbonded interactions beyond the cutoff distance of 12 Å were integrated with a time step of 5 fs. Nonbonded interactions within the cutoff distance were evaluated every 2.5 fs. Dihedral interactions were updated every 1.25 fs, and bonding and angle bending terms were evaluated every 0.625 fs. All bonds containing hydrogen were constrained using the SHAKE algorithm,<sup>92</sup> with a tolerance of  $10^{-4}$  and maximum iteration of 20. In Chapter 3, these parameters were shown to give excellent energy conservation and a ~ 2.5× speedup compared with Verlet integration with a 1 fs time step.<sup>143</sup> The Nosé-Hoover thermostat<sup>95,123</sup> and barostat were used to keep the temperature and pressure constant, with damping factors of 0.5 and 1.0 ps, respectively.

We used PACKMOL<sup>122</sup> to set up the initial configurations. These were first relaxed using conjugate gradient energy minimization, and then annealed by heating the system from 303 to 500 K and cooling to the target temperature over 2 ns. Annealing was done in the isobaric-isothermal (NPT) ensemble. The resultant configuration was then used as the input in an NPT equilibration run of 10 ns duration in which the density information was recorded during the last 4 ns.

Production runs were performed in the canonical (NVT) ensemble. To obtain better statistics, we carried out 30 independent NVT runs for each system. To initialize these, the final configuration obtained from the equilibrium run was first resized to match the 4 ns recorded average density. 30 replicas were then made with particle velocities independently resampled from the Maxwell-Boltzmann distribution. These were each run for a further 4 ns of equilibration, and followed by 10 ns of simulation over which data were collected.

The Green-Kubo relations<sup>70,72,74,124</sup> were used to calculate transport coefficients from the running time integrals of the corresponding autocorrelation functions. The self-diffusion coefficients, D, were calculated using the time integral of the velocity autocorrelation function. The ionic conductivity,  $\sigma_{GK}$ , was calculated through the time integral of the electric current autocorrelation function. The shear viscosity,  $\eta$ , was calculated from the time integral of the autocorrelation function of six independent terms of the pressure tensor. The formulas for calculating the transport coefficients, and post-processing procedure are all given in the previous chapter. The statistical uncertainties reported for each quantity are  $\pm \frac{2\sigma}{\sqrt{n}}$ , where  $\sigma$  is the standard deviation of the values obtained from each of the n = 30 runs.



Figure 4.2. Coordination numbers  $(CN_{x-y})$  of species x with species y as functions of  $\chi$  in [N3][Ac].

## 4.3 Results and Discussion

# 4.3.1 Structure

We first analyze the main structural features of these PILs by calculating the coordination numbers, pair radial distribution functions (RDFs), and spatial distribution functions (SDFs). No sign of phase separation was observed during the simulations of all PILs at all  $\chi$ , indicating that the neutral species and ions are fully miscible.

To illustrate the  $\chi$  dependence of the solution environment around each species, coordination numbers ( $CN_{x-y}$ ) were calculated over the entire range of  $\chi$ . Center-of-mass intermolecular distances (7.0 Å) were used for calculating the coordination numbers. Figure 4.2



Figure 4.3. Coordination numbers  $(CN_{x-y})$  of species x with species y as functions of  $\chi$  in [N4][Ac].

shows the variation of the coordination numbers of each species in [N3][Ac] with all other species as a function of  $\chi$ .

We first begin with the evolution of the first coordination shell of amine as  $\chi$  changes. At  $\chi = 0$ , more acid molecules are found in the coordination shell of amine than amine molecules, due to favorable hydrogen bonding interactions between amine and acetic acid molecules. This can be clearly seen in the site-site RDFs (not shown) as strong peaks between nitrogen of amine with acidic hydrogen of acetic acid, located roughly at 2.0 Å. As  $\chi$  increases the coordination with neutrals becomes weaker, while coordination with ions becomes stronger due to the decreasing number of neutral species and growing number of ions. At  $\chi > 0.5$ , ions predominate the coordination shell. As  $\chi$  increases more, amine



Figure 4.4. Coordination numbers  $(CN_{x-y})$  of species x with species y as functions of  $\chi$  in [N114][Ac].

coordinates more strongly with ammonium than acetate. Similar changes and trends are also observed in the coordination shell of acetic acid.

In the ammonium coordination profile, at  $\chi < 0.5$ , ammonium ion preferentially coordinates more strongly with acetic acid than amine. At  $\chi > 0.5$ , ions predominate in the coordination shell, and acetate ions are significantly more common than ammonium ions due to strong attractive Coulomb and hydrogen bonding interactions with ammonium. Very similar behavior is observed in the acetate coordination shell. Moreover, similar changes and trends are also observed for [N4][Ac], shown in Figure 4.3, and for [N114][Ac] in Figure 4.4.

Strong hydrogen bonds exist between ions in these PILs.<sup>146</sup> The ammonium ions act as hydrogen-bond donors through their acidic hydrogens (H), and the acetate ions act as



Figure 4.5. SDFs of acetate oxygens around a reference ammonium ion for [N3][Ac], [N4][Ac] and [N114][Ac] at  $\chi = 0.5$ . Iso-surface value is 0.02 Å<sup>-3</sup>. SDFs were calculated with Travis<sup>2</sup> and visualized in VMD.<sup>3</sup>

hydrogen-bond acceptors through their oxygens (O). To have a better picture of the spatial distributions of these interactions, the SDFs of O atoms around a reference ammonium ion were calculated for each PIL at  $\chi = 0.5$ , shown in Figure 4.5. SDFs show the probability of finding a particle at a certain position in space around a fixed reference particle, and thus provide additional orientational information not present in RDFs.<sup>2</sup> Three major regions of hydrogen bonding are observed for [N3][Ac] and [N4][Ac], while only one is seen for [N114][Ac]. This depicts a significant difference in hydrogen bonding between the primary ammonium and tertiary ammonium PILs, with the former showing more hydrogen bonds. The reason is that in the primary ammonium PIL, the ammonium ion has multiple hydrogen bond donor sites (three H atoms) available to interact with O atoms, while the tertiary ammonium only has a single H that can interact with a neighboring acetate.

To show this quantitatively, we used a distance criterion ( $r_{\text{H-O}} < 2.4$  Å) to measure the number of hydrogen bonds between ions<sup>116</sup> in each PIL. At  $\chi = 0.5$ , each O atom of acetate on average accepts 1.3, 1.3, and 0.6 hydrogen bonds from ammonium ions in [N3][Ac], [N4][Ac], and [N114][Ac], respectively. This clearly shows that in the primary ammonium PILs, more hydrogen bonds exist between cations and anions than in the tertiary PIL.



Figure 4.6. Site-site RDFs for simulated PILs at  $\chi = 1.0$ . N represents the nitrogen of ammonium ion. O and C1 represent the oxygen and carbon atoms of carboxylate group in acetate anion, respectively. C2 represents the carbon of the methyl group in acetate anion.

Strong directionality is also observed in interactions between ions, as acetate ions approach ammonium ions with their carboxylate group. This is clearly seen in site-site RDFs, shown in Figure 4.6, where the position of the N(ammonium)-O(carboxylate) peak appears first at the lowest distance, the N(ammonium)-C(carboxylate) peak occurs at larger distance, and lastly the N(ammonium)-C(methyl group) peak occurs at the largest distance. This structural feature was also observed in tertiary ammonium triflate PILs in Chapter 3, in which triflate ions preferentially approached ammonium ions with their sul-

fonate groups.<sup>6,116,143</sup> Such directionality is driven by strong hydrogen bonds between specific groups in ions as explained earlier.

### 4.3.2 Density

Figure 4.7 shows the variation of density with  $\chi$  for simulated PILs. As  $\chi$  is increased the density of the PILs in all cases increases in a nearly linear fashion. This increase is due to electrostatic interactions between the increasing number of ions, which decreases interionic separation and enhances packing. For primary ammonium PILs, the simulations underestimate the experimental results, even at  $\chi = 1.0$ . Deviations between experiment and simulations at 100% proton transfer are 3.3% and 1.3% for [N3][Ac] and [N4][Ac] PILs, respectively.

To better understand the discrepancy between simulation and experiment we also simulated the pure liquids [AcH], [N4] and [N114] at 25 °C and 0.1 MPa. Simulated densities of 1.053, 0.737 and 0.724 g/mL were obtained for pure [AcH], [N4] and [N114], respectively. The corresponding experimental densities are 1.051,<sup>151</sup> 0.74,<sup>151</sup> and 0.721 g/mL.<sup>151</sup> The simulated densities of pure neutral liquids are thus in excellent agreement with experimental data. This clearly shows that the force fields used here reproduce the experimental density of the neutral species well, suggesting that underestimation of PIL densities is due to the ionic part of the force field or to ion-neutral interactions. To test if this underestimation is caused by the charge scaling of ions we also performed simulations at  $\chi = 1.0$  and without charge scaling for [N3][Ac] and [N4][Ac]. Simulated densities were higher in this case, but still underestimated the experiment, with deviations of 1.7% and 0.9% for [N3][Ac] and [N4][Ac], respectively. Recently, Reddy and Mallik<sup>144</sup> observed comparable density underestimations in simulations of primary ammonium carboxylate PILs including ethylammonium acetate. This suggests that the underlying force field for ammonium and acetate ions could be improved, but this was not attempted here.



Figure 4.7. Density as a function of  $\chi$  for the simulated PILs. The experimental density for [N3][Ac] is taken from Chhotaray and Gardas;<sup>7</sup> [N4][Ac] and [N114][Ac] are taken from Stoimenovski et al.<sup>8</sup> Uncertainties are smaller than the symbols used.

## 4.3.3 Self-diffusion Coefficients

The self-diffusion coefficients of neutral species and ions in each PIL are shown in Figure 4.8. No experimental data was found for comparison. Generally the self-diffusion coefficients of all species decrease as the degree of proton transfer increases. This indicates that the dynamics of each PIL slows down as the PIL becomes more ionic. The PILs have the slowest dynamics at complete proton transfer. The increase of ion diffusion coefficients by neutral species is well-known from MD studies of ILs containing molecular cosolvents such



Figure 4.8. Self-diffusion coefficients as functions of  $\chi$ . Uncertainties are smaller than the symbols used.

as water<sup>6,152,153</sup> and acetonitrile.<sup>150</sup> Neutral molecules screen electrostatic interactions and disturb ion associations in ILs which leads to greater ion mobility and lowers viscosity.

Neutral species diffuse much faster than their ionic counterparts. For example, in [N3][Ac], amines diffuse 2-5 times faster than ammonium ions (depending on  $\chi$ ), and acetic acid diffusion constant is 2-3 times higher than acetate ion. Amines show higher diffusivity than acetic acid for all PILs, at all  $\chi$ , except in [N4][Ac] and [N114][Ac] at  $\chi = 0$ . We believe that at  $\chi = 0$  the diffusivities of neutrals are influenced more by their molecular mass; the acetic acid diffuses faster than amines in [N4][Ac] and [N114][Ac] because it is lighter. However, at higher  $\chi$ , the slower diffusion coefficient of acetic acid may be due to its stronger hydrogen bonding interactions with ionic species, especially with acetate<sup>154</sup> in PIL solutions. The slower diffusivity of ions than neutrals is related to stronger electrostatic and hydrogen bonding interactions between ions.

The diffusion constants of cation and anion are nearly identical at all  $\chi$  which indicates that "correlated motion" of ions is significant here. Such correlated motion can happen in the form of "ion pairing" which may be a further cause of reduced diffusion of these species. We will discuss correlated motions of ions further in Section 4.3.6.

### 4.3.4 Viscosity

The shear viscosities of the simulated PILs are shown in Figure 4.9. The experimental viscosity is shown for comparison in each plot. Viscosity increases dramatically with increasing  $\chi$ . The addition of molecular (neutral) solvents in IL solutions has been shown to have a "diluting" effect on IL solutions which promotes ion mobility through dissociation of ions, resulting in a lower viscosity.<sup>150,154</sup> For instance, Renda et al.<sup>154</sup> observed experimentally that the viscosity of 1-ethyl-3-methylimidazolium acetate IL decreased upon addition of acetic acid to the IL solution. Chaban et al.,<sup>150</sup> in MD simulations of imidazolium-based ILs, demonstrated that the viscosity of simulated ILs decreases with increasing concentration of acetonitrile. In an experimental study of acetate-based PILs, Almeida et al.<sup>51</sup> suggested that the presence of neutral species in these PILs due to the lack of complete proton transfer could be the major reason for their lower viscosity compared to the highly ionic AILs studied.

Viscosity depends on intermolecular interactions such as hydrogen bonding, and liquids with stronger hydrogen bonding interactions should display higher viscosity.<sup>41</sup> The primary ammonium acetates PILs have higher viscosity than the tertiary ammonium acetate PIL at every  $\chi$ . This difference can be related to their hydrogen bonding network structure (as explained in Section 4.3.1) in which the primary ammonium PILs make more hydrogen bonds than the tertiary ammonium PIL.



Figure 4.9. Viscosity of simulated PILs. Experimental viscosities for [N3][Ac] are taken from Chhotaray and Gardas,<sup>7</sup> [N4][Ac] from Xu,<sup>9</sup> and [N114][Ac] from Stoimenovski et al.<sup>8</sup> The vertical scale is logarithmic.

## 4.3.5 Ionic Conductivity

Figure 4.10 shows the variation of the ionic conductivity of the simulated PILs as a function of  $\chi$ . At  $\chi = 0$  there are no charge carriers (ions) and so the conductivity is zero. As  $\chi$  increases the conductivity increases in an initially linear fashion until a maximum is reached, after which conductivity decreases with further increase in  $\chi$ . This initial increase reaches maxima at 37.5%, 25% and 50% proton transfer for [N3][Ac], [N4][Ac] and [N114][Ac], respectively.

The ionic conductivity is affected by two competing factors. On one hand, the number of charge carriers (ions) increases with  $\chi$ , which increases the ionic conductivity. On the other



Figure 4.10. Ionic conductivity of simulated PILs. The experimental conductivity for [N3][Ac] is taken from Chhotaray et al.;<sup>10</sup> [N4][Ac] and [N114][Ac] are taken from Stoimenovski et al.<sup>8</sup>

hand, the dynamics becomes significantly slower as  $\chi$  increases. The diffusion constants of the charge carriers decrease rapidly with  $\chi$ , which leads to the decreasing conductivity observed at high  $\chi$ . Despite the increasing number of charge carriers, the conductivity is more influenced by the mobility of these ions at this range.

Interestingly our ionic conductivity profiles are similar to those observed by Chaban et al.<sup>150</sup> in MD simulations of dialkylimidazolium tetrafluoroborate IL mixtures with acetonitrile at varying mole fractions of ions and acetonitrile. Acetonitrile had a similar effect on ionic conductivity as the neutrals do here. With increasing mole fraction of ions (decreasing mole fraction of acetonitrile), the ionic conductivity of ILs first increased to a maximum and then decreased.

## 4.3.6 Ionicity

Ionicity is an important feature of ILs, defined as the effective fraction of ions that are available to participate in the conduction process.<sup>52</sup> Some percentage of ions do not contribute to conduction due to strongly correlated motions (ion associations), lack of complete proton transfer (presence of precursor neutral species), or a combination of these two.<sup>8,16,52</sup> Ion pairing is the simplest type of ion association, and long-lived ion pairs which are (net) neutral will not contribute to conduction.<sup>52</sup> Other forms of ion association may also appear, including clusters or aggregates involving larger groups of ions.<sup>16,52</sup> Generally, these associations can impact ionic conductivity in two ways. On one hand they decrease the mobility and independence of ions, and on the other hand, the net charge of these ionic associations is close to zero, both of which decrease the conductivity.<sup>52</sup>

Ionicity in ILs can be qualitatively demonstrated by the use of Walden plots.<sup>8,37</sup> In this approach, the Walden rule is used:

$$\Lambda \eta = k \tag{4.4}$$

Λ is molar conductivity,  $\eta$  is viscosity, and k is a constant. Λ is obtained by dividing the ionic conductivity by the molarity of the solution, which here is the total concentration of ions and neutrals per liter. The Walden rule was originally introduced for dilute aqueous solutions, but has found widespread application in ILs.<sup>8,37,52</sup> A Walden plot is constructed by plotting log Λ vs. log  $\frac{1}{\eta}$ , thus showing a simple relationship between these two transport properties. Data from 0.01 M aqueous KCl solution are used to make a reference line with unity slope.<sup>37</sup> This line represents the behavior of an ideal electrolyte solution in which ions move independently and their motion fully contributes to conductivity. Any negative deviation from the reference line is an indication of ionicity lower than ideal Walden behavior



Figure 4.11. Walden plots for PILs at different  $\chi$ .

which could be due to ion associations, or incomplete proton transfer, or a combination of these effects.<sup>16,37,52</sup> The negative (vertical) deviation from the reference line,  $\Delta W$ , has been taken as a measure of ionicity for ILs.<sup>37</sup> For example,  $\Delta W = 1$  means an IL showing only 10% of the conductivity it would exhibit if behaved ideally. Many ILs fall below this line due to ion associations in various forms.<sup>16,37,41</sup> Many PILs even fall further below due to incomplete proton transfer.<sup>8,37,52</sup>

First we constructed Walden plots for each simulated PIL at different  $\chi$ , as shown in Figure 4.11. All PILs fall below the reference line at all  $\chi$ , showing that their molar conductivity is lower than that expected from their fluidity  $(\eta^{-1})$ . The effect of  $\chi$  on ionicity of these PILs



Figure 4.12.  $\Delta W$  as a function of  $\chi$  for simulated PILs.

can be better shown by extracting  $\Delta W$  at each  $\chi$ . Figure 4.12 shows the variation of  $\Delta W$  with  $\chi$  for these PILs. Strong correlations are observed between  $\Delta W$  and  $\chi$ . As  $\chi$  increases, the ionicity of PIL is increased. Lower ionicity (larger  $\Delta W$ ) at lower  $\chi$  is mainly due to the presence of neutral molecules. The highest ionicity is observed at complete proton transfer, but still shows some deviation from the ideal behavior, presumably due to some form of ion association.

In Section 4.3.3 we showed that the cation and anion diffusion constants are nearly identical, indicating strong correlated motion of these species. To show these correlations better, we use the ionicity  $Y = \sigma_{GK}/\sigma_{NE}$ , introduced in the previous chapter, to quantify the degree of correlated motions of ions in these PILs. If  $Y \sim 1$  then the majority of cations



Figure 4.13. Y as a function of  $\chi$  for simulated PILs.

and anions move independently (their motion is uncorrelated) which contributes the most to ionic conductivity. If  $Y \sim 0$ , the ionic motion is totally correlated such that ions move together in the form of "ion pairs" or other associations, which contributes the least to the conductivity.

Y values are depicted in Figure 4.13 for all PILs at all  $\chi$ . Generally, Y increases with increasing  $\chi$ , reflecting less correlated motion of ions. This indicates that at lower  $\chi$  one is more likely to witness ion pairing or other types of ion association than at higher  $\chi$ , though the change in Y is relatively small.



Figure 4.14. Linear fits and interpolations of  $\chi$  corresponding to experimental ionic conductivity  $\sigma$ , and viscosity  $\eta$  for [N3][Ac] and [N4][Ac].

### 4.3.7 Estimation of Equilibrium $\chi$ in Experimental Systems

Here we try to estimate the  $\chi$  in experimental systems ( $\chi_{expt}$ ) using an interpolation procedure. In this procedure, simulation data including density, conductivity and viscosity were first fit to linear functions of  $\chi$ . Following this, the  $\chi$  corresponding to observed experimental density, etc., were obtained from the linear fits. At points where the experimental data is beyond the simulation data range (density in [N3][Ac] and [N4][Ac]), or the estimated  $\chi_{expt}$  lies beyond the proton transfer range (viscosity in [N3][Ac] and conductivity in [N4][Ac]) complete proton transfer ( $\chi_{expt} = 1.0$ ) is assumed. Figure 4.14(a) shows the linear fit of conductivity data for [N3][Ac]. Figure 4.14(b) shows the linear fit of viscosity data for [N4][Ac]. Figure 4.15 shows linear fits of density, conductivity and viscosity data for [N114][Ac]. Table 4.2 shows the  $\chi_{expt}$  values predicted in this way.

In [N3][Ac] and [N4][Ac], the  $\chi_{expt}$  values obtained from density, viscosity and ionic conductivity are all equal to 1. In [N114][Ac],  $\chi_{expt}$  obtained from conductivity and viscosity agree to their uncertainty, but  $\chi_{expt}$  by density is slightly higher. This disagreement may be due to the underestimation of density by the force field used as explained in Section 4.3.2. Improved performance of the force field will likely decrease the  $\chi_{expt}$  obtained from density.



Figure 4.15. Linear fits and interpolations of  $\chi$  corresponding to experimental (a) density  $\rho$ , (b) viscosity  $\eta$ , and (c) ionic conductivity  $\sigma$  for [N114][Ac].

Table 4.2. Estimated  $\chi_{expt}$  from density data  $\chi_{expt}(\rho)$ , viscosity data  $\chi_{expt}(\eta)$ , conductivity data  $\chi_{expt}(\sigma)$ , and averaged  $\overline{\chi}_{expt}$ .

PIL	$\chi_{ m expt}( ho)$	$\chi_{ m expt}(\eta)$	$\chi_{ m expt}(\sigma)$	$\overline{\chi}_{\mathrm{expt}}$
[N3][Ac]	1.0	1.0	$0.94{\pm}0.16$	0.98
[N4][Ac]	1.0	$0.96 {\pm} 0.04$	1.0	0.99
[N114][Ac]	$0.34{\pm}0.01$	$0.10 {\pm} 0.04$	$0.07 {\pm} 0.03$	0.17

There is a substantial difference in the predicted degree of proton transfer between the primary ammonium and tertiary ammonium acetate PILs. For [N3][Ac] and [N4][Ac] we predict nearly complete proton transfer, while for [N114][Ac] there is very little proton transfer. This result is consistent with recent experimental findings. Stoimenovski et al.<sup>8</sup> showed that the proton transfer is close to complete for primary ammonium acetate PILs, including [N4][Ac]. Shen et al.<sup>139</sup> also predicted that 93% of species are ions in [N3][Ac] which is in reasonable agreement with our finding of nearly complete proton transfer in this PIL.

The estimated  $\chi$  for the tertiary ammonium PIL [N114][Ac] is quite low. Stoimenovski et al.<sup>8</sup> concluded that little proton transfer takes place in tertiary ammonium acetate PILs, including [N114][Ac]. The difference in proton transfer between primary and tertiary PILs has been previously explained based on hydrogen bonding.<sup>8</sup> Stronger proton transfer in the primary ammonium acetate PILs originates from the stronger solvation of primary ammonium and acetate ions due to better hydrogen bonding (as explained in Section 4.3.1). This energetically favors the formation of more ions. In the tertiary ammonium case, frustrated hydrogen bonding provides a less-stabilising solvent environment and hence inhibits proton transfer.

### 4.3.8 Sensitivity to Charge-Scaling Factor

Results presented so far were all obtained with a charge-scaling factor of  $\gamma = 0.8$ . Here we examine the effect of this factor on PIL properties and  $\chi_{expt}$ . For this purpose, we performed simulations for [N4][Ac] and [N114][Ac] at  $\gamma = 0.7$ .

Figure 4.16 shows the effect of  $\gamma$  on different properties of PILs. Generally, PILs show higher density, higher viscosity, and lower conductivity at  $\gamma = 0.8$  than at  $\gamma = 0.7$ , mainly due to stronger electrostatic interactions. Data at these two  $\gamma$  are qualitatively similar. These plots clearly show that the effect of the scaling factor is magnified as  $\chi$  increases. These findings are consistent with previous simulations of pure ILs,<sup>110</sup> and our work in Chapter



Figure 4.16. Effect of charge-scaling factor  $\gamma$ , on density  $\rho$ , viscosity  $\eta$ , and ionic conductivity  $\sigma$  of simulated PILs.

3 on pure tertiary ammonium triflate PILs where density and transport properties showed strong dependence on  $\gamma$ .

We used the data at  $\gamma = 0.7$  to re-estimate  $\chi_{expt}$ . In [N4][Ac], the experimental density and viscosity are beyond the simulated data, and for conductivity the estimated  $\chi$  is found beyond the  $\chi$  range, so complete proton transfer is assumed here, very similar to  $\gamma = 0.8$ . In [N114][Ac], estimated  $\chi_{expt}$  of  $0.43\pm0.01$ ,  $0.16\pm0.02$  and  $0.06\pm0.02$  were derived from density, viscosity and conductivity data, respectively. The averaged  $\chi_{expt}$  at  $\gamma = 0.7$  ( $\overline{\chi} = 0.22\pm0.05$ ) is only slightly higher than average  $\chi_{expt}$  with  $\gamma = 0.8$  ( $\overline{\chi} = 0.17\pm0.08$ ).

The standard Gibbs free energy change ( $\Delta G^{\circ}$ ) for the reaction in Eq. 4.1 can be calculated by  $\Delta G^{\circ} = -RT \ln K$ .<sup>155</sup> K is the equilibrium constant, R is the gas constant, and T is the absolute temperature. In a rough approximation, assuming ideal solution behavior here, K can be estimated as  $K = \frac{[A^-][HB^+]}{[HA][B]}$ . Following this,  $\Delta G^{\circ}$  values of 6.4 and 8.0 kJ/mol are obtained for  $\gamma$  values of 0.7 and 0.8, respectively. This shows a difference of only 1.6 kJ/mol which is quite small. This indicates that  $\chi$  predicted for these PILs is not very sensitive to  $\gamma$ , if  $\gamma$  is applied in the 0.7–0.8 range often used in simulations.

## 4.4 Conclusions

We have examined the systematic effects of the degree of proton transfer  $\chi$  in two primary ammonium acetate PILs, [N3][Ac] and [N4][Ac], and one tertiary ammonium acetate PIL, [N114][Ac]. Simulations were carried out for each PIL ranging from  $\chi = 0$ , zero proton transfer (a liquid of neutral molecules), to  $\chi = 1.0$ , 100% proton transfer (a fully ionic liquid). PILs properties including density, self-diffusion constants, shear viscosity and ionic conductivity were calculated at each  $\chi$ , and their variation with  $\chi$  was studied.

Structural analysis showed that with increasing  $\chi$ , the first solvation shell of all species becomes more ionic. Strong hydrogen bonding interactions were observed between ammonium and acetate ions in these PILs. In primary ammonium PILs [N3][Ac] and [N4][Ac], more hydrogen bonds exist between ions than the tertiary [N114][Ac], indicating stronger hydrogen bonding in the former. This mainly originates from the higher number of available hydrogen-bond donors on the primary ammonium (three acidic hydrogens) than the tertiary ammonium (one acidic hydrogen) to interact with neighboring acetate ions.

Density increases almost linearly with increasing  $\chi$ . PILs are denser at higher  $\chi$  because of stronger electrostatic interactions caused by increasing number of ions. Our simulations underestimated the density of [N3][Ac] and [N4][Ac] compared to experiment, even at  $\chi = 1$ . This result, along with recent density underestimations in primary ammonium carboxylate systems,<sup>144</sup> suggests that further tuning of the force field parameters for primary ammonium and acetate ions may be needed in order to match the experimental densities.

Diffusion constants of all species in PIL solutions decrease with increasing  $\chi$ . This shows that the dynamics of these liquids slow down as they become more ionic. The neutral species facilitate the diffusion of ions as  $\chi$  decreases. The neutral molecules also show greater diffusivity than the ionic counterparts at all  $\chi$ . Ions exhibit very close diffusion coefficients at all  $\chi$ , indicating that "ion pairing" may happen in these PILs to some extent.

Viscosity increases rapidly with increasing  $\chi$ . The neutral molecules enhance the mobility of ions which results in lower viscosity. As  $\chi$  increases, more neutral molecules are replaced with ions and so these effects are diminished, and viscosity increases.

The dependence of ionic conductivity on  $\chi$  is more complex. Conductivity is determined by an interplay between the number of charge carriers and their mobility. At first, the conductivity increases steadily to a certain (maximum) point due to increasing number of charge carriers. However, following this, the conductivity starts decreasing because the mobility of ions decreases rapidly with  $\chi$ .

We used Walden plots to analyze the effect of  $\chi$  on ionicity of these PILs. All these PILs fall below the reference line at all  $\chi$  reflecting non-ideal behavior. The ionicity of these PILs all increase with  $\chi$ , indicating that more ions contribute to conduction. Ionicity is significantly lower at low  $\chi$ , mainly due to the presence of neutral species. At complete proton transfer ionicity is maximal, but still shows some deviation from the ideal electrolyte solution behavior. Analysis of correlated motion of ions also revealed that these effects are more significant at lower  $\chi$ .

Finally we used simulated data to estimate  $\chi$  in corresponding experimental systems through an interpolation procedure. The simulation data including density, viscosity, conductivity were fit to linear functions against  $\chi$ , and  $\chi$  in the experimental system was then interpolated by using experimental data for each quantity. Average  $\chi$  values of  $0.98 \pm 0.16$ ,  $0.99 \pm 0.04$  and  $0.17 \pm 0.08$  were obtained for [N3][Ac], [N4][Ac], and [N114][Ac], respectively. This shows a significant difference in the proton transfer of the primary and tertiary ammonium PILs. Primary ammonium PILs exhibit almost complete proton transfer, while the tertiary ammonium PIL shows little proton transfer.

This work showed that MD simulations can be effectively used to study the effect of the degree of proton transfer in PILs which cannot be directly studied in experiment. The extent

of proton transfer can strongly affect the structure and transport properties of these PILs. This approach can be used to study the effect of the degree of proton transfer on other PIL properties such as surface tension, thermal conductivity, etc.

### CHAPTER 5

# THERMODYNAMICS OF ACID-BASE EQUILIBRIA IN PROTIC IONIC LIQUIDS

### 5.1 Introduction

Protic ionic liquids (PILs) are a subset of ionic liquids (ILs) made by the combination of a Brønsted acid (HA) with a Brønsted base (B), such that ions are formed by proton transfer between the two.<sup>37</sup> As discussed in previous chapters, the proton transfer reaction may not be complete in some PILs, resulting in an equilibrium state between neutral precursor molecules and ions:

$$HA + B \rightleftharpoons A^{-} + HB^{+} \tag{5.1}$$

The equilibrium constants  $(K_{\rm IL})$  for these reactions can be estimated in aqueous media as will be shown below; however, they are not known in PIL environments, which are non-aqueous solutions of both reactants and products. The extent of the proton transfer reaction in various PILs has been studied experimentally and to some extent theoretically as discussed in Chapter 4, but no one has measured equilibrium constants in PIL media.

An approximate  $K_{\text{IL}}$  may be obtained by appropriate combination of the aqueous acid dissociation  $(K_{a}^{\text{aq}})$  reactions:

$$\mathrm{HA} + \mathrm{H}_{2}\mathrm{O} \implies \mathrm{A}^{-} + \mathrm{H}_{3}\mathrm{O}^{+} \qquad K_{\mathrm{a}}^{\mathrm{aq}}(\mathrm{HA})$$
(5.2)

$$HB^{+} + H_{2}O \rightleftharpoons B + H_{3}O^{+} \qquad K_{a}^{aq}(HB^{+}) \qquad (5.3)$$

$$HA + B \rightleftharpoons A^{-} + HB^{+} \qquad K_{IL}^{aq} = \frac{K_{aq}^{aq}(HA)}{K_{a}^{aq}(HB^{+})}$$
(5.4)

Here  $K_{\rm IL}{}^{\rm aq}$  is the equilibrium constant of the proton transfer reaction in water.  $K_{\rm IL}{}^{\rm aq}$ , however, is a very poor approximation of the equilibrium constant in PIL media since the solvation environment in PILs is substantially different than water, and so the acidity constants of species in PILs and aqueous media may differ significantly. Therefore, determining the actual equilibrium constants ( $K_{\rm IL}$ ) in PIL media is of high significance. The standard Gibbs free energy change ( $\Delta G^{\circ}$ ) associated with the proton transfer reaction is the key thermodynamic quantity by which one could measure the true equilibrium constant in PIL media through the well-known Gibbs free energy relation at chemical equilibrium:<sup>155</sup>

$$\Delta G^{\circ} = -RT \ln K \tag{5.5}$$

where R is the gas constant and T is the absolute temperature. In this chapter, we introduce a thermodynamic cycle (Figure 5.1) by which to calculate the  $\Delta G^{\circ}$  of the proton transfer reaction, and eventually predict the equilibrium constant and the degree of proton transfer for a typical PIL solution.

Prior molecular simulation studies of PILs have addressed many of their structural, transport and thermodynamic properties but have not addressed proton-exchange equilibria in any systematic way. The only prior MD study of proton transfer equilibria in ILs is that of Klähn et al.<sup>156</sup> who determined the free energy of proton transfer from positively charged tryptophan (HTrp<sup>+</sup>) to the anions in two ILs 1-butyl-3-methylimidazolium (BMIM) tetrafluoroborate and BMIM hexafluorophosphate using a thermodynamic cycle approach. In these calculations the absolute free energies of solvation (in the ILs) of all reacting species were determined by simulating transfer from the gas phase into solution, with the gas phase reaction free energy determined using electronic structure methods. Proton transfer from HTrp<sup>+</sup> to the IL anions was found to be disfavored due to the production of neutral species in a highly ionic environment.

In this work, we try to determine the reaction free energy and the degree of proton transfer for trimethylammonium acetate [N111][Ac] PIL using a thermodynamic cycle and constrained molecular dynamics (CMD) simulations. We will discuss all the details regarding these calculations in next section. [N111][Ac] is a tertiary ammonium acetate PIL. These are known for their low degree of proton transfer,<sup>8</sup> but no quantitative measurement has been

done to determine how low it might be. These calculations can provide us with a better picture of the acid-base equilibrium in PILs with partial proton transfer.

CMD simulations can be used to study solute transfer across liquid/liquid interfaces. In conventional CMD, the transferring molecule is constrained at different positions along a reaction coordinate, and at each position the average force on the molecule is computed and integrated to yield a free energy profile also known as the potential of mean force (PMF).<sup>157</sup> The mechanisms and thermodynamics of transfer of various species across liquid/liquid interfaces have been studied extensively by computing such free energy profiles.<sup>158,159,160</sup> Numerous studies have been done on ion transport across the interface between water and immiscible organic solvents.<sup>161,162,163,164</sup> CMD simulations have also been employed in studying gas adsorption processes into ILs by computing free energy profiles of the gas species across gas/IL interfaces.<sup>165,166,167</sup>

# 5.2 Computational Methodology

### 5.2.1 Thermodynamics

The following thermodynamic cycle will be used to determine the reaction free energies of proton transfer in the ionic liquid medium. This is an indirect scheme based on calculating the work required to transfer the species involved in a given reaction between different environments, here aqueous and PIL media, as shown in Figure 5.1. Here il indicates species in the ionic liquid solution and aq indicates aqueous solution. The desired reaction free energy for the proton transfer in PIL medium is:

$$\Delta G^{\circ,IL} = \Delta G^{\circ,aq} + \Delta G^T_{\mathrm{A}^-} + \Delta G^T_{\mathrm{HB}^+} - \Delta G^T_{\mathrm{HA}} - \Delta G^T_{\mathrm{B}}$$
$$= \Delta G^{\circ,aq} + \Delta \Delta G^T$$
(5.6)

where  $\Delta G_j^T$  is the free energy for transferring species j from aqueous to IL solution. These "transfer free energies" are calculated by a constrained mean force approach in which each

$$\begin{array}{c} \mathrm{HA}(il) + \mathrm{B}(il) & \xrightarrow{\Delta G^{\circ,IL}} & \mathrm{A}^{-}(il) + \mathrm{HB}^{+}(il) \\ & & \\ \Delta G^{T}_{\mathrm{HA}} + \Delta G^{T}_{\mathrm{B}} \\ & & \\ \mathrm{HA}(aq) + \mathrm{B}(aq) \xrightarrow{\Delta G^{\circ,aq}} & \mathrm{A}^{-}(aq) + \mathrm{HB}^{+}(aq) \end{array}$$

Figure 5.1. Thermodynamic cycle.

species is gradually transferred between the aqueous and IL regions of a two-phase simulation cell as described below. Four such calculations are required to close the thermodynamic cycle in Figure 5.1, one for each reactant or product.

 $\Delta G^{\circ,aq}$  is the standard reaction free energy in aqueous solution, for which experimental data is available for the reactions of all common weak acids and bases, including most PIL components.  $\Delta G^{\circ,aq}$  can be calculated as following. The equilibrium constant of the proton transfer reaction in aqueous solution  $K_{\rm IL}^{\rm aq}$  is (as shown earlier):

$$K_{\rm IL}{}^{\rm aq} = \frac{[{\rm A}^-][{\rm HB}^+]}{[{\rm HA}][{\rm B}]} = \frac{K_{\rm a}{}^{\rm aq}({\rm HA})}{K_{\rm a}{}^{\rm aq}({\rm HB}^+)}$$
(5.7)

By definition,  $\Delta p K_a^{aq}$  is:<sup>37</sup>

$$\Delta p K_{a}^{aq} = p K_{a}^{aq} (HB^{+}) - p K_{a}^{aq} (HA)$$
(5.8)

Eq. 5.7 can then be re-written:

$$pK_{\rm IL}{}^{\rm aq} = -\Delta pK_{\rm a}{}^{\rm aq} \tag{5.9}$$

By combining Equations 5.5 and 5.9,  $\Delta G^{\circ,aq}$  can be derived:

$$\Delta G^{\circ,aq} = -RT\Delta p K_a \ln(10) \tag{5.10}$$

To proceed we first need to establish a relationship between the degree of proton transfer  $\chi$  (defined in the previous chapter) and the equilibrium constant of the fundamental PIL

reaction (Eq. 5.1). The equilibrium constant for the fundamental PIL reaction (if behaving ideally) can be written simply as:

$$K_{\rm IL} = \frac{[{\rm A}^{-}][{\rm HB}^{+}]}{[{\rm HA}][{\rm B}]} = \frac{\frac{n({\rm A}^{-})}{V} \times \frac{n({\rm HB}^{+})}{V}}{\frac{n({\rm HA})}{V} \times \frac{n({\rm B})}{V}} = \frac{N({\rm A}^{-}) \times N({\rm HB}^{+})}{N({\rm HA}) \times N({\rm B})}$$
(5.11)

where n is the number of moles, N is the number of molecules, and V is the volume. If  $[HA]_0=[B]_0$ , this can be rewritten:

$$K_{\rm IL} = \frac{(N_{ion})^2}{(N_{neutral})^2}$$
(5.12)

 $N_{ion}$  and  $N_{neutral}$  are the numbers of ionic and neutral molecules at equilibrium, respectively.  $N_{neutral} = N_{total} - N_{ion}$ , where  $N_{total}$  is the total number of molecules:

$$K_{\rm IL} = \frac{(N_{ion})^2}{(N_{total} - N_{ion})^2} = \frac{\left(\frac{N_{ion}}{N_{total}}\right)^2}{(1 - \frac{N_{ion}}{N_{total}})^2}$$
(5.13)

In Chapter 4 we defined the degree of proton transfer  $\chi = \frac{N_{ion}}{N_{total}}$  which yields:

$$K_{\rm IL} = \frac{\chi^2}{(1-\chi)^2}$$
(5.14)

If the proton transfer reaction is nearly complete ( $\chi \approx 1$ ) the PIL composition can be assumed fully ionic. Therefore any dependence of  $\Delta G^{\circ,IL}$  on  $\chi$  is not relevant and the transfer calculations can be carried out at  $\chi = 1$ . In this scenario, the thermodynamic cycle yields the reaction free energy associated with the full proton transfer, and  $K_{\rm IL}$  can be calculated easily through Eq. 5.5. This scheme can be applied to PILs obtained from super-strong acid (base) precursors, and can be used to calculate the (very low) concentrations of neutrals in the PIL at equilibrium.

However, as explained earlier, in many PILs the proton transfer reaction is incomplete at equilibrium. In these circumstances, the free energy change may depend on the degree of proton transfer which cannot be ignored. To correctly describe such systems, we suggest an approach which takes into account the degree of proton transfer as follows. The chemical potential of a species j in the IL solution at given  $\chi$  and at some nonstandard state can be written as:<sup>168</sup>

$$\mu_j^{IL}(\chi) = \mu_j^{\circ,aq} + \Delta G_j^T(\chi) + RT \ln \frac{[j]_{\chi}}{[j]^{\circ}}$$
(5.15)

The first term on the right side is the standard chemical potential of j in the aqueous phase (considered to be at 1.0 M, but behaving as if at infinite dilution). The second term is the transfer free energy of j from the aqueous phase to the IL phase at some composition given by  $\chi$ , and the third term is the work to change [j] from standard concentration to the desired concentration. In the third term, we can use concentrations instead of activity coefficients since all the relevant interactions between j and other species are included in the  $\Delta G_j^T(\chi)$ term.<sup>168</sup> We can now write the free energy change for the fundamental PIL reaction (Eq. 5.1):

$$\Delta G^{IL}(\chi) = \mu_{\rm A^-}^{IL}(\chi) + \mu_{\rm HB^+}^{IL}(\chi) - \mu_{\rm HA}^{IL}(\chi) - \mu_{\rm B}^{IL}(\chi)$$
(5.16)

Substituting Eq. 5.15 for each species in Eq. 5.16 gives:

$$\Delta G^{IL}(\chi) = \Delta G^{\circ,aq} + \Delta \Delta G^T(\chi) + RT \ln \frac{[\mathrm{A}^-][\mathrm{HB}^+]}{[\mathrm{HA}][\mathrm{B}]}$$
(5.17)

The first term on the right side is:

$$\Delta G^{\circ,aq} = \mu_{\rm A^-}^{\circ,aq} + \mu_{\rm HB^+}^{\circ,aq} - \mu_{\rm HA}^{\circ,aq} - \mu_{\rm B}^{\circ,aq}$$
(5.18)

and the second term is:

$$\Delta\Delta G^{T}(\chi) = \Delta G^{T}_{\mathrm{A}^{-}}(\chi) + \Delta G^{T}_{\mathrm{HB}^{+}}(\chi) - \Delta G^{T}_{\mathrm{HA}}(\chi) - \Delta G^{T}_{\mathrm{B}}(\chi)$$
(5.19)

The thermodynamic condition for equilibrium is:  $\Delta G^{IL}(\chi) = 0$ , and applying Eq. 5.14 yields:

$$\Delta G^{\circ,IL}(\chi) = \Delta G^{\circ,aq} + \Delta \Delta G^T(\chi) = -RT \ln \frac{\chi^2}{(1-\chi)^2}$$
(5.20)



Figure 5.2. Chemical structures of neutrals and ions in trimethylammonium acetate PIL.

To determine the  $\chi$  for a partially proton transferred PIL with some unknown  $\chi$ , we first need to determine the  $\Delta G^{\circ,IL}(\chi)$  function. This can be achieved by completing the thermodynamic cycle at different  $\chi$  values (starting at  $\chi = 0$ ), and finding a suitable function which describes the  $\chi$  dependence of the values obtained. Once this function is determined, the equilibrium  $\chi$  can then be obtained by solving Eq. 5.20 by iteration.

## 5.2.2 Molecular Models

PILs were modeled with the OPLS-AA force field, as described in previous chapters. Figure 5.2 shows the chemical structure of the PIL components.

### 5.2.3 System Setup

Each simulation cell contains a two-phase system consisting of a PIL medium and water phase which are separated by two water/PIL interfaces. The water/PIL interface is perpendicular to the (elongated) z-axis. Rectangular simulation boxes with initial linear dimensions of  $30 \times 30 \times 100$  Å were used throughout, with period boundary conditions (PBCs) in all directions. Water/PIL systems were constructed by placing a slab of PIL molecules in the center of the simulation box with the water molecules located on both sides, as shown in Figure 5.3. Water molecules occupy two side regions, that is, 0 < z < 20 Å and 80 < z < 100



Figure 5.3. Simulation box of a two phase water/PIL system. Gray region represents the PIL phase, and the white regions show aqueous phase. Blue and red (dashed) lines show the positions of the wall potentials acting on PIL and water regions, respectively.

Å, and PIL molecules were located in 20 < z < 80 Å region. Each simulation cell contains one solute molecule, 1198 water molecules (599 in each water region initially), and 574 PIL molecules. In Figure 5.3, water appears as two distinguishable regions in the simulation cell; however, since PBCs are used water molecules can freely move between these two regions and hence there is only one water phase.

Since the water and PIL phases are miscible we used repulsive harmonic wall potentials to prevent them from mixing:

$$U_w = K_w (z - z_c)^2, \qquad z < z_c$$
 (5.21)

 $U_w$  is the potential of the wall,  $k_w$  (0.1 kcal/mol Å<sup>2</sup>) is the force constant, z is the distance from the particle to the wall potential in z-axis, and  $z_c$  is the cutoff distance at which the particle and wall no longer interact,  $z_c = 10$  Å. The energy of the wall potential is shifted so that the wall-particle interaction energy is zero at the cutoff distance.

A total of four wall potentials were used, such that one wall acts on each species in a specific direction as shown in Figure 5.3. The transfer molecules are not affected by the wall potentials. In addition to preventing the water and IL phase from mixing, the walls also prevent a transferring molecule from "dragging" any water into the IL region, and vice versa.

## 5.2.4 Free Energy Calculations

To obtain the free energy profiles associated with the transfer of each species across the water/PIL interface, "constrained molecular dynamics" was used. The reaction coordinate for the transferring molecule is defined as the z coordinate of the molecule ( direction normal to the water/PIL interface). The Gibbs free energy difference,  $\Delta G$ , between a state where the transferring molecule is located at  $z_1$ , and a state where the transferring molecule is at  $z_0$  is given by:<sup>162,163</sup>

$$\Delta G(z_1) = G(z_1) - G(z_0) = -\int_{z_0}^{z_1} \langle f_z(z) \rangle dz$$
(5.22)

 $f_z(z)$  is the z component of the total force exerted on the molecule at a given position z, averaged over the isobaric-isothermal ensemble.  $G(z_0)$  is here chosen as the free energy of the system with the transferring molecule located in the bulk water region at z = 5.0 Å.

In this technique, the center of mass of the transferring molecule is constrained at different z coordinates, here spaced in 1 Å increments. At each position, the average force acting along the z-axis is calculated, and the results integrated to obtain the free energy profile, also known as the potential of mean force (described further below). Note that the  $\Delta G$  is not affected by the wall potentials because G is a state function and so  $\Delta G$  does not depend on the transfer path.<sup>157</sup>

## 5.2.5 Simulation Details

MD simulations were performed using the LAMMPS package<sup>121</sup> at 25 °C and 1.0 bar. Standard Lorentz-Berthelot mixing rules were used to derive the cross interaction LJ parameters between different atom types. A cutoff distance of 12 Å was used for both the LJ and the real part of the Coulomb pairwise interactions. The particle-particle particle-mesh (PPPM) solver<sup>88</sup> was employed to handle long-range electrostatic interactions with a precision of  $10^{-5}$  beyond the cutoff distance. Long-range LJ tail corrections were added to the energy and pressure of the system.

All simulations were carried out in isobaric-isothermal (NPT) ensemble. The Nosé-Hoover thermostat<sup>95,123</sup> and barostat were used to keep the temperature and lateral pressure constant, with damping factors of 0.5 and 2.0 ps, respectively. Pressure in the lateral direction (xy) was held fixed, so the dimensions of the system fluctuate in x and y, while the z dimension remains constant. All bonds containing hydrogen were constrained using the SHAKE algorithm.<sup>92</sup> The Verlet integrator was used to integrate the equations of motion with a time step of 2 fs.

The transferring molecule was initially placed in the bulk water phase with the z component of its center of mass positioned at z = 5.0 Å. This position was held fixed through the use of a spring force with a force constant of 100.0 kcal/mol Å<sup>2</sup> applied to each atom. These configurations were first relaxed using conjugate gradient energy minimization, and then annealed by heating the system from 300 to 500 K and cooling to the 25 °C over 2 ns. The resultant configuration was then used as the input in an *NPT* equilibration run of 6 ns duration.

After the equilibration phase was over, the final configuration was used to start "pulling runs" which generate the initial states for final production runs. At this stage, each transfer molecule is pulled with a moving spring attached to the center of mass of the molecule. These pulling runs were performed at constant velocity  $(5 \times 10^{-4} \text{ Å/fs})$  with force constant of 100.0 kcal/mol Å<sup>2</sup>. Each molecule is pulled along the transfer coordinate, which takes it from the water phase at z = 5.0 Å to the PIL medium at z = 55.0 Å over 100 ps. During this step, configurations containing z coordinates of the center of mass of the transferring molecules, spaced at 1.0 Å are collected for the next phase of simulations. Figure 5.4 shows snapshots of pulling runs for transferring an amine molecule from the water phase to the IL phase.



amine molecule in the IL phase

Figure 5.4. Snapshots depicting the pulling runs for transferring an amine molecule across the water/IL phase. Different representation was used for the transferring amine to distinguish it from other molecules.

After configurations at different z are extracted from the pulling runs, the constrained MD simulations are conducted. In order to constrain the z coordinate of the transferring molecule, the center of mass of the molecule is attached to a spring with a force constant of 1000.0 kcal/mol Å<sup>2</sup>, tethered to the desired z coordinate (see Appendix C). Each CMD simulation is first run for 2 ns of equilibration, followed by a 20-30 ns production run in

$\chi$	%Proton Transfer	Amine	Acetic Acid	Ammonium	Acetate	
0	0	287	287	0	0	
0.1	10.0	258	258	29	29	
0.2	20.0	229	229	58	58	

Table 5.1. Specifications of PIL phase simulated at different  $\chi$ . Number of molecules

which the z component of the spring force is recorded and averaged in 1 ns blocks. Note that the f(z) in Eq. 5.23 is the opposite of the spring force here, i.e.,  $f_z(z) = -f_z^{spring}(z)$ .

As mentioned before, the thermodynamic cycle must be evaluated at a series of  $\chi$  values to determine the  $\chi$  dependence of  $\Delta G^{\circ,IL}$ . Here we carried out simulations at  $\chi$  values of 0, 0.1 and 0.2. System specifications of the PIL phase including  $\chi$ , corresponding proton transfer percentages, and respective numbers of neutrals and ions associated with each  $\chi$  are given in Table 5.1. At  $\chi = 0.1$  and 0.2, four wall potentials were used to act on each species in the PIL phase, and the  $z_c$  of the wall potentials acting on amine species was changed from 10.0 Å to 11.0 Å to yield corresponding  $\chi$  in the PIL bulk phase. Moreover, longer production runs of 30 ns were performed at  $\chi = 0.1$  and 0.2 to improve the uncertainty in the force averaging.

### 5.3 **Results and Discussion**

#### 5.3.1 Density Profiles

Density profiles were calculated by dividing the simulation cell into 200 static rectangular bins (each of 0.5 Å width) parallel to the interface, and counting the atoms in each bin, averaged over the course of simulations. The profile densities here were obtained from averaging over 10 independent simulations (replicas), each replica of 20 ns production run. We also used the symmetry of the system to improve the statistics. Figure 5.5 shows the symmetrized density profiles of water and IL phase represented for the first (left) half of the simulation box at different  $\chi$ .


Figure 5.5. Number density profiles for the simulated water/IL systems at different  $\chi$ .

The layering of liquids near the interface is a well-known effect in MD simulations,<sup>157,163,169</sup> and is observed here for both water and IL phase. Density profiles of water clearly show a first strong peak located roughly at 16 Å, indicating the first water layer which is packed against the IL phase. However, we should note that in fact such packing arises from repulsion by the wall potentials since the interface here is made artificial; this also holds for the IL phase. A second water layer is also visible at a larger distance due to the packing of water molecules against the first layer, but significantly weaker. After the second layer, water density shows a plateau, indicating bulk water behavior. Similarly, the IL phase shows a strong first peak located at 20.2 Å corresponding to the first layer of IL molecules packed against the water phase. However, the layering effect here more strongly propagates into the bulk IL phase than the water, and extends deeper into the IL phase, including almost four IL layers. However, the density oscillations in the IL phase eventually diminish well into the bulk liquid region (at z = 35 Å), and IL density reaches a plateau in the region 40 < z < 50 Å. Very similar density profiles are also observed for water/IL systems at different  $\chi$ .

To analyze the density profiles in more detail, the density of each component of the IL liquid is calculated at each  $\chi$ , shown in Figure 5.6. Water shows the same profile as discussed above, but the IL phase represents complex profiles depending on  $\chi$ . At  $\chi = 0$ , the IL phase contains only two species, that is, amine and acid molecules. These neutral species both show a first peak at roughly 20 Å, with amine having a stronger peak. Amine and acid both show density oscillations which extends into IL phase up to z = 35 Å, after which a plateau is observed.

At  $\chi = 0.1$ , the ammonium and acetate ions are also present in the IL phase along with neutral species. Ions show a first peak positioned roughly at z = 20 Å, indicating that they are concentrated in the interfacial region. Ammonium shows a stronger peak than acetate, but acetate slightly diffuses deeper into the water phase, with a broader peak. Further from the interface, the ions do not show any other peak or oscillatory behavior, and reach a plateau more quickly than neutral species, at z = 30 Å. Neutral species shows oscillations as before, however due to the presence of ions at the interface their second peak becomes stronger.

At  $\chi = 0.2$ , the density of ions at the interface is more pronounced than  $\chi = 0.1$ , indicating that ions are highly concentrated in the interface. Ammonium shows the first and strongest peak among other PIL species at roughly 20 Å. As the interface is more strongly occupied by ions, the neutral species move away further from the interface. This can be seen as the first peaks in neutral densities become weaker, showing that neutral molecules are pushed further away from the interface. The tendency of ions to locate at the interface in spite of their lower population than neutrals originates from their strong interactions with



Figure 5.6. Number density profiles for the simulated water/IL systems. The nitrogen atom of amine and ammonium molecules were taken to represent these molecules. The carbon atom of the carboxylic and carboxylate groups in acetic acid and acetate was taken to represent these molecules. The oxygen atom of water was taken to represent water molecules.

water. Here we emphasize again that all the structures observed in the interfacial region is artificial because they are induced by the wall potentials. However, they are similar to the interfacial structures often observed between two immiscible phases, e.g., water and organic solvents.<sup>163,169</sup>

#### 5.3.2 Free Energy Profiles

In this section we present the free energy profiles (PMFs) for transferring each species across the water/IL interface. Each PMF plot represents the free energy change of the transferring molecule as a function of the z coordinate of the center of mass of the transferring molecule, which is the transfer coordinate. The transfers for each species start from the bulk water at z = 5 Å, cross the water/IL interface, and finally reach the bulk IL phase at z = 55 Å. The computed free energy for each species undergoes major changes as the transferring molecule begins to cross the interface. The left-side plateaus correspond to the free energy of the transferring molecule in the bulk water phase, while the right-side plateaus correspond to the free energy of the transferring molecule in the IL phase. The difference between these two shows the free energy of transfer. Here we used the first point and the last point in PMF profiles to calculate the transfer free energies. The uncertainty for the transfer free energies was obtained by dividing the averaged force data into two blocks, and obtaining PMFs for each block. We here emphasize again that the transfer free energies are not affected by the wall potentials because G is a state function.

Figure 5.7 shows the z component of the mean force at each z constrained position of the transferring molecule at  $\chi = 0$ . The averaged force for each species undergoes major changes within the interfacial region. In the bulk water or IL regions the mean force is close to zero.

Figure 5.8 shows the free energy profiles for transfers made at  $\chi = 0$ . Figure 5.8(a) shows the PMF for transferring the amine molecule. Initially, the free energy of amine decreases monotonically as it moves toward the interfacial region, and reaches a minimum located roughly at 16 Å. The existence of such minimum is more likely due to the increase in the hydration number of the amine at this point which coincides well with the first peak of water. This shows that higher concentration of water can in fact lower the free energy. As the amine begins to move into the IL phase, the free energy increases quickly. This is due to the fact that the solution environment of amine is changing rapidly from being purely water molecules to purely IL phase components. The free energy then passes through a barrier at z = 22.5 Å. The presence of this barrier is likely due to the enhanced density of the IL



Figure 5.7. Mean force profiles across the water/IL interface at  $\chi = 0$  for transferring a (a) amine molecule, (b) acetic acid molecule, (c) ammonium ion and (d) acetate ion. Vertical scales differ between plots.

phase at this z. The free energy then oscillates very slightly for a few tens of Ångstroms, and eventually reaches a plateau in the bulk IL phase. The transfer free energy of amine is  $6.4\pm0.4$  kJ/mol, implying that the amine molecule is more soluble in water than in the IL phase.

Figure 5.8(b) shows the PMF of transferring an acetic acid molecule across the water/IL interface. The PMF profile for the acetic acid is similar to that of the amine. The free energy first decreases to a minimum, after which it increases and passes through a barrier,



Figure 5.8. Free energy profiles across the water/IL interface at  $\chi = 0$  for transferring a (a) amine molecule, (b) acetic acid molecule, (c) ammonium ion and (d) acetate ion. Vertical scales differ between plots to show fine details of each profile.

and eventually reaches a plateau in the bulk IL region. The estimated free energy of transfer for acetic acid is  $2.2\pm0.4$  kJ/mol, showing that water is also a better solvent for acetic acid than the IL phase.

However, the transfer free energy for acetic acid is lower than that for amine. We believe that this difference originates from their hydrogen bonding. The amine molecule in the IL phase can only make hydrogen bonds with acetic acid, while the acetic acid can make hydrogen bonds with other acetic acid molecules. In fact, acetic acid can donate hydrogen



Figure 5.9. Mean force profiles across the water/IL interface at  $\chi = 0.1$  for transferring a (a) amine molecule, (b) acetic acid molecule, (c) ammonium ion and (d) acetate ion. Vertical scales differ between plots.

bonds through its acidic hydrogen, and can accept hydrogen bonds through its negatively charged carboxylic oxygen. Here we used the same analysis applied in Chapter 4 to estimate the number of hydrogen bonds between different species. The hydrogen bonds were counted deep in the IL phase, averaged over 20 ns simulation. The transferred amine makes 0.8 hydrogen bonds with acetic acid molecules in the bulk IL phase, while the transferred acetic acid makes 1.8 hydrogen bonds with other acetic acid molecules, in addition to 0.8 hydrogen



Figure 5.10. Free energy profiles across the water/IL interface at  $\chi = 0.1$  for transferring a (a) amine molecule, (b) acetic acid molecule, (c) ammonium ion and (d) acetate ion. Vertical scales differ between plots.

bonds with amine. This hydrogen bonding ability makes the IL phase a better solvent for acetic acid than amine.

Figure 5.8(c) represents the free energy variation of an ammonium ion crossing the water/IL interface. The free energy first decreases and reaches a shallow minimum at 15 Å, after which it increases monotonically until it reaches a plateau in the bulk IL phase. The free energy increases much more significantly as the ammonium ion enters the IL phase



Figure 5.11. Mean force profiles across the water/IL interface at  $\chi = 0.2$  for transferring a (a) amine molecule, (b) acetic acid molecule, (c) ammonium ion and (d) acetate ion. Vertical scales differ between plots.

than it did with the neutral species. The estimated free energy of transfer for ammonium is  $35.10\pm0.4$  kJ/mol.

Figure 5.8(d) shows the free energy variation of transferring an acetate ion across the water/IL interface. Similar to the ammonium profile, the free energy first decreases and reaches a minimum, after which increases monotonically, and finally reaches a plateau in the bulk IL phase. The estimated free energy of transfer for acetate ion is  $20.9\pm0.1$  kJ/mol, showing that acetate is more soluble in water than in the IL phase. However, the transfer



Figure 5.12. Free energy profiles across the water/IL interface at  $\chi = 0.2$  for transferring a (a) amine molecule, (b) acetic acid molecule, (c) ammonium ion and (d) acetate ion. Vertical scales differ between plots.

free energy of acetate is much lower than that of ammonium. This can be explained based on the hydrogen bonding. Our hydrogen bonding calculations show that each oxygen of the transferring acetate accepts on average 1.95 hydrogen bonds from the neighboring acetic acid molecules, while ammonium only makes 0.7 and 0.2 hydrogen bonds with amine and acetic acid molecules, respectively. This makes the IL phase a better solvent for acetate than ammonium ion.

	Ammonium	Acetate	Amine	Acid
$\chi = 0$	$35.1 \pm 0.4$	$20.9 {\pm} 0.1$	$6.4{\pm}0.4$	$2.2{\pm}0.4$
$\chi = 0.1$	$22.5 \pm 0.3$	$10.1 \pm 1.1$	$8.6{\pm}0.4$	$1.5\pm0.2$
$\chi = 0.2$	$25.5 \pm 0.2$	$8.2 \pm 1.0$	$8.6{\pm}0.1$	$0.1{\pm}0.7$

Table 5.2. Computed free energy of transfer for each species. Transfer free energies (kJ/mol)

Figure 5.9 and 5.10 show the mean force and free energy profiles for transferring each species at  $\chi = 0.1$ , respectively. Generally, the free energy profiles show features similar to those observed at  $\chi = 0$ . However, the PMF profile of the ammonium ion, Figure 5.10(c), shows a slight barrier at roughly z = 22 Å which was not present at  $\chi = 0$ . This barrier is most likely due to the enhanced density of ammonium ions in this region (Figure 5.6) which strongly repel the transferring ammonium.

Figure 5.11 and 5.12 show the mean force and free energy profiles for transferring each species at  $\chi = 0.2$ , respectively. PMF profiles for neutral molecules are similar to those observed in previous cases. In the ammonium PMF, the barrier right before the bulk IL phase is more pronounced here as stronger ammonium peak exists at  $\chi = 0.2$  than  $\chi = 0.1$ .

The computed free energies of transfer are given for each species at each  $\chi$  in Table 5.2. From  $\chi = 0$  to  $\chi = 0.1$ , the transfer free energies of ammonium and acetate ions dramatically drop. This suggests that the IL phase becomes a better solvent for ions as it becomes more ionic. This is mainly because the transferring ions can now interact strongly through attractive Coulomb interactions with other ions in the IL phase. Moreover, the transferred ions can also make strong hydrogen bonds with other ions available in the IL solution which were not present at  $\chi = 0$ .

For neutrals, the transfer free energy of acetic acid also decreases with increasing  $\chi$ . This is because the acid molecules can also hydrogen bond with acetate ions. Our hydrogen bond analysis shows that the transferring acetic acid donates 0.21 hydrogen bonds to acetate ions present in the bulk IL phase. In contrast, the amine transfer free energy increases with

Table 5.3. Computed free energy of transfer for each path in the thermodynamic cycle at different  $\chi$ . Unit is kJ/mol.

	$\Delta G^{\circ,aq}$	$\Delta\Delta G$	$\Delta G^{\circ,IL}$
$\chi = 0$	-28.8	$47.4{\pm}1.3$	$18.6 \pm 1.3$
$\chi = 0.1$	-28.8	$22.5 \pm 2.0$	$-6.3 \pm 2.0$
$\chi = 0.2$	-28.8	$25.0{\pm}2.0$	$-3.8 \pm 2.0$

 $\chi$ , implying that the IL phase destabilizes the amine more as it becomes more ionic. Our hydrogen bond analysis shows that the transferred amines cannot make significant hydrogen bonds with ammonium ions. Moreover, the number of hydrogen bonds of the transferred amine with acetic acid molecules also decreases from 0.8 at  $\chi = 0$  to 0.7 at  $\chi = 0.1$  which explains the increase observed.

From  $\chi = 0.1$  to  $\chi = 0.2$ , the transfer free energies of the acetic acid and acetate decrease further. This is due to the fact that these species can make more hydrogen bonds with ions as IL becomes more ionic. For example, each oxygen of the transferred acetate on average accepts 0.5 hydrogen bonds from ammonium ions at  $\chi = 0.2$ , while only makes 0.4 at  $\chi = 0.1$ . Likewise the transferred acetic acid makes more hydrogen bonds (0.3) with acetate at  $\chi = 0.2$  than  $\chi = 0.1$  (0.2). The transfer free energy of amine does not change and stays the same. The transfer free energy of the ammonium ion increases slightly which was not expected. This in fact can be explained based on the hydrogen bonding environment. The total number of hydrogen bonds of the transferred ammonium decreases slightly from 1.1 at  $\chi = 0.1$  to 1.0 at  $\chi = 0.2$ . This shows that transferred ammonium ion struggles to donate enough hydrogen bonds as it has to compete with other hydrogen bond donors such as ammonium ions and acetic acid molecules.

#### 5.3.3 Predicting $\chi$ and $K_{IL}$ in [N111][Ac]

In this section we use the free energies of transfer at each  $\chi$  to calculate the  $\Delta G^{\circ,IL}$  at different  $\chi$ . These data are all given in Table 5.3.



Figure 5.13.  $\Delta G^{\circ,IL}$  vs  $\chi$ , along with the linear and quadratic fits.

To proceed, we plot  $\Delta G^{\circ,IL}$  against different  $\chi$ , and fit these data to a linear and a quadratic function, shown in Figure 5.13. To solve Eq. 5.20, we first rewrite it in the following format:

$$-\frac{\Delta G^{\circ,IL}(\chi)}{RT} = \ln \frac{\chi^2}{(1-\chi)^2}$$
(5.23)

Here  $\Delta G^{\circ,IL}(\chi)$  represents the linear and quadratic functions obtained by fitting. Following this, we plot both sides of the above equation for  $0 < \chi < 1.0$ , and look for the point that they cross each other, which corresponds to the solution. This plot is shown in Figure 5.14. The linear fit does not give a solution, suggesting that this is not a suitable function to describe the  $\chi$  dependence of  $\Delta G^{\circ,IL}$ . The quadratic fit gives a solution at  $\chi = 0.24$ , indicating that [N111][Ac] has a low degree of proton transfer. We further use  $\Delta G^{\circ,IL}$  value at this  $\chi$  to measure the equilibrium constant using Eq. 5.5 which predicts  $K_{\rm IL} = 2.5$ .

Unfortunately, there is no experimental  $\chi$  or  $K_{\rm IL}$  reported for this PIL. However, we can apply the approach used in Chapter 4 to estimate  $\chi_{\rm expt}$  by comparison with experimental viscosity data, shown in Figure 5.15. The interpolation procedure suggests  $\chi = 0.25$  which agrees well with the  $\chi$  obtained from the thermodynamic approach.



Figure 5.14. Plots of the linear and quadratic fits, and the natural log against  $\chi$  for Eq. 5.23.



Figure 5.15. Linear fit and interpolation of viscosity data for [N111][Ac]. The red line is the experimental value.<sup>11</sup>

#### 5.4 Computational Cost

Here we provide some information on the computational effort and simulation time spent on these calculations. In this study, the final transfer production runs were carried out on the supercomputer Lonestar 5 (LS5), located at the Texas Advanced Computing Center (TACC). LS5 has 1252 twenty-four core compute nodes (a total of 30,000 processor cores). Each transfer simulation was carried out on a single compute node, each with 24 physical cores. Each 22 ns run for  $\chi = 0$  took ~17 hours, and each 32 ns run for  $\chi = 0.1$  and 0.2 took ~24 hours in the transfer calculations. Each transfer simulation consists of 50 points which uses 50 compute nodes (1200 cores) per single transfer. Including all the production run times and nodes/cores at all  $\chi$ , this adds up to 13,000 node-hour (312,000 core-hour).

In terms of simulation time, at  $\chi = 0$ , each point in the transfer coordinate is run for 22 ns. This makes one single transfer 1.1 microseconds. There are 4 of them which makes a total of 4.4 microseconds per thermodynamic cycle. At  $\chi = 0.1$  and 0.2, each transfer point is 32 ns, which makes 6.4 microseconds per thermodynamic cycle. The sum of all the simulation times at all  $\chi$  equals to 17.2 microseconds.

#### 5.5 Conclusions

In this chapter we introduced a thermodynamic cycle by which to measure the degree of proton transfer and the equilibrium constant of the proton transfer reaction in PILs. This thermodynamic approach can be applied to all PILs ranging from partially proton transferred to fully ionic, however for the PILs with partial proton transfer the cycle needs to be repeated for a series of  $\chi$  values. This method predicted  $\chi = 0.24$  for [N111][Ac].

 $\chi$  is a central quantity in PIL acid-base chemistry, analogous to pH in aqueous media. This is the first computational prediction of  $\chi$  by molecular simulation, and demonstrate the feasibility of this approach to PIL thermodynamics. Moreover, this thermodynamic cycle can also be effectively used to study the proton transfer reaction between PIL components and other solutes. For instance, the precursor acid (HA) in the thermodynamic cycle can be replaced with any other acidic species to predict the  $pK_a$  of those acids in PIL media which is of high interest in many chemical and biological applications.

#### CHAPTER 6

#### SUMMARY AND FUTURE WORK

In this dissertation we studied protic ionic liquids (PILs) by using molecular dynamics (MD) simulations. MD simulation is a powerful technique for studying liquids, and can create conditions which are not accessible by experiment. These studies, in conjunction with experimental observations, can assist the scientific community better understand the behavior of these complex liquids at the molecular level.

In Chapter 3, we demonstrated that current well-established empirical force fields for ILs can be effectively modified with an optimal charge-scaling factor ( $\gamma$ ) applied to atomic partial charges. In this study, a family of PILs consisting of several tertiary ammonium cations paired with triflate anions was considered. Our results showed that the dynamics of simulated PILs are greatly improved, resulting in better estimation of transport coefficients, and better agreement with experiment. One of the main advantages of this method is that it does not increase the computational cost of the simulations as opposed to using polarizable models. This is significant given the current limitations in the system-size and time-scales of IL simulations.

The optimal  $\gamma$  was derived through interpolation of simulated data using experimental data, which benefits from the fact that the experimental data of many properties of PILs are now well-documented. Moreover, the value of  $\gamma$  was found to be nearly independent of the choice of experimental data and temperature used. This suggests that one could use the most rapidly and accurately obtained quantity by simulation, e.g., density or diffusion coefficient in this procedure.  $\gamma$  was also found to be reasonably transferable among these PILs, implying that this approach may be performed for only one member of a family of PILs of closely related structure.

In Chapter 4, the effects of the degree of proton transfer ( $\chi$ ) on structure and dynamical properties of PILs were studied. MD simulations allowed us to observe how the properties of PILs change as  $\chi$  changes. This is important and only achievable by simulation, as  $\chi$  is not a controllable quantity in experiment. This study also helped us better understand the behavior of neutral precursors in PILs, which is not well-understood. Finally, we showed that comparison of simulations data with experiment can give an estimate of  $\chi$  in experimental PILs, which is difficult to measure.

This type of simulations can also be extended further to study the effect of  $\chi$  on other PIL properties such as thermal conductivity or surface tension. The predictive power of these simulations in measuring  $\chi$  in experimental systems can help us establish relationships between the PIL constituents and the degree of proton transfer. These studies may be useful in designing new PILs, by determining what type of precursors will likely result in PILs with higher ionic composition or specific physical properties. Moreover, experimental  $\chi$  can be used to improve the performance of current force fields in measuring properties of interest at that particular  $\chi$ .

In Chapter 5 we developed a thermodynamic approach by which to measure the degree of proton transfer in PIL media. This is based on a thermodynamic cycle calculation of the reaction free energy associated with the proton transfer reaction. For trimethylammonium acetate, the application of this scheme gave relatively low  $\chi = 0.24$ , in good agreement with the  $\chi$  derived from the approach used in Chapter 4. In future work, we shall use this thermodynamic scheme to study acid-base equilibria in different PILs.

Moreover, the thermodynamic cycle introduced here can be effectively used in measuring the reaction free energies for proton transfer reaction between different solutes and PILs components. This can be achieved by replacing the precursor acid (base) with the solute of interest in the thermodynamic cycle. This feature adds more functionality to our approach in studying proton transfer reactions between a wide variety of solutes and PIL components. For example, it can be used to measure acidity constants of various acids in PIL media, which can then be compared with their aqueous values. These calculations can help us better understand the solvent environment in PILs, and will be valuable in optimizing their solvent properties.

# APPENDIX A FORCE FIELD PARAMETERS

The parameters that define the two triflate models and the tertiary ammonium models used in this study are given in the following tables. The tabulated partial charges are the *unscaled* charges as provided in the original force fields.<sup>118,119</sup> When simulating with a particular charge-scaling factor  $\gamma$  all these values are multiplied by  $\gamma$ .

Non-Bonded Parameters			
atom	q(e)	$\sigma(\text{\AA})$	$\epsilon$ (kcal mol <sup>-1</sup> )
С	+0.35	3.50	0.0660
F	-0.16	2.95	0.0530

0.2500

0.2100

3.55

2.96

+1.02

-0.63

Table A.1. Force field parameters for first triflate model (TM1). C: Carbon; F: Fluorine; S: Sulfur; O: Oxygen.

# Bond Stretching Parameters

 $\mathbf{S}$ 

0

bond	$K_b$ (kcal mol <sup>-1</sup> Å <sup>-2</sup> )	$r_0(\text{Å})$	
C-F	441.92	1.323	
C-S	233.03	1.818	
S-O	637.07	1.437	

# Angle-Bending Parameters

angle	$K_a$ (kcal mol <sup>-1</sup> rad <sup>-2</sup> )	$\theta_0(\mathrm{deg})$	
F-C-F	93.33	107.1	
S-C-F	82.93	111.7	
C-S-O	103.97	102.6	
O-S-O	115.80	118.5	

dihedral angle	$V_1$ (kcal mol <sup>-1</sup> )	$V_2$ (kcal mol <sup>-1</sup> )	$V_3$ (kcal mol <sup>-1</sup> )
F-C-S-O	0.00	0.00	0.3468

Tion Donaca Tarameters			
atom	q(e)	$\sigma(\text{\AA})$	$\epsilon$ (kcal mol <sup>-1</sup> )
С	+0.36	3.50	0.0660
$\mathbf{F}$	-0.12	2.95	0.0530
S	+1.37	3.55	0.3360
О	-0.79	2.96	0.1700

Table A.2. Force field parameters for second triflate model (TM2). C: Carbon; F: Fluorine;S: Sulfur; O: Oxygen.Non-Bonded Parameters

### Bond Stretching Parameters

bond	$K_b$ (kcal mol <sup>-1</sup> Å <sup>-2</sup> )	$r_0(\text{\AA})$	
C-F	367.0	1.332	
C-S	222.0	1.810	
S-O	700.0	1.440	

# Angle-Bending Parameters

angle	$K_a$ (kcal mol <sup>-1</sup> rad <sup>-2</sup> )	$\theta_0(\mathrm{deg})$	
F-C-F	77.0	109.1	
S-C-F	50.0	109.5	
C-S-O	74.0	108.9	
O-S-O	104.0	119.0	

dihedral angle	$V_1$ (kcal mol <sup>-1</sup> )	$V_2$ (kcal mol <sup>-1</sup> )	$V_3$ (kcal mol <sup>-1</sup> )
F-C-S-O	-0.1569	0.0323	-0.0725

Table A.3. Force field parameters for tertiary ammonium compounds. N3: Nitrogen; H3: Hydrogen bonded to N3;  $CT^a$ : Carbon bonded to N3.  $CT^b$ : Carbon bonded to  $CT^a$  in ethyl side chain.  $CT^c$ : Carbon bonded to  $CT^a$  in n-propyl alkyl chain.  $CT^d$ : Terminal carbon in n-propyl alkyl chain.  $HC^a$ : Hydrogen bonded to  $CT^a$ ; HC: Hydrogen bonded to  $CT^b$ ,  $CT^c$  and  $CT^d$ .

atom	q(e)	$\sigma(\text{\AA})$	$\epsilon$ (kcal mol <sup>-1</sup> )
НЗ	+0.31	0.00	0.00
N3	+0.03	3.250	0.1700
$\mathrm{CT}^{a}$	-0.17	3.50	0.0660
$\mathrm{CT}^b$	-0.05	3.50	0.0660
$\mathrm{CT}^{c}$	+0.01	3.50	0.0660
$\mathrm{CT}^d$	-0.18	3.50	0.0660
$\mathrm{HC}^{a}$	+0.13	2.50	0.0300
$\mathrm{HC}$	+0.06	2.50	0.0300

Non-Bonded Parameters

Bond Stretching Parameters

 0			
 bond	$K_b$ (kcal mol <sup>-1</sup> Å <sup>-2</sup> )	$r_0(\text{\AA})$	
H3-N3	434.00	1.0100	
CT-N3	367.00	1.4710	
CT-HC	340.00	1.0900	
CT-CT	268.00	1.5290	

#### **Angle-Bending Parameters**

0 0			
angle	$K_a$ (kcal mol <sup>-1</sup> rad <sup>-2</sup> )	$\theta_0(\mathrm{deg})$	
CT-N3-H3	35.00	109.50	
CT-CT-HC	37.50	110.70	
CT-CT-CT	58.35	112.70	
HC-CT-HC	33.00	107.80	
CT-CT-N3	80.00	111.20	
CT-N3-CT	50.00	113.00	
HC-CT-N3	35.00	109.50	

dihedral angle	$V_1$ (kcal mol <sup>-1</sup> )	$V_2(\text{kcal mol}^{-1})$	$V_3$ (kcal mol <sup>-1</sup> )
HC-CT-N3-H3	0.00	0.00	0.261
HC-CT-CT-N3	0.00	0.00	0.384
CT-CT-N3-H3	0.00	0.00	0.347
CT-CT-CT-N3	2.732	-0.229	0.485
CT-CT-N3-CT	1.740	-0.157	0.279
HC-CT-N3-CT	0.00	0.00	0.366
HC-CT-CT-HC	0.00	0.00	0.318
CT-CT-CT-HC	0.00	0.00	0.366
	116		

## APPENDIX B

# FORCE FIELD PARAMETERS

The parameters for the acetic acid and acetate models are given in this section. The tabulated partial charges are the *unscaled* charges as provided in the original force fields.<sup>147,149</sup> When simulating with a particular charge-scaling factor  $\gamma$  all these values are multiplied by  $\gamma$ .

Table B.1. Force field parameters for Acetic Acid. C2: Carbon of the methyl group; H2: Hydrogen bonded to C2; C3: Carbon of the carboxylic group; O4: Oxygen of the –OH group; H4: Hydrogen bonded to O4; O3: Oxygen bonded to C3. Non-Bonded Parameters

atom	q(e)	$\sigma(\text{\AA})$	$\epsilon$ (kcal mol <sup>-1</sup> )
H4	+0.45	0.0	0.0
O4	-0.53	3.00	0.170
C3	+0.52	3.750	0.1050
O3	-0.44	2.960	0.2100
C2	-0.18	3.500	0.0660
H2	+0.06	2.420	0.0150

Bond Stretching Parameters

bond	$K_b$ (kcal mol <sup>-1</sup> Å <sup>-2</sup> )	$r_0(\text{\AA})$	
O4-H4	552.940	0.945	
O4-C3	449.951	1.364	
C3–O3	569.938	1.229	
C2-C3	316.966	1.522	
C2-H2	339.963	1.09	

# Angle-Bending Parameters

angle	$K_a$ (kcal mol <sup>-1</sup> rad <sup>-2</sup> )	$\theta_0(\mathrm{deg})$	
H4-O4-C3	34.996	113.0	
O4-C3-O3	79.992	121.0	
O4-C3-C2	69.992	108.0	
C3-C2-H2	34.996	109.5	
O3-C3-C2	79.992	120.4	
H2-C2-H2	33.00	107.80	

dihedral angle	$V_1$ (kcal mol <sup>-1</sup> )	$V_2(\text{kcal mol}^{-1})$	$V_3$ (kcal mol <sup>-1</sup> )
H4-O4-C3-O3	0.0	2.7496	0.0
H4 - O4 - C3 - C2	0.7499	2.7496	0.0
O4-C3-C2-H2	0.0	0.0	0.0
O3-C3-C2-H2	0.0	0.0	0.0

Table B.2. Force field parameters for Acetate. C1: Carbon of the methyl group; H1: Hydrogen bonded to C1; CO: Carbon of the carboxylate group; O2: Oxygen bonded to CO. Non-Bonded Parameters

		0	
atom	$q(\mathrm{e})$	$\sigma(\mathrm{\AA})$	$\epsilon$ (kcal mol <sup>-1</sup> )
O2	-0.890	2.960	0.2100
CO	+1.027	3.400	0.08599
C1	-0.253	3.400	0.1094
H1	+0.002	2.650	0.01570
Bond Stretching Parameters			
bond	$K_b$ (kcal mol <sup>-1</sup> Å <sup>-2</sup> )	$r_0(\text{\AA})$	
CO-O2	371.341	1.264	
CO-C1	173.891	1.535	
C1-H1	211.040	1.094	
Angle-Bending Parameters			
angle	$K_a$ (kcal mol <sup>-1</sup> rad <sup>-2</sup> )	$\theta_0(\text{deg})$	
O2-CO-O2	134.300	124.90	
O2-CO-C1	141.501	117.61	
CO-C1-H1	107.608	109.50	
H1-C1-H1	33.301	106.80	
Dihedral Angle Parameters			
dihedral angle	$V_1$ (kcal mol <sup>-1</sup> )	$V_2(\text{kcal mol}^{-1})$	$V_3$ (kcal mol <sup>-1</sup> )
H1-C1-CO-O2	0.3824	0.0	0.0382

### APPENDIX C

#### FORCE CONSTANT

To check the accuracy of the time step used (2 fs) in the production runs of the CMD simulations, we checked the total energy of the CMD simulations in NVE ensemble for the constrained amine molecule at  $\chi = 0$ , with the Verlet integrators with 1 and 2 fs time steps. Results showed comparable fluctuations in the total energy for the two time steps, with no detectable drift in the total energy.



Figure C.1. Total energy fluctuations in NVE simulation of the constrained amine at z = 5.12 Å and at  $\chi = 0$ , with the force constant of 1000.0 kcal/mol Å<sup>2</sup>.

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#### **BIOGRAPHICAL SKETCH**

Amir Taghavi Nasrabadi obtained his Bachelor of Science degree in Pure Chemistry from The Yazd University in 2006. He then pursued his Master of Science degree in Nanochemistry, and graduated from The University of Tehran in 2010. In Fall 2012, he was admitted into the graduate program at The University of Texas at Dallas where he pursued his Doctor of Philosophy in Chemistry under the supervision of Dr. Lev Gelb.

## CURRICULUM VITAE

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American Chemical Society

## **Refereed Publications:**

(As of 8/6/17, 178 total citations, h-index = 6, i10-index = 5 Google Scholar).

1- <u>Amir Taghavi Nasrabadi</u> and Lev D. Gelb, "Structural and Transport Properties of Tertiary Ammonium Triflate Ionic Liquids: A Molecular Dynamics Study", The Journal of Physical Chemistry B 121 (2017): 1908-1921

2- <u>Amir Taghavi Nasrabadi</u> and Masumeh Foroutan, "Air Adsorption and Separation on Carbon Nanotube Bundles from Molecular Dynamics Simulations", Computational Materials Science 61 (2012): 134-139.

3- Amir Taghavi Nasrabadi and Masumeh Foroutan, "Ion-separation and Water-purification Using Single-walled Carbon Nanotube Electrodes", Desalination 277, (2011): 236-243.

4- Masumeh Foroutan and Amir Taghavi Nasrabadi, "Adsorption and Separation of Binary Mixtures of Noble Gases on Single-walled Carbon Nanotube Bundles", Physica E: Lowdimensional Systems and Nanostructures 43, (2011): 851-856.

5- Masumeh Foroutan and <u>Amir Taghavi Nasrabadi</u>, "Molecular Dynamics Simulation Study of Neon Adsorption on Single-walled Carbon Nanotubes", Physica E: Low-dimensional Systems and Nanostructures 43, (2010): 261-265.

6- <u>Amir Taghavi Nasrabadi</u> and Masumeh Foroutan, "Interactions Between Polymers and Single-walled Boron Nitride Nanotubes: A Molecular Dynamics Simulation Approach", The Journal of Physical Chemistry B 114, (2010): 15429-15436.

7- Masumeh Foroutan and <u>Amir Taghavi Nasrabadi</u>, "Adsorption Behavior of Ternary Mixtures of Noble Gases Inside Single-walled Carbon Nanotube Bundles", Chemical Physics Letters 497, (2010): 213-217.

8- Masumeh Foroutan and Amir Taghavi Nasrabadi. "Investigation of the Interfacial Binding Between Single-walled Carbon Nanotubes and Heterocyclic Conjugated Polymers", The Journal of Physical Chemistry B 114, (2010): 5320-5326.