

Atomistic Investigation of Polymer Electrolyte Membrane Nanostructure and Dynamics of Molecular Transport in Fuel Cells

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DOCTOR OF PHILOSOPHY

by

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CERTIFICATE

Certified that the work incorporated in the thesis entitled “*Atomistic Investigation of Polymer Electrolyte Membrane Nanostructure and Dynamics of Molecular Transport in Fuel Cells*” submitted by **Anurag Prakash Sunda** was carried out by the candidate, under my supervision. The work presented here or any part of it has not been included in any other thesis submitted previously for the award of any degree or diploma from any other University or institution.

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Declaration

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Abbreviations

ABPBI	:	Poly(2,5-benzimidazole)
AIMD	:	<i>Ab initio</i> Molecular Dynamics
BzTEA ⁺	:	Benzyltriethyl ammonium cation
BzTMA ⁺	:	Benzyltrimethyl ammonium cation
CPMD	:	Car-Parrinello Molecular Dynamics
DEMA ⁺	:	Diethylmethyl ammonium cation
EIS	:	Electro-chemical Impedance Spectroscopy
EMD	:	Equilibrium Molecular Dynamics
HF	:	Hartree-Fock
OPLS-AA	:	Optimized Potentials for Liquid Simulation-All Atom
PA	:	Phosphoric Acid
PCIL	:	Proton Conducting Ionic Liquid
PFSA	:	Perfluorosulfonic Acid
PFBu ⁻	:	Perfluorobutanesulfonate
PME	:	Particle-Mesh Ewald
QENS	:	Quasi-Elastic Neutron Scattering
m-PBI	:	Poly[2,2-(m-phenylene)-5,5-bibenzimidazole]
MD	:	Molecular Dynamics
MP2	:	Möller-Plesset Perturbation Theory (2nd order)
MSD	:	Mean Square Displacement
NEMD	:	Non-Equilibrium Molecular Dynamics
NPT	:	Isobaric Isothermal
NVT	:	Isochoric Isothermal
RDF	:	Radial Distribution Function
RH	:	Relative Humidity

SANS	:	Small Angle Neutron Scattering
SAXS	:	Small Angle X-ray Scattering
SPC	:	Simple Point Charge
SPC/E	:	Extended Simple Point Charge
TFA	:	Trifluoromethanesulfonate or Triflate ion

Abstract

In Polymer Electrolyte Membrane (PEM) fuel cells, the PEM is sandwiched between the electrodes to facilitate the proton transport from anode to cathode. A molecular study of structural and dynamical properties of various PEMs from simulations can facilitate the development of aqueous/non-aqueous PEMs for fuel cell applications. In this thesis, polymer membranes like the aliphatic Perfluorosulfonic acid (PFSA) membranes [for example: Nafion (Dupont), Aciplex (Asahi Chemicals Co.) and Dow (Dow Chemicals)] and hetero aromatic benzimidazole based membranes (ABPBI) are chosen for investigation using Molecular Dynamics (MD) simulations. A characterization of ammonium based ionic liquids (ILs) using MD simulations and experimental techniques is also presented in this thesis.

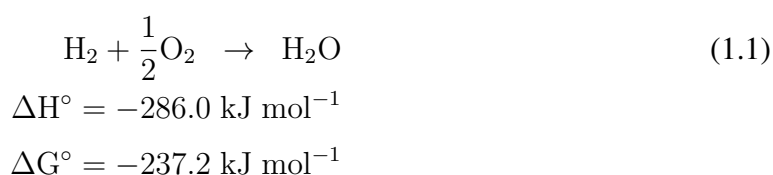
MD simulations on trifluoromethanesulfonic (triflic) acid and triflate ion-water mixtures are performed to mimic the functional group of hydrated PFSA polymer electrolyte membranes where the sulfonate group is responsible for proton conduction. Subsequently, a comparative study of pendant-water mixtures of Dow, Aciplex and Nafion membranes is performed to investigate the role of the ether oxygen in side chain and the side chain length. The nanostructure of the full Aciplex ionomer membrane and dynamics of hydronium ions and water molecules is also investigated. A molecular investigation of the hydrated ABPBI polymer membrane doped with phosphoric acid (PA) and triflate ion (TFA) is performed for high temperature PEM fuel cells. Classical MD simulations are employed to compare the structure and dynamics of ABPBI+PA, ABPBI+TFA and ABPBI+PA+TFA blends at varying hydration. The effect of different parameters such as thermostat, coupling time and system size for the accurate determination of shear viscosity is examined using an Extended Simple Point Charge (SPC/E) water model. The relation of electrostatic, cation–phenyl and C–H/phenyl interactions with the structure and dynamics of benzyl-NX₃ (X=methyl, ethyl) trifluoromethanesulfonate ILs is characterized using MD simulations and Electro-chemical Impedance Spectroscopy (EIS). The characterization of the role of asymmetry of cation and N–H/ π interactions in proton transfer using *ab initio* MD can be the focus of future activities. Such a study can provide further insights to design novel protic ILs for various technological applications.

Chapter 1

Introduction

1.1 Polymer Electrolyte Membrane fuel cells

Fuel cells (FCs) are electrochemical energy conversion devices [1] which generate power by a spontaneous (direct) electrochemical reaction of fuel and oxidant at the cell electrodes. Historically, fuel cells were invented in the 19th century followed by enhanced technological development in the 20th century and is focused on clean, portable and efficient energy in the current century. Sir William Grove first demonstrated H₂/O₂ fuel cell with spongy Platinum (Pt) electrode using sulfuric acid as an electrolyte in 1839. The analysis of the fuel cells by W. Ostwald in 1894, showed the advantages of the fuel cells over thermal engines and suggested that it is a prominent source of electrical energy from chemicals with “*no smoke, no soot, and no fire.*”



Fuel cells are classified [1, 2] on the basis of fuel cell operation at low and high temperature (see Table 1.1). Low temperature fuel cells are classified into Proton Exchange Membrane/Polymer Electrolyte Membrane Fuel Cell (PEMFC), Phosphoric Acid Fuel Cell (PAFC) and Alkaline Fuel Cell (AFC) on the basis of electrolyte medium. Similarly, high temperature fuel cells are classified into Molten Carbonate Fuel Cell (MCFC) and Solid Oxide Fuel Cell (SOFC). PEM fuel cells have attracted a lot of attention as they

Table 1.1: Classification of fuel cells.

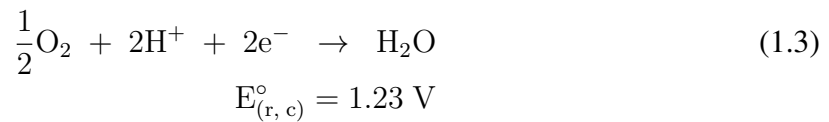
Type	Operating Temp.	Electrolyte	Charge Transport
AFC	60–120 °C	Alkaline base	OH [−] from cathode to anode
PEMFC	60–180 °C	Ion Exchange Membrane	H ⁺ from anode to cathode
PAFC	160–200 °C	Immobilized liquid H ₃ PO ₄	H ⁺ from anode to cathode
MCFC	560–660 °C	Immobilized liquid Carbonate	CO ₃ ^{2−} from cathode to anode
SOFC	750–1000 °C	Ceramics (Y ₂ O ₃ stabilized ZrO ₂)	O ₂ [−] from cathode to anode

serve as promising sources of alternative energy for stationary and portable applications. Further, they have a capability to deliver high power density with minimal pollution with fewer issues of electrolyte management. A typical PEM fuel cell consists of a Membrane Electrode Assembly (MEA) in which the solid polymer membrane is sandwiched between two Pt catalyzed porous gas diffusion electrodes (see Figure 1.1). H₂ and O₂ gases are used as a fuel in PEM fuel cell where the half cell reactions occur at the electrodes as seen from the below reactions:

At the anode:



At the Cathode:



The use of solid polymer membrane as an electrolyte in PEM fuel cells has the following advantages:

- Effective power generation for a specific power density.
- Low corrosion compared to liquid electrolyte.

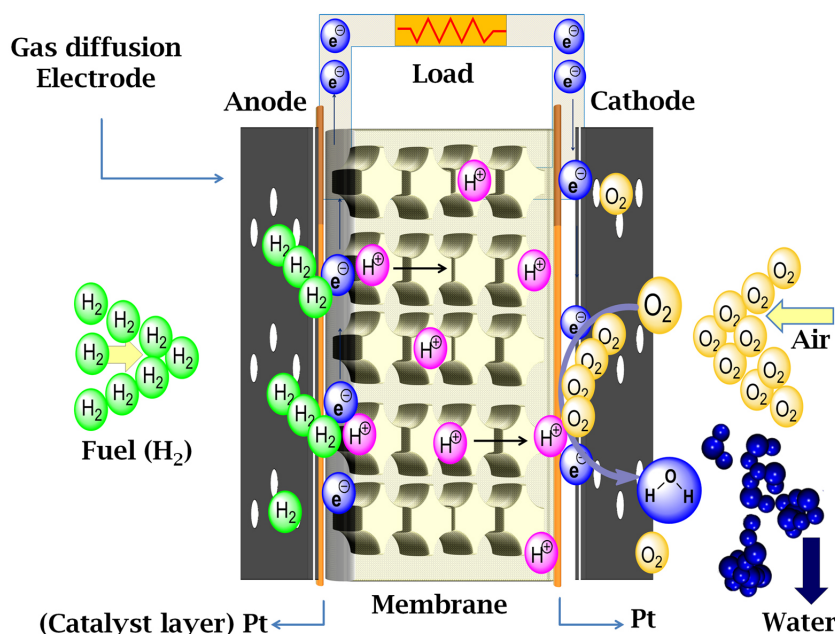


Figure 1.1: Membrane electrode assembly in PEM fuel cell.

- Large operating temperature range and quick start up.
- Fuel cell stack design and system compactness.
- Ease in electrolyte handling and power management.
- Wide range of applications: portable, stationary power generation and automotive energy applications.

1.2 Polymer membrane materials as a quasi-solid electrolytes

The polymer membrane used as quasi-solid electrolyte plays a critical role in the conductivity of the PEM fuel cell. The role of the membrane is to facilitate transport of protons from anode to cathode. The properties of an ideal PEM include high proton conductivity, durability, thermal, chemical and mechanical stability under prolonged fuel cell operation. The first PEM fuel cell based on sulfonated poly(styrene-divinylbenzene) copolymer grafted with polystyrene sulfonic acid membranes (PSSA) was tested as an

auxiliary source of power [1] in NASA Gemini Space Vehicles in early 1960s. The replacement of PSSA due to low power density ($<100 \text{ mW/cm}^2$) with shorter life time (few weeks) was achieved by the subsequent synthesis of aliphatic Perfluorosulfonic acid (PFSA) membrane called as Nafion [3, 4] by General Electric/Dupont which brought a revolution in the development of PEM fuel cells. This made it possible to achieve high power density ($>400 \text{ mW/cm}^2$) with longer lifetimes as evident by 30-day Biosatellite space mission [2] of NASA. More examples of PFSA membranes used in PEM fuel cells are Aciplex (Asahi Glass) [5, 6] Dow (Dow Chemicals) [7–9]. Further, aromatic membranes like Polyetherketones [10, 11] (PEEK, PEEKK) and Polybenzimidazole (PBI) [12] are also developed. Among these membranes, the Nafion polymer membrane has been studied extensively by experiments [3, 4, 13–15] and computational methods [16–27].

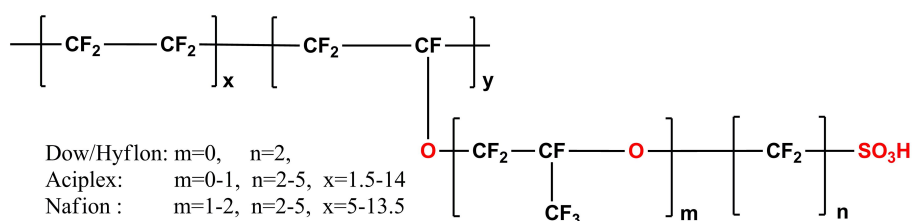


Figure 1.2: The chemical structure of PFSA polymer membranes.

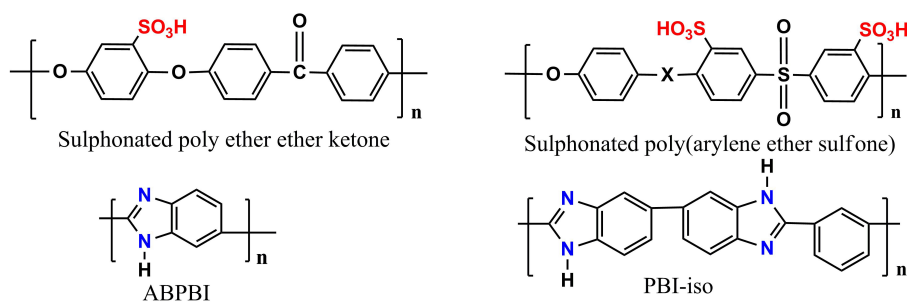


Figure 1.3: The chemical structure of aromatic polymer membranes.

The PFSA membranes (consist of terminal acidic sulfonate group) are of particular interest due to their inherent electro-chemical properties and an ability to satisfy all requirements necessary for a choice of an ideal electrolyte membrane. However, the conductivity of Nafion is strongly dependent on hydration [21–23, 28]. Further, the operating temperature of fuel cells using Nafion is limited to the boiling point of water (i.e. 100°C). At this temperature there is a low tolerance (10-20 ppm at 80°C) of the electro-catalyst like Pt

against CO poisoning and increases substantially with temperature (1000 ppm at 130 °C and 30000 ppm at 200 °C). Savinell *et al.* [29] attempted to replace water by incorporation of the highly volatile phosphoric acid (boiling point 160 °C) in Nafion to increase the fuel cell operating temperature upto 150 °C. The Nafion/H₃PO₄ electrolyte was successfully tested though a failure of the anode electrode occurred due to possible migration of anion and consequent electrode flooding.

Table 1.2: Commercially available PFSA polymer electrolyte membranes.

Type	Equivalent weight	Thickness (μm)
Dow	800	125
Aciplex-S	1000	25-100
Nafion 112	1100	50
Nafion 115	1100	125
Nafion 117	1100	175

A modification of PFSA membranes like Nafion and other membranes were also investigated to sustain high CO tolerance and thermal, water management [30]. Aromatic polymer membranes like poly(ether ether ketone), poly(arylene ether sulfone) were also developed and modified with sulfonation but were found to be limited to the boiling point of water. In high temperature fuel cells, aromatic membranes based on benzimidazole (which are basic in nature) are found to be effective to operate up to 200 °C. The simplest polymer electrolyte with a benzimidazole functional group called poly(2,5-benzimidazole) (ABPBI) polymer membrane, was synthesized by the polymerization of 3,4-diamino benzoic acid (DABA) [12, 30–32]. Several derivatives of benzimidazole based membranes were synthesized (see Figure 1.3) to improve fuel cell efficiency. For example, blends of phosphoric acid (PA) with the poly[2,2-(m-phenylene)-5,5-bibenzimidazole] (m-PBI) was successfully tested [33] in fuel cells to operate up to 200 °C. These membranes doped with phosphoric acid (PA) serve as replacement of water for transport of protons. The specific choice of dopant (water, PA etc.) in polymer membranes is crucial for proton conductivity and fuel cell operating temperature. The performance of polymer membranes and proton conductivity is limited by the dopant which plays a key role in proton transport. In the next section, the mechanism of proton transport in hydrated or PA doped polymer membranes is discussed.

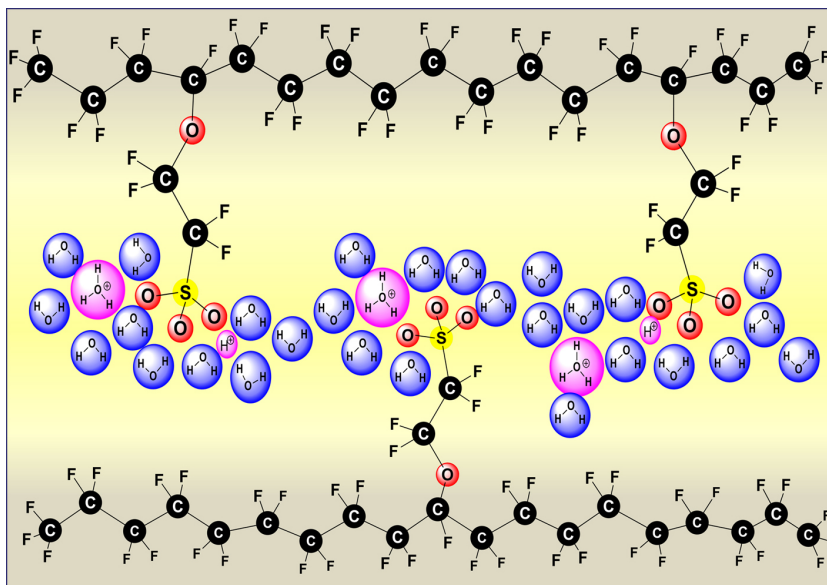


Figure 1.4: A schematic view of water-proton nano-channels in hydrated rod shaped side chains of a PFSA polymer matrix.

1.3 Mechanism of proton transport

PFSA polymer membranes have a terminal sulfonate group which acts as an acidic site and is responsible for proton transport in the presence of water (see Figure 1.4). The contribution of bulk water in proton conduction is known as “vehicular diffusion”. In vehicular diffusion, the proton does not migrate as H^+ , but move as OH_3^+ (hydronium ion) or NH_4^+ (ammonium ion) [34] bonded to a “vehicle” like H_2O and NH_3 . The contribution of vehicular diffusion to proton transport in PFSA membranes is associated with the self-diffusion of water [$D_{H_2O}(\text{bulk}) \sim 2.5 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$] and strongly depends on the level of hydration. In PFSA membranes, the vehicular proton transport occurs via a hydronium ion diffusion through water nano-channels. These water channels are formed around the sulfonate group of the pendant chain as depicted (see Figure 1.4) in a sandwich [35] model. There are several models proposed to illustrate morphology of water nano-channels in the PFSA polymer matrix from Small Angle Neutron Scattering (SANS) and Small Angle Neutron Scattering (SAXS) studies with the assumption of distribution of water in rod [35] and spherical [36] like aggregates. It is difficult to directly distinguish between the spherical and rod like aggregates from SAXS and SANS experimental studies [9, 35–38] due to limitations of the scattering range. Schmidt-Rohr and

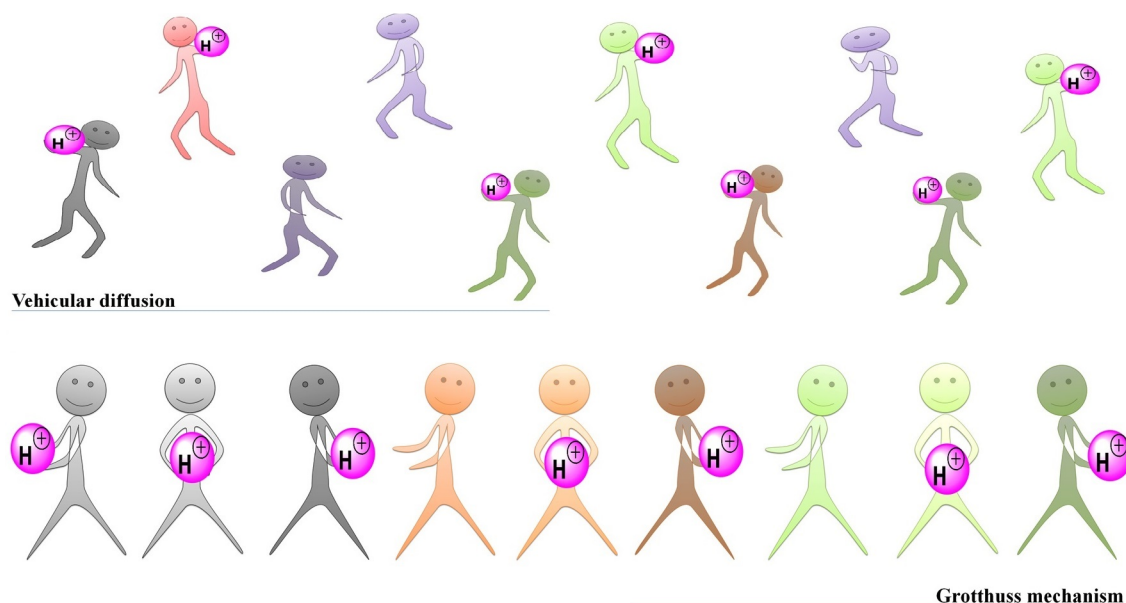


Figure 1.5: A schematic illustration of vehicular diffusion and structural diffusion.

Chen [39] proposed a parallel cylindrical water channel model in Nafion membrane by analyzing SAXS scattering data from simulation and a modified inverted micelles model proposed by Gierke *et al.* [37] and Gebel [9].

In previous studies, apart from the vehicular diffusion of protons, the mobility of protons was proposed to be associated with an infinite network of hydrogen bonds through water molecules which occur in two steps. First, the translation of a proton from an oxonium ion to a water molecule by tunneling in a hydrogen bond and subsequent reorientation (rotation) of the water molecule [34]. The reorientation (rotation) of the water molecules leads to an abstraction or donation of the next proton (see Figure 1.5). Further, a microscopic picture of proton transport through hydrogen bond networks have also been characterized by experiments and theoretical methods [40–42]. The proton associated with a single water molecule gives rise to a hydronium ion (H_3O^+) which consists of three equivalent protons. The hydrated hydronium ion can bind with three water molecules due to strong hydrogen bonding, which is called an Eigen-ion [43]. If a proton is shared between two water molecules in a symmetric intermediate complex, it is called as a Zundel-ion [44] (see Figure 1.6). The hopping of a proton from a proton donor such as H_3O^+ to neighboring water molecules leads to a structural diffusion (also known as “Grotthuss Mechanism”).

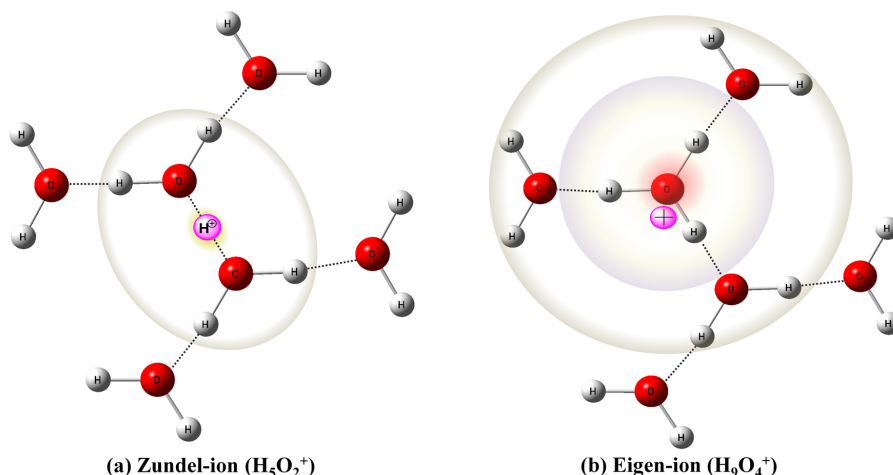


Figure 1.6: Proton conduction in through water molecules where proton diffuses by displacement of center of symmetry between a) Zundel-ion and b) Eigen-ion.

The structural diffusion occurs via a hydrogen bonded network which involves a displacement of center of symmetry from the proton (H^+) to oxygen (O) atom in the Zundel-ion and the Eigen-ion respectively and *vice versa* (see Figure 1.6). A small energy barrier of $\sim 2.4 \text{ kJ mol}^{-1}$ [40,45] between the Eigen-ion and the Zundel-ion leads to a consecutive chain of hydrogen bond breaking and hydrogen bond formation in “Eigen–to–Zundel” and “Zundel–to–Eigen” ion transitions respectively. Marx *et al.* [40] examined the nature of the hydrated excess proton in water by considering a time-independent thermal equilibrium and quantum fluctuations of all nuclei in simulation. The authors observed that the quantum fluctuations lead to a fluxional defect (delocalized over several hydrogen bonds) in the hydrated proton. Hence, first and/or second solvation-shell rearrangements in water molecules can strongly influence dynamic nature of hydrogen-bonds and contribute to the structural diffusion of protons. Chandra *et al.* [46] showed that the kinetics of proton transport depends on the solvation of protons involved in hydrogen bonding. The authors showed that “*proton rattling*” involves an actual charge-displacement event through hydrogen-bond network where the proton (charge defect) returns to the oxygen atom (O^* or O of the H_3O^+) from which it originated. Berkelbach *et al.* [47] showed a concerted proton transfer from simulation driven by hydrogen-bond breaking and formation at different sites of hydronium ion within the first and second solvation-shell of water molecules (see Figure 1.7). Recently, Hassanali *et al.* [48] characterized structural diffusion using first-principle simulations and demonstrated proton transfer in water is a multi-scale and multi-dynamical process. Hence, it is important to understand that how

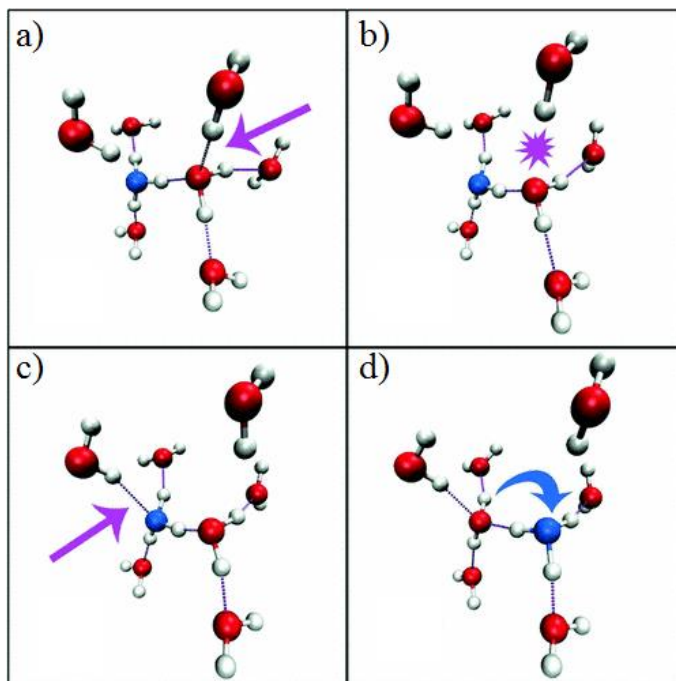


Figure 1.7: Snapshots of an example of proton-transfer event from the actual simulation where O^* is blue, oxygen atoms are red, hydrogen atoms are white, and hydrogen-bonds are purple. [Reprinted (figure) with permission from Berkelbach *et al.* [47] Copyright (2009) by the American Physical Society]

proton transport occurs in quasi-solid polymer electrolyte membranes which require solvent molecules as a charge carrier.

1.4 Review of prior work: molecular modeling and simulations

The polymer membrane used as a quasi-solid electrolyte plays a critical role in proton conductivity. There are certain parameters which influences the performance of PEM fuel cells using PFSA membrane such as hydration, solvent/water uptake, electrode water flooding and operation at low temperature ($<80^\circ\text{C}$). A detailed structural description and study of membrane morphology at a molecular level can facilitate the design of new or alternate cost effective membrane materials. Experimental methods such as Transmission Electron Microscopy (TEM), SAXS and SANS are quite expensive and are not very accu-

rate to provide molecular level insights on membrane nanostructure. However, molecular modeling and simulation methods have been used to characterize membrane morphology and dynamical properties. Classical Molecular Dynamics (MD) simulations can provide atomistic details of water orientation in membrane matrix.

Mauritz and Moore [4] reviewed several aspects of PFSA membranes using Nafion as a model membrane. Wu *et al.* [49] studied effect of molecular weight on hydrated morphology of PFSA membranes using Dissipative Particle Dynamics (DPD) and found that increase in molecular weight induces phase segregations which results in larger/elongated water domains at high molecular weight. Liu *et al.* [28] studied relationship between the structure and hydrated morphology of PFSA membranes. The authors concluded that water diffusivity enhances with decrease in polymer equivalent weight due to better connectivity and reduced confinement of polymer backbone. The molecular modeling study of PFSA membranes by Paddison and Elliot [20] suggested that structural diffusion occur in-spite of strong sulfonate-water interactions. The authors also concluded that connectivity between the sulfonate groups of two side chains through a hydrogen bond network of water molecules depends on CF_2 units which separates two side chains. Jang *et al.* [50] studied the monomeric sequence effect on nanophase segregation and transport in Nafion 117 using MD simulations. The authors concluded that water diffusion was larger in blocky sequence compared to the dispersed phase due to the formation of large water clusters and nano channels in the blocky sequence. The diffusion of hydronium ions was 6-10 times lower compared to water as seen in the work of Venkatnathan *et al.* [21] and Devanathan *et al.* [22,23] from MD simulations in hydrated Nafion. Perrin *et al.* [15] examined dynamics of molecular transport in hydrated Nafion using Quasi-Elastic Neutron Scattering (QENS). The authors observed slower hydronium ion diffusion due to 2.5-4.5 times larger mean residence time of hydronium ion compared to water. Hayes *et al.* [51] studied proton transport in triflic acid hydrates to mimic hydrated PFSA membrane sulfonate group using Path Integral Car-Parrinello Molecular Dynamics simulations. The authors concluded that proton transferred to water molecules most strongly binds with a sulfonate group via a Grotthuss-type mechanism and quickly returns to the most solvated bulky CF_3SO_3^- defect structure. Among the several simulation studies reported so far, classical MD simulations have been extensively used to characterize membrane nanostructure and water-proton dynamics. The accuracy of MD simulations and determination of macroscopic properties depends on the choice of force-field parameters. A brief description of force-field, its advantages and limitations are presented in the next Section.

1.5 Force-field

The potential energy of a molecular system consists of bonding and nonbonding interactions. The bonding interactions are bond, angles, proper and improper dihedrals. The non-bonding interactions energies are van der Waals and electrostatic interactions. The total potential energy is written as:

$$V_{\text{Total}} = V_{\text{bonding}} + V_{\text{non-bonding}} \quad (1.4)$$

$$V_{\text{bonding}} = \sum_{\text{bond}} \frac{k_b}{2} (r - r_0)^2 + \sum_{\text{angle}} \frac{k_\theta}{2} (\theta - \theta_0)^2 + \sum_{\text{dihedral}}^{n=0-5} C_n (\cos(\psi))^n \quad (1.5)$$

where, k_b and k_θ are force constants for bonds and angles respectively, C_n is dihedral coefficient, $\psi = \phi - 180^\circ$, where ϕ denotes a dihedral angle.

$$V_{\text{non-bonding}} = \sum_{i,j} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{\epsilon_r r_{ij}} \quad (1.6)$$

where, σ_{ij} and ϵ_{ij} are van der Waals parameters and calculated by using an arithmetic average for sigma and a geometric average for epsilon. The ϵ_0 is permittivity of vacuum, ϵ_r is relative dielectric constant and q_i and q_j denotes partial charges on different atoms. The mathematical expression in Eqn. 1.5 and 1.6 is called as force-field, where all parameters are either obtained from experiments or from quantum calculations. It is a tedious task to derive a sufficiently accurate force-field for a molecular system of interest which is based on assumptions, approximations and simplifications of the molecular model. The reliability of force-field and their contributions to the overall accuracy of simulations is significantly subjected to the property of interest, methodology and adopted algorithms [52].

1.5.1 Empirical force-fields

Classical MD simulations which employ empirical force-fields have attained tremendous popularity for several decades due to its application to characterize numerous macroscopic properties of macromolecular and bimolecular systems at an atomistic level. Empirical models allow numerical simulations at fairly low computational cost at longer time scale (upto microseconds) and larger length scale (upto hundreds of nanometers). The param-

eters of these empirical force-fields are derived from experimental observables and/or *ab initio* calculations. However, empirical force-fields severely lack the ability to study the following physical and chemical process:

- molecular motion at low-temperature (0-10 K),
- motion of light atoms (such as hydrogen atoms) even at room temperature,
- chemical reactions which include bond breaking and bond formation.

Apart from these limitations [52], electronic polarization and nuclear quantum effects are generally not included in such molecular force fields. The inclusion of these effects in empirical models enhances the accuracy of target properties and brings it closer to experiment.

1.5.1.1 Polarizable force-fields

The accuracy of molecular interactions for ions, ion–pair interactions, and cation– π interactions which may reflect into condensed phase properties of a system requires an explicit description of electronic polarization (accounts a local displacement of charge) in the force-field [41, 53, 54]. The current electrostatic models include electronic polarizability implicitly by choosing partial atomic charges which overestimate molecular dipoles. The improvement in structure and energetics can be performed by an explicit description of electronic polarization in force-field such as:

$$U_{\text{Pol.}} = \frac{1}{2} \sum_i \mu_i E_i \quad (1.7)$$

where, μ_i is the dipole moment and E_i is the electrostatic field at atom i , respectively. Lamoureux *et al.* [55] found that the success of polarizable force-field models in macromolecular systems is not so clear due to the inability to directly transfer gas phase molecular polarizabilities to the condensed phase. The authors suggested that “*such effects arise due to the energy associated with overlapping of electronic clouds in the condensed phase due to Pauli’s exclusion principle opposing induction*” [55].

1.5.1.2 Nuclear quantum effects

Nuclear quantum effects (NQEs) play a significant role in characterization of hydrogen bond interactions and proton transport. Tuckerman *et al.* [56] employed *ab initio* tech-

niques to explore the quantum character of the shared proton in the hydrogen-bonded complexes of water molecules (H_5O_2^+ and H_3O_2^-). The authors found that oxygen-oxygen separation (hence the strength of the hydrogen bond) was strongly influenced by the quantum character of protons. The authors also concluded that NQEs were more pronounced in H_3O_2^- compared to H_5O_2^+ . Raugei and Klein [57] investigated the role of NQEs on hydrogen bonding in liquids. The authors concluded that inclusion of NQEs can lead to stronger hydrogen bonds (compared to classical results) in strongly Hydrogen bonded liquids. Chen *et al.* [58] performed path integral CPMD simulations and analyzed hydrogen bonding in water. The authors found an enhancement in the dipole moment of water due to inclusion of zero-point energy. Morrone and Car [59] showed that inclusion of NQEs leads to softening of water structure. Ceriotti *et al.* [60] found that nuclear motion have a qualitative impact on the hydrogen bond fluctuations and increase in fluctuations may leads to a partial dissociation of the covalent OH bond (see Figure 1.8). However, *ab initio* MD simulations which include NQEs have a prohibitively high computational cost and remains limited to simulation on small time and length scales.

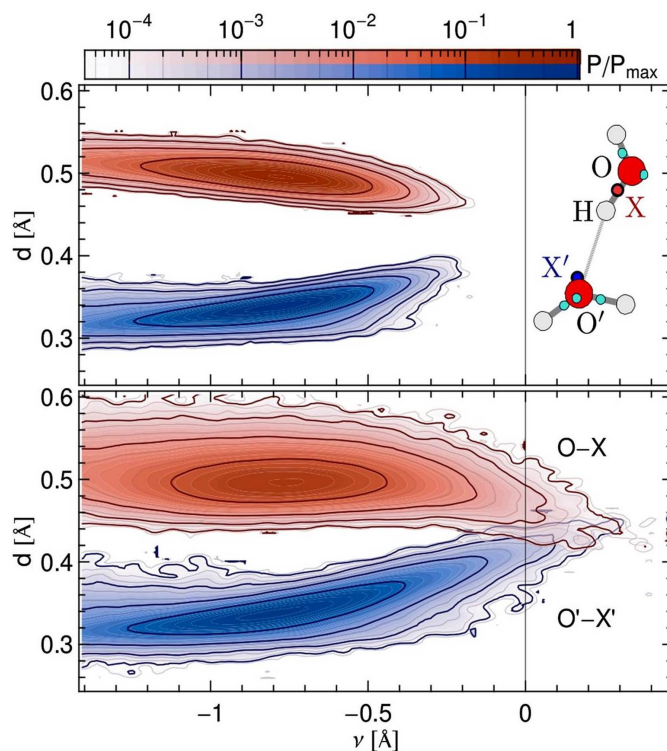


Figure 1.8: A classical simulation of liquid water (Upper) and a simulation that includes NQEs (Lower) (Adapted from Ceriotti *et al.* [60] Copyright 2013 National Academy of Sciences, USA).

1.5.2 Reactive force-fields

Reactive force-fields such as Reactive Empirical Bond Order (REBO) [61–63], Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) [64], and ReaxFF [65] have been developed to model chemical reactions which include bond breaking and formation. In general, these force-fields employ a bond length/bond order relationship, where the bond orders are updated at each time step. The other bonded interactions such as angles and torsions are also made bond-order dependent to ensure that their energy contributions disappear upon the bond dissociation [61–65]. van Duin *et al.* [65] developed a Reactive Force-Field (ReaxFF) to study complex chemical reactions in hydrocarbons using MD simulations for a system containing thousands of atoms. The authors showed that simulations using reactive force-field were much faster compared to *ab initio* methods. Chenoweth *et al.* [66] parameterized a reactive force-field to model C-Si systems and investigated the thermal decomposition of poly(dimethylsiloxane) polymer. Wang and Voth [67] developed the multi-state empirical valence bond (MS-EVB) reactive MD method to describe the physics of excess hydrated protons in water. Selvan *et al.* [68] parameterized reactive force-field to model proton transport in Nafion and found that diffusion coefficients of water molecules in hydrated Nafion was closer to experiments due to inclusion of structural diffusion of protons (modelled by the reactive force-field). While reactive force-fields are more accurate compared to empirical force-fields, the parameterization of reactive force-fields for macromolecular systems is time consuming and an arduous task.

1.6 Classical force-fields: an application to PEM

Proton transport, rearrangement of the proton solvent network, and polymer dynamics take place on different time and length scales. Though, classical MD simulations cannot describe structural diffusion of protons, it does possess certain advantages over *ab initio* MD and reactive MD simulation methods. For example, for a large macromolecular system (~ 100000 atoms), the diffusion of water molecules and water network formation (water clusters in polymer matrix) can be studied using classical MD with empirical force fields, accounting all polymeric interactions and chain conformations. Further, these simulations can be performed using reasonable computational effort for longer time scale (hundreds of nanoseconds). In the present thesis, to investigate structural and dynamical properties of large polymeric system at different hydration and acid concentration,

classical MD simulations are employed using empirical force-fields. In the next Section, the understanding of theoretical concepts and general protocol of input design, simulation parameters, analysis of output and visualization (see Figure 1.9) using classical MD simulations is discussed.

1.7 Methodology: simulation protocol, analysis and visualization

In this thesis, the GROMACS software program is used to perform MD simulations, though other simulation codes can also be used. The details of input preparation, simulation protocol and simulation parameters are described (by choosing Aciplex as model polymer membrane) as follows:

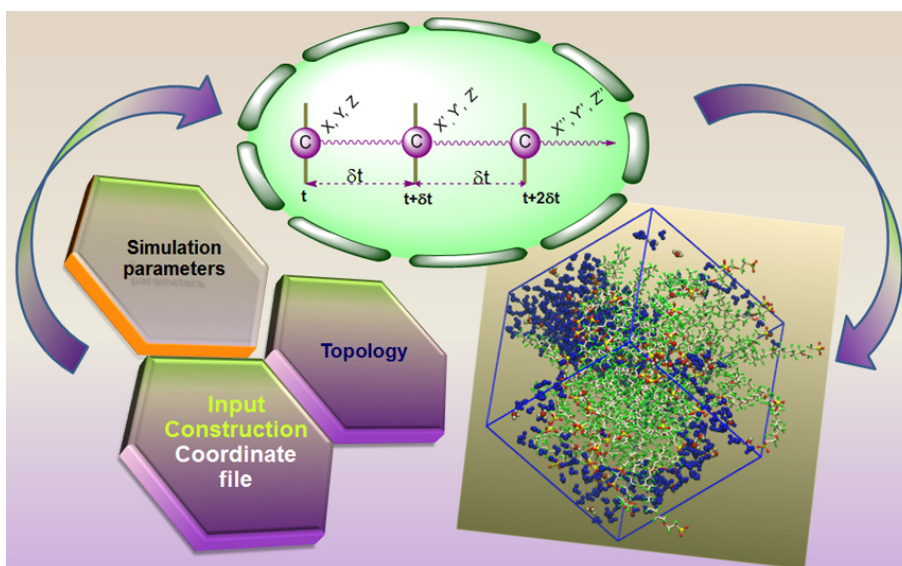


Figure 1.9: A schematic view of design and setup of a MD simulation.

1.7.1 Atomic coordinates of molecular structure and topology

The atomic coordinates of any molecular structure in three dimensions can be represented either as a Z-matrix, protein data bank (pdb) or a gro file format. The molecular structure is generated using a molecule builder software like MOLDEN [69], VMD [70], Gaussview [71]. The input molecule should be placed in a simulation box which can be cubic ($a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$), hexagonal ($a = b \neq c$, $\alpha = \gamma = 90^\circ$ and

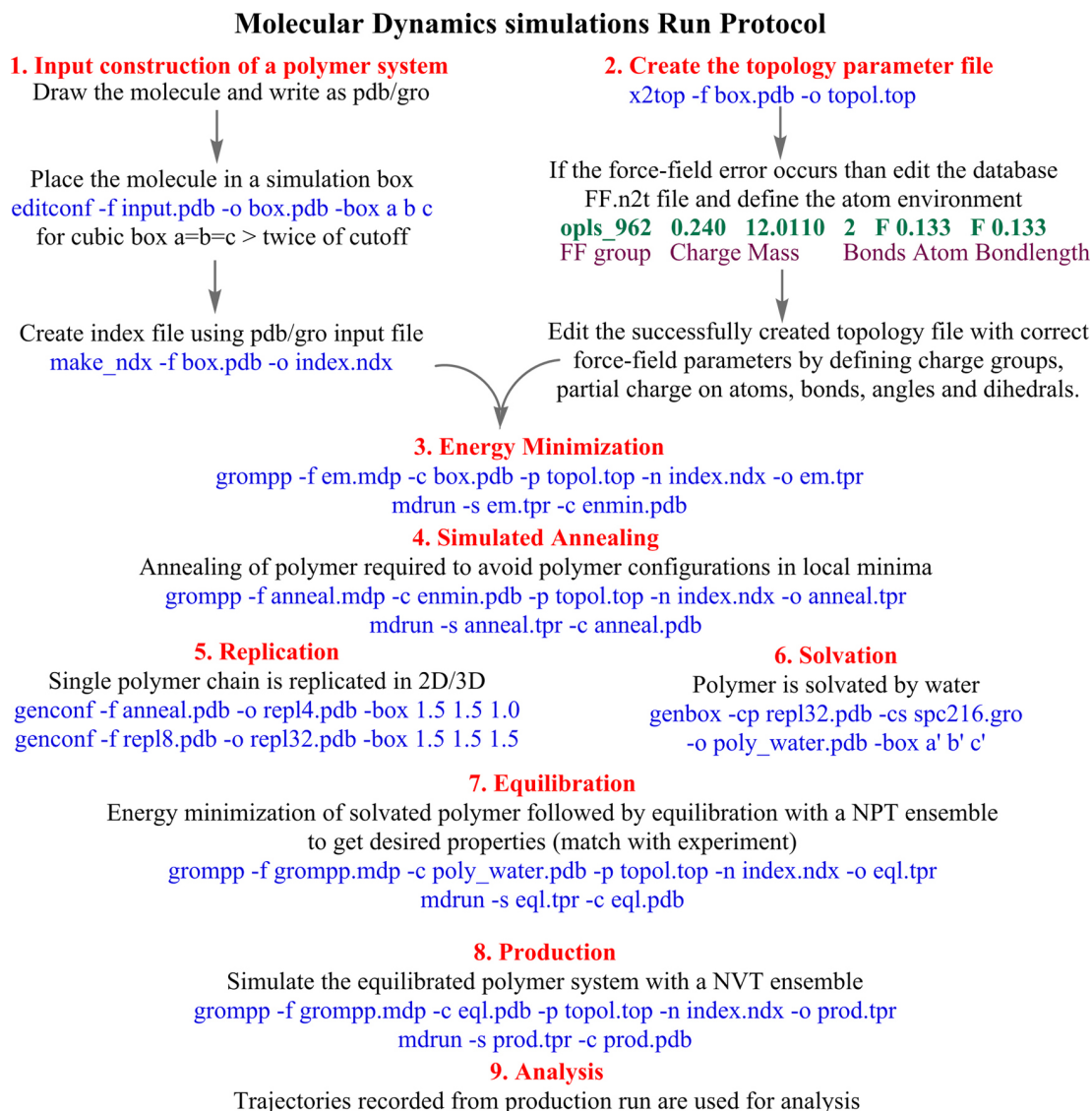


Figure 1.10: MD simulation protocol for hydrated polymer using GROMACS.

$\beta = 120^\circ$) or Triclinic ($a \neq b \neq c$ and $\alpha = \beta = \gamma \neq 90^\circ$). For example, a single polymer chain of PFSA (Aciplex) polymer membrane can be created in a cubic box as shown in step-1 of Figure 1.10. In the present study, the force-field parameters for polymer membranes are taken from the OPLS-AA (see Figure 1.10, step-2) force-field database [72].

1.7.2 Energy minimization, annealing, replication and solvation

A single polymer unit (For example, Aciplex ionomer membrane along with hydronium ion) was energy minimized (see Figure 1.10, step-3) using a steepest descent algorithm [73]. Energy minimization removes bad contacts present in initial molecular geometry of system. The energy minimized configuration was used as an input and a simulated annealing (see Figure 1.10, step-4) was performed by heating from 300 K to 750/1000 K and cooled back to 300 K with an annealing time. The annealing points were chosen with a temperature increase of 50 K with a time-step of 50 ps.

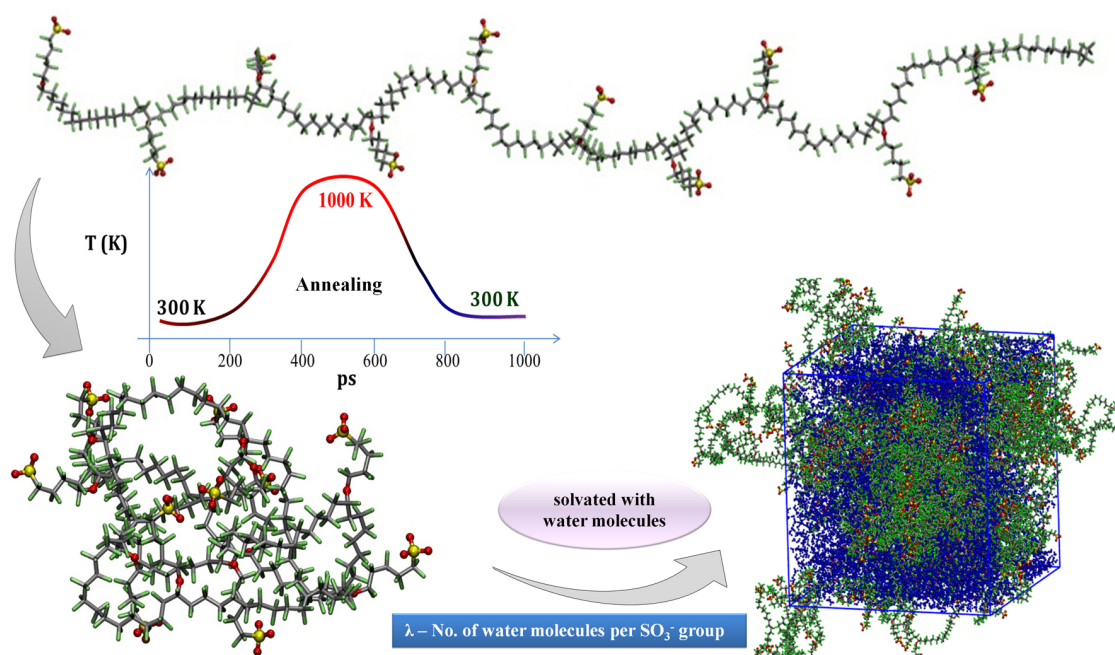


Figure 1.11: A schematic illustration of simulated annealing followed by replication and water solvation for PFSA (Aciplex) polymer chain.

The simulated annealing procedure was repeated till the simulated density is in agreement with the experimental density. The final configuration from the annealing procedure was used to create a larger system. For example, a single polymer chain of Aciplex ionomer along with hydronium ion was replicated 4 times in 2 dimension space (see Figure 1.10, step-5) and output configuration was used to replicate 8 times in 3 dimension space. The system with 32 polymer chains was used to generate a hydrated polymer configuration of Aciplex + water. Aciplex polymer chains was solvated with water molecules using a water input file (spc216.gro) to generate a specific ratio of ionomer and water (see

Figure 1.10, step-6). A schematic of simulated annealing for Aciplex polymer chain followed by replication and water solvation is shown in Figure 1.11. In the present thesis, a similar protocol was adopted for input design to perform classical MD simulations on hydrated, acid doped polymer membranes and Ionic Liquids (ILs).

1.7.3 Analysis

1.7.3.1 Radial Distribution Function

The structural properties of the membranes or ILs and interactions with solvent (water) can be examined from Radial Distribution Functions (RDFs). The RDF of any particle B around the reference particle A is calculated [74] as:

$$g_{AB}(r) = \frac{1}{\langle \rho_B \rangle_{\text{local}} N_A} \sum_{i \in A}^{N_A} \sum_{j \in B}^{N_B} \frac{\delta(r_{ij} - r)}{4\pi r^2} \quad (1.8)$$

where, $\langle \rho_B \rangle_{\text{local}}$ is the particle density of particle B, averaged over all spheres around reference particle A.

1.7.3.2 Scattering Intensity and Structure factor

The structure factor [75] calculated from a Fourier transform of the RDF, $g(r)$, and is written as:

$$S_{ij}(Q) = 4\pi\rho \int_0^\infty r^2 dr (g_{ij}(r) - 1) \frac{\sin Qr_{ij}}{Qr_{ij}} \quad (1.9)$$

where, ρ is the atomic density, $Q = 2\pi/\lambda_S$ is momentum transfer, λ_S is the scattering wavelength, $g_{ij}(r)$ is the radial distribution function from atom types i and j , r_{ij} is the inter-molecular distance between atom i and j .

The calculation of scattering intensity, $I_{ij}(Q)$, is defined as:

$$I_{ij}(Q) = \sum_{ij} x_i x_j f_i(Q) f_j(Q) \frac{\sin Qr_{ij}}{Qr_{ij}} + \sum_{i \leq j} x_i x_j f_i(Q) f_j(Q) S_{ij}(Q) \quad (1.10)$$

where, x_i and x_j are the atomic fraction of atoms i and j respectively, $f_i(Q)$ and $f_j(Q)$ are the Q dependent atomic scattering factor for atoms i and j respectively [75].

1.7.3.3 Radius of gyration

The radius of gyration of a polymer chain [76, 77] is calculated as:

$$R_g = \sqrt{\frac{\sum_i \|r_i\|^2 m_i}{\sum_i m_i}} \quad (1.11)$$

where, m_i is the mass of atom i , r_i is the position of atom i with respect to the center of mass of the polymer chain.

1.7.3.4 Mean Square Displacement

The Mean Square Displacement (MSD) is calculated using the Einstein relationship [74] and can be written as:

$$\lim_{t \rightarrow \infty} \langle \|r_i(t) - r_i(0)\|^2 \rangle_{i \in A} = 6D_A t \quad (1.12)$$

where r_i is the center of mass position of any molecule and D_A is the corresponding self-diffusion coefficient.

1.7.3.5 Nernst-Einstein ionic conductivity

The ionic conductivity is calculated using the Nernst-Einstein equation [78] from the diffusion coefficients (D_A) of cations and anions and can be written as:

$$\sigma_{NE} = \frac{N_{\text{pair}}}{V k_B T} (q_+^2 D_+ + q_-^2 D_-) \quad (1.13)$$

where N_{pair} is the number of total ion-pair in system, V is the simulation box volume, k_B is the Boltzmann constant and T is temperature. q_+ and q_- are the total charge of the cations and anions respectively. D_+ and D_- are the corresponding self-diffusion coefficient of cation and anion respectively.

1.7.3.6 Activation Energy

From the diffusion coefficients (D_A), the energy of activation (E_A) of diffusion is calculated using an Arrhenius equation and can be written as:

$$\ln D_A = \ln D_0 - \frac{E_A}{RT} \quad (1.14)$$

1.7.4 Visualization

A visual inspection/representation can be achieved by a visual molecular dynamics program (VMD 1.9.1) [70] or Chimera [79]. The visualization of output coordinates can be represented by Perspective, Orthographic and Surface representation. For example, Figure 1.12a shows a surface view of the hydrophobic backbone of the hydrated PFSA membrane and water channel formation. A Licorice view, orthographic view and perspective view of water molecules, hydronium ions and PFSA ionomer are shown in Figure 1.12(b-d) respectively.

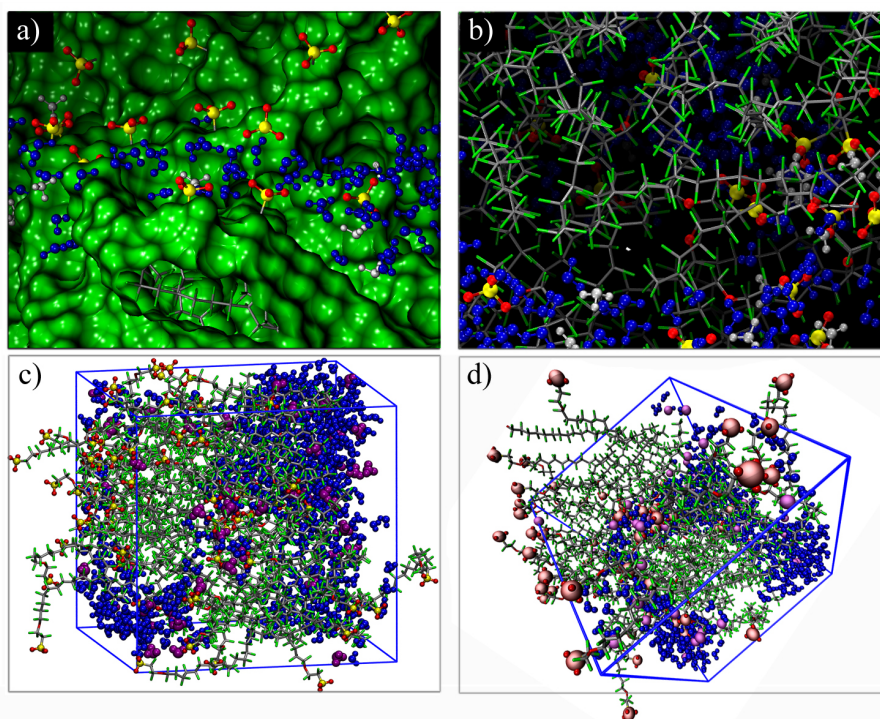


Figure 1.12: Snapshot of hydrated PFSA ionomer (a) shows water channels in hydrophobic (surface view); water molecules in polymer matrix (b) Licorice view, (c) orthographic view and (d) perspective view.

Apart from MD simulations on PEMs, this thesis also includes synthesis and characterization of benzyl-NX₃ (X=Methyl, Ethyl) trifluoromethanesulfonate (TFA) ILs as electrolytes in fuel cells. The conductivity of these ILs is crucial for fuel cell applications and is characterized by Electrochemical Impedance Spectroscopy (EIS). A brief description of impedance and ionic conductivity measurement using EIS is discussed in the next Section.

1.8 Impedance measurement: Electrochemical Impedance Spectroscopy

Impedance of ILs is measured using BioLogic Science Instrument and RH is controlled in ESPEC (SH-241) benchtop type temperature and humidity chamber. EIS measurement is performed by two probe method in the following manner: A cell is composed of two electrical conducting electrodes and a thin sandwiched layer of IL (see Figure 1.13a). These electrodes are prepared by Fluorine-doped tin oxide (FTO) coated glass electrodes. The inter-electrode space is filled with the solid IL (300 μm thickness) in an effective electrode area of $1 \times 1 \text{ cm}^2$. The obtained data from EIS can be fitted to Randles circuits of mixed kinetics and diffusion control model (see Figure 1.13b).

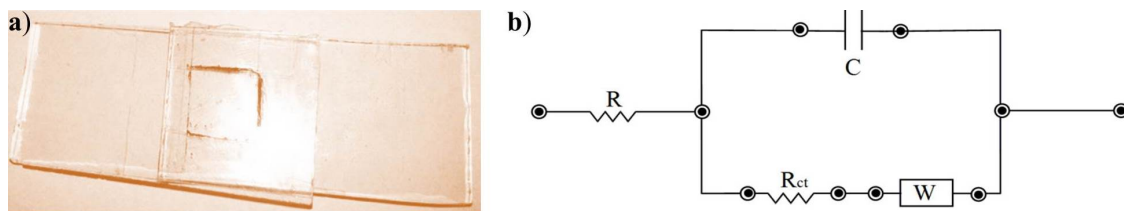


Figure 1.13: a) Snap of a cell, and b) Randles circuit of mixed kinetics and diffusion control model.

1.9 Aim/scope of the thesis

Chapter 2 describes a MD simulation study of Trifluoromethanesulfonic Acid (triflic acid). Triflic acid mimics the functional group of PFSA polymer electrolyte membranes where the sulfonate group is responsible for proton conduction. The objective of this study is to develop force-field parameters to investigate the effect of temperature and hydration on structure and dynamics of triflic acid. Some of the force-field parameters of triflic acid and triflate ion (in hydrated conditions) have been developed by using *ab initio* calculations and these parameters are integrated with the Optimized Potential for Liquid Simulations-All Atom (OPLS-AA) force-field. The developed force-field is validated with available experimental data. Classical MD simulations have been employed to characterize structural and dynamical properties of triflic acid (270 K to 450 K) and triflate ion-water mixtures (300 K).

Chapter 3 describes a comparative study of pendant-water mixtures of PFSA mem-

branes such as Dow, Aciplex and Nafion. These membranes have a similar backbone but differ in side chain. This study probes the role of side chain ether oxygen and side chain length on membrane nanostructure and water-hydronium ion dynamics as a function of hydration and temperature. Classical MD simulations have been performed on pendant-water mixtures of Dow, Aciplex and Nafion at 300 K and 350 K at varying hydration from low water content ($\lambda=3$) to high water content ($\lambda=15$). The calculated structure factors and scattering intensities reproduce the characteristic features of SANS and SAXS profiles of Dow and Nafion, and confirms the existence of spherical water aggregates in the rod shaped pendant nanostructure of Nafion. The effect of hydration on the mobility of hydronium ions at 300 K and 350 K has been investigated and the trends have been compared with experimental data. The activation energy of diffusion of hydronium ions and water molecules in Nafion pendant-water mixtures (14-25 kJ mol⁻¹) validate experimental observations (16-22 kJ mol⁻¹).

Chapter 4 describes an extensive investigation of the nanostructure of the Aciplex ionomer membrane and dynamics of hydronium ions and water molecules transport at varying hydration and temperature. The impact of polymer chain conformations and hydrophobicity with inclusion of polymer backbone on structural and dynamical properties have been examined, which were not included in the simulation study of Chapter 3. The effect of stiffness of side chain on the *intra-chain* or *inter-chain* interactions between sulfonate groups as a function of hydration and temperature has been discussed. The impact of an enlargement of hydrophobic domains assisted by the rigid side chain and polymer backbone flexibility in the Aciplex membrane on mobility of water molecules has been examined and compared with Nafion.

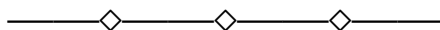
Chapter 5 describes a molecular investigation of the ABPBI polymer membrane doped with PA which is promising membrane material for high temperature PEM fuel cells. Water plays a critical role in PA doped ABPBI membrane where PA can leak out from the membrane in humidified conditions. To minimize the PA leaching from the ABPBI membrane, triflic acid (in form of triflate ion or TFA) has been proposed as a dopant. Classical MD simulations have been employed to compare the structure and dynamics in ABPBI + PA, ABPBI + TFA and ABPBI + PA + TFA blends with varying hydration. The stability of the polymer membrane under various hydrated acidic environments has been examined from the RDFs, end-to-end polymer chain distance and radius of gyration. The number of PA, TFA and water molecules in a cluster around the polymer membrane (skewed and extended form) with the extent of hydration have also been

investigated. The mobility of water molecules has also been investigated to study the effectiveness of TFA doping in reducing the leaching of acid from the membrane matrix.

Chapter 6 describes a parameter dependent study is crucial for the accurate determination of shear viscosity which is an important macroscopic property of a polymer. The effect of various simulation parameters such as thermostat, coupling time and system size is crucial for the accurate determination of shear viscosity and needs to be examined. In this study, an Extended Simple Point Charge (SPC/E) water model has been used for simplicity. A transverse current auto correlation function using Equilibrium Molecular Dynamics (EMD) and the periodic perturbation method using Non-Equilibrium Molecular Dynamics (NEMD) simulations have been employed to calculate the shear viscosity. The thermodynamics stability of different thermostat such as Berendsen, velocity-rescale, Nose'-Hoover on EMD and NEMD simulations have been examined for various coupling times (0.1 to 2.5 ps) and system sizes (900 to 7200 water molecules).

Chapter 7 describes a molecular investigation of the structure relationship with dynamics in benzyl-NX₃ (X=Methyl, Ethyl) trifluoromethanesulfonate (TFA) ILs. The effect of electrostatic, cation-phenyl and C-H/phenyl interactions on cation, anion, and IL mobility is investigated and validated by examination of ionic conductivity at varying temperature and Relative Humidity (RH) using EIS. The effect of hydration on the presence of strong inter-molecular C-H/phenyl interaction is also examined and validated by conductivity measurements.

Chapter 8 summarizes the salient results of structure property relationships of various polymer membranes with dynamics of molecular transport. A significant effect of inter/intra-molecular interactions (for example, electrostatic, cation- π and C-H/ π etc.) on water-proton mobility is summarized. A molecular study of structural and dynamical properties of IL doped polymer membranes from simulations and experiments can facilitate the development of non-aqueous composite PEM for high temperature fuel cell applications. The role of cationic asymmetry and N-H or N-H/ π interactions in protic ILs in the design of novel protic ILs for various technological applications (fuel cells, batteries etc.), which can be the focus of future activities is also discussed.



Chapter 2

Triflic acid and triflate ion-water mixtures: a proton conducting electrolyte component in fuel cells

2.1 Introduction

Triflic acid mimics the functional group of perfluorosulfonated polymer electrolyte membranes [3, 4] where the sulfonate group is responsible for proton conduction in fuel cells. Triflic acid is a strong proton donor and is used in many applications related to catalysis, synthesis of co-ordination compounds and organometallic chemistry [80]. A review of properties of triflic acid and its reaction chemistry have been discussed by Howells and McCown [81]. The variation of dissociation constant of triflic acid along the liquid-vapor interface has been studied by Paddison *et al.* [82]. It was found that the dissociation becomes unfavorable at temperatures above 500 K. Hayes *et al.* [51] reported the use of path integral MD to study proton transport in triflic acid hydrates. The authors concluded that the protonic charge on the sulfonic group gets redistributed over two or more water molecules. The conductivity of immobilized imidazole doped with various proportions of triflic acid was studied by Schuster *et al.* [83]. The authors found that the doping of triflic acid results in the increase of conductivity by 50 times as compared to pure imidazole. It was also found that the proton conductivity of PBI based membranes is enhanced in presence of ammonium trifluoromethanesulphonate [84]. *Ab initio* calculations by Liao *et al.* [85] suggests that inter-molecular proton transfer is much easier between triflic acid and imidazole as compared to triflic acid and water. Habenicht *et al.* [86, 87] investigated the proton transfer in SO₃H functionalized Carbon Nanotubes (CNT) at very low water content using *ab initio* molecular dynamics (AIMD) simulations. The authors investigated

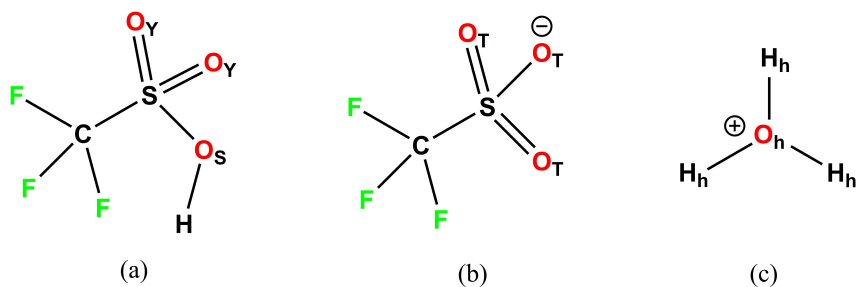


Figure 2.1: Chemical structure of a) triflic acid, b) triflate ion and c) hydronium ion.

the role of hydrogen bonding when proton transfers from the SO₃H group in the presence of different hydrophobic CNT environments. The authors concluded that even at $\lambda = 3$ (where λ denotes the degree of hydration) there is a complete dissociation of the acidic proton from the SO₃H functional groups.

While there has been some work on triflic acid hydrates [51] and triflate ion [82, 88–90], there has been very little investigation on pure triflic acid. In this chapter, a force-field of triflic acid have been developed by deriving force-field parameters from *ab initio* calculations and incorporated the derived parameters with the OPLS-AA force-field [72]. Since triflic acid undergo dissociation [51, 82] to form triflate ions at extremely low hydration, a force-field model which describes the dissociated form of triflic acid is required. However, due to the classical nature of the force-field employed in this work, the force-field developed for triflic acid cannot be used to describe its dissociated form. Hence, a force-field has been developed for the triflate ion in the present study which describes the dissociated form of triflic acid. The dissociated form is modeled using a triflate ion-hydronium ion pair. The “triflate ion-water mixtures” has been defined as configurations which contain triflate ion-hydronium pairs with varying amount of water molecules. The derivation of force-field parameters for triflic acid and triflate ions and details of MD simulations are described in Section 2.2. The structural and dynamical properties of triflic acid (270 K to 450 K) and triflate ion-water mixtures (300 K) obtained from the MD simulations are presented in Section 2.3. A summary of salient results concludes the chapter.

2.2 Computational details

2.2.1 Force-field

The chemical structure of triflic acid, triflate ion and hydronium ion is shown in Figure 2.1. All MD simulations were performed using the GROMACS [91] 4.0.7 program. The total potential energy is shown in Eqn. 1.4. For triflic acid and triflate ion, all van der Waals parameters and the partial charges for CF_3 group were extracted from the OPLS-AA force-field [72]. The partial charges for SO_3H group (triflic acid) and SO_3^- group (triflate ion) have been computed from the *ab initio* calculations using Gaussian 03 [92] in the following manner: The structure of a single triflic acid molecule and triflate ion was independently optimized using the HF/6-31G** basis set. The optimized geometry obtained using the HF calculation was re-optimized using the MP2/6-31G** basis set. The converged geometry from the MP2/6-31G** basis set calculation was used to compute partial charges for SO_3H group (triflic acid) and SO_3^- group (triflate ion) respectively using the CHELP [93] method. All bonds, angles and their force constants for triflic acid and triflate ion were extracted from the OPLS-AA force-field except for the C-S-O_S angle (triflic acid) angle and dihedral angles. The C-S-O_S angle was taken from the *ab initio* calculation reported by Gejji *et al.* [94] as it was not found in the OPLS-AA [72] database.

2.2.2 Dihedral parameterization

The dihedral potentials for triflic acid and triflate ion were computed using the MP2/6-31G** basis set. The dihedral energies were scanned for F-C-S-O_S (triflic acid), F-C-S-O_T (triflate ion) and C-S-O_S-H (triflic acid) dihedral angles in steps of 18 degrees. The computed dihedral energy for the F-C-S-O_S dihedral angle was fitted by using a proper dihedral function (see Figure 2.2a), where the functional form is written as:

$$V_d(\phi) = \frac{1}{2} [C_0(1 + \cos(\phi)) + C_1(1 + \cos(2\phi)) + C_2(1 + \cos(3\phi)) + C_3(1 + \cos(4\phi))] \quad (2.1)$$

Parameters C_0 to C_3 derived from the fit were called as dihedral coefficients. Similarly, the dihedral energy computed for the F-C-S-O_T dihedral angle was fitted using Eqn.2.1 (see Figure 2.2b). The dihedral energy of the C-S-O_S-H dihedral angle was fitted using a Fourier dihedral function (see Figure 2.2c). The functional form of the Fourier

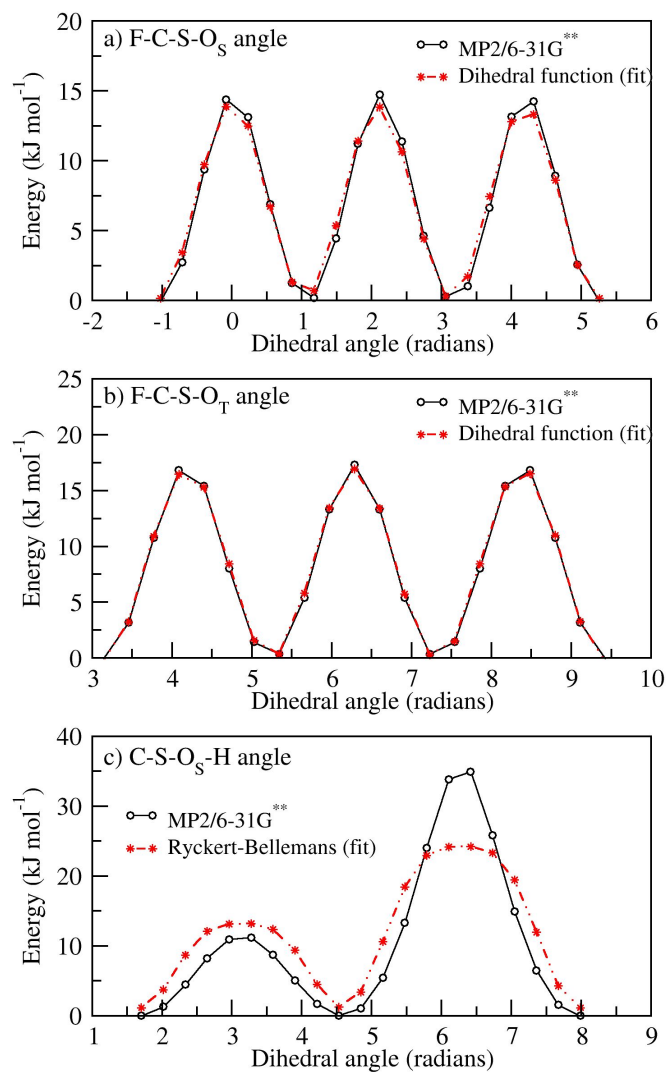


Figure 2.2: Dihedral energy for a) F-C-S-O_S, b) F-C-S-O_T and c) C-S-O_S-H angle.

dihedral function is written as:

$$V_{\text{rb}}(\phi) = \frac{1}{2} [f_1(1 + \cos(\phi)) + f_2(1 - \cos(2\phi)) + f_3(1 + \cos(3\phi)) + f_4(1 - \cos(4\phi))] \quad (2.2)$$

where, f_1 , f_2 , f_3 and f_4 are the Fourier dihedral coefficients which can be transformed into Ryckert-Bellemans dihedral coefficient parameters as seen in Eqn. 2.3:

$$\begin{aligned}
 C_0 &= f_2 + \frac{1}{2}(f_1 + f_3) \\
 C_1 &= \frac{1}{2}(-f_1 + 3f_3) \\
 C_2 &= -f_2 + 4f_4 \\
 C_3 &= -3f_3 \\
 C_4 &= -4f_4 \\
 C_5 &= 0
 \end{aligned} \tag{2.3}$$

For the sake of completeness, all force-field parameters for triflic acid and the triflate ion are provided in Table A2-1 and Table A2-2 respectively (see Appendix A). The force-field parameters for hydronium ion were taken from the work of Jang *et al.* [50]

2.2.3 Simulation details

The starting geometry used for MD simulations on triflic acid was obtained as follows: An energy minimized triflic acid molecule was replicated to generate a cubic box containing 1008 triflic acid molecules. MD simulations at 270 K, 300 K, 330 K, 360 K, 390 K, 420 K and 450 K were performed on triflic acid. The triflate ion-water mixtures were created as follows: An energy minimized triflate ion was replicated to generate a cubic box containing 500 triflate ions. To maintain charge neutrality on the system, 500 hydronium ions were added. The resultant configuration (500 triflate ion-hydronium ion pairs) was used as an input and a simulated annealing was performed by heating from 300 K to 750 K and cooling back to 300 K in with an annealing time of 6 ns. The annealing procedure was repeated 3 times. The final configuration obtained from the simulated annealing procedure was used as a template and solvated with 500, 1500, 3000 and 4500 SPC/E [95] water molecules to generate varying triflate ion-water mixtures denoted as $\lambda=1, 3, 6$ and 9 (λ represents the number of water molecules per triflate ion or triflate ion-hydronium ion pair). MD simulations for the triflate ion-water mixtures were performed at 300 K. For all MD simulations, the cut-off distance for van der Waals and electrostatic interactions for non-bonded interactions were chosen as 10 Å. The leapfrog algorithm [74] was chosen as an integrator using a time step of 1 fs. Each MD simulation was equilibrated for 10 ns using the NPT ensemble with a 1 bar isotropic pressure and a Berendsen barostat [96].

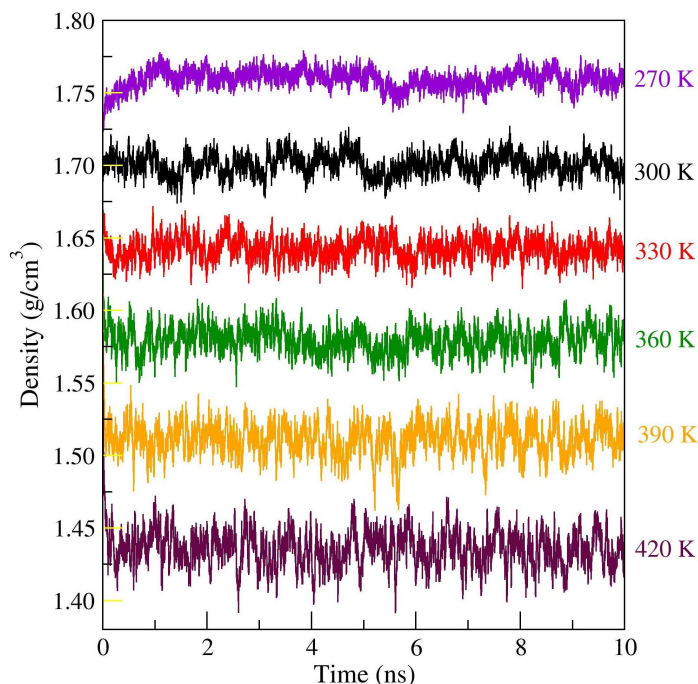


Figure 2.3: Density of triflic acid from a 10 ns MD equilibration.

Temperature was kept constant by using a velocity-rescale thermostat [97] with a coupling time of 0.1 ps. The Particle-Mesh Ewald (PME) [98, 99] method was used to calculate long-range electrostatic interactions. Equilibration was followed by a 20 ns production run using the NVT ensemble. Trajectories from the production run were recorded every 5 ps to compute structural and dynamical properties.

2.3 Results and discussion

2.3.1 Density

The initial test of our developed force-field for triflic acid is used to compute the density of triflic acid. For example, the density of triflic acid computed at various temperatures from the 10 ns MD equilibration is shown in Figure 2.3. As seen, the computed densities show a steady fluctuation around the mean temperature. The box sizes and densities obtained from equilibration are shown in Table 2.1. The computed triflic acid density is 1.692 g cm^{-3} at 300 K and is in excellent agreement with the experimental [100] density of 1.698 g cm^{-3} at 298.15 K. As expected, the density decreases with an increase in

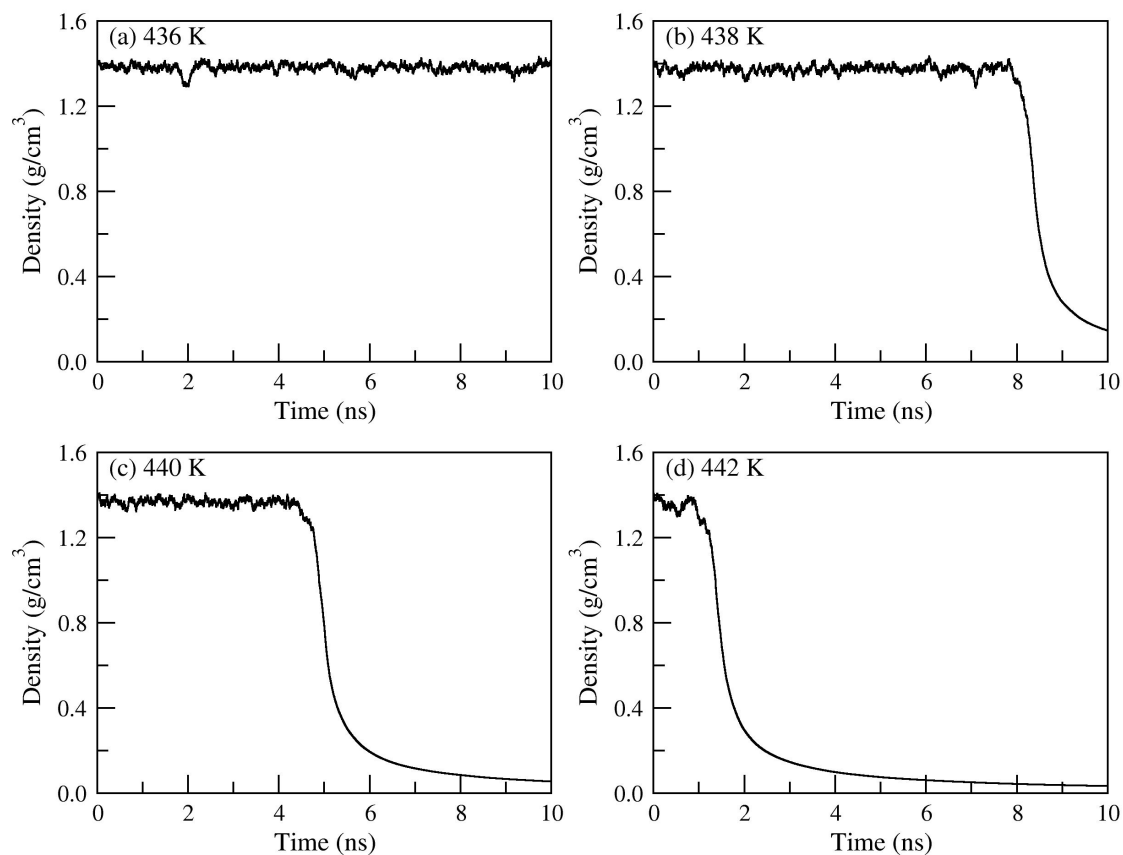


Figure 2.4: The density profile of triflic acid above the experimental boiling point.

temperature. While, no experimental data on the density of triflic acid is reported for temperatures except at 298.15 K, the computed density at various temperatures are in good agreement with the experimental density of triflic acid monohydrate reported by Barthel and Meier [101]. For example, the density obtained from our MD simulations at 330 K is 1.642 g cm^{-3} which agrees extremely well with the value reported by Barthel *et al.* at 333.15 K (density = 1.645 g cm^{-3}). Similarly, the computed density at 360 K (density = 1.579 g cm^{-3}) is close to the value at 358.15 K (density = 1.616 g cm^{-3}). The experimental [100] boiling point of triflic acid is 435 K. MD equilibration at 436 K, 438 K, 440 K and 442 K are performed to show the effect of the developed force-field on the density. The densities shown in the Figure 2.4 demonstrates the behavior of the force-field for temperatures above the experimental boiling point.

A more detailed analysis on the behavior of density is seen by performing a MD simulation at 450 K. For example, Figure 2.5 shows a change in the density and snapshots

(from a 10 ns equilibration) of triflic acid at 450 K from 1.352 g cm^{-3} (initial) to a density (final) of 0.028 g cm^{-3} during the course of the 10 ns equilibration. The density at 450 K is extremely low compared to the density of 1.435 g cm^{-3} at 420 K and hence the density at 450 K does not represent the liquid state of triflic acid. Further an examination of the low density is evident by the change in the simulation box length and snapshots at various time intervals during the course of the simulation. The length of box show a increase from $53.32 \text{ \AA}$ ($t=0$), $83.92 \text{ \AA}$ ($t=1 \text{ ns}$), $113.22 \text{ \AA}$ ($t=2 \text{ ns}$), $158.76 \text{ \AA}$ ($t=5 \text{ ns}$), $206.31 \text{ \AA}$ ($t=10 \text{ ns}$). A visual inspection of the snapshots (using periodic boundaries) shows that groups of triflic acid molecules coalesce and separate during the course of the simulation. Our force-field model does not include modifications of the van der Waals parameters required for the description of vapor phase of triflic acid. A view of the final snapshot ($t=10 \text{ ns}$) shows a large simulation box full of isolated clusters of triflic acid molecules, rather than a true liquid to gas phase transition. The densities of triflate ion-water mixtures are shown in Table 2.2. As expected, the densities of the triflate ion-water mixtures decrease with increasing water content. For example, the difference in density from $\lambda=1$ to $\lambda=3$ is 0.136 g cm^{-3} , $\lambda=3$ to $\lambda=6$ is 0.114 g cm^{-3} , and $\lambda=6$ to $\lambda=9$ is 0.073 g cm^{-3} respectively which shows that the difference in density at higher hydration ($\lambda=6$ to $\lambda=9$) is lower than the

Table 2.1: Box length (l) and average densities (ρ) obtained from a 10 ns equilibration run for triflic acid.

Temp. (K)	l ($\text{\AA}$)	ρ (g cm^{-3})
270	51.096	1.759
300	51.745	1.692
330	52.380	1.642
360	52.883	1.579
390	52.791	1.512
420	54.909	1.435

Table 2.2: Box length (l) and average densities (ρ) from a 10 ns equilibration run at 300 K for triflate ion-water mixtures.

λ	l ($\text{\AA}$)	ρ (g cm^{-3})
1	45.440	1.642
3	49.701	1.506
6	54.792	1.392
9	59.256	1.319

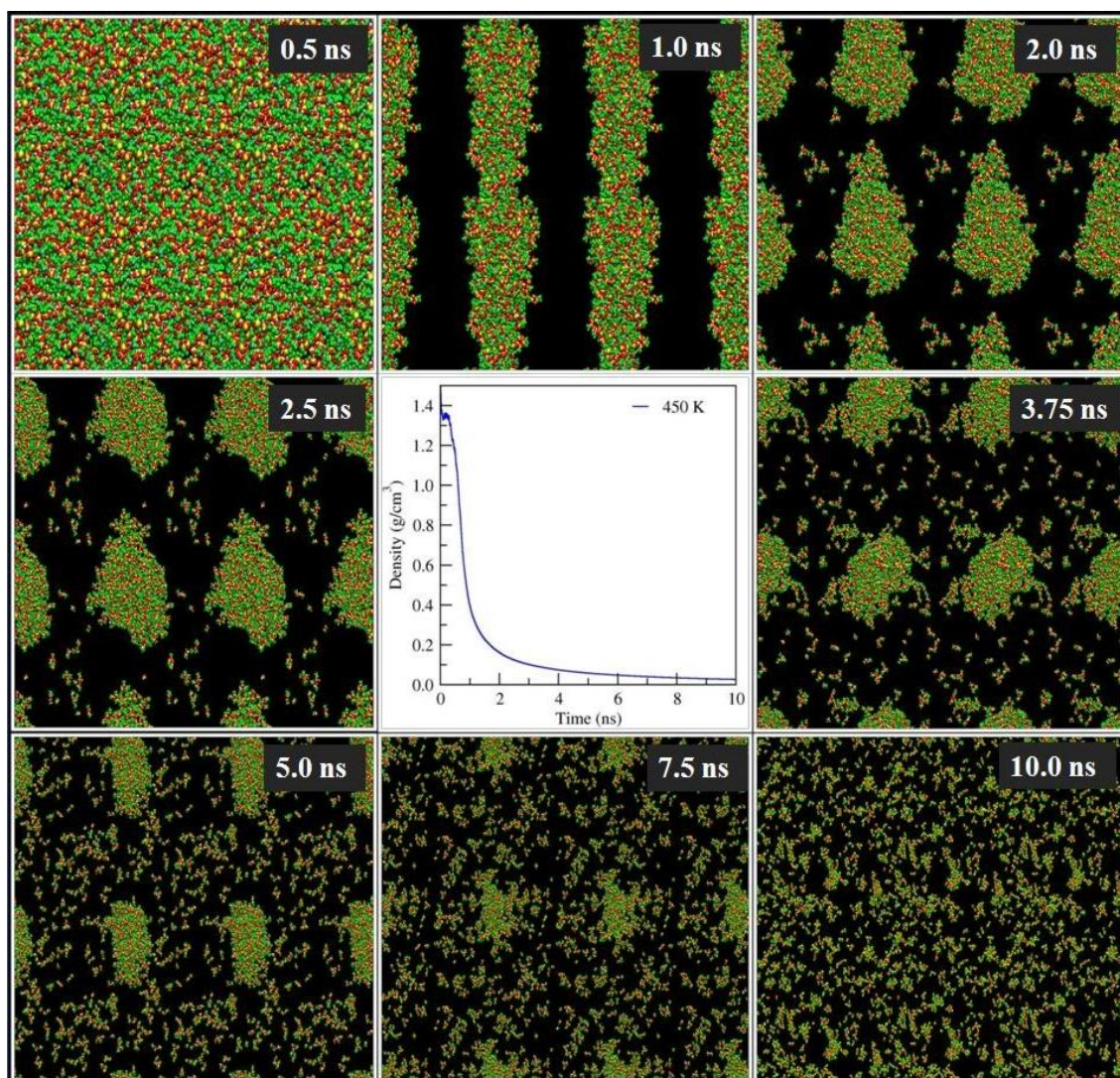


Figure 2.5: Density and snapshots of triflic acid from a 10 ns MD equilibration at 450 K.

differences in density at low hydration ($\lambda=1$ to $\lambda=3$).

2.3.2 Effect of temperature on neat triflic acid

The structural environment of triflic acid at different temperatures is investigated by an examination of the RDFs. As seen in Figure 2.6, the qualitative and quantitative features of RDFs are very similar for temperatures from 270 K to 420 K. This shows that temperature produces no effect on different RDFs. A detailed examination of the RDFs is done as follows: The C-S RDF in Figure 2.6a shows a small shoulder at 5.2 Å which shows

the hydrophobic nature of the CF_3 group. For temperatures from 270 K to 420 K, the S-S RDFs in Figure 2.6b shows a first solvation minima at 5.7 Å which corresponds to a co-ordination number of 6. Thus six triflic acid molecules appear in the first solvation shell of a triflic acid. Further, the peak corresponding to the first S-S solvation shell appears at 4.5 Å which agrees well with the peak seen in S-S RDF for triflic acid hydrates by Hayes *et al.* [51]. Similar to the behavior observed in density, we see that the quantitative behavior of S-S RDFs at 450 K (inset of Figure 2.6b) is different from the S-S RDFs at other temperatures. The RDF profiles at 450 K show that hydrogen bonding ex-

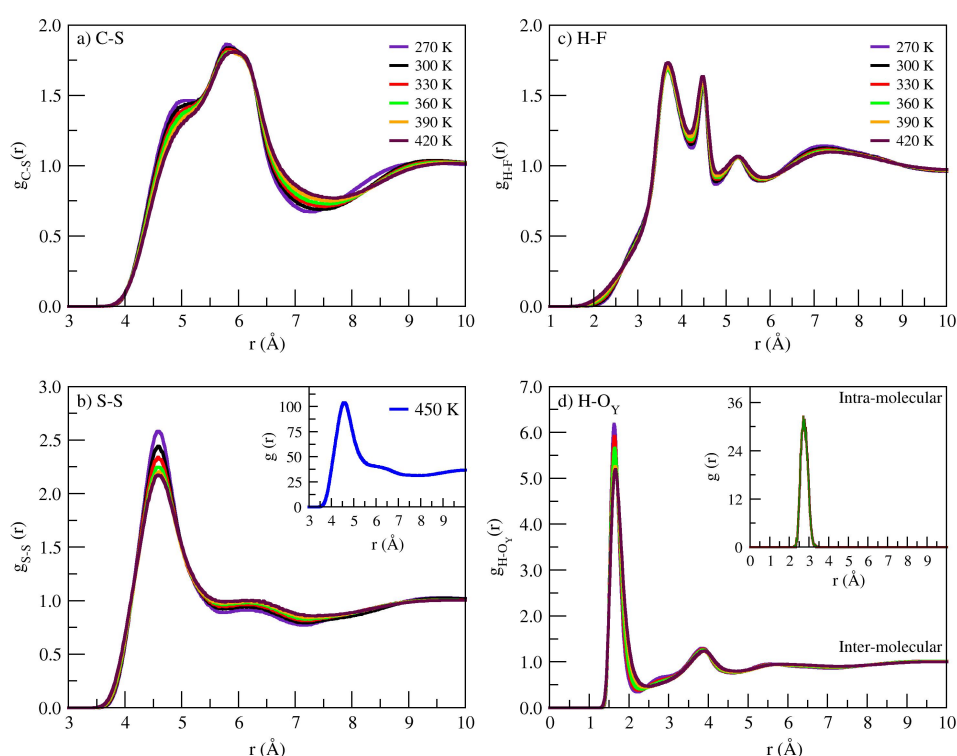


Figure 2.6: RDFs of triflic acid: a) C-S, b) S-S, c) H-F and d) H-O_Y.

ists between two or more sulfonate groups (i.e. $\text{F}_3\text{CSO}_3\text{—H—O}_3\text{SCF}_3$) due to presence of isolated clusters of triflic acid molecules, rather than a true liquid or gas phase. An examination of the H-F and H-O_Y RDFs shows the nature of hydrogen bonding in triflic acid. The H-F RDFs shown in Figure 2.6c show the presence of three peaks corresponding to different solvation shells. For example, the H-F RDFs show a first solvation minima at 4.2 Å with a co-ordination number of 6. The H-O_Y RDFs shown in Figure 2.6d includes inter-molecular and intra-molecular (in inset) hydrogen bonding. A sharp peak at 1.8 Å

shows the presence of strong inter-molecular hydrogen bonding which corresponds to co-ordination number of 1 at a cutoff of 2.2 Å. A clear view of the intra-molecular hydrogen bonding at 2.75 Å is seen in the inset of Figure 2.6d and corresponding co-ordination number is 2 at a cutoff of 3.45 Å.

2.3.3 Effect of hydration on triflate ion-water mixtures

The structural rearrangement in triflate ion-water mixtures can be seen from an examination of the various RDFs (see Figure 2.7) and the corresponding co-ordination numbers obtained from these RDFs (see Table 2.3). For example, the S-S RDFs in various triflate ion-water mixtures are shown in Figure 2.7a. The radius of the first solvation shell of a triflate ion is much larger compared to that of neat triflic acid (5.7 Å). For example, the first solvation minima for $\lambda=1$ appears at 6.9 Å. The minima increases to 7.4 Å with increase in hydration ($\lambda=3, 6$ and 9). The co-ordination number (see Table 2.3) at the first minima from the S-S RDFs shows a decrease of 7 ($\lambda=1$) to 3.5 ($\lambda=9$). The decrease in co-ordination number with increasing hydration is because water molecules prefer to orient around the hydrophilic SO_3^- group of the triflate ion. The hydrophilic character of the SO_3^- group can also be seen from the S- O_w RDFs (Figure 2.7b) where the first solvation minima appears at 4.2 Å for all hydration. The co-ordination number at the first minima increases from 2.0 ($\lambda=1$) to 6.1 ($\lambda=9$) due to the increase in number of water molecules around the SO_3^- group. The trends observed from the co-ordination numbers reported in this work are similar to the results of Venkatnathan *et al.* [21] using the Nafion membrane. The interaction of the hydronium ion with the SO_3^- group is seen by an examination of the S- O_h RDFs. The co-ordination number of hydronium ions is 3.7 at ($\lambda=1$) at the first minima of 4.5 Å where there is a presence of stable triflate ion-hydronium ion complex. However, with an increase in hydration, there is a decrease in the stability of the triflate ion-hydronium ion complex and hence the co-ordination number of hydronium ions de-

Table 2.3: Co-ordination number at the first minima of triflate ion-water mixtures RDFs at 300 K.

λ	S-S (7.4 Å)	S- O_w (4.2 Å)	S- O_h (4.5 Å)	O_h - O_h (5.7 Å)	O_h - O_w (3.1 Å)	O_w - O_w (3.0 Å)
1	7.0	2.0	3.7	3.7	0.3	1.0
3	6.8	4.2	2.5	2.4	1.1	1.9
6	4.8	5.6	1.6	1.5	1.6	2.6
9	3.5	6.1	1.2	1.0	2.0	2.8

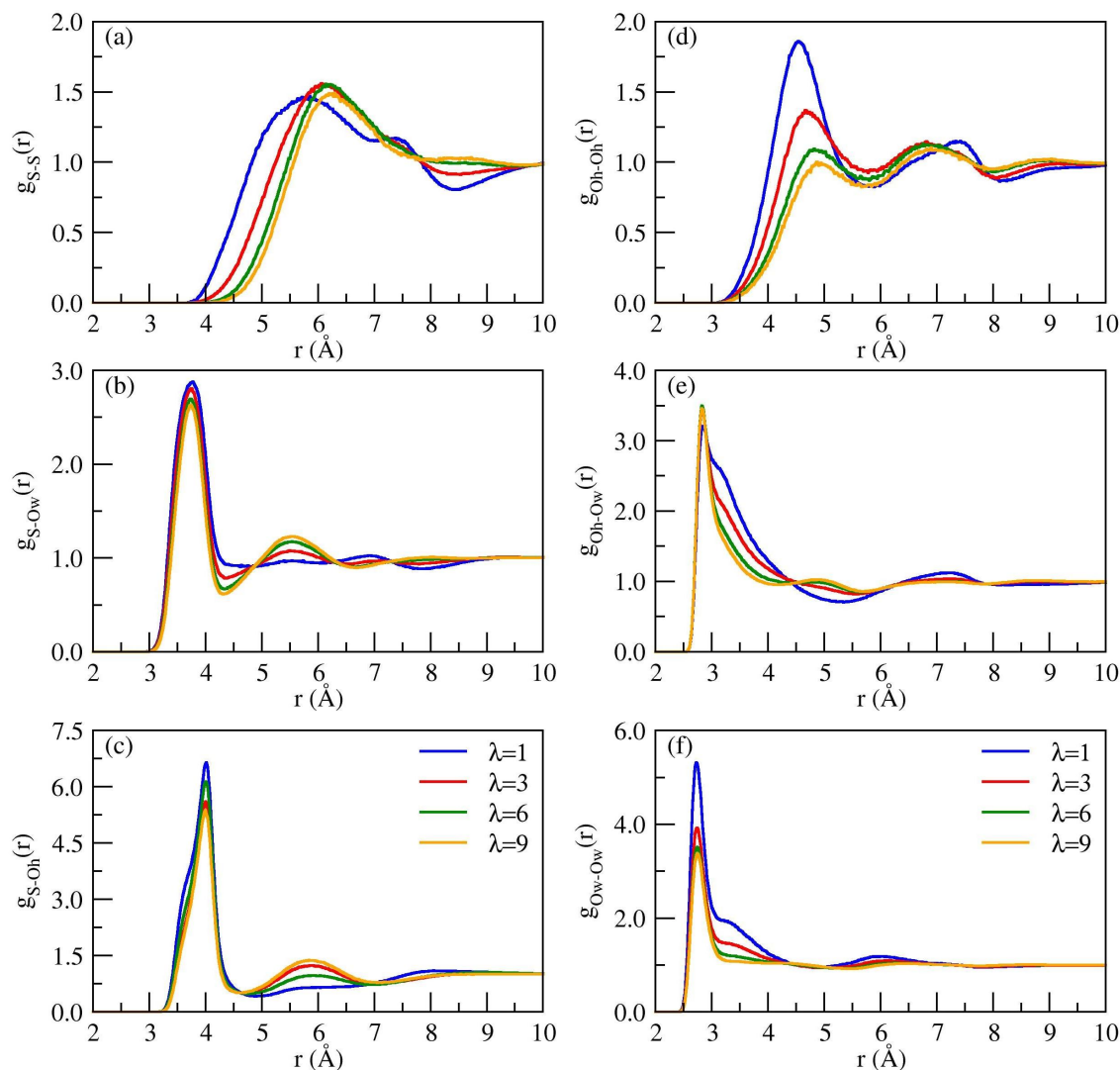


Figure 2.7: RDFs of triflate ion-water mixtures at 300 K: a) S-S, b) S-O_w, c) S-O_h, d) O_h-O_h, e) O_h-O_w and f) O_w-O_w.

creases to 1.2 ($\lambda=9$).

The decrease in stability of the triflate ion-hydronium ion complex due to increasing hydration can also be confirmed by an examination of the interactions between hydronium ions and water molecules seen from the O_h-O_h (see Figure 2.7d) and O_h-O_w RDFs (see Figure 2.7e). The decrease in the intensity of the first peak in the O_h-O_h RDFs with increasing hydration shows that this is due to the increase in solvation of water molecules around the hydronium ion. An increase in hydration results in the decrease in co-ordination number from 3.7 ($\lambda=1$) to 1.0 ($\lambda=9$) at the first solvation minima (5.7 Å)

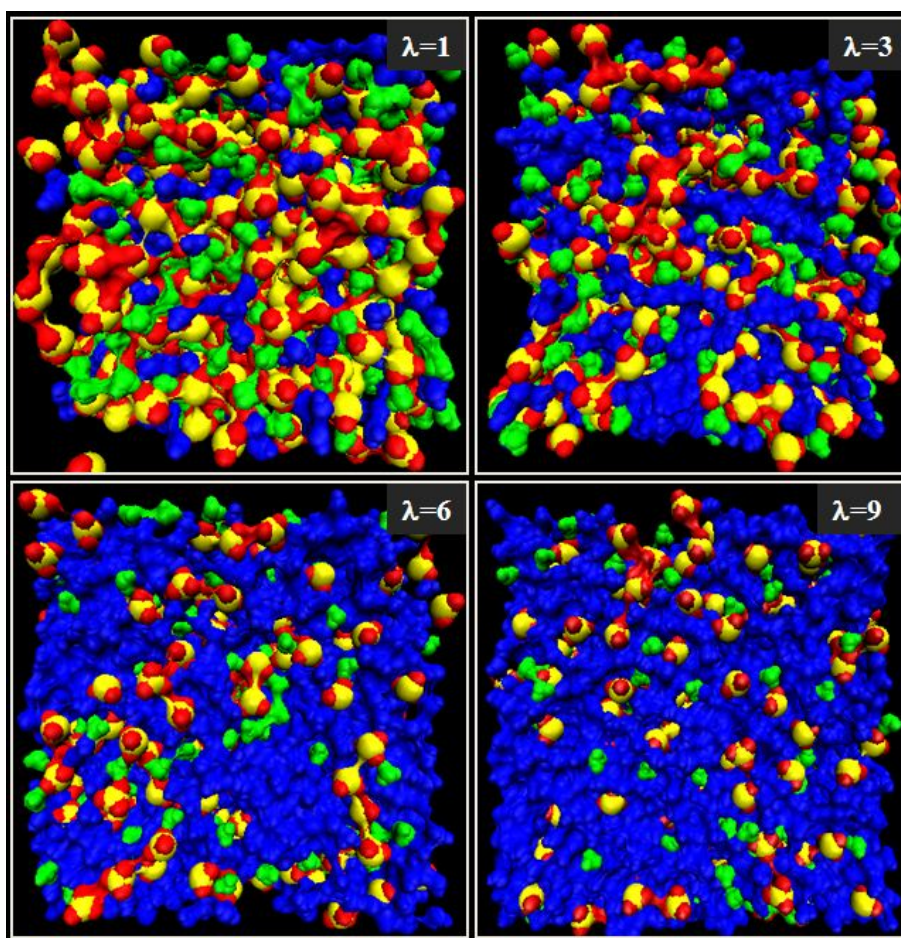


Figure 2.8: Snapshots of triflate ion-water mixtures at 300 K. [hydronium ion (green), water (dark blue), SO_3^- (yellow and red) and CF_3 is not displayed].

of the $\text{O}_\text{h}-\text{O}_\text{h}$ RDFs. The co-ordination number for water molecules obtained from the first solvation minima (3.1 Å) of $\text{O}_\text{h}-\text{O}_\text{w}$ RDFs shows an increase from 0.3 ($\lambda=1$) to 2.0 ($\lambda=9$) which again demonstrates that water molecules solvate the hydronium ions. The solvation of water molecules around other water molecules can be seen from the $\text{O}_\text{w}-\text{O}_\text{w}$ RDFs (see Figure 2.7f). The co-ordination number of water molecules from the first solvation minima (3 Å) of the $\text{O}_\text{w}-\text{O}_\text{w}$ RDFs increases from 1.0 ($\lambda=1$) to 2.8 ($\lambda=9$). Also, the first solvation minima of the $\text{O}_\text{w}-\text{O}_\text{w}$ RDFs is similar to the water solvation minima reported in the work of Venkatnathan *et al.* [21], Urata *et al.* [18] and Cui *et al.* [25] where they employed the PFSA membranes. Thus the effect of hydration shows that some water molecules orient around the SO_3^- group, while others solvate the hydronium ions and water molecules. The effect of hydration is also seen by the visual inspection of the final

snapshots (extracted from the production run) of triflate ion-water mixtures (see Figure 2.8). For example, the hydrophilic nature of SO_3^- group can be seen clearly at $\lambda=1$ and $\lambda=3$. At $\lambda=1$, there is a presence of small disconnected water clusters in close proximity to the SO_3^- group. However, at $\lambda=3$, there are water clusters and water channels which again are aligned around the SO_3^- group. Further increase in hydration ($\lambda=6$ and 9) leads to interconnected water channels which also orient around the SO_3^- group.

2.3.4 Diffusion of neat triflic acid and triflate ion

The mobility of triflic acid is analyzed from the MSD using the Einstein relationship [74]. As seen in Figure 2.9a, the MSD of triflic acid increases with temperature. The diffusion coefficients are computed from the linear regime of MSD and tabulated in Table 2.4. It can be seen that the diffusion coefficient of triflic acid increases by a factor of 6 from 270 K to 300 K, whereas the diffusion coefficient increases by a factor of ~ 2 with increase in temperature for every 30 K from 300 K. While, no experimental data on diffusion coefficient of triflic acid is reported so far, the diffusion coefficients obtained in this work requires experimental validation.

The mobility of triflate ion, hydronium ion and water molecules is seen by an examination of the MSD (see Figure 2.9) and the calculated diffusion coefficients are shown in Table 2.5. As expected, the MSD of water molecules is larger than the hydronium ions and triflate ions for all hydration. It is also observed at the lowest hydration ($\lambda=1$), the MSD of triflate ion and hydronium ion are extremely low which again confirms the existence of stable triflate ion-hydronium ion complex. The diffusion of triflate ion increases by a factor of 16 from $\lambda=1$ to $\lambda=3$. Such a large increase in the diffusion of triflate ion can be attributed to the fact that the water solvation around the triflate ion in $\lambda=1$ is very low due to the presence of stable triflate ion-hydronium ion complex. With increasing hydration,

Table 2.4: Diffusion coefficient (D_A) of triflic acid from a 20 ns production run.

Temp. (K)	$D_A (\times 10^{-5} \text{ cm}^2 \text{ s}^{-1})$
270	0.0088 ± 0.0003
300	0.0562 ± 0.0020
330	0.1551 ± 0.0032
360	0.3653 ± 0.0146
390	0.7706 ± 0.0058

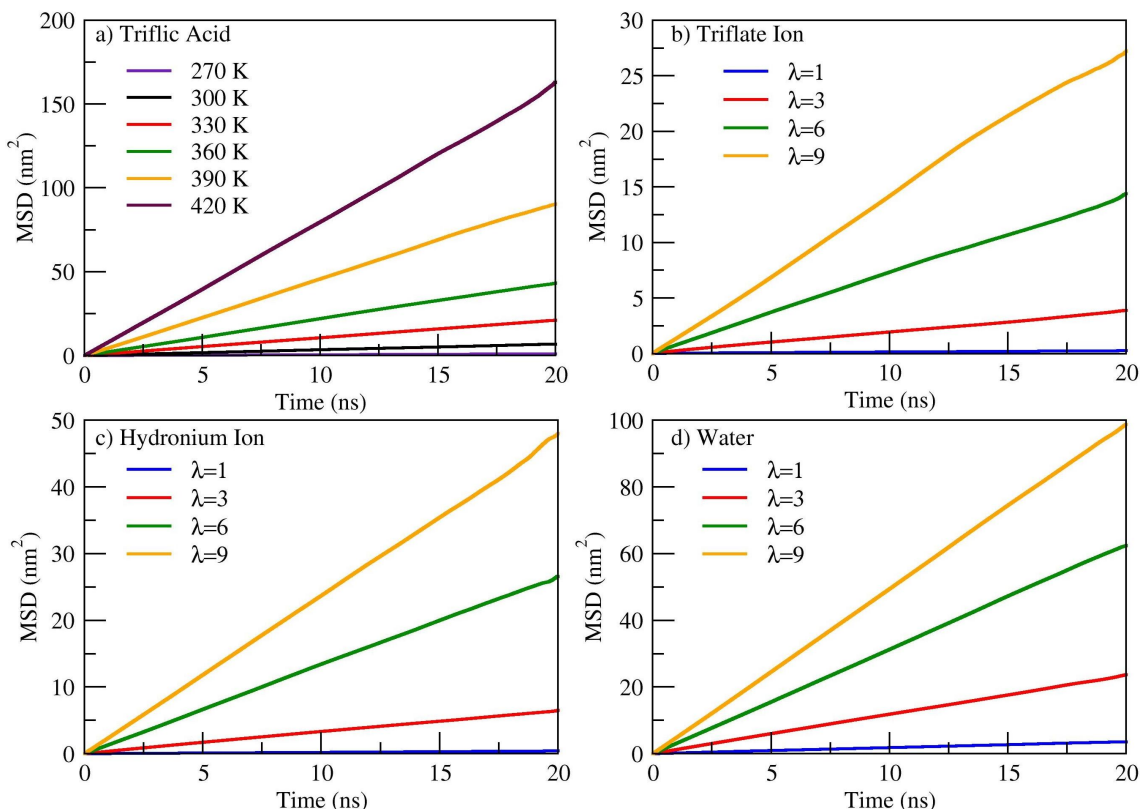


Figure 2.9: Mean Square Displacement of a) triflic acid, b) triflate ion, c) hydronium ion and d) water.

water molecules infiltrate and break the stable triflate ion-hydronium ion complex which leads to an increase in diffusion. However, the increase in hydration from $\lambda=3$ to $\lambda=6$ result in the increase of diffusion coefficient of triflate ion by only a factor of only 3.8. A subsequent increase in hydration from $\lambda=6$ to $\lambda=9$ results in the increase of diffusion coefficient of triflate ion by a factor of ~ 2 .

The effect of hydration on the diffusion of hydronium ions is found to be very similar to the diffusion behavior of triflate ion. The diffusion of hydronium ion increases by a factor of 15.55 from $\lambda=1$ to $\lambda=3$. A subsequent increase in hydration from $\lambda=3$ to $\lambda=6$, and $\lambda=6$ to $\lambda=9$ shows an increase of diffusion coefficient of hydronium ion by a factor of ~ 4.2 and 1.76 respectively. The diffusion coefficient of triflate ion at $\lambda=1$ is 30 times lower than the diffusion of triflic acid at 300 K which again demonstrates the stability of triflate ion-hydronium ion complex. The stability of this complex decreases with an increase in solvation of water molecules around triflate ions and hydronium ions at $\lambda=3$ and hence an enhanced diffusion of hydronium ions is observed. Similar to the behavior

Table 2.5: Diffusion coefficient (D_A) and Nernst-Einstein conductivity (σ_{NE}) of triflate ion-water mixtures from a 20 ns production run.

λ	$CF_3SO_3^-$	(D_A) H_3O^+	Water	σ_{NE} (S/m)
1	0.0019	0.0034	0.0296	0.1787
3	0.0303	0.0529	0.1942	2.0231
6	0.1161	0.2222	0.5272	5.8629
9	0.2385	0.3928	0.8303	8.2296

of triflate ions and hydronium ions, the diffusion of water molecules increases by a factor of 7 from $\lambda=1$ to $\lambda=3$. Further increase in hydration from $\lambda=3$ to $\lambda=6$, and $\lambda=6$ to $\lambda=9$ results in the increase of diffusion coefficient of water molecules only by a factor of ~ 2 . The water molecules exist in the form of mixture of water clusters and water channels at $\lambda=3$. However at $\lambda=6$, there is an abundant amount of water channels which is consistent with the snapshots (see Figure 2.8). At $\lambda=6$, the diffusion of hydronium ions and water molecules reported in this work is found to be 10 and 1.7 times higher compared to the corresponding diffusion coefficients reported by Venkatnathan *et al.* [21] where they have employed the Nafion membrane for study. The lower diffusion coefficients from the work of Venkatnathan *et al.* [21] is due to the confinement effect of the hydrophobic polymer backbone in Nafion. Finally, a collective examination of the RDFs, diffusion coefficients and the hydrated snapshots of triflate ion-water mixtures show that $\lambda=6$ will be a sufficient amount of water required by triflate ions for proton conduction. Such an observation also confirms the computational findings of Devanathan *et al.* [27] and the experimental work of Laporta *et al.* [102] where the PFSA membranes were used for study. The Nernst-Einstein conductivity (σ_{NE}) (using Eqn. 1.13) is also calculated from diffusion coefficients (see Table 2.5) and is in agreement with ionic conductivity from experiment (1-10 S/m) [103] of triflic acid monohydrate solid.

2.3.5 Activation energy

From the diffusion coefficients, the energy of activation for diffusion (E_A) is calculated by using an Arrhenius equation (see Eqn. 1.14). A plot of the logarithm of diffusion coefficient with reciprocal of temperature is shown in Figure 2.10. A linear fit to the simulation data gives an E_A of 31.01 kJ mol⁻¹. Since no corresponding experimental data is available for triflic acid, the computed activation energy of diffusion is compared to the

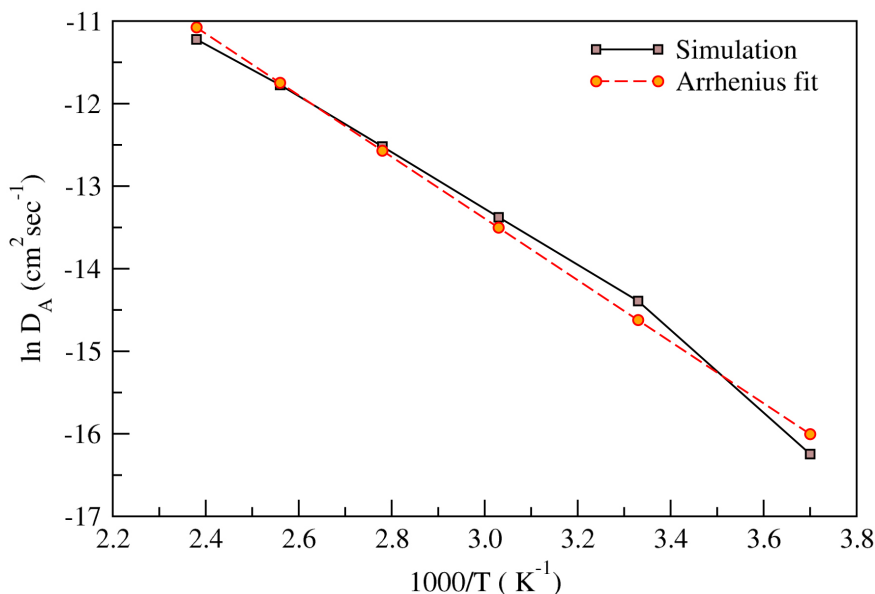


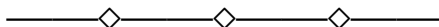
Figure 2.10: Activation energy of diffusion (E_A) of triflic acid.

activation energy for conductivity (0.3 eV or 28.9 kJ mol⁻¹) for triflic acid mono hydrate reported by Paddison *et al.* [82].

2.4 Conclusions

A force field for triflic acid and triflate ion has been developed by deriving parameters from *ab initio* calculations and combined these parameters with OPLS-AA force-field. The developed force-field have been tested by computing structural and dynamical properties of triflic acid and triflate ion-water mixtures. The RDFs suggest that temperature does not have any significant effect on the structural changes in triflic acid in between temperature range of 270 K to 420 K. The radius of the first solvation shell of a triflate ion (at $\lambda=1$ is 6.9 Å and further increased to 7.4 Å at higher hydration) is much larger compared to that of neat triflic acid (5.7 Å). This is due to the solvation of water molecules around the sulfonate group which results in a larger solvation shell of the triflate ion. The structural analysis of triflate ion/water mixtures shows that the stability of triflate ion-hydronium ion complex is broken by the solvation of water molecules. The diffusion of triflate ion, hydronium ion and water molecules increases with hydration in triflate ion/water mixtures which shows that water plays a role in the mobility of triflic acid. The increase in hydration results in the solvation around triflate ions and hydronium ions which is necessary to

facilitate proton transport in PEM fuel cells. The coordination numbers and the diffusion coefficients of triflate ions, hydronium ions and water molecules presented in this work resemble qualitatively the findings of Venkatnathan *et al.* [21], Urata *et al.* [18] and Cui *et al.* [24,25] where they employed PFSA membranes. The connectivity of water molecules around sulfonate group through water channels is observed at $\lambda=3$ which is enhanced to provide better connectivity at $\lambda=6$ as seen from the snapshots. Thus, triflic acid and triflate ions can prove to be a promising electrolyte component in fuel cell membranes such as PFSA and PBI membranes, where it enhances the conductivity as observed by Schuster *et al.* [83] at sufficient hydration.



Chapter 3

Atomistic probe into the nanostructure of side chain and water dynamics in PFSA membranes

3.1 Introduction

The aliphatic PFSA membranes like Nafion (Dupont) [3, 4], Aciplex (Asahi-Glass) [10, 11, 104], Dow (Dow Chemical's) [7–9] consists of a polytetrafluoroethylene (PTFE) polymeric backbone with a side chain terminated by a sulfonate group (responsible for proton conduction). The side chain is a key difference between PFSA membranes such as Dow, Aciplex and Nafion (see Figure 3.1). The Dow membrane has the shortest side chain and has been commercialized by Solvay-Solexis and called as Hyflon Ion [105–107]. Among all the PFSA membranes, the Nafion membrane has been studied extensively by experiments [4, 13, 14] and computational methods [16–18, 20, 25, 108]. The presence of water is essential to the functioning of these membranes, where the proton dissociates from the sulfonate group of the PFSA membranes. The role of water is to facilitate transport [109] of the dissociated proton from the sulfonate group and also to serve as a medium for protons to transfer either via a Grötthuss proton shuttling mechanism [44] (structural diffusion) or a vehicular mechanism.

The conductivity of PFSA membranes is found to depend on hydration [22–24] and temperature [21]. For example, the effect of hydration on proton dissociation in hydrated Dow membranes was studied by Paddison and Elliott [16] using an *ab initio* self-consistent field (SCF) molecular orbital and Density Functional theory with Beckes three parameter functional (B3LYP). The authors concluded that the number of water molecules required for proton dissociation from the sulfonate group depends on the number of di-

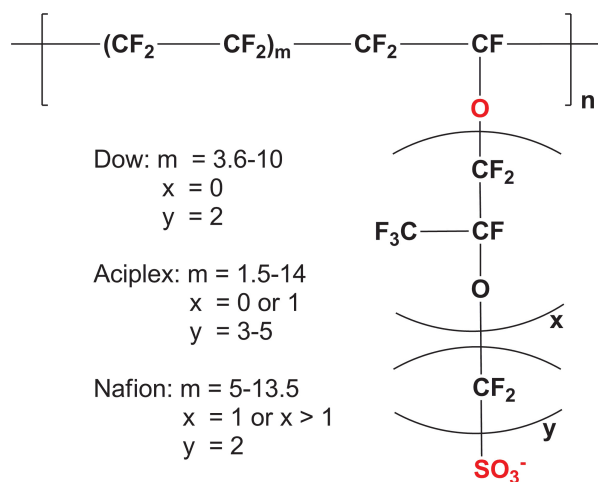


Figure 3.1: Chemical structure of PFSA polymer electrolyte membranes (ionomer form).

fluoromethylene (CF_2) groups which separates two successive pendant chains in the Dow polymer membrane. Urata *et al.* [18] performed MD simulations on PFSA membranes and concluded that the sulfonate group is a unique site to bind water molecule, and the pendant side chains of membrane prefer to orient perpendicular to the hydrophilic/hydrophobic interface. The effect of side chain connectivity and local hydration in PFSA membranes was investigated by Clark and Paddison [110]. The authors found that the side chain connectivity in the sulfonate group of a fully extended polymer backbone depends on the presence of neighboring water molecules. The chemical bond strength in the pendants of PFSA membranes was also analyzed by Tokumasu *et al.* [111]. The authors concluded that the ionization of sulfonate group strengthens the C-S bond and weakens the C-O bond of ether group which connects the pendant with the polymer backbone. Habenicht *et al.* [86, 87] investigated proton transfer from the sulfonate group of PFSA membranes in a carbon nanotube environment using an AIMD method. The authors found that a hydronium ion forms a bridge between two sulfonate groups and prevents water molecules from a full solvation of the acidic proton.

A comparative study of Dow, Aciplex and Nafion membranes have been reported by Brandell *et al.* [112] at two degrees of hydration. The authors concluded that the Nafion membrane represents an optimal compromise between the hydrophobic and hydrophilic region due to an ideal length to promote side chain motion. Apart from these studies, a phase separated nanostructure is obtained in the morphological studies [36–38, 113–115] of hydrated PFSA membranes where the water molecule resides in the hydrophilic do-

main. Such two phase nanostructure have been validated by theoretical studies [116–118] and scattering experiments [35, 39, 119, 120] as well. Devanathan and Dupuis [121] investigated the effect of side chain length by comparing Dow (short side chain) and Nafion (long side chain) using classical MD simulations. The authors concluded that the water molecules forms more clusters around the sulfonate group in Dow compared to Nafion. Further, the authors observed that the side chain of Nafion membrane remains bent at all hydration and bears close resemblance in structural properties to Dow membrane. While, results from their work have provided a molecular understanding of some interactions which occur in humidified conditions of these membranes, it is difficult to distinguish the contributions which arise from side chains and polymer backbone to the various structural and dynamical properties. Hence, while previous studies [112, 121] have included the polymer backbone, in this work only the side chains consider as candidates for study. The lack of polymeric membrane in this study suggests that effects like polymer backbone conformation and their orientations are not included. However, these effects occur on relatively longer simulation time scales compared to the motions of side chains, water molecules and hydrated protons. Such a study can provide an understanding of how the side chain and pendant ether oxygen of PFSA membranes can influence proton transport and water dynamics. In the present work, we choose the ionomeric form of the side chains of Dow ($-\text{OCF}_2\text{CF}_2\text{SO}_3^-$), Aciplex ($-\text{O}(\text{CF}_2)_5\text{SO}_3^-$) and Nafion ($-\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_3^-$) and employ MD simulations to characterize the nanostructure of side chains and the dynamical properties of water molecules and hydronium ions (hydrated proton), at varying hydration and temperature.

Due to the limitations of classical force-fields, only the vehicular diffusion of protons (in the form of hydronium ions) can be studied. The derivation of force-field parameters of side chains and details of MD simulations are described in section 3.2. The nanostructured arrangement and water-hydronium ion dynamics in Dow, Aciplex and Nafion side chains with varying hydration (300 K and 350 K) obtained from MD simulations, validation with experimental data are presented in the section 3.3. The results presented in this chapter provides a comprehensive examination of interaction of various sites of the side chains with hydrated protons and water molecules, interaction among water molecules and between the hydrated protons and water molecules. In this chapter, a comparison of the calculated structure factors and scattering intensities is also presented with suitable experimental data. The dynamics of hydrated protons and water molecules like Mean Square Displacement, diffusion coefficients and activation energy of diffusion are also

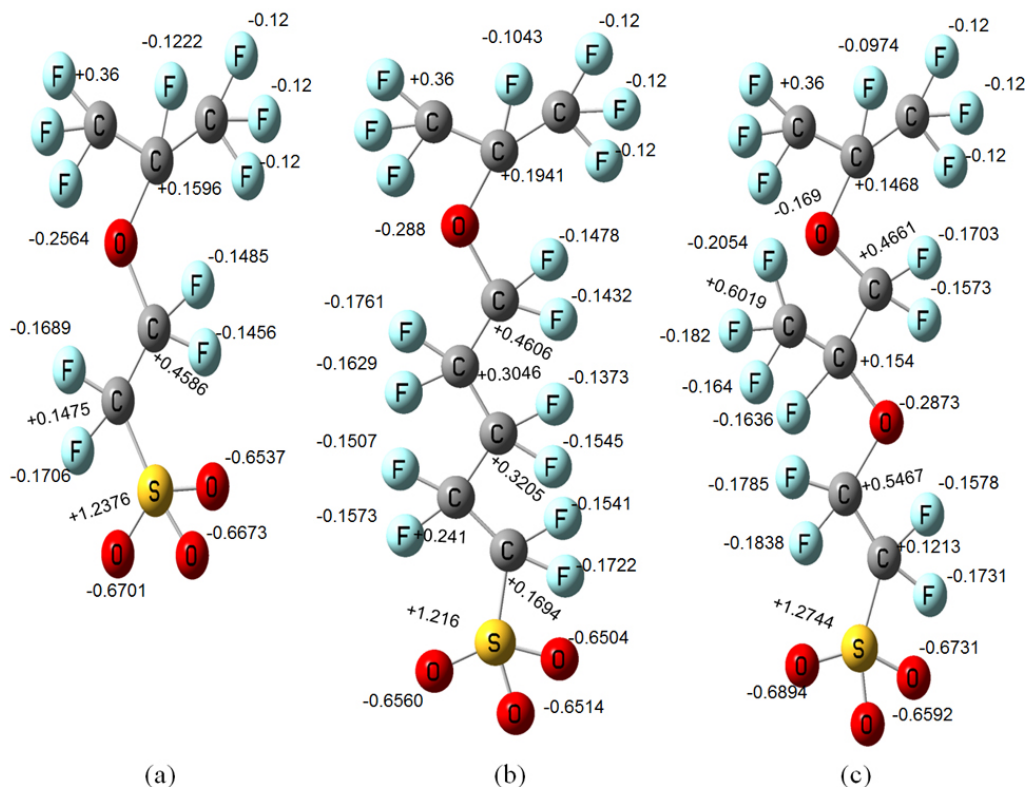


Figure 3.2: CHELPG charges for PFSA polymer electrolyte membranes a) Dow, b) Aciplex and c) Nafion.

presented. A summary of salient results concludes the chapter.

3.2 Computational details

3.2.1 Force-field

All MD simulations were performed using the GROMACS [91] 4.5.4 program. For Dow, Aciplex and Nafion side chains, all van der Waals parameters and the partial charges for the terminal CF₃ group were extracted from the OPLS-AA force field [72] database. The partial charges are computed from *ab initio* calculations using the Gaussian 03 [92] program in the following manner: The structure of a single Dow, Aciplex and Nafion side chain was independently optimized using the HF/6-31G** basis set. The optimized geometry obtained using the HF calculation was used as an input for a subsequent optimization

using the MP2/6-31G** basis set. The optimized geometry from the MP2/6-31G** basis set calculation was used to compute partial charges for the side chain of Dow, Aciplex and Nafion membrane respectively using the CHELPG [122] method. The full set of partial charges is shown in Figure 3.2. All bonds, angles and their force constants except the dihedral angles for side chains were extracted from the OPLS-AA force-field [72] database.

3.2.2 Dihedral parameterization

The dihedral coefficients for Dow, Aciplex and Nafion side chains were computed by choosing the Dow side chain as a template and optimized using the MP2/6-31G** basis set. The dihedral energies were scanned for C-C-C-F, F-C-C-F, F-C-C-O, C-C-S-O, C-C-O-C and F-C-O-C dihedral angles in steps of 18 degrees. The computed dihedral energy for C-C-C-F, F-C-C-F, F-C-C-O, C-C-S-O dihedral angles (see Figure 3.3a-d) was fitted by using a proper dihedral function as shown below:

$$V_d(\phi) = \frac{1}{2} [C_0(1 + \cos(\phi)) + C_1(1 + \cos(2\phi)) + C_2(1 + \cos(3\phi)) + C_3(1 + \cos(4\phi))] \quad (3.1)$$

Parameters C_0 to C_3 derived from the fit were called as dihedral coefficients. While the dihedral energy for the C-C-O-C and F-C-O-C dihedral angles was fitted by using a proper dihedral function as shown in Eqn. 3.2 (see Figure 3.3e-f)) where the functional form of the periodic function is written as:

$$V_d(\phi) = \frac{1}{2} [C_0(1 + \cos(\phi)) + C_1(1 + \cos(2\phi))] \quad (3.2)$$

The full set of force-field parameters for the Dow, Aciplex and Nafion side chains is provided in Table A3-1 (see Appendix A). The force-field parameters for the hydronium ion were taken from the work of Jang *et al.* [50]

3.2.3 Simulation details

The starting geometry used for MD simulations on Dow, Aciplex and Nafion side chain was created as follows: An energy minimization was performed on a single side chain and hydronium ion pair. The energy minimized side chain-hydronium ion pair was replicated to generate a cubic box containing 512 pairs. The resultant configuration was used as an input and a simulated annealing was performed by heating from 300 K to 1000 K and cooled back to 300 K with an annealing time of 6 ns. The annealing procedure was re-

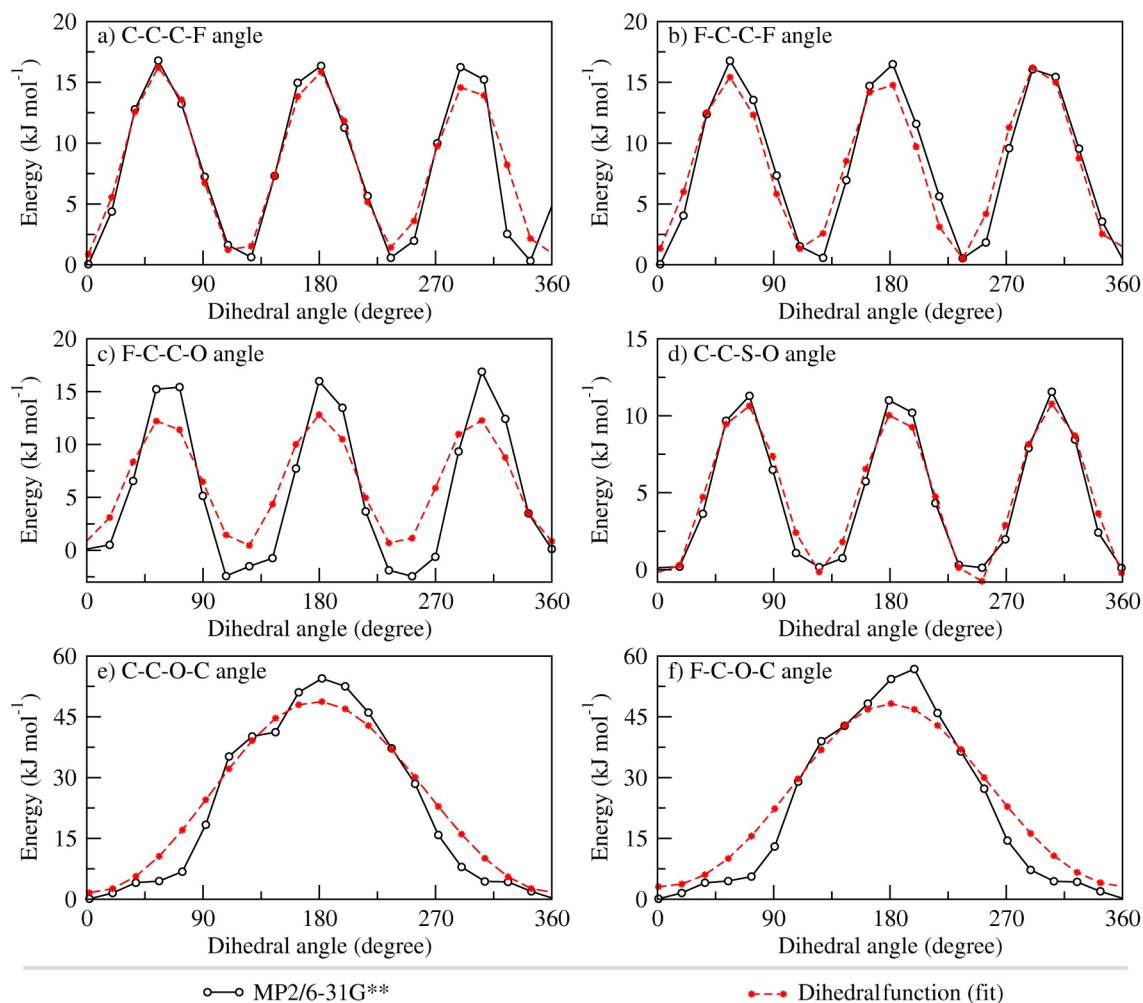


Figure 3.3: Dihedral energies of a) C-C-C-F, b) F-C-C-F, c) F-C-C-O, d) C-C-S-O, e) C-C-O-C and f) F-C-O-C angle.

peated 2 times. The final configuration obtained from the simulated annealing procedure was used as a template and solvated with 1536, 3072, 4608, 6144 and 7680 SPC/E [95] water molecules to generate configurations which contained Dow, Aciplex, Nafion side chain-hydronium ion pairs with varying water content denoted as $\lambda=3, 6, 9, 12$ and 15 (λ represent the number of water molecules for each side chain-hydronium ion pair). Concisely, we call these configurations as pendant-water mixtures. The smallest system ($\lambda=3$) of Dow pendant-water mixtures contains 17,408 atoms and the largest system ($\lambda=15$) of Nafion pendant-water mixtures contains 40,960 atoms. MD simulations on Dow, Aciplex and Nafion pendant-water mixtures were performed at 300 K and 350 K. For all MD simulations, the cut-off distance for van der Waals and electrostatic interactions for non-

bonded interactions were chosen as 10 Å. The leapfrog algorithm [74] was chosen as an integrator using a time step of 1 fs. Each MD simulation was equilibrated for 10 ns using the NPT ensemble with a 1 bar isotropic pressure and a Berendsen barostat [96]. Temperature was kept constant with a velocity-rescale thermostat [97] and a coupling time of 0.1 ps. The PME [98, 99] method was used to calculate long-range electrostatic interactions. Equilibration was followed by a 20 ns production run using the NVT ensemble. Trajectories from the production run were recorded every 5 ps to compute structural and dynamical properties.

3.3 Results and discussion

3.3.1 Density

MD simulations are performed on Dow, Aciplex and Nafion pendant-water mixtures and density is calculated at $\lambda=3, 6, 9, 12$ and 15 at 300 K and 350 K. The box sizes and the computed densities obtained from a 10 ns NPT equilibration are given in the Table A3-2 for 300 K and Table A3-3 (see Appendix A) for 350 K respectively. The density profile for Dow, Aciplex and Nafion pendant-water mixtures (see Figure 3.4) resemble closely with the density profile of the work of Sunda *et al.* [123] on triflate ion/water mixtures. The density profile (see Figure 3.4(a-c)) at 300 K shows that density decreases with increasing hydration. For example the density of Dow pendant-water mixtures is 1.68 g cm^{-3} ($\lambda=3$) and decreases with increase in hydration to 1.56 g cm^{-3} ($\lambda=6$), 1.47 g cm^{-3} ($\lambda=9$), 1.41 g cm^{-3} ($\lambda=12$) and 1.37 g cm^{-3} ($\lambda=15$) respectively. The density of Aciplex and Nafion pendant-water mixture are similar due to close resemblance in chemical structure. For example the density at $\lambda=3$ is 1.736 g cm^{-3} and 1.732 g cm^{-3} in Aciplex and Nafion side chain pendants/water mixtures respectively at 300 K. The density of Nafion pendant-water mixtures at 300 K is 1.732 g cm^{-3} ($\lambda=3$) and agrees with the experimental [124, 125] density (1.75 g cm^{-3}) of Nafion. The density from all side chain pendants/water mixtures shows a decrease with hydration as seen in this work; though the trends in density with hydration is insignificant in the work of Urata *et al.* [18], Venkatnathan *et al.* [21] and Brandell *et al.* [112] where they have employed a full polymer chain for simulation. The density of all pendant-water mixtures decreases with temperature for all hydration. For example the density of Dow pendant-water mixture for $\lambda=3$ is 1.68 g cm^{-3} at 300 K and decreases to 1.590 g cm^{-3} at 350 K. Similarly, the density of Aciplex and Nafion pendant-water mixtures at $\lambda=3$ is 1.736 g cm^{-3} and 1.732 g cm^{-3} at 300 K, and decreases to 1.631

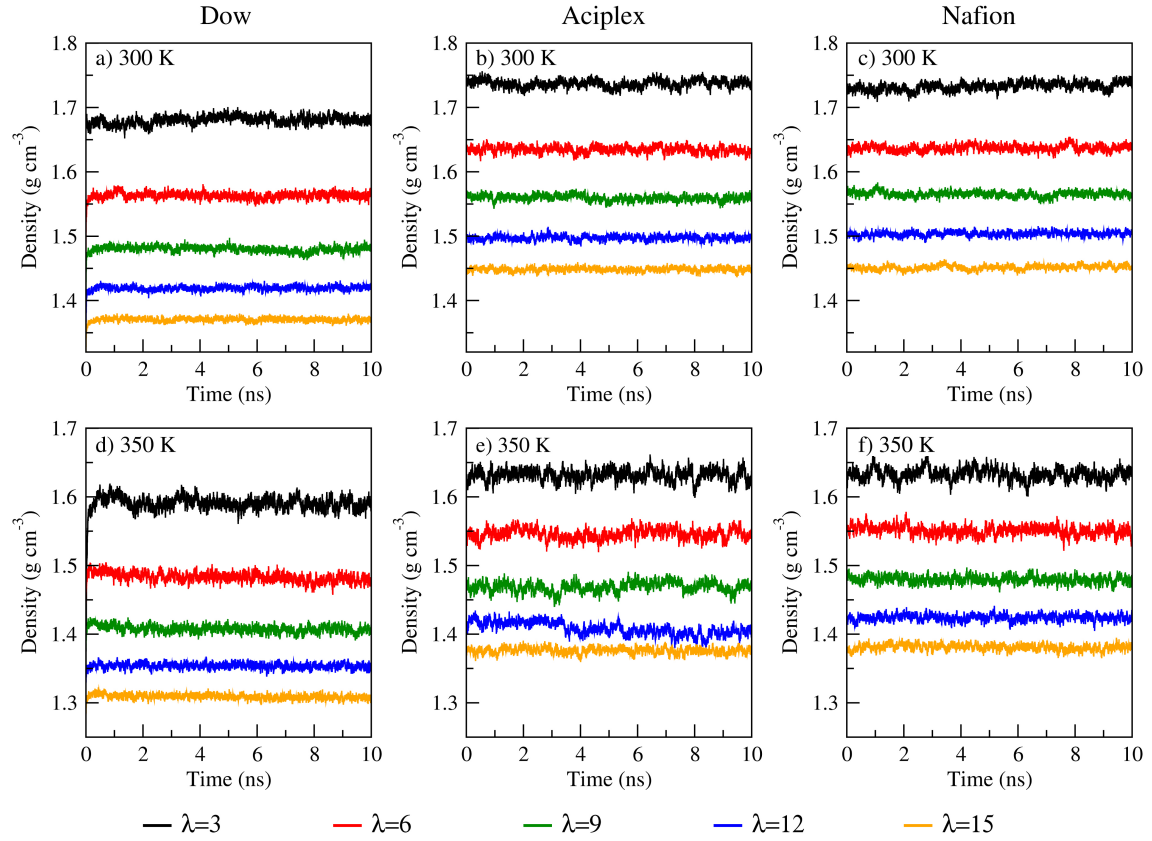


Figure 3.4: Densities of Dow, Aciplex and Nafion pendant-water mixtures at (a-c) 300 K and (d-f) 350 K.

g cm^{-3} and 1.632 g cm^{-3} at 350 K.

3.3.2 Influence of hydration and temperature on pendant nanostructure

The change in membrane nanostructure of Dow, Aciplex and Nafion side chain pendants with varying hydration at 300 K and 350 K is seen by an examination of the RDFs. The interaction among sulfonate groups is seen from the S-S RDFs (see Figure 3.5(a-c)). The sulfonate-sulfonate interaction decreases with increasing hydration in Dow and Aciplex pendant-water mixtures due to the increase in solvation of water molecules around the sulfonate group. The strongest sulfonate-sulfonate interactions are observed in Nafion pendant-water mixtures, where an anomalous behavior is observed at $\lambda=9$. For example, the peak intensity of sulfonate-sulfonate interactions in Nafion side chain pendant is

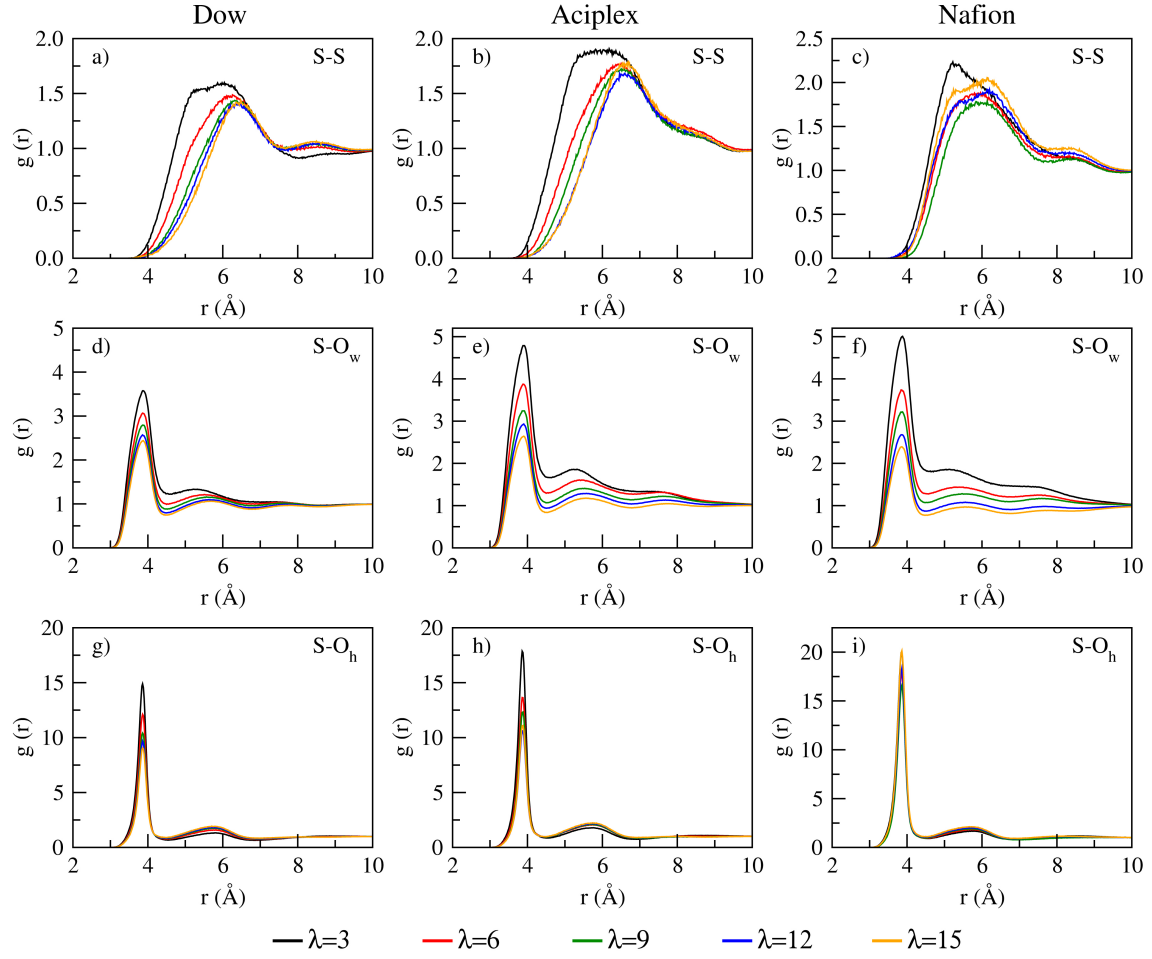


Figure 3.5: (a-c) S-S, (d-f) S-O_w and (g-i) S-O_h RDFs at 300 K.

higher at $\lambda=15$ compared to $\lambda=12$. The S-S RDF profiles seen in $\lambda=9$ from the Nafion pendant-water mixtures are similar to the S-S RDF profile obtained for Dow pendant-water mixtures at $\lambda=3$, where a bi-fragmented [123] peak at 5.5 Å is observed. This suggests that at low hydration ($\lambda=3$) in Dow pendant-water mixtures, and at higher hydration ($\lambda \geq 9$) of Nafion pendant-water mixtures, there is close proximity of water molecules around the sulfonate group. The bi-fragmented peaks disappear at 350 K for all hydration in Dow and Nafion pendant-water mixtures (see Figure 3.6). The first minima (7.75 Å) from the S-S RDFs in Dow, Aciplex and Nafion pendant-water mixtures is similar to previous work [28, 104] on hydrated PFSA membranes. The coordination numbers obtained from the S-S RDFs (as seen in Table 3.1) show a decrease with increasing hydration, whereas the effect of hydration on the co-ordination number is insignificant at $\lambda \geq 9$.

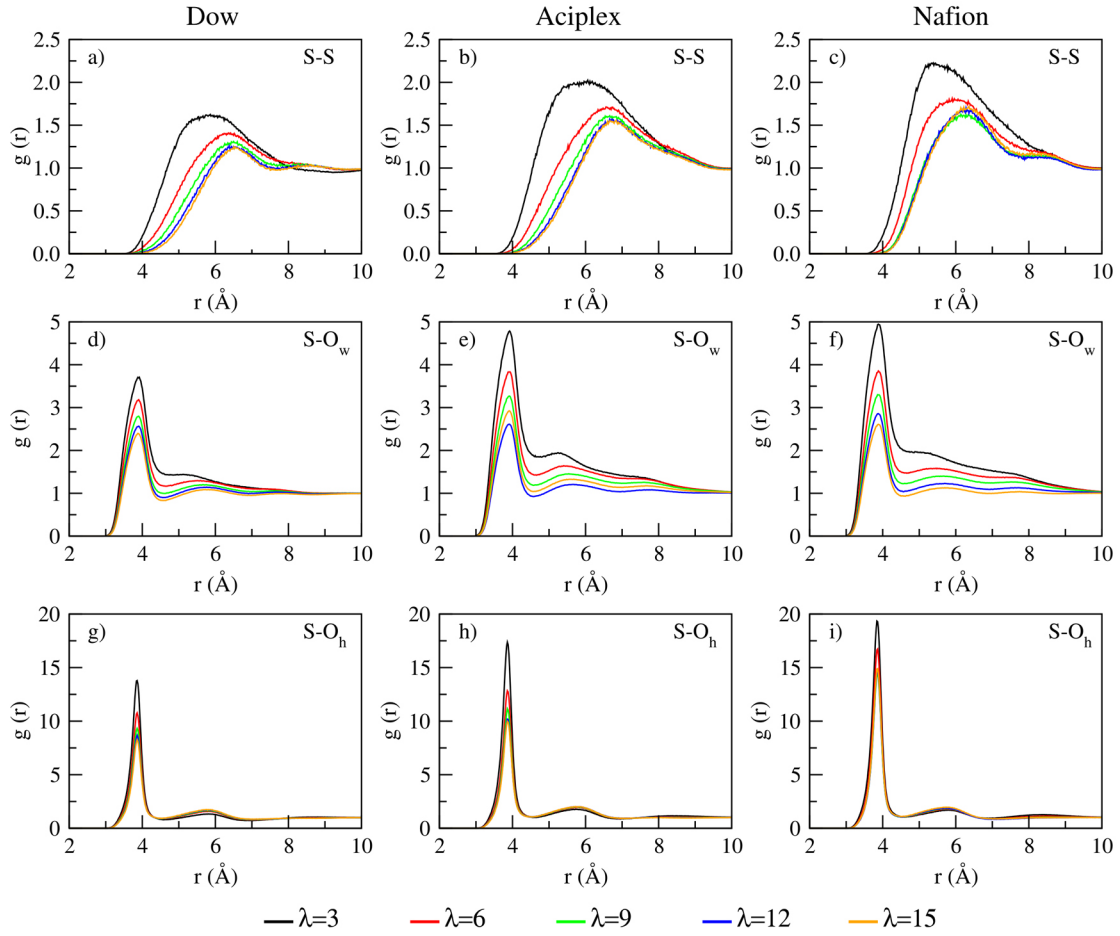


Figure 3.6: (a-c) S-S, (d-f) S-O_w and (g-i) S-O_h RDFs at 350 K.

in Nafion pendant-water mixtures. The coordination number slightly decreases from 2.9 ($\lambda=9$) to 2.7 ($\lambda=15$) in Nafion pendant-water mixtures but is found to be higher compared to Dow (2.0 at $\lambda=15$) and Aciplex (2.2 at $\lambda=15$) pendant-water mixtures. The coordination number from the S-S RDFs in Aciplex pendant-water mixtures is in excellent agreement with Sunda *et al.* [104] on hydrated Aciplex polymer membrane. Similarly, the coordination number obtained from the S-S RDFs in Nafion pendant-water mixtures agrees well with the work of Venkatnathan *et al.* [21] on Nafion.

The influence of hydration on sulfonate-water interactions is examined from the S-O_w RDFs (see Figure 3.5(d-f)) for Dow, Aciplex and Nafion pendant-water mixture respectively. The peak intensity of sulfonate-water interactions decreases with increase in hydration. This shows that water molecules are loosely bound to the sulfonate group with

Table 3.1: Co-ordination number calculated at the first minima in pendant-water mixtures of Dow, Aciplex and Nafion respectively.

g(r)	Pendant	$\lambda=3$	$\lambda=6$	$\lambda=9$	$\lambda=12$	$\lambda=15$
S-S (7.75 Å)	Dow	4.8	3.6	2.8	2.4	2.0
	Aciplex	4.5	3.4	2.8	2.4	2.2
	Nafion	4.6	3.6	2.9	2.8	2.7
S-O_w (4.5 Å)	Dow	3.5	5.0	5.8	6.1	6.4
	Aciplex	3.8	5.1	5.8	6.1	6.1
	Nafion	3.8	4.8	5.4	5.4	5.4
S-O_h (4.5 Å)	Dow	2.1	1.5	1.1	0.9	0.75
	Aciplex	2.0	1.3	1.1	0.9	0.75
	Nafion	2.1	1.6	1.3	1.3	1.3
O_h-O_h (7.5 Å)	Dow	4.2	3.1	2.5	2.0	1.7
	Aciplex	3.8	2.8	2.2	1.75	1.5
	Nafion	4.2	3.2	2.4	2.4	2.3
O_h-O_e (7.2 Å)	Dow	3.7	3.0	2.5	2.25	2.0
	Aciplex	—	—	—	—	—
	Nafion	2.1	1.8	1.6	1.6	1.6
O_h-O_w (3.5 Å)	Dow	2.0	3.0	3.5	3.75	4.0
	Aciplex	2.1	3.0	3.4	3.75	3.8
	Nafion	2.0	2.7	3.2	3.2	3.2
O_w-O_w (3.4 Å)	Dow	2.5	3.1	3.5	3.8	3.9
	Aciplex	2.2	3.0	3.5	3.7	3.9
	Nafion	2.5	3.3	3.6	3.8	3.9

increase in hydration. The peak intensity of sulfonate-water interactions is higher in Aciplex and Nafion pendant-water mixtures compared to the Dow pendant-water mixtures. The interactions of water molecules with the sulfonate group are stronger in Aciplex and Nafion pendant-water mixtures and weaker in Dow pendant-water mixtures. The first minima from the S-O_w RDFs in Dow, Aciplex and Nafion pendant-water mixtures is 4.5 Å and is similar to the work of Urata *et al.* [18], Venkatnathan *et al.* [21] and Liu *et al.* [28] on hydrated PFSA membranes. The coordination number is 6.4 (Dow pendant-water mixtures at $\lambda=15$) while the coordination number remains unchanged at $\lambda \geq 9$ in Nafion pendant-water mixtures (5.4 at $\lambda \geq 9$). The water solvation around the sulfonate group is found to be higher in Dow pendant-water mixtures. The water solvation around the sulfonate

group remains unaffected with temperature. For example, the S-O_w peak profile and solvation minima remains unchanged at 350 K for all hydration in Dow, Aciplex and Nafion pendant-water mixtures (see Figure 3.6(d-f)). The sulfonate-hydronium ion interaction is seen from the S-O_h RDFs (see Figure 3.5(g-i)). As expected, the strength of sulfonate-hydronium ion complex is highest/strongest at $\lambda=3$ and decreases with increase in hydration, and is lowest/weakest at $\lambda=15$ in Dow and Aciplex pendant-water mixtures. The peak intensity decreases with increase in hydration as water molecules mediate the sulfonate-hydronium ion interactions. In Nafion pendant-water mixtures, the peak intensity of sulfonate-hydronium ion is highest at $\lambda=15$ due to strong sulfonate-hydronium ion interactions. The sulfonate-hydronium ion interaction decreases with hydration as seen in the Dow and Aciplex pendant-water mixture which leads to enhanced hydronium ion diffusion. The sulfonate-hydronium ion interactions are affected by temperature as seen in Figure 3.6(g-i).

The peak intensity of from the S-O_h RDF is lower at 350 K compared to 300 K for Dow, Aciplex and Nafion pendant-water mixtures. However, the solvation minima remain unchanged. The influence of temperature is found significant in Nafion pendant-water mixtures at $\lambda=15$. The strength of sulfonate-hydronium ion interactions is weaker at 350 K compared to 300 K for $\lambda=15$, but still higher compared to Dow and Aciplex pendant-water mixtures. The first minima from the S-O_h RDFs in Dow, Aciplex and Nafion pendant-water mixtures is 4.5 Å. The coordination number of hydronium ions around the sulfonate group is ~ 2 in Dow and Aciplex pendant-water mixtures (at $\lambda=3$) and decreases with hydration. However, in Nafion pendant-water mixtures, the coordination number remains unchanged at $\lambda \geq 9$. The coordination numbers from the S-O_h and S-O_w RDFs from the Aciplex and Nafion pendant-water mixtures are in good agreement with the work of Sunda *et al.* [104] on hydrated Aciplex and Venkatnathan *et al.* [21] on hydrated Nafion respectively, though quantitative differences are observed at $\lambda \geq 9$ which could be due to the absence of polymer backbone in this work.

The O_h-O_h RDFs (see Figure 3.7(a-c)) are similar in Dow, Aciplex and Nafion pendant-water mixtures with the observation of two small shoulders at 4.5 Å and 5.6 Å respectively. The presence of the shoulder is more prominent in Nafion pendant-water mixtures and closely resembles the hydronium ion interactions seen in the work of Venkatnathan *et al.* [21] on the Nafion polymer membrane. The coordination number obtained at the first minima (7.5 Å) of the O_h-O_h RDFs is 4.2, 3.6 and 4.2 in Dow, Aciplex and Nafion pendant-water mixtures respectively at $\lambda=3$ (300 K). The coordination number de-

creases with hydration in Dow and Aciplex pendant-water mixtures, but remains constant in Nafion pendant-water mixtures at $\lambda \geq 9$.

3.3.3 Chain length variation and pendant nanostructure

The variation in pendant chain length with hydration and flexibility of side chain pendant is seen by a calculation of the average chain length (from 4000 frames of a 20 ns simulation trajectories) between the ether bonded backbone carbon and sulfur atom of the terminal sulfonate group at 300 K for all hydration in Dow, Aciplex and Nafion side chain pendants as seen in Figure 3.8(b-d). The Dow side chain pendant has shows a small variation of 0.8 Å in ~ 10 -15 % chain residues from an average chain length (5 Å). The Aciplex

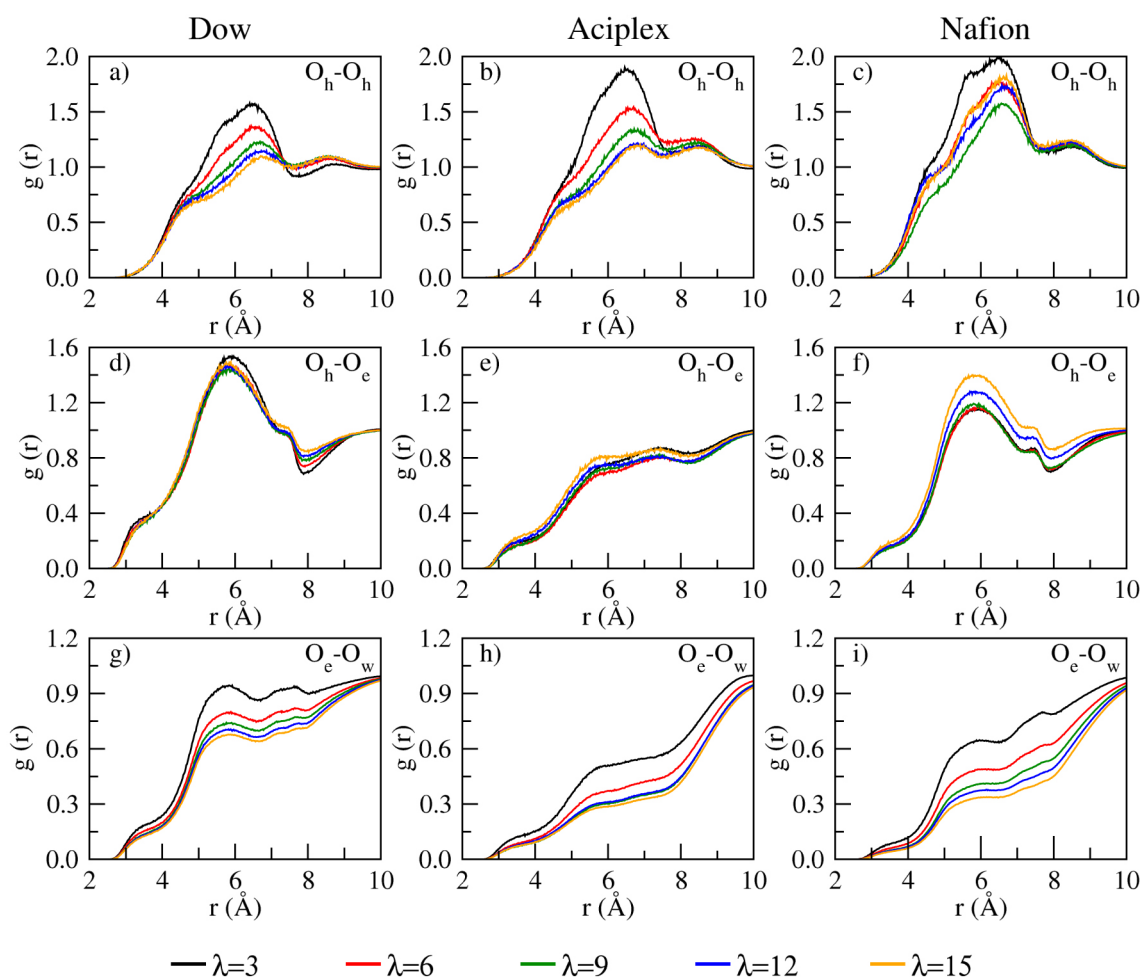


Figure 3.7: (a-c) O_h-O_h , (d-f) O_h-O_e and (g-i) O_e-O_w RDFs at 300 K.

side chain pendant has 60 % longer side chain length (7.9 Å) compared to Dow side chain pendant and shows a variation of 1.3 Å in ~ 10 -15 chain residues from the average chain length (7.9 Å). The presence of an extra ether oxygen in Nafion side chain pendant compared to Aciplex results in more flexibility and shows pendant chain length variation of 2.1 Å in ~ 10 % chain residues from average chain length (7.9 Å). This higher flexibility in Nafion pendant results in an elastic deformation with the pendant chain length variation of 1.0 Å in ~ 40 -50% chain residues from average chain length (7.9 Å). The impact of

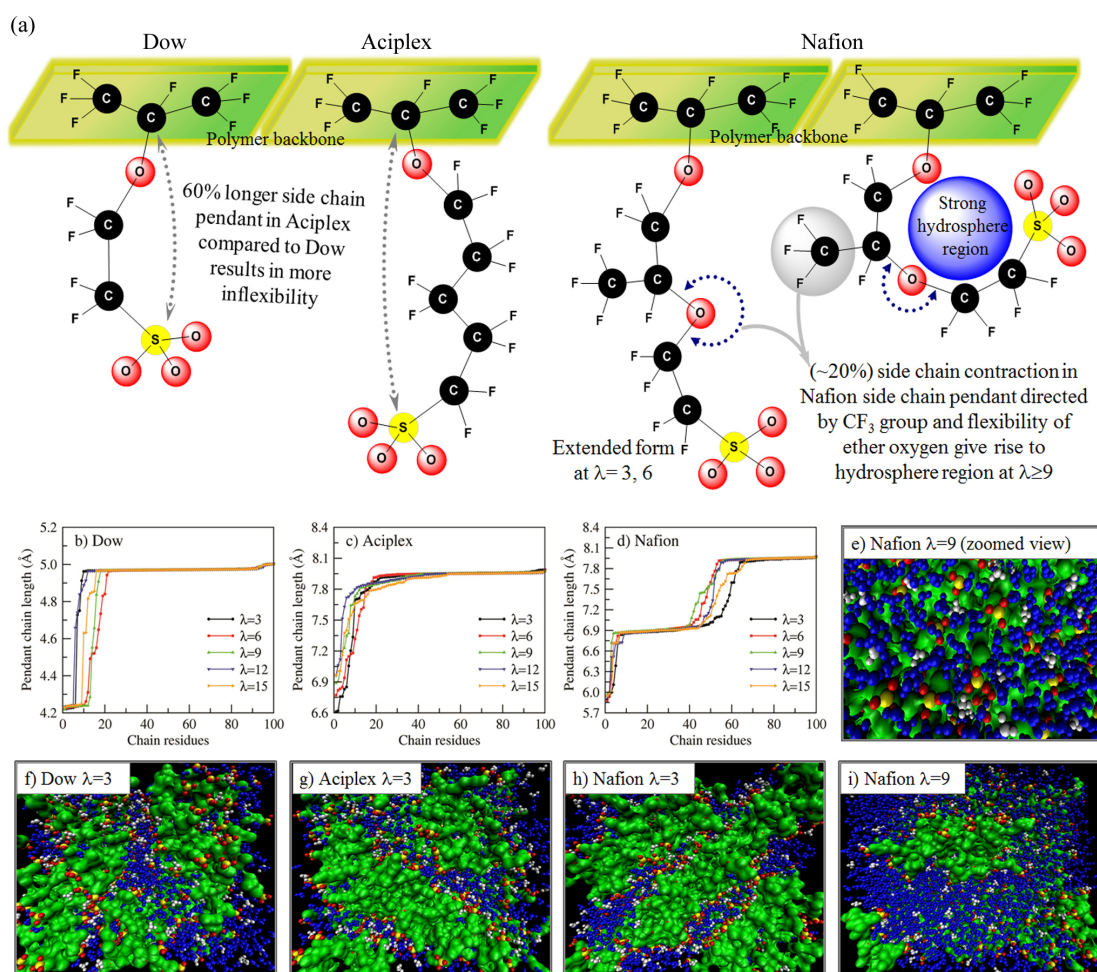


Figure 3.8: a) Schematic diagram of variation in pendant chain length; b-d) variation in C-S pendant chain length from simulations for Dow, Aciplex and Nafion side chain pendant respectively; and e-i) Snapshots (perspective view) of pendant-water mixtures at 300 K. [Hydronium ion (white), Water (dark blue), SO_3^- (yellow and red), Carbon (green surface) and fluorine atoms are not displayed]

this pendant chain length variation, chain flexibility and the role of ether oxygen is further illustrated by the RDF between the oxygen atom of hydronium ion and the ether oxygen of side chain pendant attached to backbone carbon as observed in O_h-O_e RDF (see Figure 3.7(d-f)). The Dow side chain pendant which has a shorter pendant chain length shows a larger hydronium ion solvation shell minima around the ether oxygen atom at 7.2 Å, which remains unaffected by hydration. The O_h-O_e RDF for Aciplex side chain pendant shows a flattened profile and the pair-pair interaction, $g(r)$ below unity indicates phase segregation. This flattened profile is also observed in the interaction between the pendant ether oxygen atom and water molecules as observed in O_e-O_w RDF (see Figure 3.7(h)). The hydrophobicity created by the longer side chain length consists of difluoromethylene (CF_2) group which is responsible for phase segregation in the hydrophobic and hydrophilic region. The appearance of phase segregation is seen in Dow pendant-water mixtures but become more pronounced in Aciplex pendant-water mixtures. A clear view (see Figure 3.8) of phase segregation in Aciplex pendant-water mixtures can be seen by comparing the snapshots with Dow pendant-water mixtures at $\lambda=3$. Such a phase segregation is also observed in Nafion pendant-water mixtures as seen in snapshots at $\lambda=3$. However, the phase segregation which exists in Nafion pendant-water mixtures at $\lambda=3$, disappears on increasing hydration. This is due to the flexibility of the side chain pendant, unlike the Aciplex and Dow pendants.

The O_h-O_e RDF of the Nafion pendant-water mixtures shows that the interaction between the hydronium ions and the pendant ether oxygen atom increases with hydration (see Figure 3.7(f)). The coordination number of hydronium ions around the pendant ether oxygen atom decreases with increase in hydration in Dow pendant-water mixtures but remain intact in Nafion pendant-water mixture at $\lambda \geq 9$. The interaction of water molecules with the pendant ether oxygen atom is seen from O_e-O_w RDFs (see Figure 3.7(i)). The flattened O_e-O_w RDF profiles in Aciplex pendant-water mixtures resemble the O_e-O_w RDFs which suggests that hydronium ions and water molecules prefer to stay away from the pendant ether oxygen atom. The interaction between hydronium ions and water molecules is seen from the O_h-O_w RDF (see Figure 3.9(a-c)). The solvation of hydronium ions with water molecules increases with hydration in Dow and Aciplex pendant-water mixtures but remain intact in Nafion pendant-water mixtures at $\lambda \geq 9$. The coordination number is ~ 2 at $\lambda=3$ in Dow, Aciplex and Nafion pendant-water mixtures; at $\lambda=15$ the coordination number is 4 in Dow pendant-water mixtures, 3.8 and 3.2 in Aciplex and Nafion pendant-water mixtures respectively at 300 K. The effect of temperature on O_h-O_w RDF

is insignificant, where peak profiles at 350 K are similar to 300 K (see Figure B3-2(a-c) of Appendix B). The water-water interactions are found to be unaffected with pendant chain length and flexibility, while the peak intensity from the O_w-O_w RDFs is highest in Nafion pendant-water mixtures (see Figure 3.9(d-f)). The coordination number of water at $\lambda=12$ or 15 from these RDFs resembles that of bulk water. A schematic change in the nanostructured arrangement with increase in hydration shows the cumulative impact of chain length and flexibility and the presence of an extra ether oxygen atom in Nafion side chain pendant is shown in Figure 3.8a). At higher hydration, the contraction in chain length and the hydrophobicity of the CF_3 group in the side chain pendant chain give rise to a hydrosphere cavity which can trap hydronium ions and water molecules. The presence of a hydrosphere cavity in Nafion validates the “Elbow” or “Hook” like structure in the pendant tail of Nafion as proposed in the work of Brandell *et al.* [112] and Devanathan *et al.* [121]

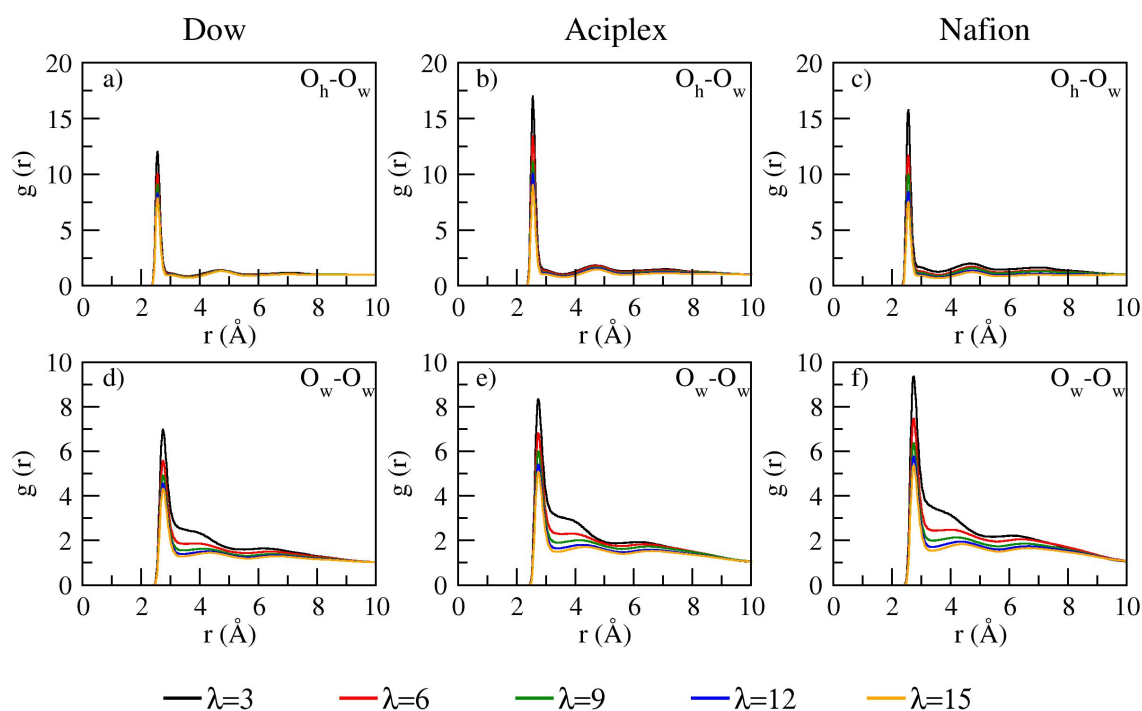


Figure 3.9: (a-c) O_h-O_w and (d-f) O_w-O_w RDFs at 300 K.

3.3.4 Structure factor and scattering intensities

The nanostructured arrangement of PFSA polymer membranes and the existence of hydrophilic water nano-domains inside the polymer matrix have been debated over the last one decade. Several structural models have been proposed from structure factor and scattering intensities recorded from SAXS and SANS studies with the assumption of distribution of water in spherical and rod like aggregates. However, it is not possible to directly distinguish between the spherical and rod like aggregates from SAXS and SANS experimental studies due to limitations in the scattering range. Schmidt-Rohr and Chen [39] proposed a parallel cylindrical water channel model (see Figure 3.10) in Nafion membrane by analyzing SAXS scattering data from simulation and a modified inverted micelle model proposed by Gierke *et al.* [37] and Gebel [9]. However, the role of water in the reorgani-

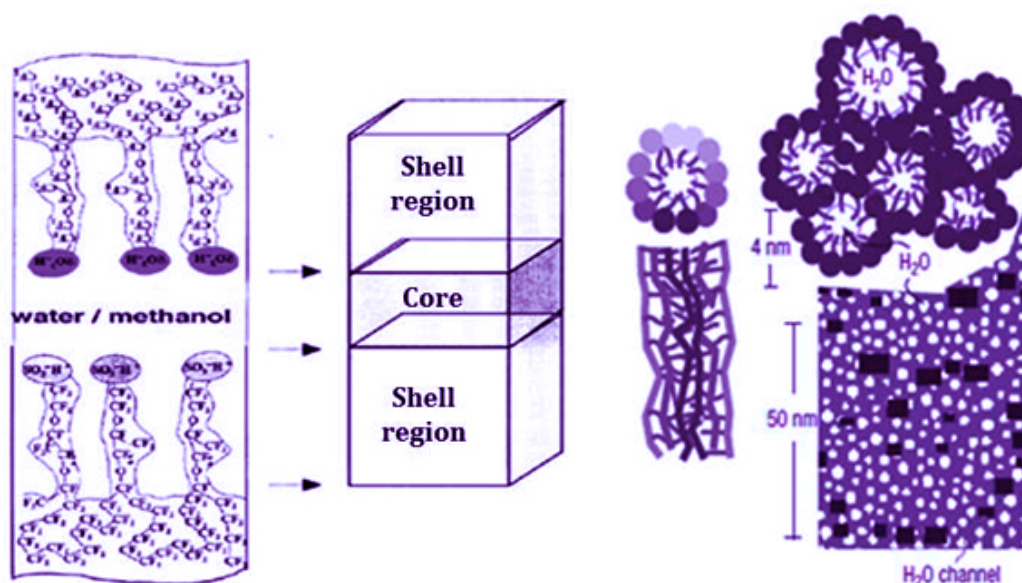


Figure 3.10: Schematic diagram of sandwich model and parallel cylindrical model (Adapted from Haubold *et al.* [35] Copyright 2001 Elsevier Science Ltd. and Schmidt-Rohr *et al.* [39] Copyright 2008 Nature Materials, Macmillan Publishers Ltd.).

zation of ionic clusters at different hydration is not completely clear. We have calculated the structure factor from simulation between the oxygen atoms of water molecules, since oxygen atoms contribute to 85 % of the total scattering in SAXS profile. The structure factor calculated from a Fourier transform of the RDF (see Eqn. 1.9). The structure factor at $\lambda=3$ shows a low flattened peak at $0.3 \text{ \AA}^{-1}$ in Dow pendant-water mixtures and at 0.24

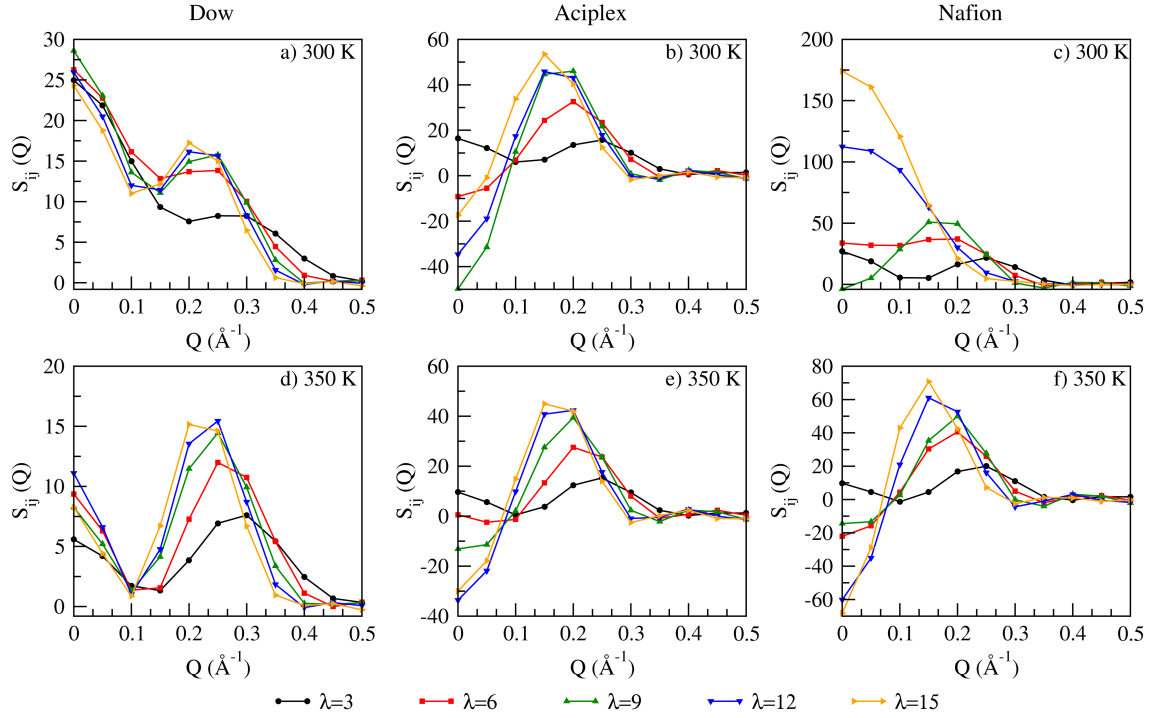


Figure 3.11: Structure factor calculated for O_w-O_w (water) atoms a-c) at 300 K and d-f) at 350 K.

$\text{\AA}^{-1}$ in Aciplex and Nafion pendant-water mixtures (see Figure 3.11). The peak patterns at $\lambda=3$ in Aciplex and Nafion pendant-water mixtures are similar [75] to bulk SPC/E water at the lower wave region. At $\lambda=3$, a comparison of the structure factors with the snapshots of Aciplex and Nafion pendant-water mixtures (see Figure 3.8g and Figure 3.8h) shows a segregated phase of hydrophilic and hydrophobic domains. The maximum volume of water remains in hydrophilic domain and a cumulative impact is seen in structure factor which resembles bulk water. The rigid pendant chains of Aciplex and the extended form of Nafion pendant exist as a rod like structure which is consistent with the sandwich model of Haubold *et al.* [35] from SAXS data analysis. The structure factor peak of $0.18 \text{ \AA}^{-1}$ at $\lambda=9$ of Nafion pendant-water mixtures (see Fig.3.11c) agrees well with the SANS experiment peak obtained in the work of Perrin *et al.* [15] at $0.18 \text{ \AA}^{-1}$ for hydrated Nafion at $\lambda=11$ (see Figure 3.12a). The sharpness of structure factor peak increases with hydration with the peaks shifted towards the lower wave region which is similar to the SANS structure factor profile (see Figure 3.12a). The deviation from bulk water behavior is seen from the snapshot of Nafion pendant-water mixtures at $\lambda=9$ which shows the distributions of the water as spherical aggregates of water domain around the sulfonate groups. The impact of

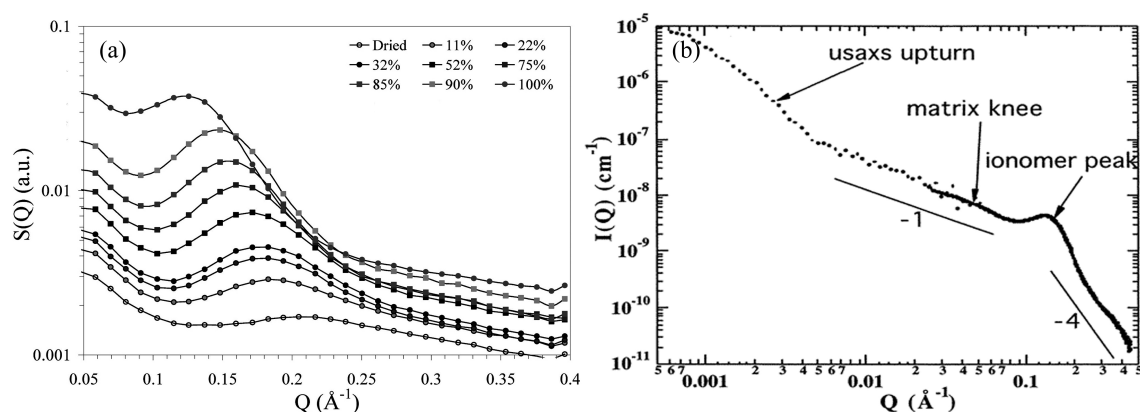


Figure 3.12: a) SANS structure factors of hydrated Nafion (Adapted from Perrin *et al.* [15] Copyright 2007 American Chemical Society), and b) A log-log representation of a standard small-angle X-ray scattering curve from a swollen Nafion 117 film (Adapted from Rubatat *et al.* [126] Copyright 2002 American Chemical Society).

the scattered water domains (see Figure 3.8e) on structure factor peak is found at higher hydration ($\lambda > 9$) due to presence of hydrosphere region in the polymer pendant matrix of Nafion side chain pendant/water mixtures at 300 K. The peak intensities are lowest in Dow pendant-water mixtures at higher hydration and moderate in Aciplex pendant-water mixtures. It is clear that the contraction of the pendant chain due to the chain flexibility in Nafion side chain pendant disturbs the rod like structure due to the swelling at $\lambda \geq 9$. Temperature has a pronounced effect on the structure factor peak intensities which are reduced upto ~ 50 at 350 K in Dow and Nafion pendant-water mixtures whereas the structure factor peak intensities are found similar at 300 K and 350 K in Aciplex pendant-water mixtures which shows the rigidity of the Aciplex side chain pendant.

Such observations are confirmed by the calculation of scattering intensity (see Equation 1.10). The calculated scattering peak at $\sim 3.2 \text{ \AA}^{-1}$ is shifted compared to the ionomer peak at $3.2 \text{ \AA}^{-1}$ obtained from the SAXS experiment of Rubatat *et al.* [126] (see Figure 3.12b). The difference in peak position could be due to the inclusion of polymer membrane in the SAXS experiment. The intensity of this peak increases with hydration due to increase in solvation around the sulfonate group as seen in Figure 3.13. The ionomer peak is broad at 300 K while it becomes smooth due to more uniformity in distribution of water molecules in the pendant matrix at 350 K. The calculated scattering intensities in Dow, Aciplex and Nafion pendant-water mixtures are similar and agree well the SAXS and SANS scattering intensities profile obtained for Dow [127] and Nafion [35, 119, 120].

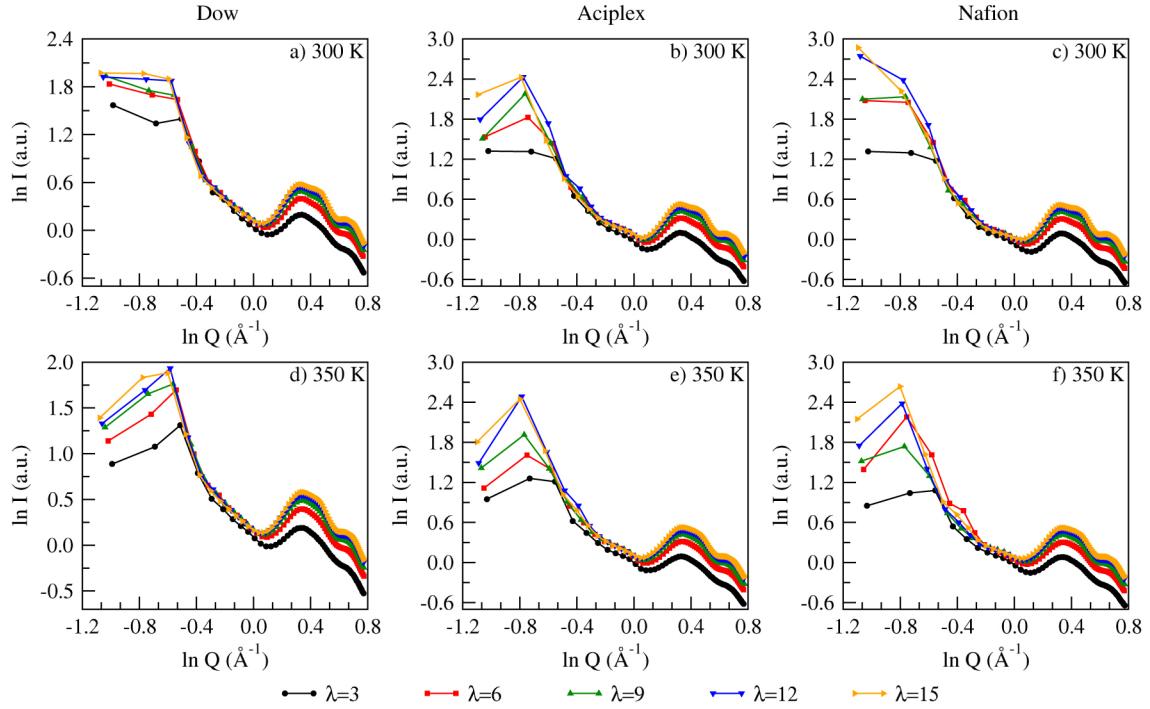


Figure 3.13: A log-log representation of scattering intensity obtained for O_w-O_w (water) atoms a-c) at 300 K and d-f) at 350 K.

The second low intense peak obtained at $\sim 0.68 \text{ \AA}^{-1}$ shows a solvation of water molecules around the hydronium ions. This peak is not observed in experimental studies. The peak positions of the side chain pendant ionomer and hydronium ions remain unaffected by temperature which is found to be consistent with the high temperature SAXS study of Mistry *et al.* [127] on Nafion and Hyflon polymer membranes.

3.3.5 Influence of hydration and temperature on water-proton dynamics

The mobility of hydronium ion and water in side chain pendants-water mixtures is determined by the MSD using the Einstein relationship [74]. The diffusion coefficients are computed from the linear regime of MSD and are tabulated in Table A3-4 and Table A3-5 (see Appendix A). The MSD shows a linear behavior for all hydration in Dow, Aciplex, Nafion pendant-water mixtures. The diffusion coefficient of hydronium ions increases with hydration. It is found highest for the Dow pendant-water mixtures and lowest in Nafion pendant-water mixtures (see Figure 3.14a). The diffusion of hydronium ions in-

creases by factor of 4 from $\lambda=3$ to $\lambda=6$ in Dow pendant-water mixtures at 300 K. Subsequent increase in hydration from $\lambda=6$ to $\lambda=9$, $\lambda=9$ to $\lambda=12$, and $\lambda=12$ to $\lambda=15$ increases hydronium ion diffusion by a factor of 1.86, 1.48 and 1.28 respectively. The phase segregation in Aciplex and Nafion (as discussed earlier) also affects the mobility of hydronium ions. The diffusion coefficient of hydronium ions at $(\lambda)=3$ is ~ 2 times lower in Aciplex and Nafion pendant-water mixtures compared to Dow pendant-water mixtures. The diffusion coefficient of hydronium ion increases by a factor of 5.59, 1.86, 1.56 and 1.12 with subsequent increase in hydration from $\lambda=3$ to $\lambda=6$, $\lambda=6$ to $\lambda=9$, $\lambda=9$ to $\lambda=12$, and $\lambda=12$ to $\lambda=15$ in Aciplex pendant-water mixtures. In case of Nafion, the diffusion of hydronium ions is the lowest. At $\lambda > 9$, the effect of hydration on diffusion is insignificant. The increase in sulfonate-hydronium ion interaction with increase in hydration as seen in RDFs and also depicted in the schematic diagram, results in the slower diffusion of hydronium ion at higher hydration in Nafion. The diffusion coefficient of hydronium ions increases by a factor of 4.17, 1.9, 1.53 and 1.03 with subsequent increase in hydration from $\lambda=3$ to $\lambda=6$, $\lambda=6$ to $\lambda=9$, $\lambda=9$ to $\lambda=12$, $\lambda=12$ and $\lambda=15$ in Nafion pendant-water mixtures. The hydrosphere region in Nafion pendant-water mixtures prevents extra water molecules to enter the hydrosphere cavity (at $\lambda \geq 9$). At all hydration at 300 K, the trends in hydronium ion diffusion coefficients are in qualitative agreement with that from a QENS experiment [15] in hydrated Nafion. The quantitative differences with experimental observations are due to the limitations of classical force-fields which cannot describe the structural diffusion of protons. However, the structural diffusion of protons can be studied using reactive MD [128–130] or AIMD simulations [131–134] methods. Temperature shows significant effect on hydronium ion diffusion. The hydronium ion diffusion increases by a factor of 4.85, 5.64 and 4.3 at $\lambda=3$ in Dow, Aciplex and Nafion pendant-water mixtures from 300 K to 350 K. Similar trends are also observed at other hydration.

The diffusion of water molecules in Dow, Aciplex and Nafion pendant-water mixtures is shown in Figure 3.14b. The diffusion of water molecules is fastest in Dow pendant-water mixtures and slowest in Nafion pendant-water mixtures. For example, the diffusion coefficient of water ($\lambda=6$) is 0.5201, 0.4545 and 0.3978 ($\times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$) for Dow, Aciplex and Nafion pendant-water mixtures at 300 K. The diffusion coefficient from simulations at 300 K is in good agreement with experiment [135] diffusion coefficient of Nafion polymer membrane (see Figure 3.14b). The higher diffusion coefficients of water molecules in Dow compared to Nafion is also consistent with the observations of Karo *et al.* [136] The increase in temperature increases the motion of water molecules leading to

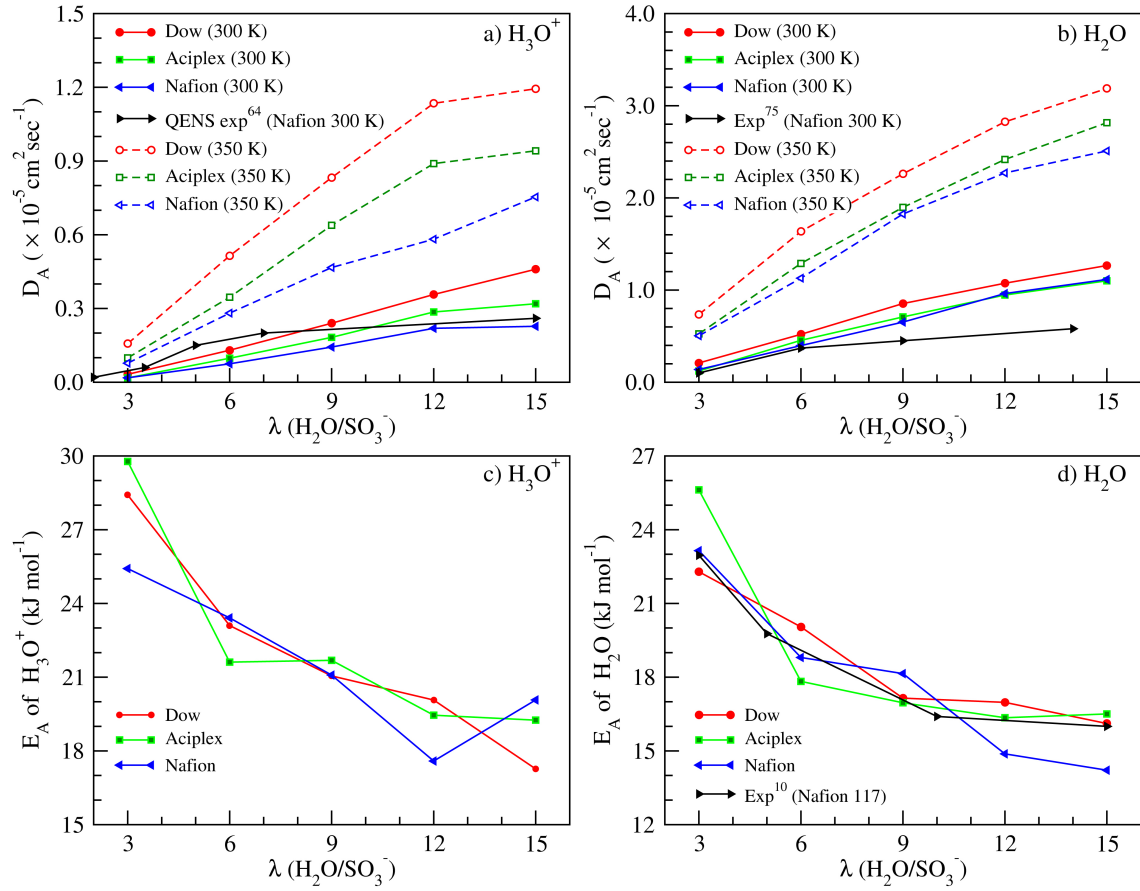


Figure 3.14: D_A of a) hydronium ions and b) water molecules; Activation energy of diffusion of c) hydronium ions and d) water molecules.

higher diffusion. The diffusion coefficient of water increases by a factor of 3.5, 4.3 and 3.65 for $\lambda=3$ in Dow, Aciplex and Nafion pendant-water mixtures at 350 K compared to 300 K. Further, the influence of hydration on water and hydronium ion mobility is also examined from the activation energy of diffusion.

3.3.6 Activation energy

To provide an accurate value of activation energy of diffusion, we have also performed MD simulations at 320 K and 335 K for $\lambda=3, 6, 9, 12$ and 15. The diffusion coefficients of hydronium ions and water molecules obtained from simulations performed at 300 K, 320 K, 335 K and 350 K are used to calculate the activation energy of diffusion for each hydration. The E_A obtained from a slope of a linear fit for hydronium ions and water

molecules are shown in Figure 3.14c and Figure 3.14d respectively and value are given in Table A3-6 (see Appendix A). The E_A of hydronium ions and water molecules decrease with hydration in Dow side chain pendant water mixtures whereas the E_A of hydronium ions become constant at $\lambda \geq 9$ in Aciplex pendant-water mixtures. However, in Nafion pendant-water mixtures, the E_A of hydronium ions is lowest at $\lambda=12$ (17.58 kJ mol⁻¹), but increases to 20.07 kJ mol⁻¹ at $\lambda=15$. This slight increase in E_A of hydronium ions at $\lambda=15$ in Nafion pendant-water mixtures is due to strongest hydronium interaction with the ether oxygen of the side chain pendant and the sulfonate group in hydrosphere region (as discussed earlier). The E_A of hydronium ions at $\lambda=15$ is 17.26, 19.25 and 20.07 kJ mol⁻¹ for Dow, Aciplex and Nafion pendant-water mixtures respectively. The calculated E_A of hydronium ions at $\lambda=15$ for the Nafion pendant-water mixtures is reasonable agreement with the experimental [137] value of E_A (16.5 kJ mol⁻¹) at $\lambda=14$ for Nafion polymer membrane. The calculated E_A of water molecules from simulation at $\lambda=3$ is 22.28, 25.62, 23.14 kJ mol⁻¹ for Dow, Aciplex and Nafion pendant-water mixtures respectively and is in excellent agreement with the experimental [10] E_A of 22.96 kJ mol⁻¹ at $\lambda=3$ in Nafion 117. The calculated E_A of water molecules at $\lambda=6, 9, 12$ and 15 for Nafion pendant-water mixtures are 18.80, 18.14 and 14.88 and 14.21 kJ mol⁻¹ respectively and are in the range of experimental [10] E_A values (19.77, 16.69, 16.4 kJ mol⁻¹ respectively for $\lambda=5, 10$ and 15) in Nafion 117. Finally, the decrease in E_A of water molecules with hydration in pendant-water mixtures is similar to the experimental work of Kreuer *et al.* [10] and simulation studies of Nafion 117 by Jang *et al.* [50] which shows enhanced mobility of water molecules.

Due to the exclusion of polymer backbone membrane in this work, effects like polymer backbone conformation, effect of hydrophobicity and polymer chain molecular weight [28] could not be examined. However, these limitations do not seem to significantly impact the structural and dynamical properties presented in this chapter. For example, various RDFs obtained from the different pendant-water mixtures resemble closely with the RDFs calculated using previous studies on the hydrated polymer (PFSA) membranes which contain these side chains pendants. Similar trends are also seen from the calculated scattering intensities of pendant-water mixtures which agree well with the experimental SAXS spectra on the hydrated polymer membrane. However, certain differences in structural properties can be seen from the use of side chain pendants compared to the full polymer membrane. For example, the effect of temperature on RDFs can be further reduced if the full polymer membrane is included, where the side chain pendant gets

thermal stability from the polymer backbone. Further, the inclusion of polymer backbone shows flattened O_h-O_e and O_e-O_w RDF profiles for Dow [121], Aciplex [104] and Nafion [21, 28] membranes, though such features are observed only in the Aciplex side chain pendant water/mixtures in this present study. The diffusion coefficients reported in this work on pendant-water mixtures also are in close agreement with the diffusion coefficients obtained from investigations on the hydrated polymer membrane. These observations are also consistent with the work of Liu *et al.* [28] where they have shown that diffusion coefficients change insignificantly with polymer equivalent weight.

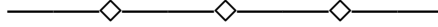
3.4 Conclusions

The side chain pendants of PFSA membranes like Dow, Aciplex and Nafion have similar atom types but differ in side chain pendant length. The pendant chain length influence pendant nanostructure and water hydronium ion mobility which are further sensitive to hydration and temperature. The presence of extra three CF_2 units in Aciplex side chain pendant compared to the Dow results in a 60% longer rigid side chain pendant. This inflexibility of Aciplex pendant results in phase segregation. This phase segregation remains intact even at higher temperature (350 K) and hydration which results in slow hydronium ion diffusion due to the restriction of its mobility in hydrophilic domains. Hydration enhances the mobility of hydronium ions and water molecules. The increase of temperature from 300 K to 350 K results in an increase of water molecules diffusion by a factor of $\sim 3-4$ for all hydration in all pendant-water mixtures.

The presence of an extra ether oxygen atom in Nafion side chain pendant provides extra flexibility to the sulfonate group to move towards the hydrophilic region and away from the hydrophobic regions. The Nafion side chain pendant are present in a rod like structure at low hydration $\lambda=3$ and 6, similar to the Aciplex side chain pendant and also shows phase segregation. The flexibility of the Nafion side chain pendant results in 20 contraction in pendant chain length which is assisted by the hydrophobicity of the side chain pendant CF_3 groups. This elastic deformation due to pendant chain length contraction in the Nafion side chain pendant gives rise to a hydrosphere region at $\lambda \geq 9$ which contains a spherical region of strongly bound hydronium ions and water molecules. The hydrosphere region can accommodate 5 to 6 water molecules and one hydronium ion and does not allow any extra water molecules to enter inside. This form of the segregated nanostructure could destroy any water nano-channel connectivity in Nafion pendant-water mix-

tures which could affect proton conductivity at higher hydration. The anomalous behavior seen in the nanostructure of Nafion pendant-water mixtures at $\lambda \geq 9$ provides evidence to experimental studies that Nafion is adversely affected by higher hydration, which validates the experimental (Infra-Red spectroscopy) work of Laporta *et al.* [102] that $\lambda=6$ is a sufficient water content for high proton conductivity.

The inclusion of polymer backbone membrane which includes the effects like polymer backbone conformation, effect of hydrophobicity and polymer chain molecular weight [28] need to be examined. In the next chapter, a detailed investigation of structural and dynamical properties of Aciplex polymer membrane with inclusion of full polymer membrane (with backbone) is presented.



Chapter 4

Atomistic simulations of structure and dynamics of hydrated Aciplex polymer electrolyte membrane

4.1 Introduction

A large number of studies have been devoted to Nafion as a membrane for fuel cells application. However, the Aciplex membrane which resembles closely with Nafion (see Figure 3.1) has received far less attention. The sulfonate group of the membrane remains in the dissociated form (ionomer form) even at extremely low water content. Adjemian *et al.* [138] compared Aciplex and Nafion based PFSA silicon oxide composite membranes with varying membrane thickness and showed that the Aciplex 1004/silicon oxide has the lowest resistivity at elevated temperature (130 °C) which makes the membrane an attractive alternative to Nafion. Tanaka [139] demonstrated an effective use of the Aciplex membrane as an ion exchange material in the desalination of water. Brandell *et al.* [112] employed MD simulations on Nafion, Aciplex and Dow membrane at two levels of hydration and at 300 K. The authors concluded that optimal water-channel network connectivity at high hydration was observed from Nafion at 300 K. Further, the Aciplex membrane used by these authors consist of a secondary ether oxygen ($x=1$) with extra CF_2 unit ($y=3$) in the pendant side chain which closely resembles with Nafion (see Figure 3.1). Devanathan and Dupuis [121] performed classical MD simulations on Dow (short side chain) and Nafion (long side chain) and investigated the role of pendant side chain length on structure and transport properties. The authors concluded that the side chain in Nafion membrane remains bent at all hydration due to the presence of secondary ether oxygen and is almost equivalent to the short side chain. Asahi Chemical Industry manufactured

a series of Aciplex membrane [140, 141] with an equivalent weight of 1000-1200 with or without secondary ether oxygen in pendant side chain ($x=0$ or 1). In this chapter, the Aciplex-S [6, 30, 142, 143] membrane (henceforth referred to as Aciplex) has been chosen to characterize the structure and dynamics of water molecules and hydronium ions at varying degrees of membrane (from very dry to extremely large amount of water) hydration at 300 K and 350 K using classical MD simulations. The Aciplex membrane used in this work has a repeating unit ($m=7$) with $O(CF_2)_5SO_3^-$ pendant side chain ($x=0$, $y=5$) corresponding to an equivalent weight of 1130.

The details of MD simulations are presented in Section 4.2. As there is no experimental data available on the actual Aciplex membrane, the calculated properties presented in this work are compared to experimental/theoretical data on Nafion. The calculated structural and dynamical properties in hydrated Aciplex membranes are described in Section 4.3. A summary of salient results concludes the chapter.

4.2 Computational details

The chemical structure of the Aciplex polymer membrane includes a $O(CF_2)_5SO_3^-$ pendant side chain ($x=0$, $y=5$) (see Figure 3.1) in the ionomer form). MD simulations were performed using the GROMACS [91] 4.5.4 program. The force-field parameters for the Aciplex polymer backbone were extracted from the OPLS-AA database [72]. The force-field parameters for the pendant side chain membrane are shown in Table A3-1 (see Appendix A). Force-field parameters for the hydronium ion were taken from the work of Jang *et al.* [50] The starting geometry used for MD simulations on Aciplex ionomer membrane was obtained as follows: A single chain (constructed from 10 monomeric units with a total of 672 atoms in each chain) of an energy minimized Aciplex ionomer membrane along with 10 hydronium ions was replicated 48 times. The resultant configuration contained 48 chains of Aciplex ionomer membrane and 480 hydronium ions. The replicated configuration was chosen as an input for a simulated annealing which was performed by heating from 300 K to 1000 K and cooled back to 300 K with a total simulation time of 9 ns. The annealing procedure was repeated three times. The final configuration from the annealing procedure was used as a template and solvated with 1440 ($\lambda=3$), 2880 ($\lambda=6$), 4320 ($\lambda=9$), 5760 ($\lambda=12$) and 7200 ($\lambda=15$) SPC/E [95] water molecules (λ denotes the number of water molecules per sulfonate group). The solvation of the membrane is achieved by a random insertion of water molecules which leads to an increase in box size to accom-

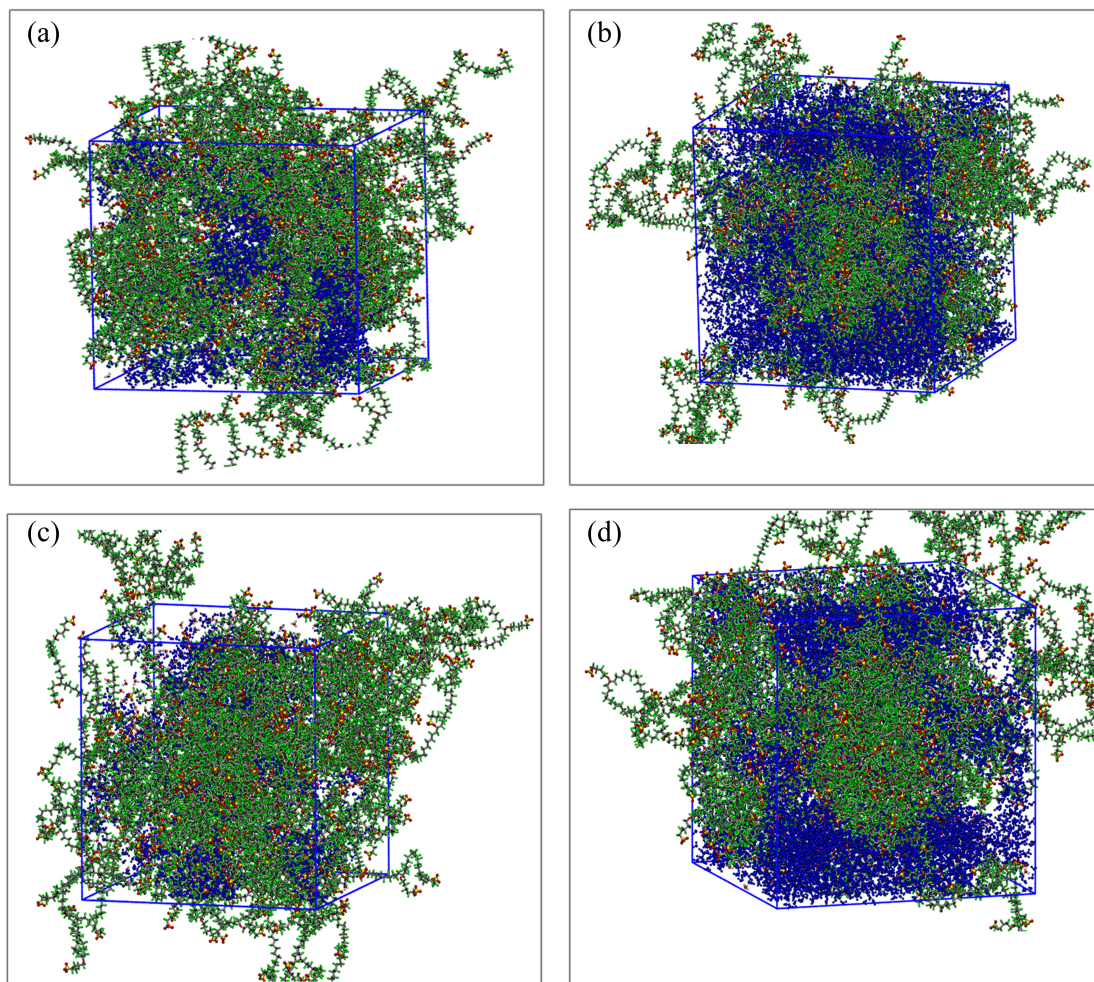


Figure 4.1: Snapshots of Aciplex ionomer membrane-water mixtures at 300 K (a and b) Initial configuration of randomly inserted water molecules in membrane matrix at $\lambda=3$ and $\lambda=15$ respectively; (c and d) Final configuration of production run at $\lambda=3$ and $\lambda=15$ respectively.

moderate water molecules to obtain a required λ . Each hydrated configuration was energy minimized using a steepest descent algorithm [73] followed by a 1 ns pre-equilibration using the NPT ensemble at 300 K and the final geometry was used as input for subsequent MD simulations.

MD simulations on the Aciplex ionomer membrane-water mixtures were performed at 300 K and 350 K. The cut-off distance for non-bonded interactions was chosen as 10 Å. The equations of motion were integrated using the leapfrog algorithm [74] with a time step of 1 fs. MD simulation on each Aciplex ionomer membrane-water mixtures was equilibrated for 10 ns using the NPT ensemble with a 1 bar isotropic pressure and the Berendsen

barostat [96]. Temperature was maintained using a velocity-rescale thermostat [97] with a coupling time of 0.1 ps. The PME [98,99] method was used for description of long range electrostatic interactions. Equilibration was followed by a 20 ns production run using the NVT ensemble. Trajectories from the production run were saved periodically for 5 ps to calculate structural and dynamical properties.

4.3 Results and discussion

4.3.1 Density

The smallest system ($\lambda=3$) of Aciplex ionomer membrane-water mixtures contains 41,376 atoms and the largest system ($\lambda=15$) of Aciplex ionomer membrane-water mixtures contains 58,656 atoms. A representative snapshot of input and output configuration of hydrated membrane at $\lambda=3$ and $\lambda=15$ is shown in Figure 4.1. The cubic box length and density for each hydration from the equilibration run is shown in Table 4.1. The density profiles for all hydration at 300 K and 350 K are shown in Figure 4.2. The calculated densities are found to be in the range of experimental density (1.75-1.80 g cm⁻³) [124,125]. The calculated densities decrease with an increase in hydration. For example, the average densities of Aciplex ionomer membrane-water mixtures are 1.78 g cm⁻³, 1.75 g cm⁻³, 1.73 g cm⁻³, 1.69 g cm⁻³ and 1.65 g cm⁻³ at $\lambda=3, 6, 9, 12$ and 15 respectively at 300 K.

Table 4.1: Box length (l) and average densities (ρ) of Aciplex ionomer membrane-water mixtures from a 10 ns equilibration run.

λ	l (Å)		ρ (g cm ⁻³)	
	300 K	350 K	300 K	350 K
3	81.307	81.860	1.782	1.745
6	82.922	83.456	1.758	1.718
9	84.586	85.380	1.730	1.680
12	86.377	87.289	1.690	1.637
15	88.187	89.124	1.650	1.592

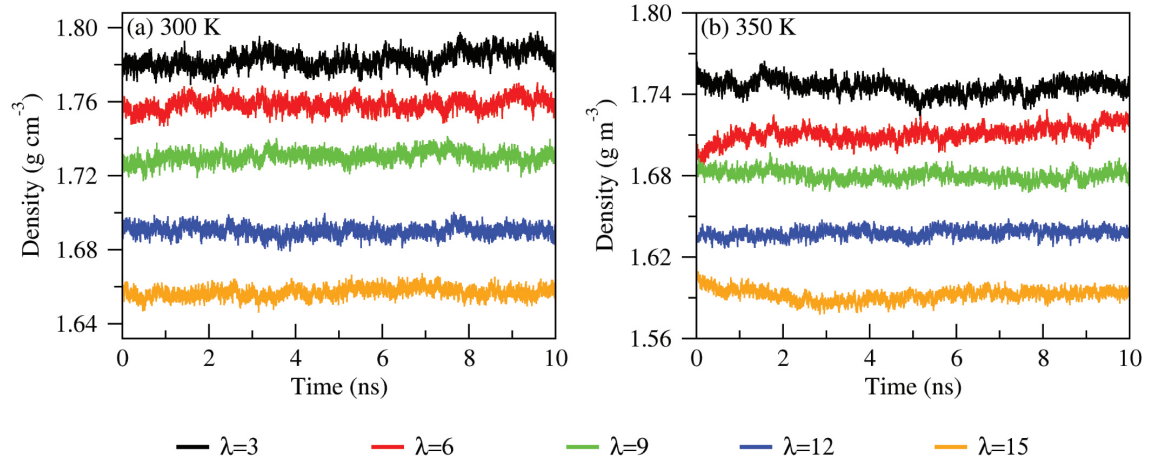


Figure 4.2: Density of Aciplex ionomer membrane-water mixtures at a) 300 K and b) 350 K.

4.3.2 Effect of hydration and temperature on membrane nanostructure

The effect of hydration on the membrane nanostructure and interactions between the pendant side chain and water domains inside the membrane matrix at 300 K and 350 K is seen by an examination of the RDFs. The sulfonate-sulfonate interactions are seen from the S-S RDFs (see Figure 4.3a), where the sulfonate group is an active part of the polymer membrane. The sulfonate-sulfonate interaction decreases with increasing hydration. A bi-fragmented peak is seen from the S-S RDF peak which shows broad features at higher hydration ($\lambda > 9$). The intensity of the first peak of the S-S RDFs decreases with hydration and shows a large solvation shell (8.5 Å). These results are similar to the work of Liu *et al.* [28] on hydrated morphology of PFSA membranes and the work of Venkatnathan *et al.* [21] on Nafion 117. The co-ordination number calculated at the first minima from the S-S RDFs (see Table 4.2) decreases with increasing hydration which suggests that water mediates the sulfonate-sulfonate interactions [123]. The sulfonate-water interactions are characterized by the S-O_w RDF shown (see Figure 4.3b). An intense S-O_w RDF peak at 4 Å shows a decrease in peak intensity with hydration and is similar to previous findings on Nafion [18, 21, 24, 28]. The coordination number is lowest at $\lambda=3$ and increases to 3.9, 4.4, 5.0 and 5.1 at $\lambda=6, 9, 12$ and 15 respectively which shows that water molecules prefer to interact with sulfonate groups. The interaction between the sulfonate group and hydronium ions can be observed from the S-O_h RDFs (see Figure 4.3c). The co-ordination number calculated at the first minima of the S-O_h RDF is highest at $\lambda=3$ and decreases

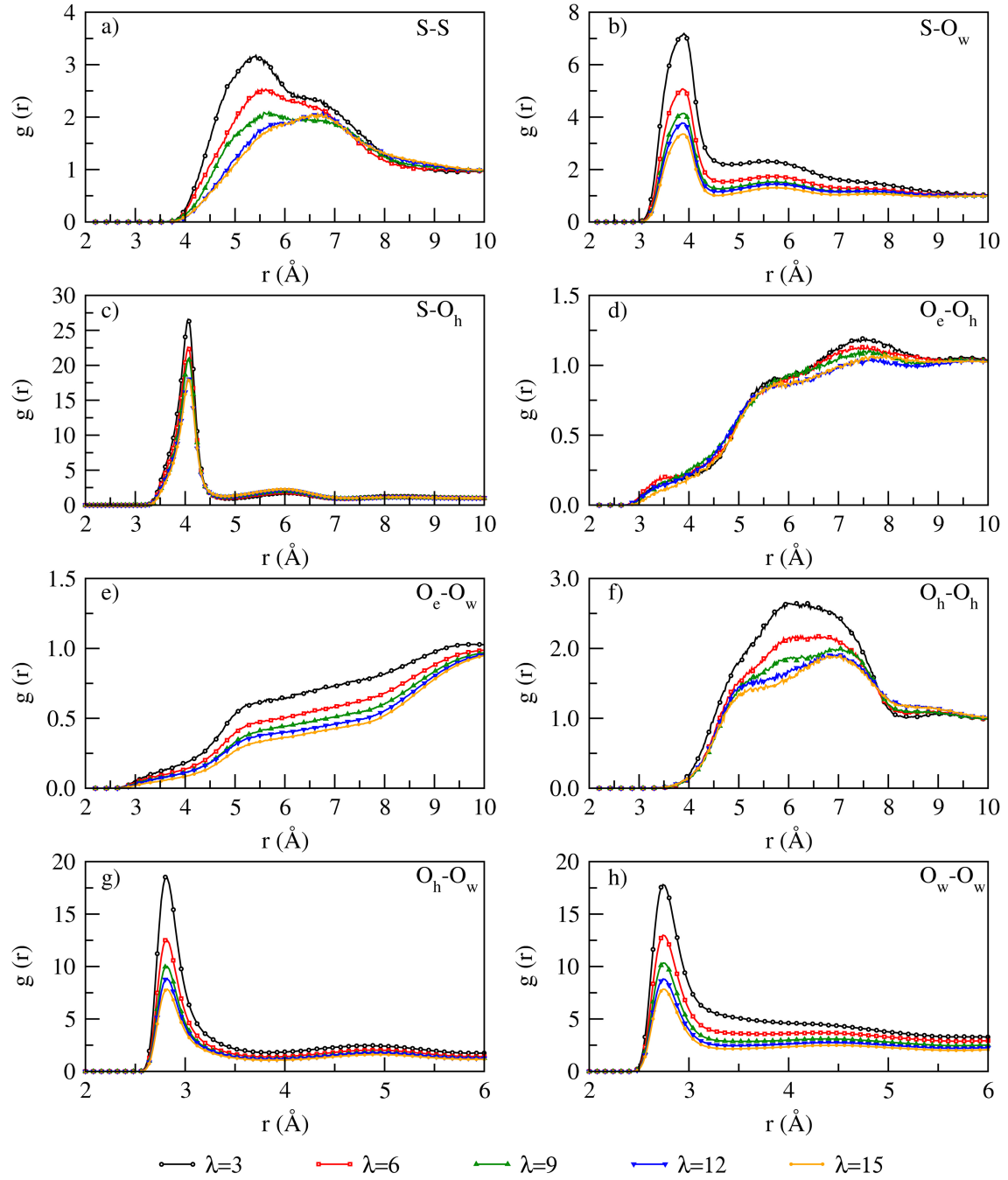


Figure 4.3: RDFs of (a) S-S, (b) S-O_w, (c) S-O_h, (d) O_e-O_h, (e) O_e-O_w, (f) O_h-O_h, (g) O_h-O_w and (h) O_w-O_w at 300 K.

to 1.8, 1.6, 1.35 and 1.25 at $\lambda=6, 9, 12$ and 15 respectively. The coordination number for S-O_h RDF is found higher for Aciplex compared to the reported [21] results on Nafion. For example, the co-ordination number for the S-O_h RDF are 1.51, 0.84 and 0.67 at $\lambda=6,$

11 and 15 respectively in the work of Venkatnathan *et al.* [21] on Nafion. At low water content, the sulfonate-sulfonate repulsion is higher but the positively charge hydronium ion brings the sulfonate group nearby which is seen in three times higher peak intensities from the S-O_h RDFs compared to S-O_w RDFs (see Figure 4.3(b and c)). The attraction between the sulfonate groups and hydronium ions decrease with hydration, due to the solvation of sulfonate groups and hydronium ions by water molecules and this is also seen from the examination of coordination numbers obtained from the S-O_h and S-O_w RDFs.

The interaction of hydronium ions with the pendant side chain ether oxygen is observed from the O_e-O_h RDF (see Figure 4.3d) which gives a flattened peak profile with pair-pair interaction below unity. A very similar pair-pair correlation is observed from the O_e-O_w RDF (see Figure 4.3e). The O_e-O_h and O_e-O_w RDFs shows the presence of phase segregations where interactions of hydronium ions and water molecules are largely confined only to the terminal sulfonate group. The hydronium ion-hydronium ion interaction is observed from the O_h-O_h RDF (see Figure 4.3f). A broad peak similar to S-S RDF with a larger solvation shell of ~ 8 Å is obtained which shows bi-fragmentation at higher hydration ($\lambda=12$ and $\lambda=15$). The O_h-O_h RDFs shows a broad feature and are more intense in Aciplex compared to Nafion [22, 24, 28]. The co-ordination number is highest (3.4) at $\lambda=3$ and decreases to 2.8, 2.4, 2.2 and 2.0 at $\lambda= 6, 9, 12$ and 15 respectively. The interaction of hydronium ions with water molecules is observed from the O_h-O_w RDFs (see Figure 4.3g). The first peak of the O_h-O_w RDFs at 2.75 Å appears at larger distance compared to the characteristic peak of Nafion [21] at 2.4 Å. This corresponds to the distance between the hydronium oxygen and water oxygen. The peak intensity decreases with increase in hydration and is similar to the previous findings on Nafion [21, 25, 28]. The coordination number is lowest at $\lambda=3$ and increases to 2.9, 3.4, 3.9 and 4.1 at $\lambda=6, 9, 12$ and 15 respectively which shows an increase in water solvation of hydronium ions with

Table 4.2: Co-ordination number calculated at the first minima in Aciplex ionomer membrane-water mixtures from a 20 ns production run (300 K).

λ	S-S (8.5 Å)	S-O _w (4.5 Å)	S-O _h (4.85 Å)	O _h -O _h (8.0 Å)	O _h -O _w (3.8 Å)	O _w -O _w (3.5 Å)
3	4.0	3.0	2.2	3.4	2.2	2.5
6	3.2	3.9	1.8	2.8	2.9	3.4
9	2.8	4.4	1.6	2.4	3.4	3.7
12	2.6	5.0	1.3	2.2	3.9	4.0
15	2.4	5.1	1.2	2.0	4.1	4.2

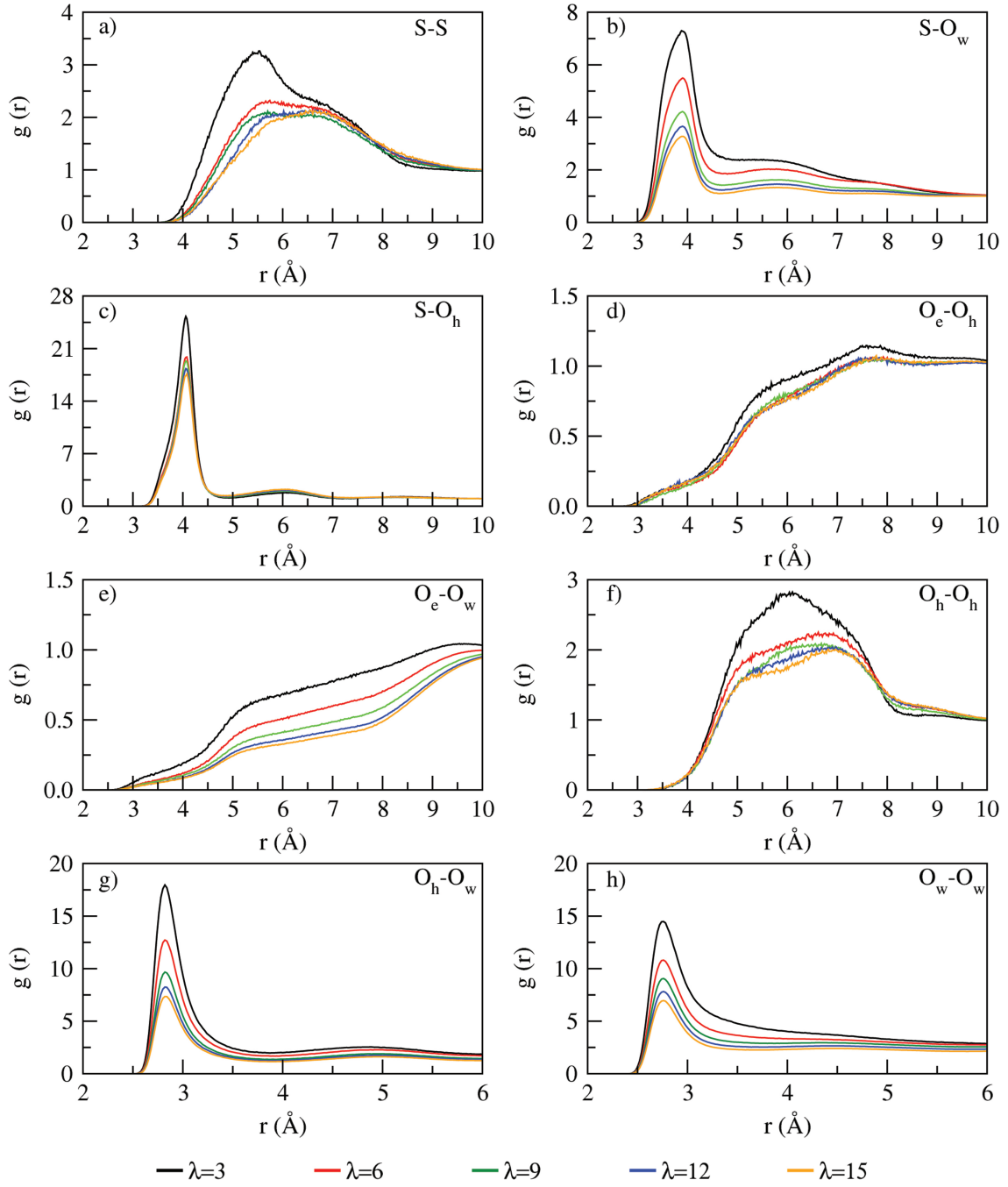


Figure 4.4: RDFs of (a) S-S, (b) S-O_w, (c) S-O_h, (d) O_e-O_h, (e) O_e-O_w, (f) O_h-O_h, (g) O_h-O_w and (h) O_w-O_w at 350 K.

hydration. The peak intensity decreases and coordination number increases with increase in hydration for interactions among water molecules as seen from the O_w-O_w RDFs (see

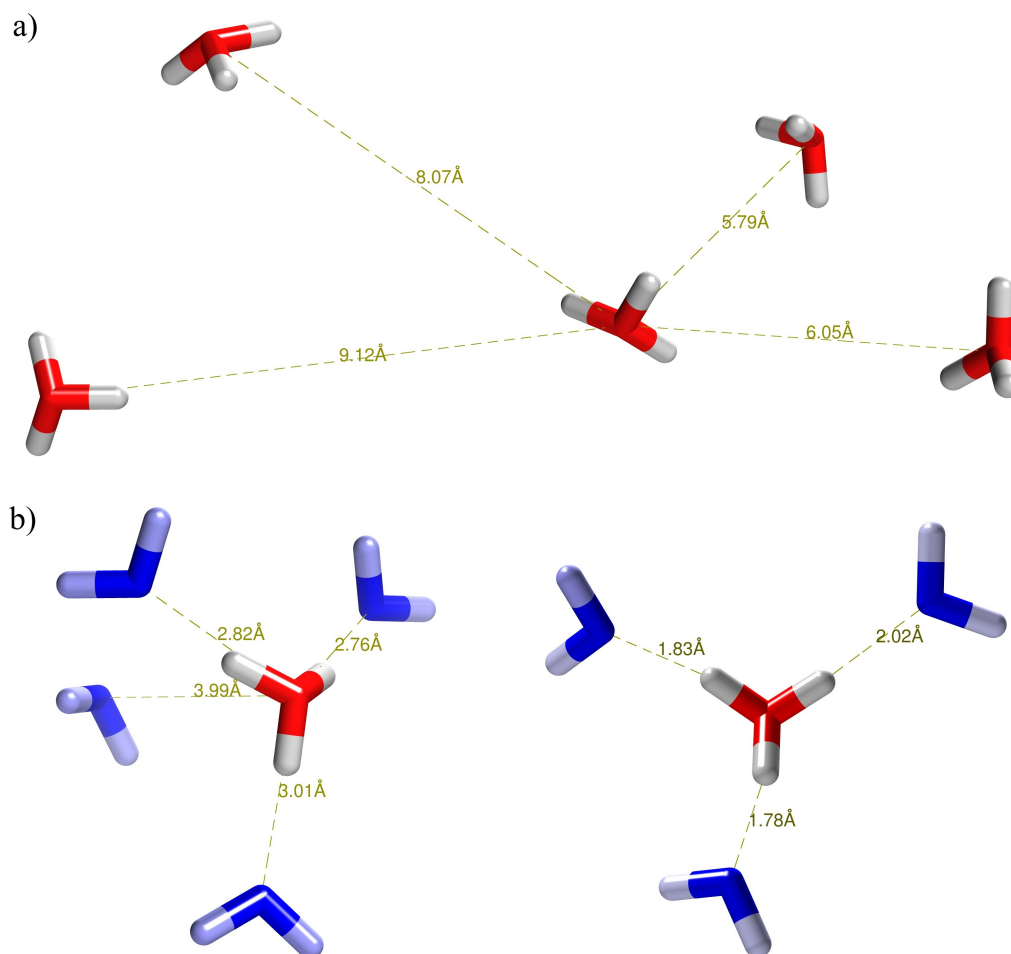


Figure 4.5: Snapshot of the hydronium ion cluster at 300 K shows first solvation shell of (a) hydronium ions at $\lambda=3$ with O_h-O_h distances and (b) water molecules at $\lambda=15$ with O_h-O_w distances (left) and hydrogen bond H_h-O_w distances (right). [Hydronium ion oxygen - red (Licorice), water oxygen - blue (Licorice)]

Figure 4.3h) and the corresponding coordination numbers. Similarly, all RDFs at 350 K are shown in Figure 4.4. A comparison of RDFs at 300 K and 350 K shows that temperature has insignificant effect on the RDFs in hydrated Aciplex membrane whereas effect of temperature was found to be significant on the peak intensities of RDFs in Nafion [21]. This shows that the Aciplex membrane could be more suitable to operate on a wider fuel cell operating temperature.

The understanding of local structure of hydronium ions and water molecules is seen from a cluster analysis performed using the Gromos algorithm [144] calculated as an average from all frames of the 20 ns production run. To investigate the presence of hydronium

ions within a cluster, a 10 Å distance cutoff is chosen from the center of mass of reference hydronium ion at 300 K. Due to higher coordination of hydronium ions at lower hydration, the cluster of hydronium ions around a reference hydronium ion is calculated at $\lambda=3$. A representative snapshot (see Figure 4.5a) of hydronium ions in this cluster at $\lambda=3$ (four hydronium ions in the first solvation shell) using a visualization software Chimera [79]. The average O_h-O_h distance of 7.2 Å in this cluster is similar to the reported value of 7.1 Å from Karo *et al.* [136] on Nafion/Dow and Devanathan *et al.* [22] on Nafion. We also characterize the presence of water molecules in a cluster around the first solvation shell of hydronium ion using a 4 Å distance cutoff from the center of mass of reference hydronium ion at 300 K. The water cluster around the hydronium ions is characterized at $\lambda=15$ due to higher coordination of water molecules around the hydronium ion at this hydration. A snapshot of four water molecules in the first solvation around the reference hydronium ion is shown in Figure 4.5b. The average O_h-O_w distance is 3.1 Å. An average hydrogen bond distance of 1.87 Å is obtained between the hydrogen atom of hydronium ion and water oxygen in the water cluster in Aciplex and these observations are similar to the work of Karo *et al.* [136] reported on Nafion (1.9 Å).

4.3.3 Structure factor and scattering intensity

The orientation of hydrophilic water domains inside the polymer matrix which shows nano-phase segregations due to presence of hydrophobic polymer backbone is characterized by the structure factor and scattering intensities recorded from SAXS and SANS studies on PFSA membranes. The structure factor has been calculated for the oxygen atoms of water molecules from a Fourier transform of the RDF, $g(r)$ (see Eqn. 1.9). The structure factor at $\lambda=3$ shows a low flattened peak at 1.3 nm^{-1} in Aciplex ionomer membrane-water mixtures at 300 K (see Figure 4.6a). The peaks of the structure factor agrees well with the experimental peak [113, 127] of 1.3 nm^{-1} of Nafion. The peak intensity of the structure factor increases with hydration. The peaks are shifted towards lower wave region and are similar to the work of Cui *et al.* [25] on Nafion. A similarity in peak intensities at 300 K and 350 K (for all hydration) is observed which provide evidence that membrane nano-structure remains unaffected by temperature (see Figure 4.6b).

These observations are also confirmed by the calculation of scattering intensity, $I_{ij}(q)$ (see Eqn. 1.10). The calculated scattering intensities in Aciplex ionomer membrane-water mixtures (for all hydration) are similar to the SAXS and SANS scattering intensities of Dow [9] and Nafion [39, 119]. The characteristic ionomer peak of PFSA membranes

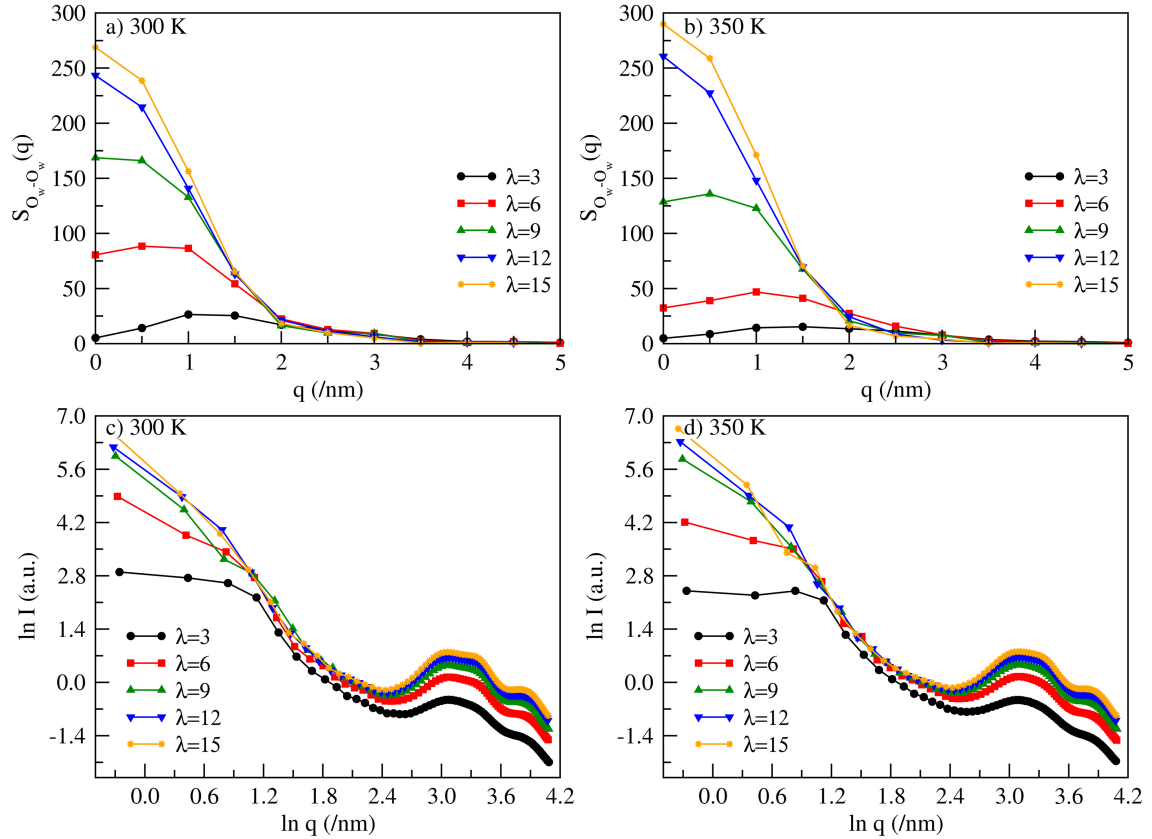


Figure 4.6: Structure factor ($S_{O_w-O_w}$) calculated for water molecules at (a) 300 K, (b) 350 K; and scattering intensity at (c) 300 K and (d) 350 K.

shows a scattering peak at 3.2 nm^{-1} and the intensity of ionomer peak increases with hydration due to increase in solvation around the sulfonate group. The effect of temperature on the ionomer peak is insignificant (see Figure 4.6(c and d)). The peak position and intensity remain unchanged with temperature. A second low intensity peak at 3.8 nm^{-1} assigned to hydronium ions is also observed from present simulations.

4.3.4 Variation in polymer backbone chain and side chain length

The flexibility in polymer backbone, side chain and the length of side chain in PFSA membranes are key features of proton exchange membrane which influence membrane morphology and size of water domains/clusters and water-proton diffusivity inside the membrane matrix. Devanathan and Dupuis [121] investigated the role of pendant side chain length using Dow and Nafion as model membrane and found that Dow shows larger cluster size of water molecules compared to Nafion around the sulfonate group. In this

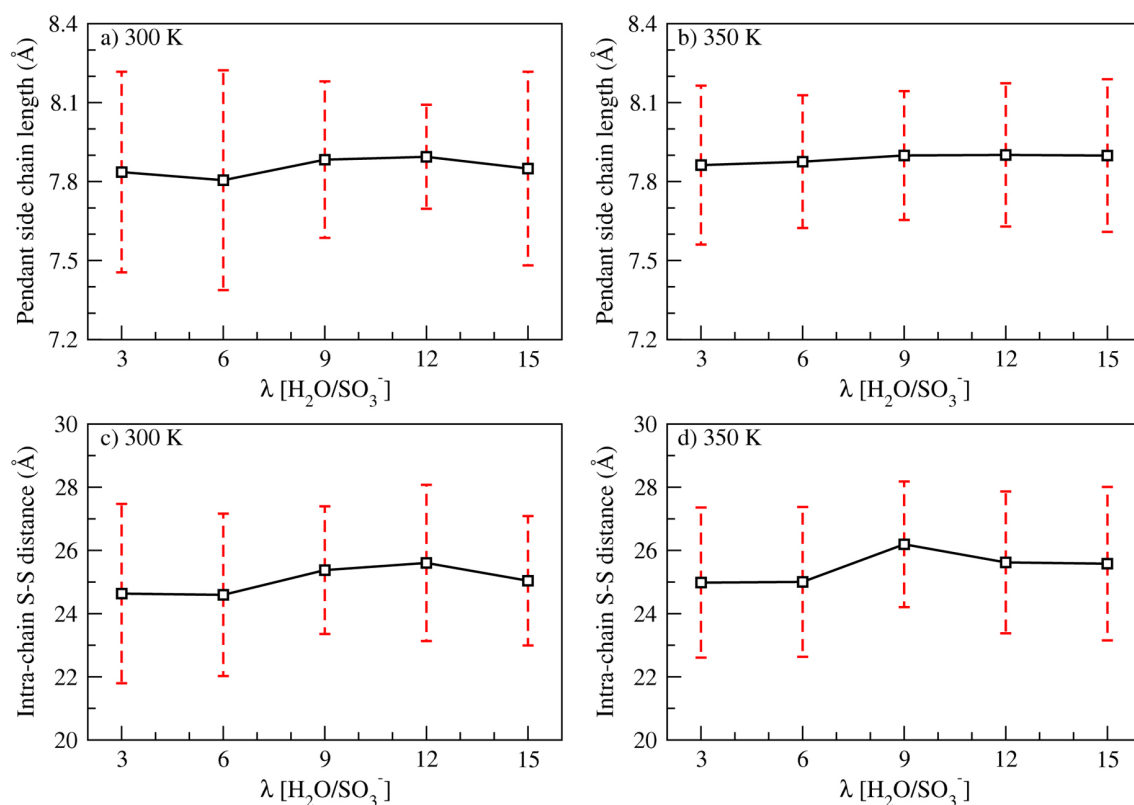


Figure 4.7: (a and b) The variation in C-S pendant side chain length at 300 K and 350 K; (c and d) variation in intra-chain average S-S distance between adjacent pendant side chain terminal sulfonate groups at 300 K and 350 K. (Error bar shown in red represents the standard deviation)

study, we investigate the effect of hydration and temperature on pendant chain length and polymer backbone. The pendant side chain length and polymer backbone chain length of Aciplex ionomer membrane is calculated for 20 polymer chains (out of 48 chains) and the average value from the entire trajectory of a 20 ns simulation is shown in Figure 4.7.

An examination of the pendant side chain length between the ether bonded backbone carbon and the sulfur atom of the sulfonate group at 300 K and 350 K is seen in Figure 4.7(a and b). The average length of the pendant side chain is 7.85 Å with a small variation of 0.3 Å. The variation in pendant side chain length remains less affected by hydration and temperature. The influence of polymer backbone flexibility in interactions between the terminal sulfonate groups is seen from the average intra-chain S-S distance between two adjacent sulfonate groups of Aciplex ionomer membrane (see Figure 4.7(c and d)). The chain separation between two adjacent sulfonate groups shows a variation of 3 Å from the average intra-chain S-S (15 CF₂ units which separate the adjacent pendants) distance of 25

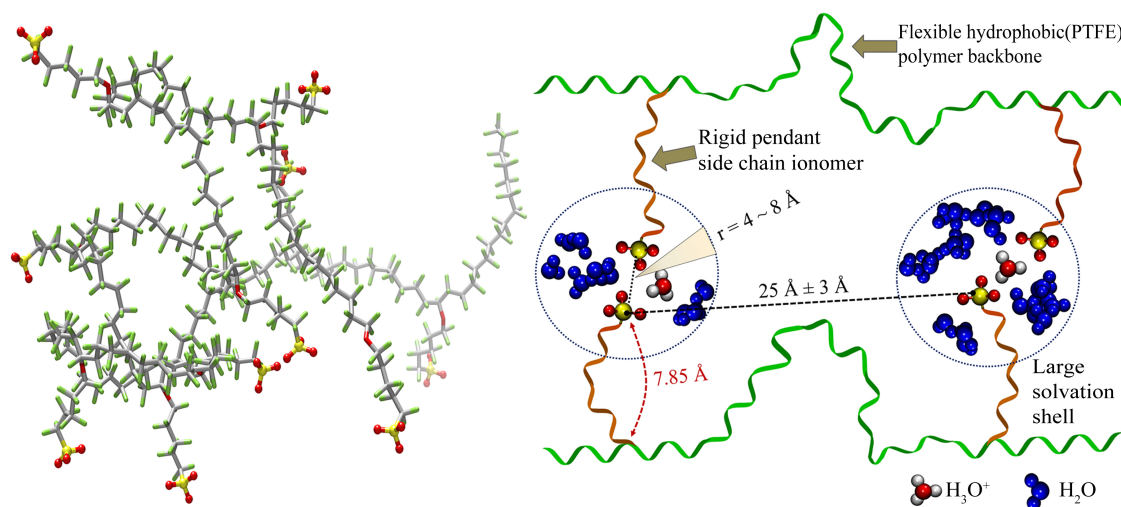


Figure 4.8: Snapshot (left) of a single Aciplex ionomer polymer chain (from $\lambda=3$ at 300 K) which shows a polymer backbone with pendant side chain with a schematic (right) to illustrate inter-chain S-S interactions, rigid pendant side chain and adjacent intra-chain distance between terminal sulfonate groups.

Å. The effect of hydration and temperature on average intra-chain S-S distance is found to be insignificant. The large adjacent intra-chain S-S distance minimizes the possibility of sulfonate-sulfonate interactions within adjacent intra-chain pendant sulfonate groups even at low hydration. We have also investigated other probable S-S intra-chain interactions and found these occur at very large distance (>10 Å). Hence, sulfonate-sulfonate interactions occur only between 4 Å to 8 Å (see S-S RDF) as illustrated in the schematic diagram of Figure 4.8.

The interactions between sulfonate groups are mainly due to inter-chain interactions even though Aciplex ($x=0$, $y=5$) have a long pendant side chain. The rigidity of the pendant side chain minimizes the possibility of intra-chain sulfonate interactions and hence differs from intra-chain interactions in Nafion and Dow membranes especially at low hydration, though there are similarities at higher hydration. For example, Cui *et al.* [25] investigated intra-chain chain sulfonate-sulfonate interactions in Dow and Nafion. The authors found that at low hydration ($\lambda=4.4$) both these membranes show intra-chain (higher in Nafion) interactions, though they diminish at higher hydration. Brandell *et al.* [112] found that the sulfonate group in Nafion ($x=1$, $y=2$) act as paddle-wheels due to the presence of the secondary ether oxygen atom in the pendant side chain which promotes its mobility, whereas the Aciplex membrane ($x=1$, $n=3$) shows lower sulfonate group mo-

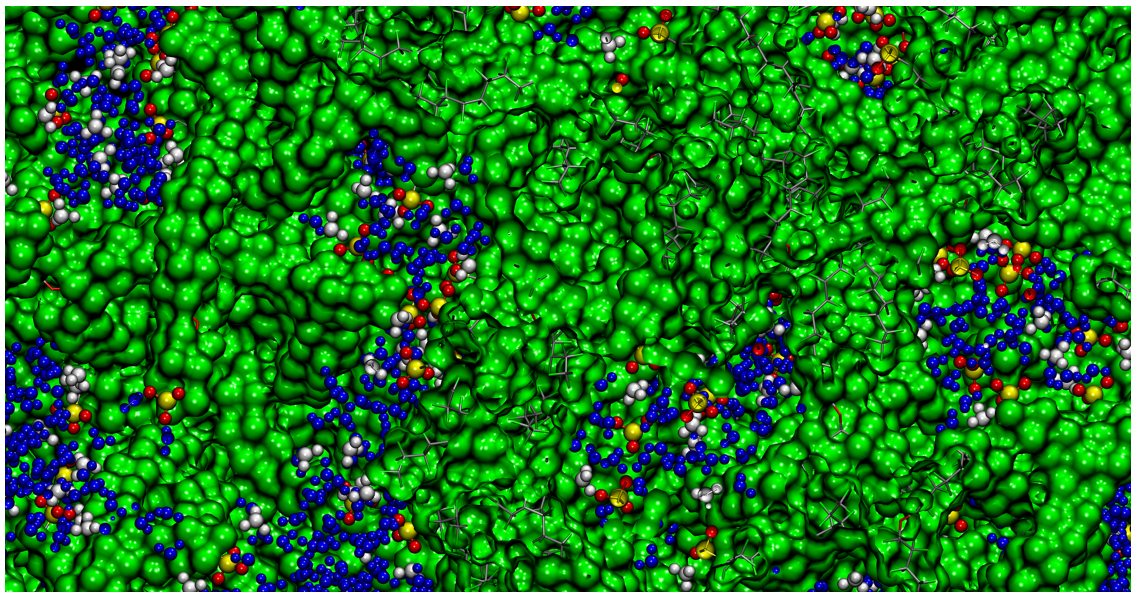


Figure 4.9: Snapshot of Aciplex ionomer membrane-water mixture ($\lambda=15$) to illustrate restricted water domains in the phase-segregated hydrophobic polymer backbone. [Carbon chain silver (line), ether oxygen red (line), sulfonate group- yellow and red (CPK), hydronium ion- white (CPK), water- blue (CPK) and F atom as green surface.]

bility. However, the flexibility of polymeric backbone in Aciplex (as seen in Figure 4.8) provides possible rearrangements of ionomer pendant and water domains to orient for efficient ion-water interactions which remains unaffected by hydration and temperature. The orientation of water molecules in the polymer membrane at $\lambda=15$ is shown in Figure 4.9. An examination of the snapshot shows phase segregated hydrophilic domains where water molecules are predominantly found close to the sulfonate groups.

4.3.5 Radius of gyration

The radius of gyration (R_g) of the Aciplex polymer chain is obtained using Eqn. 1.11. The radius of gyration is calculated for all hydration ($\lambda=3, 6, 9, 12$ and 15) of 48 polymer chains from the trajectory of 20 ns simulation. The average radius of gyration with hydration is shown in Figure 4.10. The radius of gyration shows a variation of $\sim 3 \text{ \AA}$ from average value of $16.8 \text{ \AA}$ at 300 K (see Figure 4.10a) The radius of gyration remains unaffected with hydration. This is due to less dispersive force between the polymer membrane and water molecules which results in relatively less chain expansion even at higher hydration. A similar trend is observed in the radius of gyration at 350 K (see Figure 4.10b).

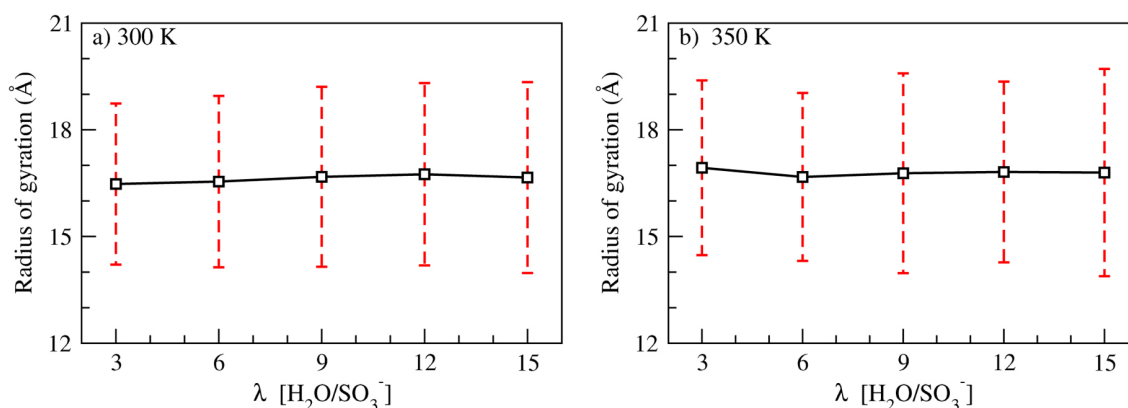


Figure 4.10: Radius of gyration (Rg) at (a) 300 K and (b) 350 K. (Error bar shown in red represents the standard deviation)

These results are in agreement with experiment [145] where the radius of gyration of ionic domains remains unchanged (30.1 and 31.4 Å) with an increase in number of sulfonic acid sites per volume in a PFSA polymer chain. This shows that the effect of temperature is insignificant on Aciplex polymer membrane which makes it more suitable for a prolonged fuel cell operation.

4.3.6 Dynamics of hydronium ions and water molecules

The MSD of hydronium and water molecules in Aciplex ionomer membrane-water mixtures are linear and increases with hydration and temperature (see Figure 4.11). A significant increase in MSD for hydronium ions and water molecules is obtained at $\lambda > 9$ compared to low hydration ($\lambda = 3, 6$) at 300 K. The effect of temperature on mobility of hydronium ions and water molecules is significant. For all hydration, the MSD at 350 K increases by a factor of ~ 2 compared to the corresponding MSD at 300 K. Similar trends with hydration and temperature were also observed in MSD for Nafion in the work of Venkatnathan *et al.* [21] and Devanathan *et al.* [22] The diffusion coefficients are computed from the linear regime of MSD (see Table 4.3). The diffusion of hydronium ions increases with hydration. The hydronium ion diffusion increases by a factor of 3.47 from $\lambda = 3$ to $\lambda = 6$ at 300 K. A subsequent increase in hydration from $\lambda = 6$ to $\lambda = 9$, $\lambda = 9$ to $\lambda = 12$, $\lambda = 12$ to $\lambda = 15$ increases the diffusion of hydronium ions by a factor of 2.64, 1.91, and 1.43 respectively. The trends in hydronium ion diffusion coefficients in Aciplex ionomer membrane-water mixtures are qualitatively similar to the QENS experimental diffusion coefficient for Nafion reported by Perrin *et al.* [15] However, quantitative differences from

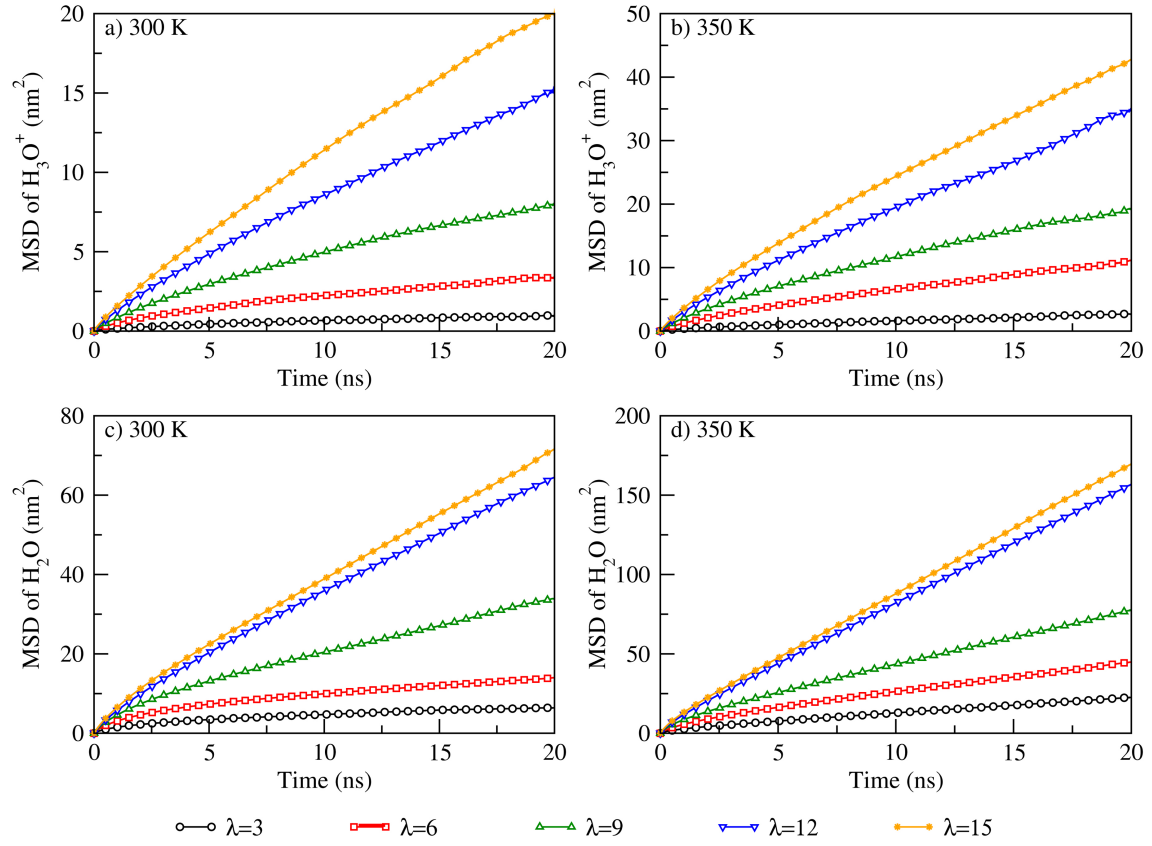


Figure 4.11: MSD of (a and b) hydronium ion and (c and d) water in Aciplex ionomer membrane-water mixtures at 300 K and 350 K.

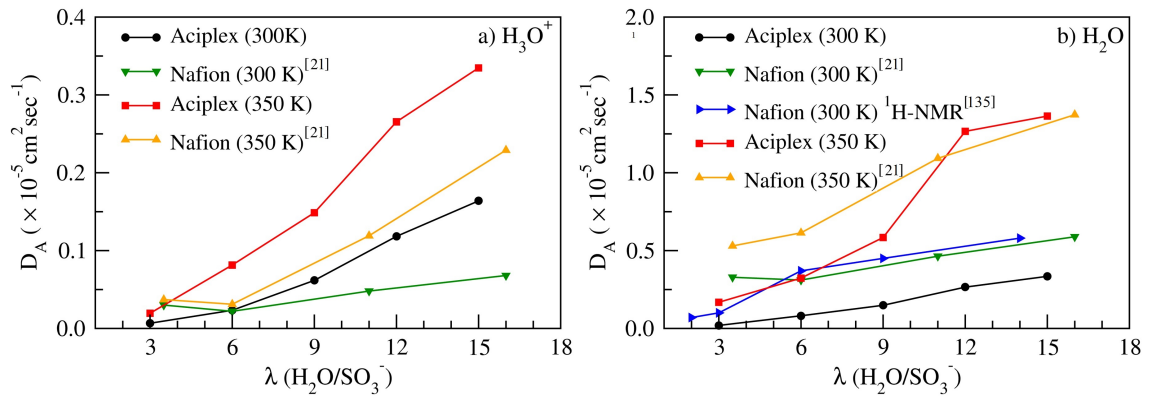
experiment arise due to the lack of description of structural diffusion due to limitations of classical force-fields used in present MD simulations. For all hydration, the hydronium ion diffusion coefficients for Aciplex are higher than the corresponding simulated diffusion coefficients of hydronium ion in Nafion at 300 K. Similar trends are also observed at 350 K, where temperature increases hydronium ion mobility at all hydration. The temperature increase (from 300 K to 350 K) enhances diffusion coefficient of hydronium ions at $\lambda=3, 6, 9, 12$ and 15 by a factor of 2.9, 3.5, 2.4, 2.2 and 2.0 respectively. At 350 K, for all hydration, the hydronium ion diffusion coefficients from this work are higher than corresponding simulated diffusion coefficients of hydronium ion in Nafion [21] and these comparisons are shown in Figure 4.12a.

The mobility of water molecules inside the membrane matrix contribute to water flux which also reflect the overall proton conductivity of Aciplex ionomer membrane. The increase in hydration enhances diffusion of water molecules. The diffusion coefficient of

Table 4.3: Diffusion coefficients ($D_A \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$) of hydronium ion and water obtained for Aciplex ionomer membrane-water mixtures from a 20 ns production run.

λ	D_A of H_3O^+		D_A of H_2O	
	300 K	350 K	300 K	350 K
3	0.0067 ± 0.0032	0.0195 ± 0.0027	0.0401 ± 0.0181	0.1678 ± 0.0160
6	0.0233 ± 0.0097	0.0814 ± 0.0167	0.0822 ± 0.0389	0.3230 ± 0.0536
9	0.0617 ± 0.0213	0.1487 ± 0.0362	0.2389 ± 0.0363	0.5841 ± 0.0525
12	0.1183 ± 0.0208	0.2654 ± 0.0464	0.5060 ± 0.0522	1.2661 ± 0.0253
15	0.1639 ± 0.0265	0.3347 ± 0.0599	0.5503 ± 0.0299	1.3637 ± 0.0254

water increases by a factor of 2.05 from $\lambda=3$ to $\lambda=6$ at 300 K. A subsequent increase in hydration from $\lambda=6$ to $\lambda=9$, $\lambda=9$ to $\lambda=12$, and $\lambda=12$ to $\lambda=15$ results in an increase of diffusion coefficient of water molecules by a factor of 2.9, 2.11 and 1.08 respectively. A similar trend is observed in the diffusion coefficient of water molecules at 350 K. The increase in temperature (from 300 K to 350 K) enhances diffusion coefficient of water molecules by a factor of 4.18 and 3.9 at $\lambda=3$ and $\lambda=6$ respectively; whereas at $\lambda>9$ the diffusion coefficient of water molecules increases by a factor of ~ 2.5 . The trends in diffusion coefficient of water molecules in Aciplex ionomer membrane-water mixtures at 300 K resemble the experimental [135] diffusion of water molecules in Nafion (see Figure 4.12b). At 300 K, the diffusion coefficient of water molecules from this work is lower compared to the reported [21, 135] diffusion coefficient of water molecules in Nafion for all hydration. The lower mobility of water molecules in the Aciplex membrane is due to an enlarged hydrophobic domain which is assisted by the rigid pendant side chain. Similar

**Figure 4.12:** Diffusion coefficients (D_A) of (a) hydronium ions and (b) water molecules.

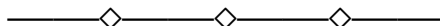
observations are seen from the work of Brandell *et al.* [112] on Aciplex membrane ($x=1$, $y=3$) where the extra CF_2 units provide stiffness to the pendant compared to Nafion ($x=1$, $y=2$) thereby resulting in lower mobility of water molecules. The pendant tail of Nafion shows a “*Elbow*” or “*Hook*” like structure [112, 121] due to the presence of a secondary ether oxygen atom and is found to resemble in functionality with the short side chain of Dow where the mobility of water molecules is higher [112] than the corresponding hydrated Aciplex membranes. However, at 350 K, for all hydration, the diffusion coefficient of water molecules from this work is similar to the simulated diffusion coefficient of water molecules of Venkatnathan *et al.* [21] on hydrated Nafion.

4.4 Conclusions

A molecular understanding of structure and dynamics of Aciplex polymer membrane using classical MD simulations is presented in this study. The effect of hydration in Aciplex membrane shows a decrease in sulfonate-hydronium ion interactions due to an increase in the solvation of water molecules around the sulfonate group and hydronium ions. Such observations are also seen in Nafion which closely resembles the Aciplex membrane. The influence of temperature on structure factor and scattering intensities is insignificant. The radius of gyration is independent of hydration and temperature. The dispersive force between the polymer and water molecules causes very less chain expansion. The simulations show phase segregation in hydrated Aciplex membrane, which remains intact even at higher hydration where water molecules are found locally around the sulfonate groups of the pendant side chain. The MSD at 350 K increases by a factor of ~ 2 for all hydration compared to the corresponding MSD at 300 K which is similar to the trends observed in MSD for Nafion [21, 23].

The presence of rigid pendant side chain ($x=0$, $y=5$) in Aciplex results in certain differences in structure and dynamics with Nafion ($x=1$, $y=2$). The significant differences obtained from present simulations are as follows: **a)** a comparison of RDFs at 300 K and 350 K show the influence of temperature is negligible on the pendant side chain nanostructure of hydrated Aciplex membrane, **b)** for all hydration, the coordination of hydronium ions around the sulfonate group (seen from the S-O_h RDF) is higher in Aciplex compared to Nafion [21], **c)** for all hydration, the first peak of the $\text{O}_h\text{-O}_w$ RDFs in Aciplex appears at 2.75 Å which differs significantly from the characteristic peak [21] of Nafion at 2.4 Å, **d)** the strong interactions between the sulfonate groups (within a large solvation shell of 4-8

Å) in Aciplex arise predominantly from inter-chain, **e)** The mobility of hydronium ions in hydrated Aciplex is higher than the mobility of hydronium ion in hydrated Nafion, **f)** the mobility of water molecules is lower by a factor of ~ 1.8 at 300 K for $\lambda > 9$ in Aciplex membrane due to enlarged hydrophobic domains assisted by the rigid pendant side chain of Aciplex ionomer compared to Nafion.



Chapter 5

Nanostructure and dynamics of Phosphoric/Triflic acid blends of hydrated ABPBI Polymer Membrane

5.1 Introduction

A large number of studies [3,4,16–18,20–27,129,130,136,146–148] have been devoted to the application of Perfluorosulfonic acid (PFSA) membrane as solid electrolytes [149,150] and the influence of hydration and temperature on proton conductivity. Further, effects of polymer chain length [28], side chain pendant [104,110,112,121,151], and membrane morphology [152–155] of PFSA membranes have also been investigated. As an alternate to PFSA membranes, cost effective membranes such as cross-linked sulfonated poly(1,3-cyclohexadiene) [156,157] and hetero aromatic benzimidazole based membranes like *m*-PBI and ABPBI doped with PA have also been developed [12,30–32,148,158]. These membranes are known to sustain high CO tolerance, offer better thermal management, operate over wider temperature range and exhibit high proton conductivity [12,30,148].

ABPBI doped with PA membrane have attracted attention, due to improved thermo-chemical properties compared to PBI [31,33,159–163]. Hughes *et al.* [164] employed a magic-angle spinning NMR technique to probe the structure and dynamics in PA doped PBI. The authors observed that proton transport in PA doped PBI occurs via a Grötthuss [44] mechanism and vehicular transport. Diaz *et al.* [165] studied the influence of low and high temperature casting on water and PA uptake by ABPBI membrane. The authors found that higher water/acid uptake was obtained from the low temperature membrane casting technique. While experiments have provided some insights into the performance of PA doped ABPBI membrane as a fuel cell electrolyte, there has been relatively very

less work towards a molecular understanding of membrane nanostructure and dynamics of molecular transport, especially with hydration. Li *et al.* [166] employed MD simulations on neat, hydrated and PA doped ABPBI and PBI membranes at 298 K. The authors observed that compared to PBI, ABPBI has higher affinity for PA. However, their study remains limited to structural properties at a single hydration. In order to investigate the effect of hydration, ABPBI+PA blend has been chosen in the present study which vary in water content. The Infrared spectroscopy study of Glipa *et al.* [167] has shown that even at higher degrees of doping (two PA molecules per imidazole), neutral PA exist in equilibrium with its corresponding ionic species in PA doped PBI membranes. Ma *et al.* [168] observed a significant amount of neutral PA exists at various temperatures (60-180 °C) and Relative Humidity. Based on experiments, only the neutral form of PA has been included in the present study.

The proton conductivity of PA doped ABPBI membrane was found to increase with an inclusion of sulfonate group (either via sulfonation of the membrane or using triflic acid as a dopant). For example, Asensio *et al.* [160] employed a sulfonated ABPBI membrane and found enhanced PA uptake with a maximum proton conductivity of $3.5 \times 10^{-2} \text{ S cm}^{-2}$ at 185 °C. Schuster *et al.* [83] studied proton conductivity of an immobilized imidazole doped with an aqueous solution of PA and triflic acid. The authors found that triflic acid enhances proton conductivity. The hydration of triflic acid shows efficient transport of protons due to the formation of triflic acid hydrates [51, 82, 169]. In addition, triflic acid can be considered as a promising dopant to minimize PA leaching from the membrane which occurs under humidified conditions. The large dissociation constant [170] of triflic acid results in a dissociated form as CF_3SO_3^- (henceforth called as TFA) even at extremely low hydration [51, 82]. In order to investigate the influence of TFA, ABPBI+TFA and ABPBI+PA+TFA blends have been chosen as candidates for investigation in this chapter.

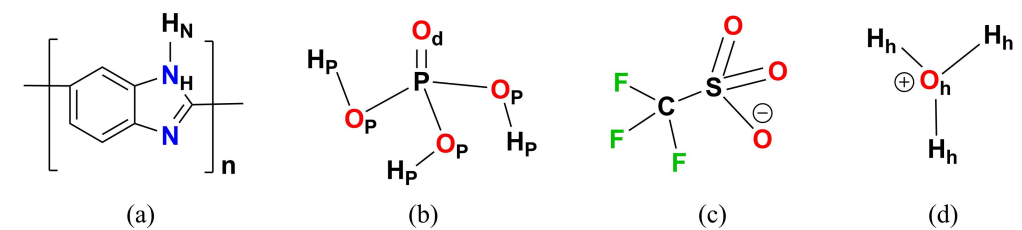


Figure 5.1: Chemical structure of a) ABPBI polymer membrane, b) PA, c) TFA and d) hydronium ion.

The computational details are presented in Section 5.2. The characterization and comparison of structural (RDFs, end-to-end polymer chain distance and radius of gyration) and dynamical properties (cluster formation and diffusion) of ABPBI+PA, ABPBI+TFA and ABPBI+PA+TFA blends with varying hydration at 353 K are presented in Section 5.3. A summary of salient results concludes the chapter.

5.2 Computational details

5.2.1 Force-field

The chemical structure of ABPBI, PA, TFA and hydronium ion is shown in Figure 5.1. All MD simulations were performed using the GROMACS [91] 4.5.4 program. The force-field parameters of ABPBI polymer membrane were taken from the OPLS-AA force-field database [72]. Force-field parameters of PA were taken from the work of Spieser *et al.* [171]. Force-field parameters for TFA were taken from the work of Sunda *et al.* [123]. Force-field parameters for hydronium ions was obtained from the work of Jang *et al.* [50].

5.2.2 Simulation details

The input configurations were obtained as follows: An energy minimized ABPBI polymer chain (constructed from 10 monomer units with a total of 132 atoms in each chain) was replicated to generate a cubic box of 64 polymer chains. The resultant configuration was used as an input and a simulated annealing was performed by heating from 300 K to 1000 K and cooled back to 300 K with an annealing time of 6.75 ns. The annealing procedure was repeated 5 times. The final configuration from the annealing procedure was used to create various acid doped hydrated ABPBI blends. These blends were created as follows: a) ABPBI+PA blends: The ABPBI membrane was solvated with 1280 molecules of well equilibrated PA to generate a ratio of 1:2 (monomeric unit of ABPBI : PA). The choice of two PA molecules per monomeric unit of ABPBI membrane was based on the experimental work of Glipa *et al.* [167], Ma *et al.* [168] and Bouchet *et al.* [172]. b) ABPBI+TFA blends: The ABPBI membrane was solvated with 1280 TFA to maintain a ratio of 1:2 (monomeric unit of ABPBI : TFA). c) ABPBI+PA+TFA blends: The ABPBI membrane was solvated with 1280 PA and 1280 TFA to maintain a ratio of 1:2:2 (monomeric unit of ABPBI : PA : TFA). To maintain charge neutrality in the system, 1280 hydronium ions were also included in the ABPBI+TFA and ABPBI+PA+TFA blends. The ABPBI+PA,

Table 5.1: Hydration levels in acid blends of ABPBI, number of water molecules (N_{water}), total number of atoms (N_{atoms}), box length (l), and system density (ρ) at 353 K.

System	λ	N_{water}	N_{atoms}	l (Å)	ρ (g cm ⁻³)
ABPBI+PA	0	—	18688	58.805	1.630
	1	1280	22528	62.264	1.535
	3	3840	30208	68.386	1.395
	6	7680	41728	76.090	1.275
ABPBI+TFA	1	1280	27648	69.647	1.538
	3	3840	35328	74.351	1.449
	6	7680	46848	80.658	1.354
ABPBI+PA+TFA	1	1280	27648	69.647	1.538
	3	3840	35328	74.351	1.449
	6	7680	46848	80.658	1.354

ABPBI+TFA and ABPBI+PA+TFA blends were chosen as template to create configurations which vary only in amount of water. A parameter, λ has been defined which denotes the number of water molecules per nitrogen atom of the monomeric unit of the ABPBI membrane. Each blend was solvated with 1280 ($\lambda=1$), 3840 ($\lambda=3$) and 7860 ($\lambda=6$) SPC/E [95] water molecules to simulate a various acid doped hydrated ABPBI blends. For PA and TFA, the acid to water ratio is 1:1, 1:3, and 1:6 for hydration level of $\lambda=1$, 3 and 6 respectively.

MD simulations were performed for all ABPBI blends at $\lambda=1, 3, 6$ (353 K). The leapfrog algorithm [74] was chosen as an integrator with a time step of 1 fs. The cut-off for van der Waals and electrostatic interactions were chosen as 10 Å. The long-range electrostatic interactions was described by the PME method [98, 99]. The input configuration of each ABPBI blend was used for equilibration for 10 ns using the NPT ensemble with a 1 bar isotropic pressure and a Berendsen barostat [96]. The velocity-rescale thermostat [97] was used to maintain a constant temperature with a coupling time of 0.1 ps. The system size, box length and density (calculated from equilibration) for various acid doped hydrated ABPBI blends is shown in Table 5.1. As a benchmark, the simulated density (1.36 g cm⁻³, 300 K) of dry ABPBI membrane is close to the experimental [173] density (1.4-1.6 g cm⁻³, 298 K). Equilibration was followed by a 20 ns production run using the NVT ensemble. Trajectories generated from the production run were saved every 5 ps for calculation of structural and dynamical properties in various acidic hydrated ABPBI

blends. The results presented in sections 5.1–5.4 use the ABPBI polymer membrane constructed from 10 monomers in a single chain.

The effect of polymer chain length have also investigated in present study by creating an ABPBI polymer chain of 20 monomer units ($n=20$). We choose the hydrated ($\lambda=3$) ABPBI+PA+TFA blend to show the effect of polymer chain length on structural and dynamical properties (see section 5.5). The hydrated ($\lambda=3$) ABPBI+PA+TFA blend containing 20 monomer units was generated in the following manner: An energy minimized ABPBI polymer chain (constructed from 20 monomer units with a total of 262 atoms in each chain) was replicated to generate a cubic box containing 64 polymer chains. The resultant configuration was used as input for a simulated annealing procedure as described earlier. The final configuration from the annealing procedure was solvated with 2560 PA and 2560 TFA to maintain a ratio of 1:2:2 (monomeric unit of ABPBI: PA: TFA). To maintain charge neutrality in the system, 2560 hydronium ions were added. The ABPBI+PA+TFA blend was solvated with 7860 ($\lambda=3$) SPC/E [95] water molecules, where the total system contains 91008 atoms. The hydrated configuration was pre-equilibrated for 1 ns using the NPT ensemble and followed by a 5 ns NPT equilibration at 353 K. Equilibration was followed by a 10 ns production run using the NVT ensemble. The structural and dynamical properties (calculated from the trajectories of the production run) were compared with hydrated ($\lambda=3$) ABPBI+PA+TFA blend created from a polymer chain of 10 monomer units.

5.3 Results and discussion

5.3.1 Interactions in hydrated ABPBI membrane

The various interactions in ABPBI membrane are seen from the N-N, N-N_H and N-H_N RDFs (see Figure 5.2) and the corresponding coordination numbers (see Table 5.2). The RDFs illustrates that the N-N, N-N_H and N-H_N interactions are stronger in ABPBI+TFA compared to ABPBI+PA blends, and strongest in ABPBI+PA+TFA blends. Further, for each blend, the peak intensities and coordination numbers increase with increasing hydration. A schematic view of inter-chain and intra-chain distances (corresponding to the peak position from RDFs) is also depicted in Figure 5.3. The peaks from the N-N RDFs which depict inter-chain and intra-chain interactions appear at 4.8 Å and 6.1 Å respectively. The N-N_H RDFs (see Figure 5.2d-f) is similar to N-N RDFs. The first peak of the N-N_H RDFs at 3 Å corresponds to inter-chain interactions and appears at a shorter dis-

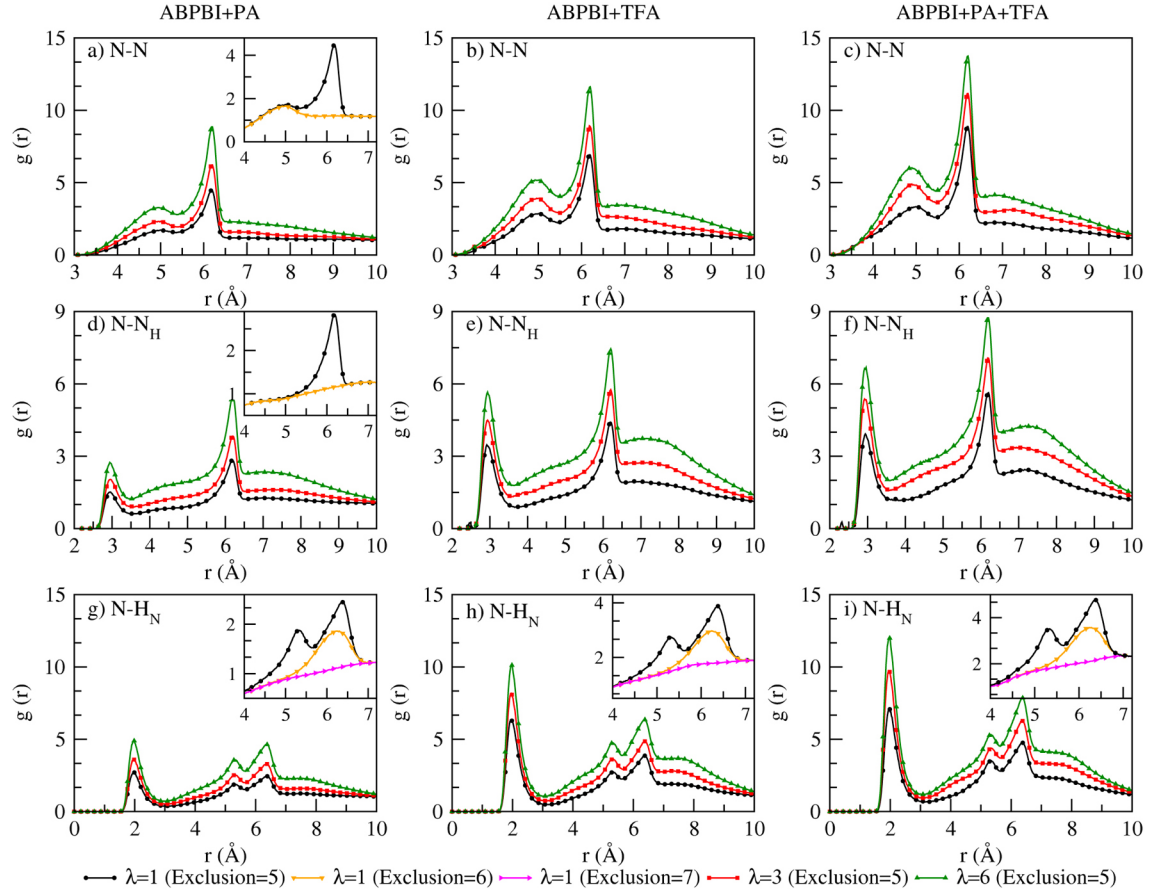


Figure 5.2: RDFs for imidazole interactions in polymer membrane a-c) N-N, d-f) N-N_H and g-i) N-H_N.

tance compared to the first peak of the N-N RDFs. However, the peak corresponding to the intra-chain N-N_H interactions appears at 6.1 Å, and is similar to the peak position of the intra-chain N-N interactions. Similar to N-N and N-N_H RDFs, the N-H_N interactions (see Figure 5.2g-i) increase with hydration. The peaks which correspond to the N-H_H inter-chain interaction appear at 2 Å corresponds to typical hydrogen bond distance. The peaks at 5.2 Å and 6.2 Å correspond to intra-chain N-H_N interactions. The N_H-N_H interactions show a broad peak at ~4-5 Å and increases with hydration as seen from in Fig. 5.4. The interaction of the polymer membrane with water and interactions among water molecules are seen from the H_N-O_w (see Figure 5.5a-c) and O_w-O_w RDFs (see Figure 5.5d-f) respectively. The peak position of the H_N-O_w and O_w-O_w RDFs remains unchanged with hydration and choice of blend. However, for each hydration, the peak intensity (coordination number) of the H_N-O_w and O_w-O_w RDF is highest in ABPBI+TFA blends and lowest

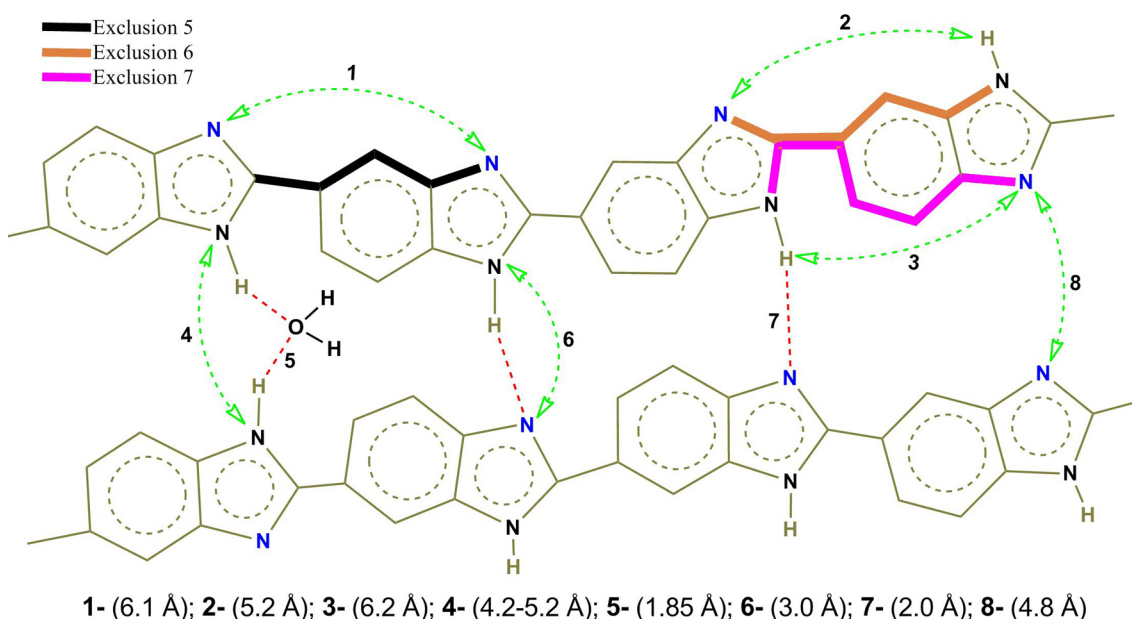


Figure 5.3: A schematic view of inter-chain and intra-chain distance in ABPBI polymer membrane.

in ABPBI+PA blends. This suggests that addition of TFA to various blends exhibit strong interaction of TFA with water molecules [123], and the strong imidazole-TFA interactions is concomitant with water molecules in close proximity to the membrane. These observa-

Table 5.2: Co-ordination number calculated using the first minima (in parenthesis) for interactions in hydrated ABPBI membrane.

System	λ	N-N (5.8 Å)	N-N _H (3.6 Å)	N-H _N (3.2 Å)	H _N -O _w (2.6 Å)	O _w -O _w (4.2 Å)
ABPBI+PA	1	1.98	0.27	0.28	0.12	2.31
	3	2.05	0.28	0.29	0.28	4.96
	6	2.13	0.28	0.28	0.33	6.56
ABPBI+TFA	1	2.31	0.41	0.41	0.19	1.94
	3	2.58	0.43	0.44	0.31	4.09
	6	2.74	0.44	0.44	0.36	5.61
ABPBI+PA+TFA	1	2.09	0.35	0.36	0.12	1.25
	3	2.56	0.41	0.41	0.22	3.17
	6	2.56	0.42	0.43	0.28	4.81

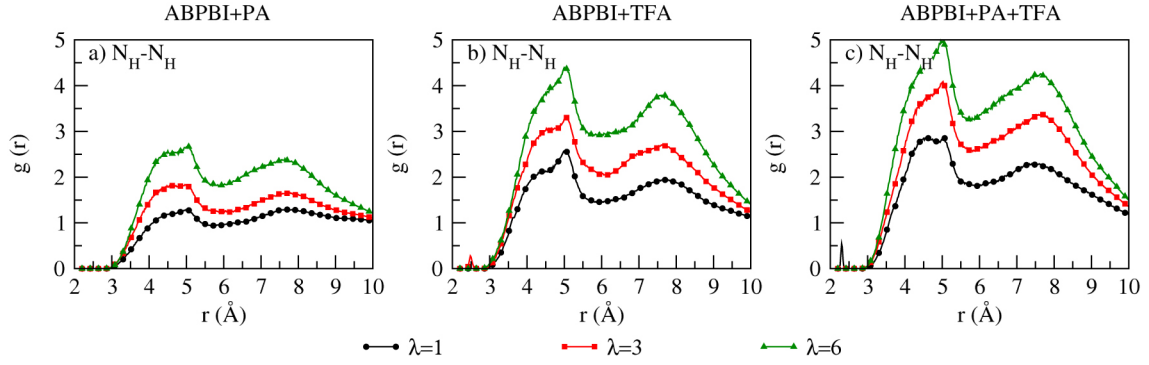


Figure 5.4: N_H-N_H RDFs from a) ABPBI+PA blends, b) ABPBI+TFA blends and c) ABPBI+PA+TFA blends.

tions are also seen from snapshots (see Figure 5.6) created using VMD [70] where water molecules are found closer to TFA (see Figure 5.6c-f). Further, the water molecules in the membrane matrix are found to be uniformly distributed in ABPBI+TFA (see Figure 5.6c and d) and ABPBI+PA+TFA (see Figure 5.6e and f) blends, compared to ABPBI+PA blends (see Figure 5.6a and b).

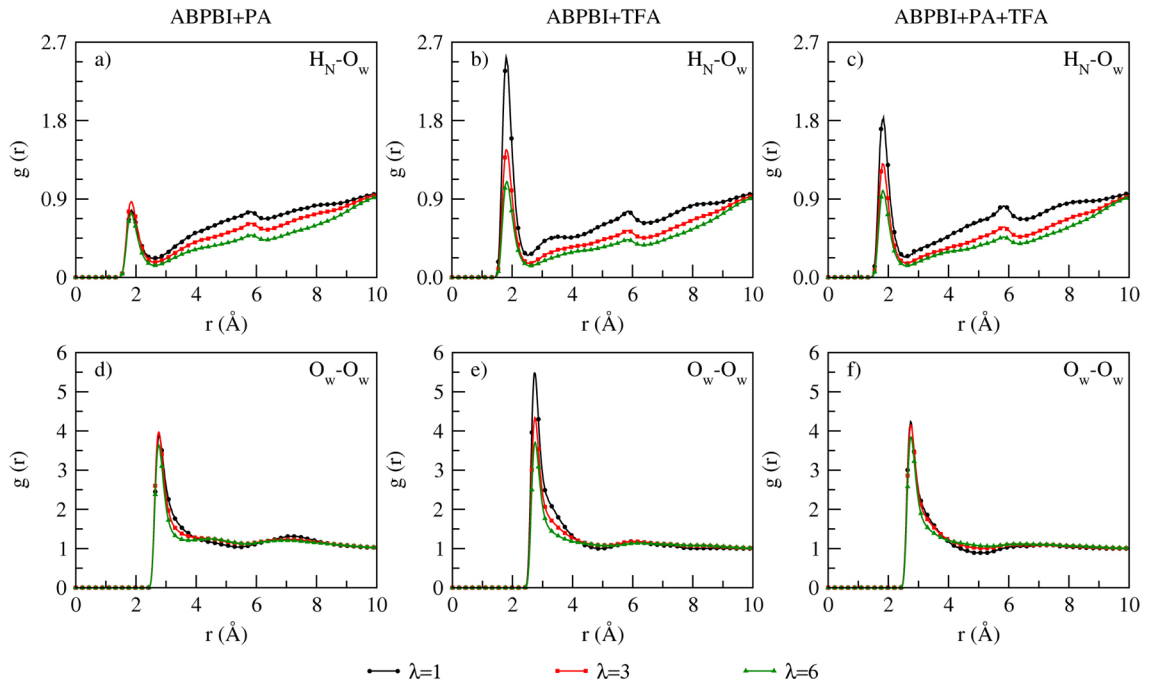


Figure 5.5: RDFs for water interactions with polymer membrane a-c) H_N-O_w and d-f) O_w-O_w .

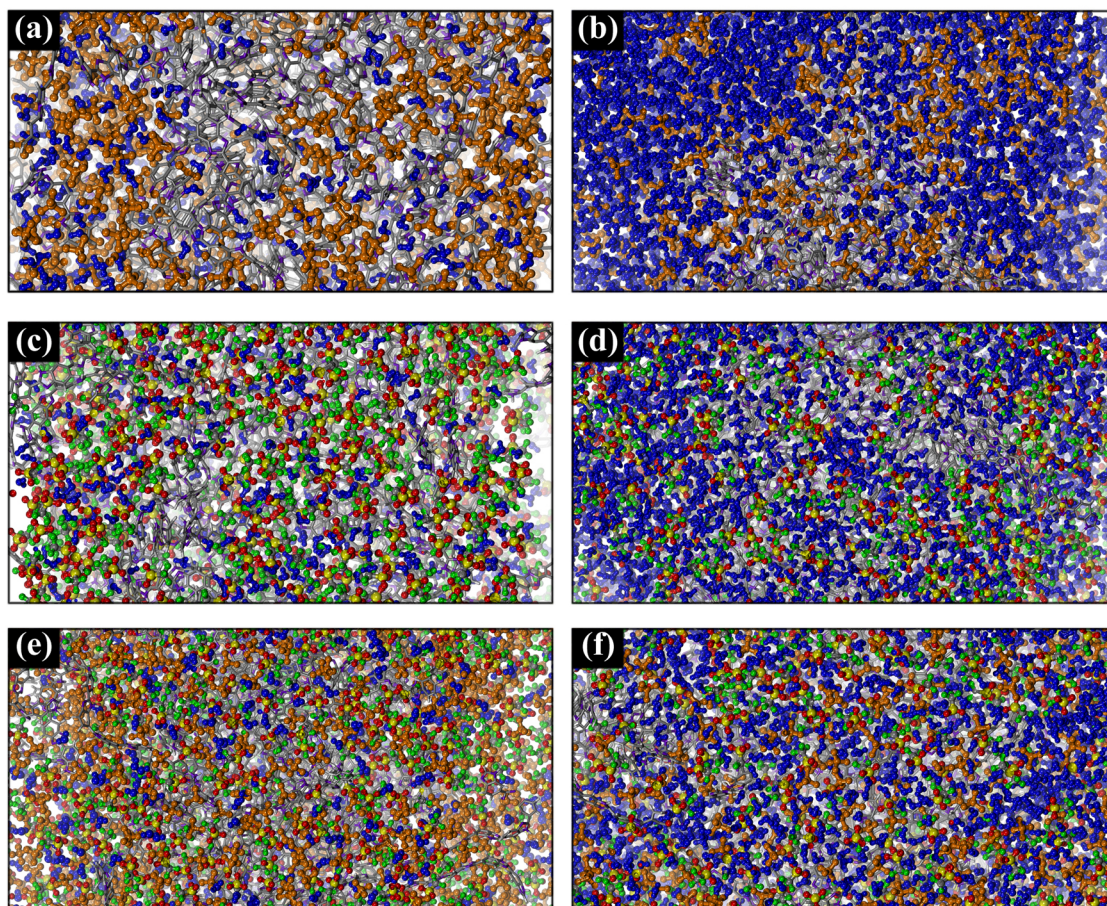


Figure 5.6: Final snapshot from the production run (orthographic view) of (a and b) ABPBI+PA blend at $\lambda=1$ and $\lambda=6$, (c and d) ABPBI+TFA blend at $\lambda=1$ and $\lambda=6$ and (e and f) ABPBI+PA+TFA blend at $\lambda=1$ and $\lambda=6$ respectively. [benzimidazole ring carbon: grey; hydrogen: white; nitrogen: violet; sulfur: yellow; oxygen (TFA): red; fluorine: green; phosphorus and oxygen of PA: orange; water molecule: blue, hydrogen of PA and hydronium ions are not displayed]

5.3.2 Interactions in phosphoric acid and triflic acid

The interactions of PA are seen from various RDFs (see Figure 5.7) and their corresponding coordination numbers (see Table 5.3). As expected, due to influence of TFA, the P-P interactions are weaker in ABPBI+PA+TFA blends. For ABPBI+PA and ABPBI+PA+TFA blends, the coordination number from the P-P RDFs shows a decrease with hydration (see Table 5.3). The interaction between the double bonded oxygen atom of PA (O_d) and the hydrogen atom of PA (H_P) results in an increase with hydration. The first peak from the O_d - H_P RDF is in agreement with a previously reported value [174] of 1.47 Å. For each

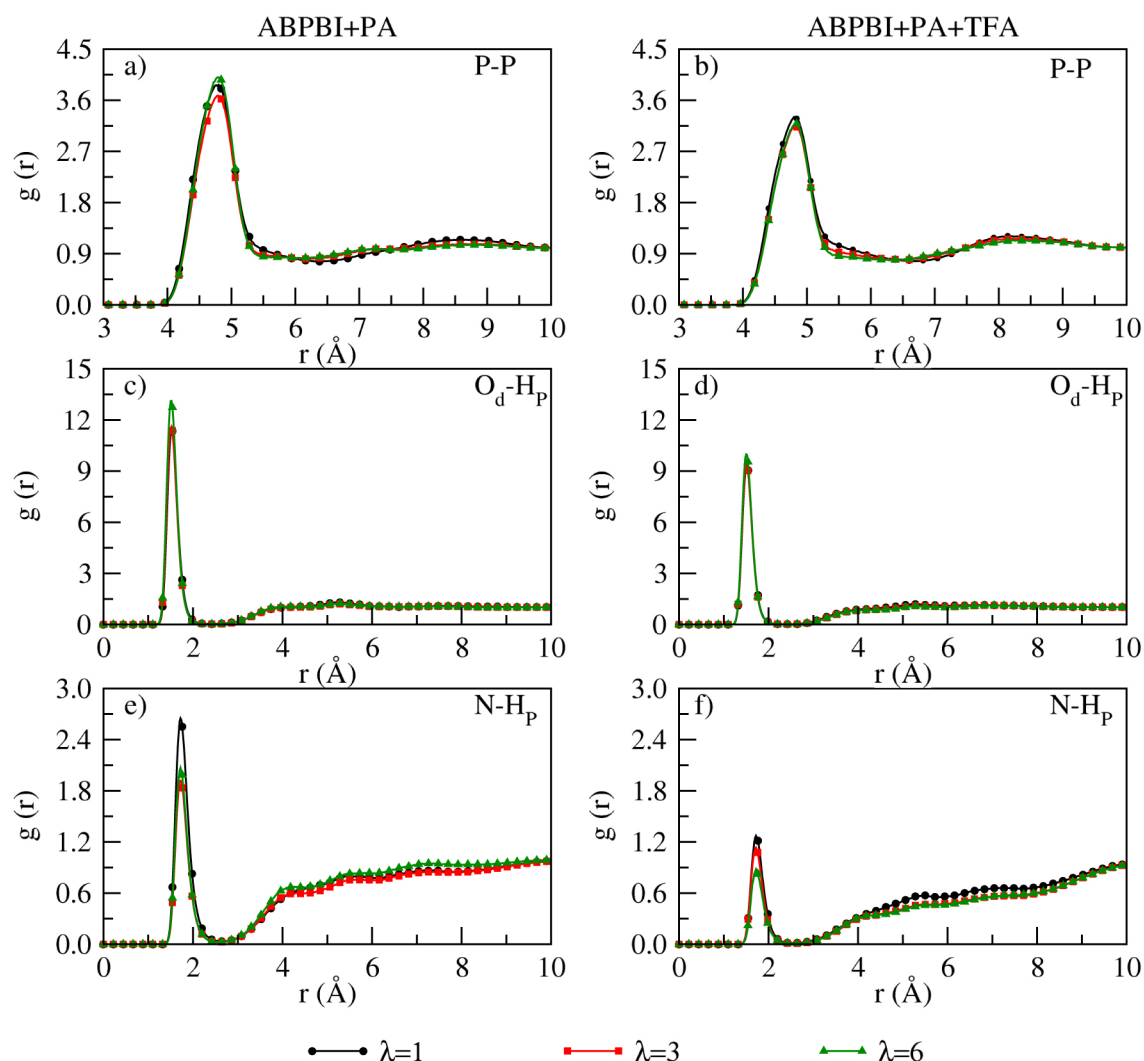


Figure 5.7: RDFs for PA interactions (a and b) P-P, (c and d) O_d-H_P and (e and f) $N-H_P$.

blend, the coordination numbers from the O_d-H_P , H_P-N , O_d-H_N RDFs show a decrease with hydration. The coordination number of water around the PA oxygen (O_P) increases with hydration in ABPBI+PA blends, and is higher compared to ABPBI+PA+TFA blends. The O_d-O_w interaction is stronger in ABPBI+PA+TFA blends compared to ABPBI+PA blends (see Figure 5.8(e and f)).

The effect of TFA is seen from the S-S RDFs shown in Figure 5.9(a and b). For all blends and hydration, the first solvation shell from the S-S RDFs appear at 7.8 Å and is consistent with the findings of Sunda *et al.* [123] on triflate ion-water mixtures. The first peak from the S-S RDFs at $\lambda=1$ appears at shorter distance (compared to higher hydration)

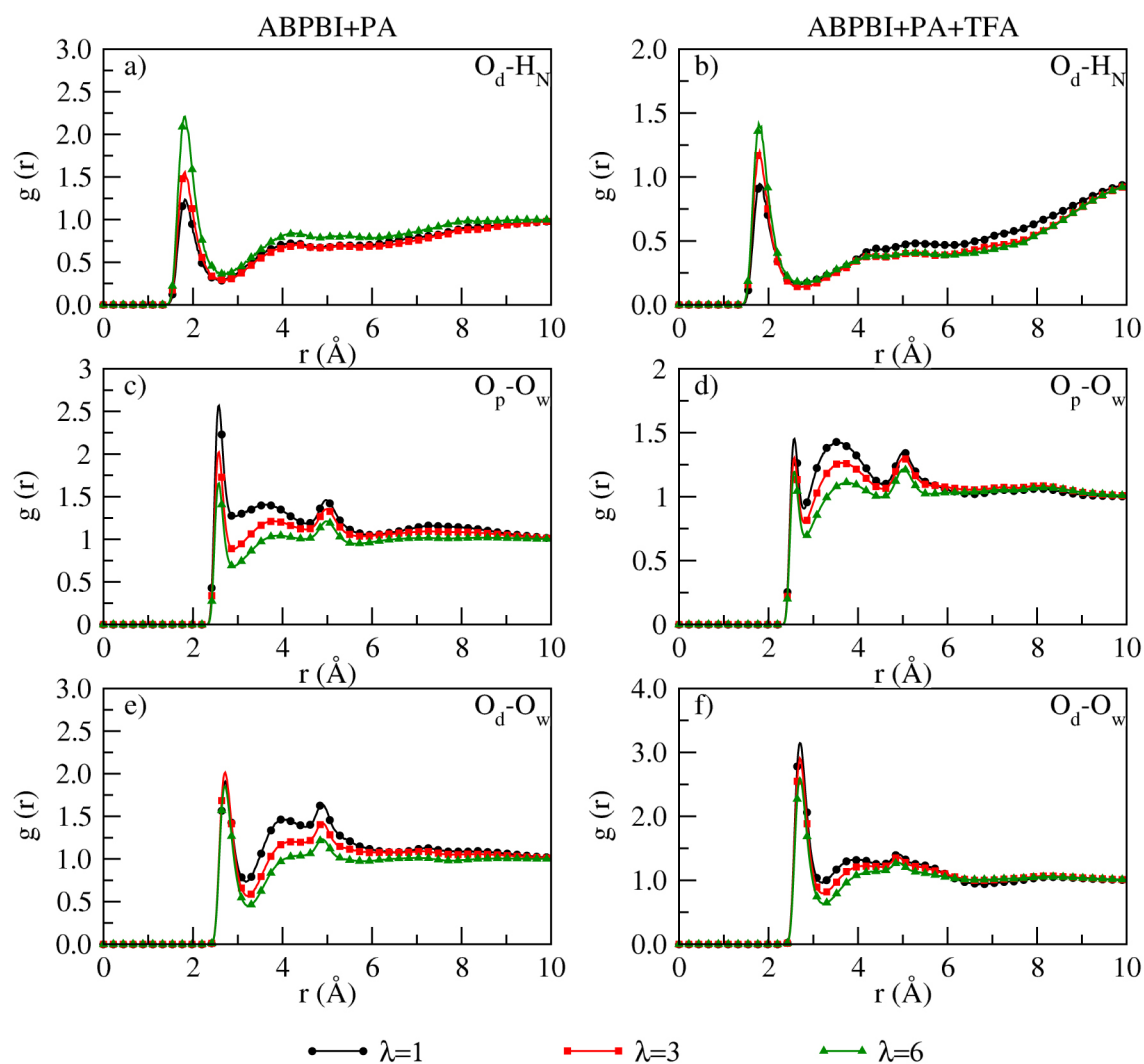


Figure 5.8: RDFs for PA interactions (a and b) O_d-H_N , (c and d) O_p-O_w and (e and f) O_d-O_w .

due to strong interactions between TFA and hydronium ions. With increasing hydration, the peak disappears due to the decrease in interaction between TFA and hydronium ions facilitated by water molecules. The sulfonate-water and sulfonate-hydronium ion interactions decrease with hydration in ABPBI+TFA and ABPBI+PA+TFA blends as seen in $S-O_w$ (see Figure 5.9(c and d)) and $S-O_h$ RDFs (see Figure 5.9(e and f)) respectively. The co-ordination number (see Table 5.4) calculated from the $S-O_w$ and $S-O_h$ RDFs shows a decrease with hydration. The solvation of water molecules and hydronium ion around the sulfonate group is lower in ABPBI+PA+TFA blends compared to ABPBI+TFA blends. The interaction of hydronium ions with water molecules is seen from the O_h-O_w RDF

Table 5.3: Co-ordination number calculated using the first minima (in parenthesis) for PA interactions in hydrated ABPBI+PA and ABPBI+PA+TFA blends.

System	λ	P-P (5.5 Å)	O _d -H _P (2.5 Å)	H _P -N (2.6 Å)	O _d -H _N (2.6 Å)	O _P -O _w (3.0 Å)
ABPBI+PA	1	4.78	0.39	0.10	0.14	0.46
	3	3.33	0.29	0.05	0.12	0.78
	6	2.56	0.23	0.04	0.11	0.91
ABPBI+PA+TFA	1	2.24	0.23	0.03	0.08	0.16
	3	1.77	0.20	0.02	0.07	0.36
	6	1.44	0.17	0.01	0.07	0.52

Table 5.4: Co-ordination number calculated using the first minima (in parenthesis) for TFA interactions in hydrated ABPBI+TFA and ABPBI+PA+TFA blends.

System	λ	S-S (7.8 Å)	S-O _w (4.5 Å)	S-O _h (4.6 Å)	O _h -O _w (4.5 Å)
ABPBI+TFA	1	8.73	1.94	3.46	2.24
	3	6.84	1.38	2.54	4.92
	6	4.94	0.94	1.81	6.86
ABPBI+PA+TFA	1	5.73	1.26	2.16	1.57
	3	4.83	0.98	1.65	3.86
	6	3.68	0.70	1.23	5.76

(see Figure 5.9(g and h)). The O_h-O_w interactions decrease due to the presence of PA (ABPBI+PA+TFA). The examination of coordination numbers show that the solvation of water molecules around the hydronium ion is higher in ABPBI+TFA blends compared to ABPBI+PA+TFA blends.

5.3.3 End-to-end distance, radius of gyration and cluster analysis

The effect of hydration and acid on ABPBI polymer chain is examined by a comparison of an average end-to-end polymer chain distance (R_{E-E}) and radius of gyration (R_g) of polymer chains in various acid doped hydrated ABPBI blends. For each blend and hydration, the average end-to-end distance of polymer chains and radius of gyration (calculated from 64 polymer chains) is calculated from the trajectory of a 20 ns simulation. The average end-to-end polymer chain distance is 31 Å with a standard deviation

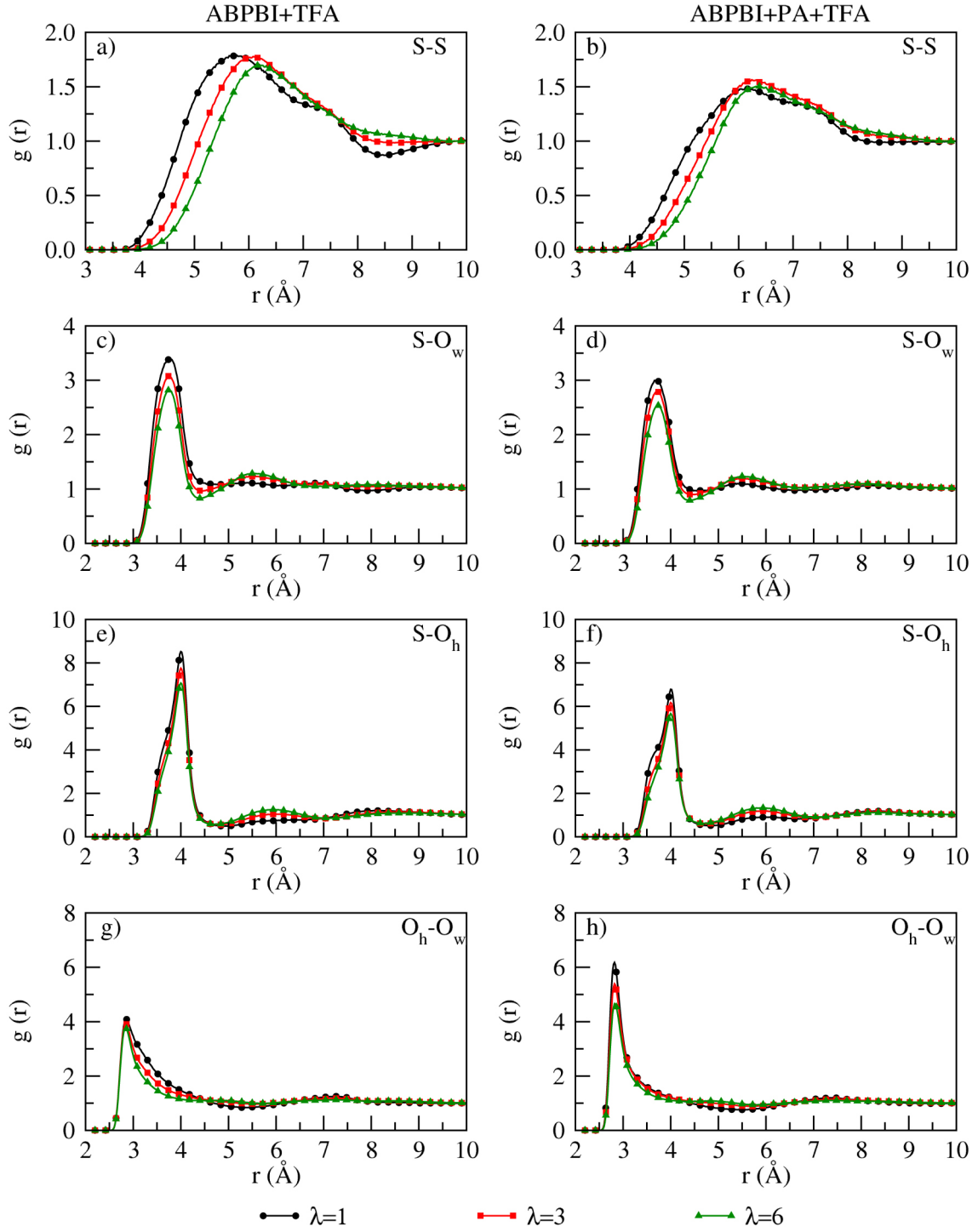


Figure 5.9: RDFs for TFA interactions (a and b) S-S, (c and d) S-O_w, (e and f) S-O_h and (g, h) O_h-O_w.

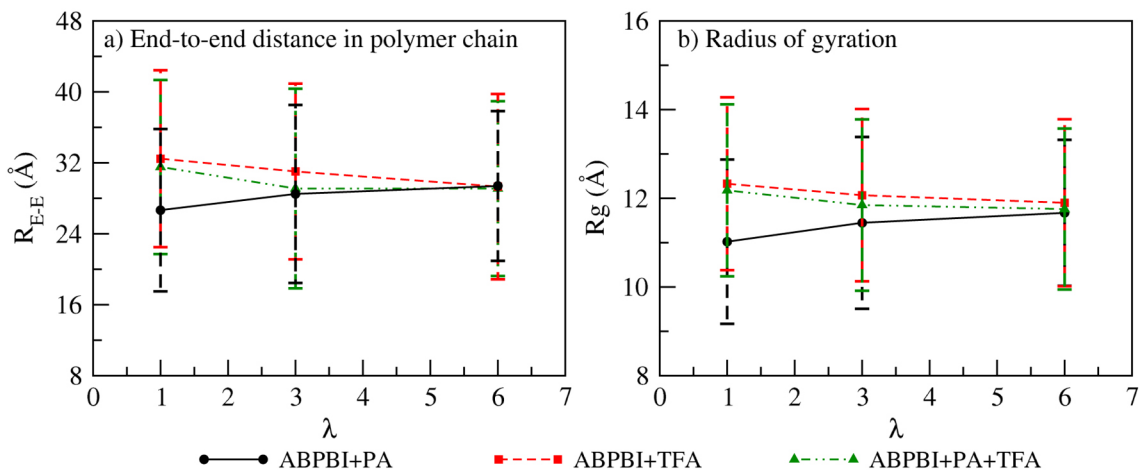


Figure 5.10: a) Average end-to-end polymer chain distance (R_{E-E}) and b) average radius of gyration (R_g) of ABPBI polymer chains. [Error bar represents standard deviation]

of ~ 9 Å (see Figure 5.10a). For each blend and hydration, the average radius of gyration is 12 Å with a standard deviation of 2 Å (see Figure 5.10b). For a long chain linear polymer, [76, 77, 175, 176] the theoretical value of R_{E-E}/R_g value is 2.45. The calculated R_{E-E}/R_g value is found to be ~ 2.4 for all acid doped hydrated ABPBI blends which suggest the existence of some chains which deviate from linearity. The end-to-end polymer chain distance and radius of gyration is invariant to change in blend and hydration, which demonstrates the stability of the polymer membrane. The stability of the polymer membrane from present simulations falls within the experimental study on stability of the polymer membrane. For example, Asensio *et al.* [159] employed thermal gravimetric analysis (TGA) on ABPBI+PA blends and observed a first weight loss (due to water) at 150 °C and a second weight loss (due to PA) at 205-210 °C.

The polymer chain with a lowest value (skewed) and highest value (extended) of radius of gyration has been chosen which can provide insights into the number of PA, TFA and water molecules in a cluster around these polymer chains. The cluster analysis is performed using the Gromos algorithm [144] where a 10 Å distance (the cutoff used in MD simulations for non-bonding interactions) of any molecule from the center of mass of polymer chain is chosen as a cutoff for inclusion of molecules in a cluster. A snapshot of PA, TFA and water molecules around the skewed and extended polymer chains ($\lambda=3$) in ABPBI+PA+TFA blend using a visualization software Chimera [79] is shown in Figure 5.11. The average number of PA, TFA and water molecules around the skewed and extended ABPBI polymer chain for ABPBI+PA+TFA blends are shown in Figure 5.12. The

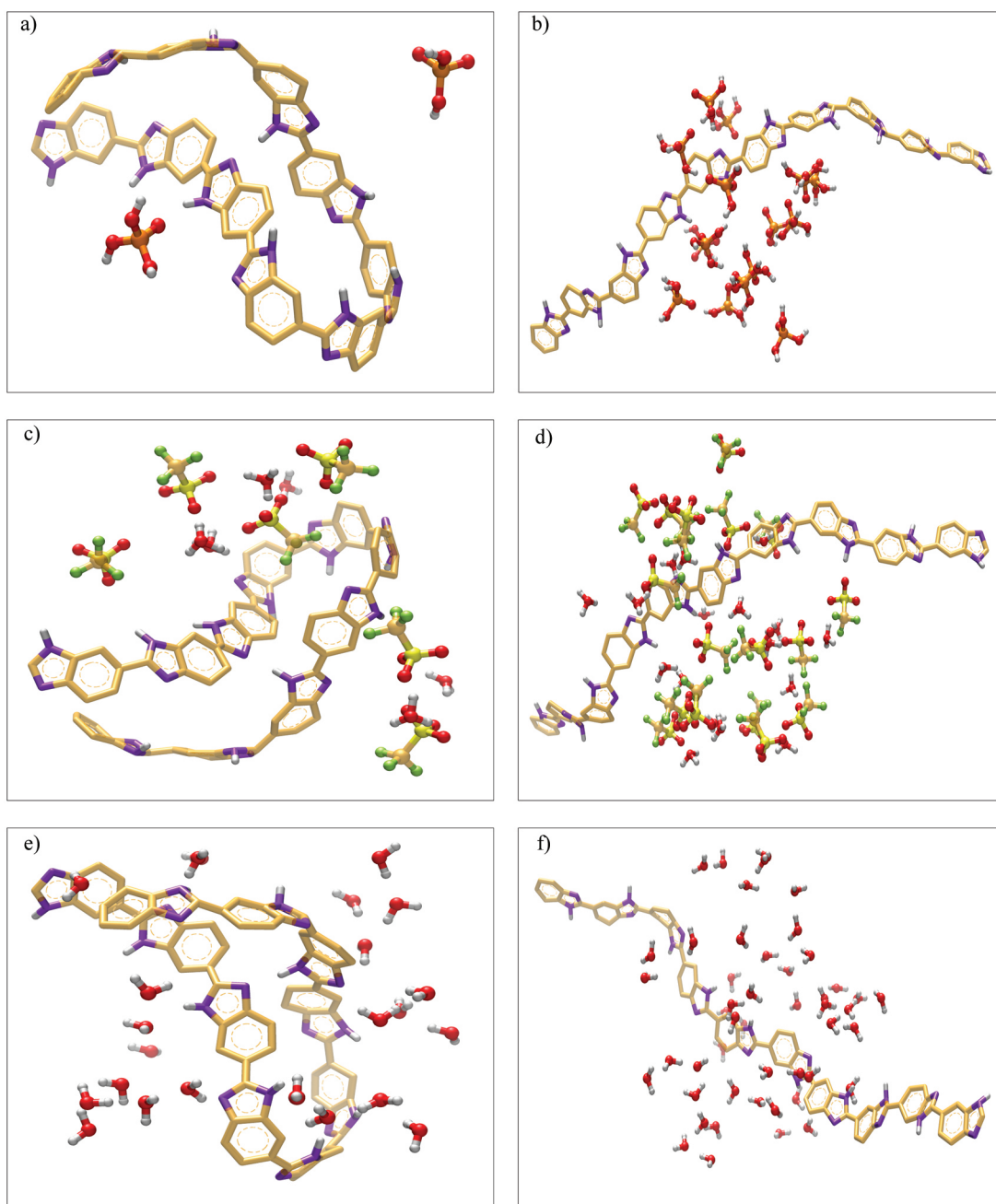


Figure 5.11: Snapshots of skewed and extended ABPBI polymer membrane of ABPBI + PA + TFA blend ($\lambda=3$) shows molecules in a cluster of (a and b) PA, (c and d) TFA and hydronium ions and (e and f) water molecules. [benzimidazole ring: white; hydrogen: grey; oxygen: red; nitrogen: violet; fluorine: green; phosphorus: orange and sulfur: yellow]

average number of PA molecules around the skewed chain increases from 0.5 ($\lambda=1$) to 1.8 ($\lambda=6$). However, the average number of PA molecules around the extended chain show a decrease from 12 ($\lambda=1$) to 6 ($\lambda=6$). The average number of TFA molecules around the skewed chain decrease from 9 ($\lambda=1$) to 1.1 ($\lambda=6$). Similarly, the average number of TFA molecules around the extended chain decreases from 9 ($\lambda=1$) to 5.6 ($\lambda=6$). However, the average number of water molecules around the skewed chain increases from 5.1 ($\lambda=1$) to 17.3 ($\lambda=3$) and remains constant with increase in hydration. Similarly, the average number of water molecules around the extended chain increases from 8.6 ($\lambda=1$) to 33.3 ($\lambda=3$) and remains constant with increase in hydration. The average number of PA, TFA and water molecules around the skewed and extended ABPBI polymer chain for ABPBI+PA and ABPBI+TFA blends are shown in Figure 5.13a and Figure 5.13b respectively. The effect of hydration is significant in the number of clusters in ABPBI+PA blends. For example, in the skewed and extended polymer chain of ABPBI+PA blend, the average number of PA molecules decreases and water molecules increases with hydration. At $\lambda < 3$, 9-12 PA molecules surround the extended polymer chain, compared to 3-5 PA molecules in the skewed polymer chain. Similar trends are also seen in ABPBI+TFA blends.

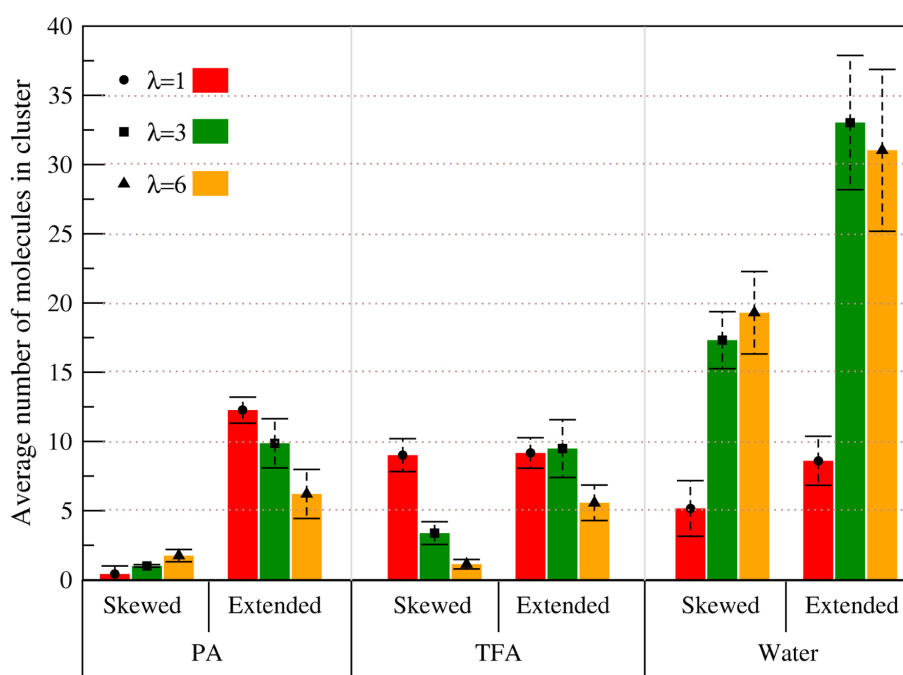


Figure 5.12: Average number of PA, TFA and water molecules in skewed and extended ABPBI polymer membrane of ABPBI + PA + TFA blend. [Error bar represents standard deviation]

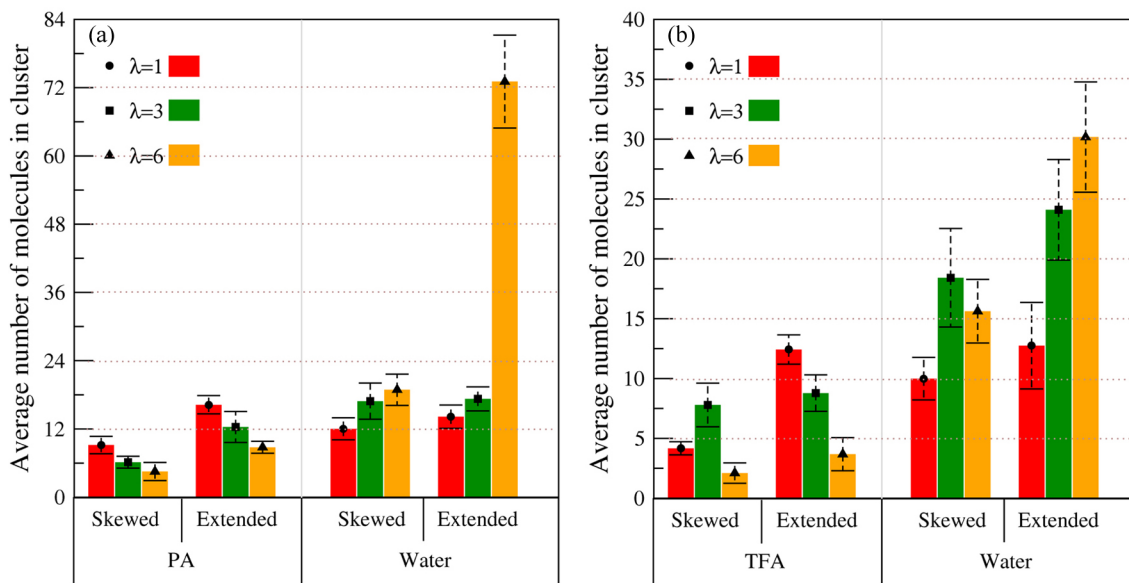


Figure 5.13: Average number of a) PA and water molecules in a cluster from ABPBI + PA blends and b) TFA and water molecules in a cluster from ABPBI + TFA blends. [Error bar represents standard deviation]

5.3.4 Influence of hydration on molecular transport

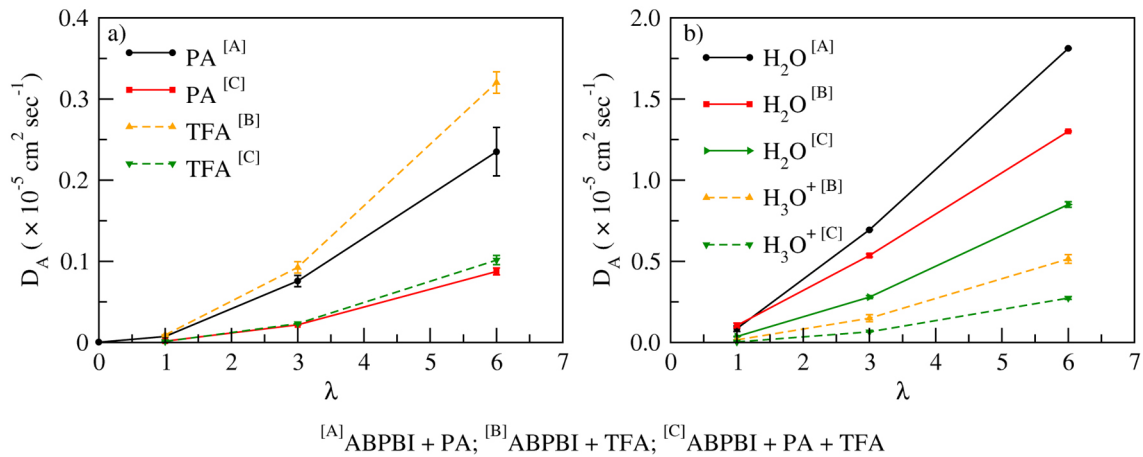
The mobility of PA, TFA, hydronium ions and water molecules are shown as MSDs (see Figure B5-1, Figure B5-2 and Figure B5-3 of Appendix B). The calculated diffusion coefficients (D_A) are shown in Figure 5.14 and D_A values are provided in Table 5.5. The diffusion of PA (see Figure 5.14a) in ABPBI+PA blends is lowest in the absence of water ($\lambda=0$). The diffusion coefficient of PA increases by factor of ~ 25 from $\lambda=0$ to $\lambda=1$. The diffusion coefficient of PA at $\lambda=1$ ($0.0073 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$) is similar to a previously reported diffusion of PA ($0.0177 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ at 298 K) by Li *et al.* [177] A subsequent increase in hydration increases the diffusion coefficient of PA by a factor of 10.36 ($\lambda=1$ to $\lambda=3$) and 3.10 ($\lambda=3$ to $\lambda=6$) respectively. The effect of TFA on the diffusion of PA is seen as follows: For example, at $\lambda=1$, the diffusion coefficient of PA in ABPBI+PA+TFA blends is 4.5 times lower than ABPBI+PA blends. Compared to ABPBI+PA blends, the diffusion coefficient of PA is lower by 3.48 ($\lambda=3$) and 2.68 ($\lambda=6$) in ABPBI+PA+TFA blends. Such observations show that the inclusion of TFA reduces the diffusion of PA.

The diffusion of TFA (see Figure 5.14a) and hydronium ions (see Figure 5.14b) shows very similar trends with increase in hydration. For example, at $\lambda=3$, compared to ABPBI+PA+TFA blends, the diffusion coefficients of TFA and hydronium ions is 4 and 2

Table 5.5: Diffusion coefficients ($D_A \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$) of PA, H_3O^+ (hydronium ions), TFA and water molecules at 353 K.

System	λ	PA	H_3O^+	TFA	water
ABPBI+PA	0	0.0003	—	—	—
	1	0.0073	—	—	0.0850
	3	0.0757	—	—	0.6943
	6	0.2351	—	—	1.8115
ABPBI+TFA	1	—	0.0160	0.0092	0.1047
	3	—	0.1496	0.0925	0.5359
	6	—	0.5146	0.3203	1.3007
ABPBI+PA+TFA	1	0.0016	0.0031	0.0012	0.0365
	3	0.0217	0.0655	0.0232	0.2792
	6	0.0875	0.2732	0.1015	0.8497

times higher in ABPBI+TFA blends. Similar trends are seen from $\lambda = 1$ and 6. The higher mobility of hydronium ions in ABPBI+TFA and ABPBI+PA+TFA blends is consistent with the observations of Schuster *et al.* [83], where an increase in the proton conductivity of immobilized imidazole is observed when TFA is used as a dopant. The inclusion of PA reduces the effective hydronium ion interactions with water molecules as seen from $\text{O}_h\text{-O}_w$ RDFs which results in lower hydronium ion mobility in ABPBI+PA+TFA blends, compared to ABPBI+TFA blends. The mobility of water molecules is highest

**Figure 5.14:** Diffusion coefficients (D_A) of PA, hydronium ions, TFA and water molecules. [Error bar represents standard deviation]

in ABPBI+PA blends and lowest in ABPBI+PA+TFA blends (see Figure 5.14b). The diffusion coefficient of water molecules increase by a factor of 8.2 from $\lambda=1$ to $\lambda=3$ in ABPBI+PA blends. A subsequent increase in hydration from $\lambda=3$ to $\lambda=6$ increases diffusion of water molecules by a factor of 2.6. The inclusion of TFA lowers the mobility of water molecules. At $\lambda=3$, compared to ABPBI+PA blends, the diffusion coefficient of water molecules in ABPBI+TFA and ABPBI+PA+TFA blends is lower by a factor of 1.3 and 2.5 respectively. Similar trends are also seen at $\lambda=6$.

5.3.5 Influence of polymer chain length on structure and dynamics

The influence of polymer chain length is examined by a comparison of the structural and dynamical properties in hydrated ($\lambda=3$) ABPBI+PA+TFA blend using a polymer chain consisting of $n=10$ and $n=20$ monomer units. The densities obtained from simulations on hydrated ($\lambda=3$) ABPBI+PA+TFA blends with different polymer chain lengths are found to be in excellent agreement with each other (see Table A5-1 of Appendix A). The effect of polymer chain length on membrane nanostructure is examined by a comparison of the N-N, N-N_H, N-H_N and H_N-O_w RDFs (see Figure B5-4 of Appendix B). The similarity in RDFs and the respective coordination numbers (see Table A5-2 of Appendix A) illustrates that increase in polymer chain length ($n=10$ to $n=20$) show negligible effect

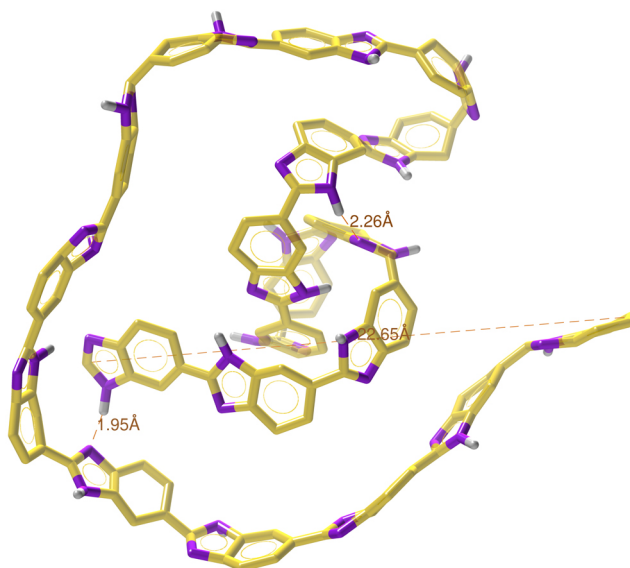


Figure 5.15: Snapshot of skewed ABPBI polymer membrane ($n=20$) of ABPBI + PA + TFA blend ($\lambda=3$). [benzimidazole ring: white; hydrogen: grey; nitrogen: violet]

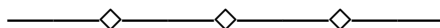
on structural properties. Similar trends are also observed in dynamical properties as seen from the MSDs (see Figure B5-5 of Appendix B) and diffusion coefficients (see Table A5-1 of Appendix A). While the end-to-end polymer chain distance (R_{E-E}) decrease with increasing polymer chain length (see Table A5-1 of Appendix A), the radius of gyration remains unchanged. The snapshots shown in Figure 5.11 ($n=10$) and Figure 5.15 ($n=20$) suggest that the ABPBI polymer chain can exist in a coil or a worm like configuration. This is due to the presence of van der Waals and hydrogen bonding interactions between various sites ($N-H_N$ interactions shown in Figure 5.2(g-i) and Figure 5.3) in the ABPBI polymer membrane. Additionally, the free rotation around the C-C bond (which connects monomeric segments) leads to polymer chain semi-flexibility and random orientations of the polymer chain.

5.4 Conclusions

A molecular understanding of acid doped hydrated ABPBI polymer membranes using classical MD simulations is presented in this chapter. The RDFs show that the interactions of TFA with the membrane are stronger compared to PA. The interactions of the imidazole moiety of the ABPBI membrane with water are strongest in ABPBI+TFA blends and weakest in ABPBI+PA blends. The RDFs shows that the distance between two adjacent imidazole units of the ABPBI polymer chain is ~ 6 Å and is invariant with hydration and type of blend. The influence of hydration and blend is negligible on the end-to-end polymer chain distance and the radius of gyration, which shows the stability of the polymer membrane. For all blends, the increase in hydration shows a decrease in acid molecules around the skewed and extended polymer chain. The increase in interaction between the ABPBI membrane and water in the presence of TFA leads to significant decrease in water mobility and this blend could be most suited to reduce the leaching of PA from the membrane.

Due to limitations of classical force-fields employed in this work, the calculated diffusion coefficient describes only the vehicular mechanism of protons. Nevertheless, the calculated diffusion coefficients offer a good benchmark for future experimental investigations. Further, in order to reduce the level of complexity in present simulations, the presence of phosphate ions (dissociated form of PA) and pyro-phosphoric acids (formed due to condensation reactions between PA molecules) was not considered. The characterization of structural diffusion of protons and the effect of temperature on the structural and

dynamical properties requires an extensive investigation by AIMD methods [134]. Such a study can provide further insights on the Grotthuss mechanism of proton transfer in PA and TFA doped ABPBI polymer membranes over a wide fuel cell operating temperature.



Chapter 6

Parametric dependence on shear viscosity of SPC/E water from equilibrium and non-equilibrium molecular dynamics simulations

6.1 Introduction

The calculation of transport coefficients such as shear viscosity of liquids, polymers, materials and bio-molecules is crucial for the understanding of various physical and chemical phenomena which occurs on nanosecond time scales. Equilibrium Molecular Dynamics (EMD) and non-equilibrium Molecular Dynamics (NEMD) simulations have been used for the determination of shear viscosity. Holian and Evans [178] observed similar values of shear viscosity of a Lennard-Jones fluid calculated using Green-Kubo EMD and NEMD methods. Schoen and Hoheisel [179] used the Green-Kubo EMD on a Lennard-Jones fluid and found that the accuracy of shear viscosity was dependent on the length of correlation function and system size. Hayes and Preston [180] used EMD simulations and found that the calculated shear viscosity of model binary mixtures of inert gases matches with experiment. Pas and Zwolinski [181] used EMD simulations and calculated the bulk viscosity of binary mixtures of inert gases. The authors observed that the accuracy of bulk viscosity was sensitive to the length of the correlation function. Hayes [182] used the Green-Kubo EMD and calculated the bulk viscosity of liquid binary mixtures. The author found the calculated shear viscosity was dependent on the composition of liquid binary mixtures.

Balasubramanian *et al.* [183] reported the shear viscosity of SPC/E [95] water from

EMD and NEMD simulations. The authors employed a chain of variables i.e. Nose'-Hoover chains [184] instead of a single thermostat variable. The authors concluded that both methods yield similar values of shear viscosity. Rowley and Painter [185] used EMD simulations using a modified Einstein method and found that the calculated shear viscosity of liquid argon was in excellent agreement with experiment. Hess [186] calculated the shear viscosities of SPC and SPC/E water using EMD and NEMD using different cutoffs for electrostatic interactions and Berendsen [187] thermostat. The author compared the accuracy and efficiency of EMD (transverse auto-correlation function) and NEMD (periodic perturbation and SLLOD algorithm) simulation methods. The author found that the NEMD methods were computationally more efficient compared to EMD. Furthermore, the author concluded that the SLLOD method suffers from a drawback due to generation of force from velocity. Bordat and Müller-Plathe [188] used a reverse NEMD for calculation of shear viscosity of simple molecular fluids. The authors found that that reverse NEMD method with a isochoric (NVE) ensemble provide accurate values of shear viscosity, whereas the shear viscosity calculated using the isochoric-isothermal (NVT) ensemble leads to deviations from experiment. Thomas and Rowley [189] developed a transient MD method to obtain the shear viscosity of a Lennard-Jones fluid. The authors showed that depending on the fluid density, two different models have to be chosen for estimation of shear viscosity. Kuang and Gezelter [190] developed a reversible NEMD method based on a non-isotropic velocity rescaling to calculate the thermal conductivity of solids, liquids and interfacial systems. However, the authors concluded that their method had limited applicability in the determination of shear viscosity of liquids.

Although EMD and NEMD methods and its variants have been used for the determination of shear viscosity, there has been no study to characterize the impact of several input parameters which play an important role in the accurate determination of shear viscosity. The objective of this study was to vary input parameters such as thermostat, coupling time and system size to investigate the effect on shear viscosity using EMD and NEMD simulations. Similar to the study of Balasubramanian *et al.* [183] and Hess, [186] the SPC/E [95] water model has been used in the present study. The Berendsen, [187] velocity-rescale [97] and Nose'-Hoover [191, 192] thermostats have been used for thermostatting the system temperature. The Berendsen thermostat scales the velocities of each particle in the system by using a time dependent scaling factor, λ , given by

$$\lambda = \left[1 + \frac{\Delta t}{T_T} \left(\frac{T_0}{T(t)} - 1 \right) \right]^{\frac{1}{2}} \quad (6.1)$$

where T_0 and $T(t)$ are the target temperature and temperatures at a particular time t (instantaneous temperature) of the system and T_T is time constant. The coupling time, τ_B , can be written as:

$$\tau_B = \frac{2C_v T_T}{N_f k_b} \quad (6.2)$$

where N_f is the number of degrees of freedom of the system, C_v is the heat capacity at constant volume and k_b is the Boltzmann constant. The velocity-rescale thermostat is similar to the Berendsen thermostat except that it uses an additional stochastic term which can be written as follows:

$$dK = (K_0 - K) \frac{dt}{T_T} + 2 \sqrt{\frac{K K_0}{N_f}} \frac{dW}{\sqrt{T_T}} \quad (6.3)$$

where K_0 and K are the kinetic energies of the system at T_0 and $T(t)$, respectively and dW is called as a Wiener noise [97]. The Nose'-Hoover [191, 192] thermostat includes a friction force with a friction heat bath parameter ξ , where the equation of motion can be written as:

$$\frac{d^2 r_i}{dt^2} = \frac{F_i}{m_i} - \xi \frac{dr_i}{dt} \quad (6.4)$$

The equation of motion for the heat bath parameter ξ can be written as:

$$\frac{d\xi}{dt} = \frac{1}{Q} (T - T_0) \quad \text{where } Q = \frac{T_T^2}{4\pi^2} T_0 \quad (6.5)$$

A brief description of methods used in the calculation of shear viscosity is described in Section 6.2. The effect of thermostats, coupling time and system size on system temperature and shear viscosity is presented in Section 6.3. A summary of salient results concludes the chapter.

6.2 Computational details

The transverse current auto-correlation [193] method (EMD) and periodic perturbation [194] method (NEMD) are used in this study for calculation of shear viscosity. The details of these methods are described extensively in the study of Hess [186]. However, for the sake of completeness only the governing equations are provided:

6.2.1 Transverse current auto-correlation method

The flow of liquid can be described by the well-known Navier-Stokes equation:

$$\rho \frac{\partial u}{\partial t} + \rho (u \cdot \nabla) u = \rho \mathbf{a} - \nabla p - \eta \nabla^2 u \quad (6.6)$$

where ρ is the liquid density and $\mathbf{a}$ is acceleration. The velocity of liquid particles consists of plane waves in the x direction. The transverse current auto-correlation function (TCAF) corresponding to various $\mathbf{k}$ - vectors can be written as:

$$u_x(z, t) = u_0 e^{-\beta} \left(\cosh(\Omega \beta) + \frac{1}{\beta} \sinh(\Omega \beta) \right) \cos(kz) \quad (6.7)$$

where $\beta = \frac{t}{2\tau_m}$ and τ_m is relaxation time. Ω is k dependent and is defined as:

$$\Omega = \sqrt{1 - \tau_m \frac{\eta}{\rho} k^2} \quad (6.8)$$

The shear viscosity is calculated using a second order approximation and can be written as:

$$\eta(k) = \eta(0) (1 - ck^2) \quad (6.9)$$

An extrapolation to $k=0$ provides the macroscopic shear viscosity.

6.2.2 Periodic perturbation method

In the periodic perturbation method, energy is fed into the system by external forces and is dissipated through viscous friction. The external force leads to velocity, where the flow of liquid can be described by the Navier-Stokes equation:

$$\rho \frac{\partial u_x(z)}{\partial t} = \rho a_x(z) + \eta \frac{\partial^2 u_x(z)}{\partial z^2} \quad (6.10)$$

where

$$a_x(z) = A \cos\left(\frac{2\pi}{l_z} z\right) \quad (6.11)$$

and l_z is the height of the box. The generated velocity can be written as:

$$u_x(z, t) = A \left(1 - e^{-\frac{\eta k^2}{\rho} t} \right) \cos(kz) \quad (6.12)$$

The shear viscosity is calculated as follows:

$$\eta = \frac{A}{v} \frac{\rho}{k^2} \quad (6.13)$$

The details of calculation of v is described in the study of Hess [186].

6.2.3 Simulation details

All MD simulations were carried out using the GROMACS [91] 4.0.7 program at 300 K. The leapfrog algorithm [74] with a time step of 1 fs was used to integrate the equations of motion. The cut-off distance for van der Waals and electrostatic interactions was chosen as 10 Å. The PME [98, 99] method was used for calculation of long-range electrostatic interactions. The starting input for all MD simulations was obtained as follows: An energy minimized water molecule was replicated in a cubic box to generate four configurations containing 900, 1800, 3600 and 7200 SPC/E [95] water molecules. Each configuration was well equilibrated for a 10 ns simulation time using a NPT ensemble at a 1 bar isotropic pressure maintained by a Berendsen barostat [96]. The equilibration was followed by a 20 ns production run using a NVT ensemble. The equilibration and production runs used a velocity-rescale [97] thermostat and a coupling time of 0.1 ps. The final configuration obtained from the production run was used as an input for subsequent calculations. For the calculation of shear viscosity, a series of EMD and NEMD simulations were carried out for a simulation time of 2 ns using a NVT ensemble with a constant acceleration of 0.1 nm ps^{-2} with three thermostats (Berendsen, velocity-rescale and Nose'-Hoover) and six coupling times (0.1 ps, 0.5 ps, 1.0 ps, 1.5 ps, 2.0 ps, 2.5 ps). Nose' [195] and Holian *et al.* [196] concluded that to avoid artifacts in simulations, the choice of coupling rate (inverse of coupling time) should be in the range of collision frequency of an N-body system size fluid and hence coupling times from 0.1 ps to 2.5 ps have been chosen in this study. In addition, for NEMD simulations, a small shear with a cosine acceleration of 0.1 nm ps^{-2} was also applied in the x direction (see Eqn. 6.11). Similar to the study of Hess [186], an externally applied shear is chosen to avoid any non-linear [197–199] variations in fluid temperature.

6.3 Results and Discussion

The decay of the transverse current autocorrelation function (TCAF) is shown in Figure 6.1. As seen, the decay of the TCAF is invariant to the choice of the thermostat and coupling time. However, in a large system (7200 water molecules) the decay of TCAFs is slower compared to the decay seen in smaller system (900 water molecules). The k -dependent shear viscosity calculated (see Eqn. 6.9) using the transverse current autocorrelation method with various thermostats for a system sizes of 900 and 7200 water molecules at 0.1 ps and 2.5 ps coupling time is shown in Figure 6.2. The shear viscosity (extrapolated value at $k = 0$) for 900 and 7200 water molecules at various coupling times is shown in Figure 6.3. As seen, the shear viscosities are found to vary with coupling time. For example the shear viscosity is 1.14, 0.57 and 0.69 ($\times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$) from the

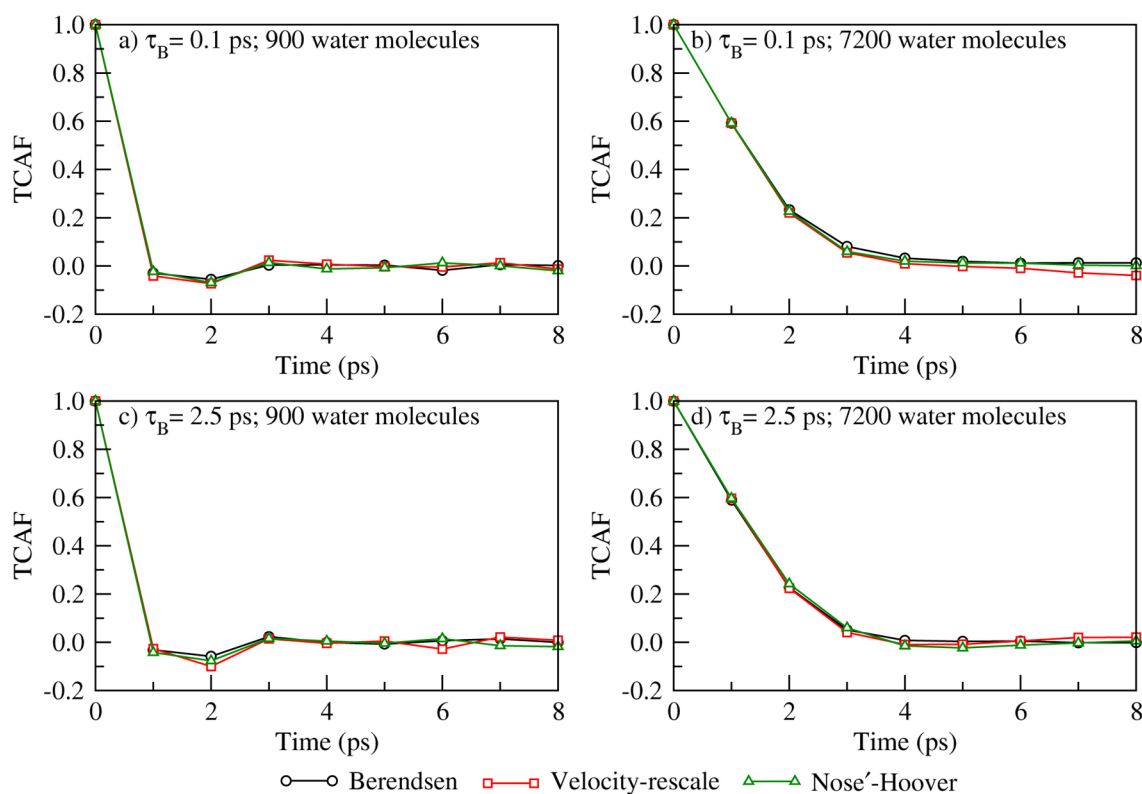


Figure 6.1: The decay of transverse current autocorrelation function with different thermostats: a) 0.1 ps coupling time in a 900 water molecules system, b) 2.5 ps coupling time in a 7200 molecule system, c) 0.1 ps coupling time in a 900 water molecules system and d) 2.5 ps coupling time in a 7200 water molecules system.

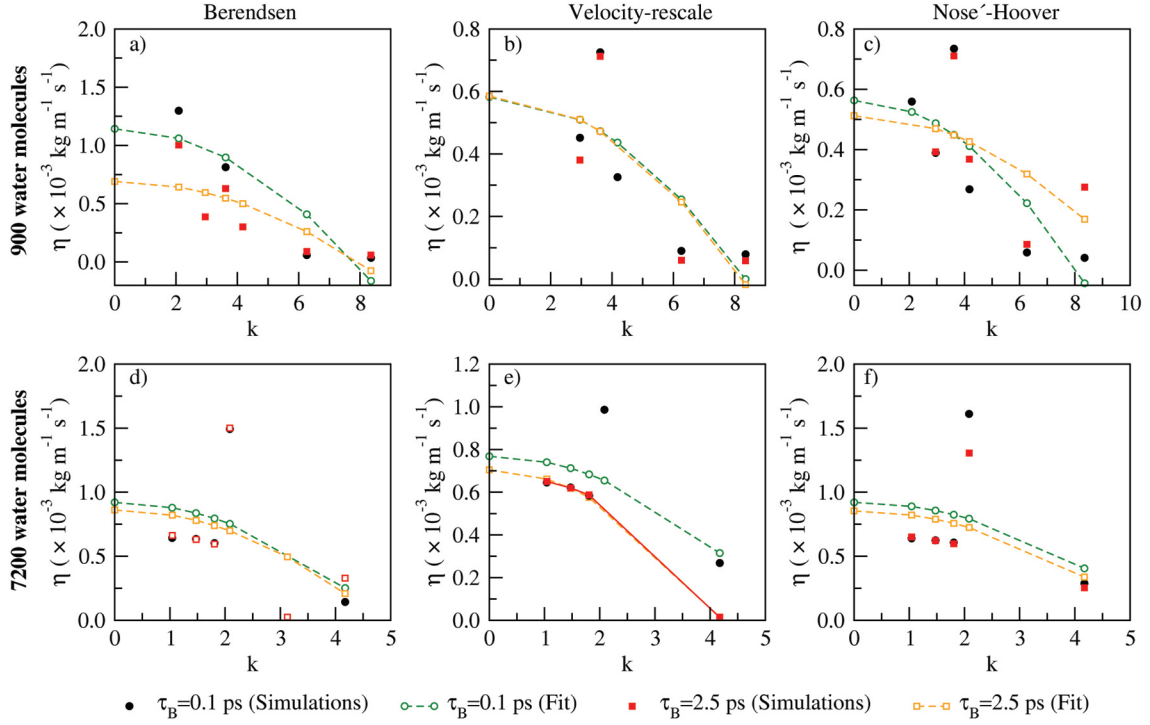


Figure 6.2: Shear viscosity computed from a 2 ns EMD simulation using the transverse current auto-correlation method: a-c) 900 molecules system and d-f) 7200 molecule system. (Filled symbols are viscosity for average k values and dotted lines are second order approximation of viscosity using Eqn. 6.9 extrapolated to $k=0$)

Berendsen thermostat at 0.1, 1.5 and 2.5 ps coupling time for 900 water molecules respectively. Similarly, the shear viscosity is 0.58, 0.64 and $0.90 (\times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})$ from the velocity-rescale thermostat at 0.1, 1.5 and 2.5 ps coupling time for 900 water molecules respectively. The shear viscosity for 900 water molecules is 0.56, 0.39 and $0.51 (\times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})$ at 0.1, 1.5 and 2.5 ps coupling time respectively using the Nose'-Hoover thermostat. Similar trends in shear viscosity are observed for the 7200 water molecules system (see Figure 6.3b). Thus, the transverse current autocorrelation function from the EMD simulations cannot provide a consistent value of shear viscosity.

A significant effect of thermostat on the temperature stability is observed from NEMD simulations performed using the periodic perturbation method. The average temperature shows a significant drift from the target temperature (300 K) especially with increasing coupling time with the use of Berendsen (see Figure 6.4a) and velocity-rescale thermostats (see Figure 6.4b). For example, the drift of average temperature from the target temperature for a system containing 900 water molecules is 3.5 K using the Berendsen thermostat.

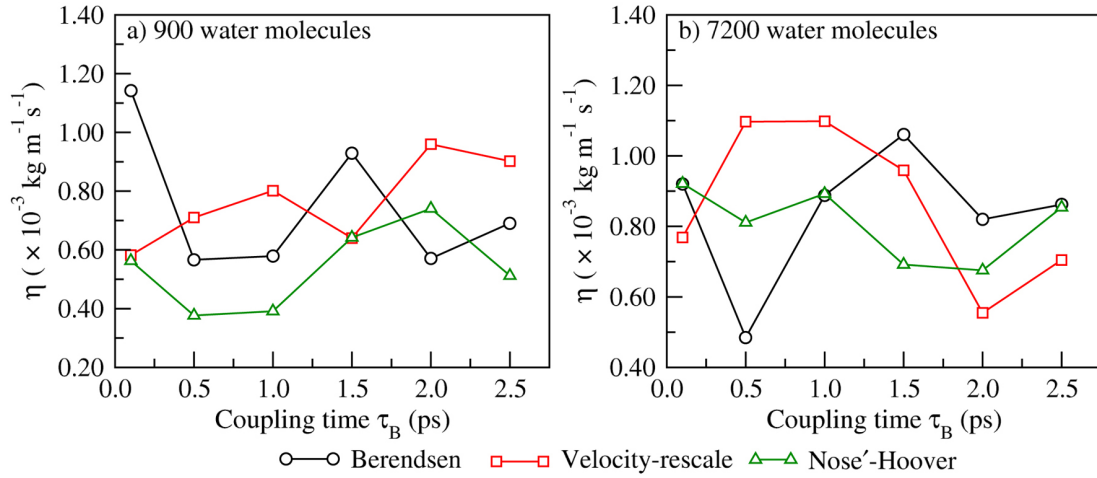


Figure 6.3: Shear viscosity computed from a 2 ns EMD simulation using various coupling time and thermostats and the transverse current autocorrelation method: a) 900 water molecules system and b) 7200 molecule system.

While this drift may appear less significant, the drifts are found to increase with system size. For a system containing 7200 water molecules, the drift is 18.2 K which is significant. Similar trends (see Figure 6.4b) are seen in the velocity-rescale thermostat due to its close resemblance with the Berendsen thermostat. The drift from the target temperature from the use of Berendsen and velocity-rescale thermostats with increasing coupling time can be understood from their definitions in Eqn. 6.1 and Eqn. 6.3. The scaling factor of the particle velocities will reduce significantly at larger coupling time and hence an accurate ensemble of configurations to produce an average temperature close to the target temperature will not be generated. Similar effects in the scaling factor are also seen with increasing system size. However, the coupling time appears in the equation of motion as a friction heat bath parameter ξ (see Eqn. 6.6) in the Nose'-Hoover thermostat which maintains the system at the target temperature. Hence, the average temperature computed using the Nose'-Hoover thermostat is found close to the target temperature for all system sizes. As expected, with increasing system size, the standard deviation (see Figure 6.4c) from the average temperature is reduced. Hence, the use of Nose'-Hoover thermostat provide excellent thermodynamic stability in NEMD simulations.

The shear viscosity calculated using the periodic perturbation method from NEMD simulation which use the Berendsen and velocity-rescale thermostats shows significant change with coupling time and system size (see Figure 6.5). In particular, for the 7200 water molecule system, the shear viscosities decrease linearly with coupling time and this

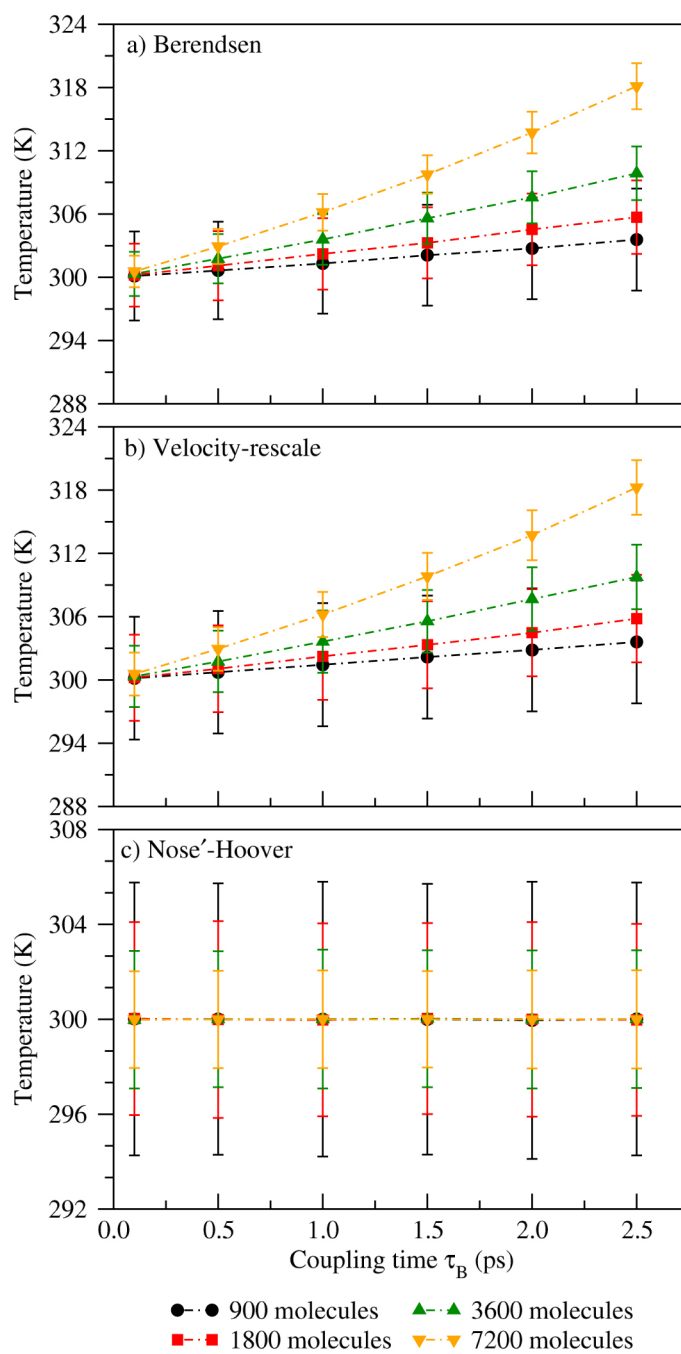


Figure 6.4: Average temperature (K) computed from a 2 ns NEMD simulation using various coupling time and thermostats and the periodic perturbation method: a) Berendsen, b) Velocity-rescale and c) Nose'-Hoover thermostat (Error bar shows standard deviation from the average temperature).

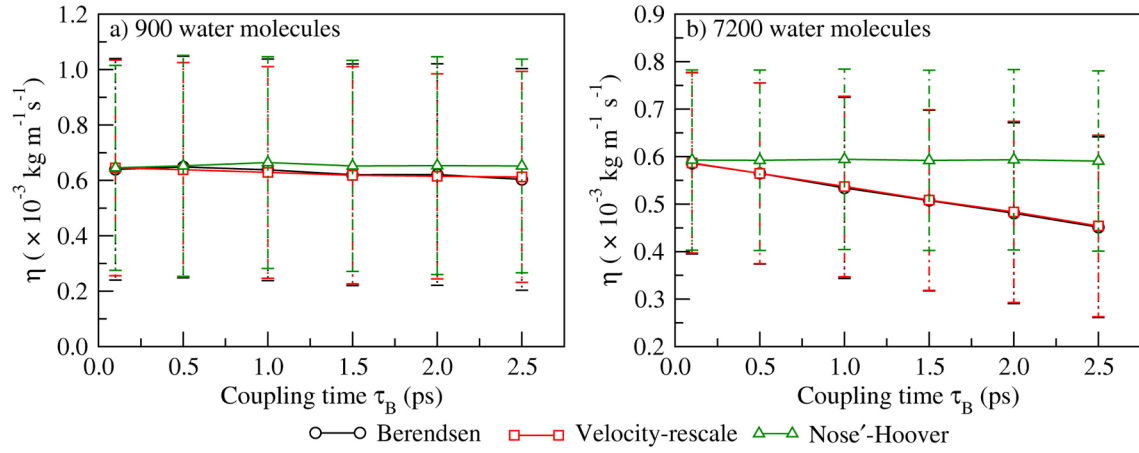
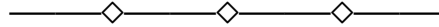


Figure 6.5: Shear viscosity computed from a 2 ns NEMD simulation using various coupling time and the periodic perturbation method: a) 900 water molecules system and b) 7200 molecule system (Error bar shows standard deviation in shear viscosity).

behavior is consistent with the increasing drift in average temperature with coupling time (see Fig 6.4a and b). The calculated shear viscosity ($0.63 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$) on a system size of 7200 water molecules (Berendsen thermostat, coupling time = 0.1 ps) is similar to the shear viscosity of ($0.64 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$) reported by Hess [186] on a system size of 6912 water molecules (Berendsen thermostat, coupling time = 0.1 ps), though the calculated viscosities are lower than the experimental [200] shear viscosity ($0.85 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$). The use of Nose'-Hoover thermostat provides a consistent shear viscosity for all coupling times and system size. For example, the shear viscosity for 900 water molecule system is $0.64\text{--}0.66 (\times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})$. The shear viscosity calculated using a system containing 7200 water molecule is $0.59 \pm 0.18 (\times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})$ at all coupling times. A shear viscosity of $0.86\text{--}0.06 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$ is reported by Bordat and Müller-Plathe [188] on a system containing 1536 water molecules using a reverse NEMD simulation method (Nose'-Hoover thermostat, coupling time = 0.2 ps). The differences in the calculated shear viscosity with the results of Bordat and Müller-Plathe [188] can be largely attributed to the different NEMD algorithms used for the calculation of shear viscosity.

6.4 Conclusions

A parametric dependent study for the determination of shear viscosity of SPC/E water from EMD and NEMD is presented in this chapter. The shear viscosities calculated using the transverse current autocorrelation method from EMD simulations vary with coupling time and system size. The shear viscosity calculated using the periodic perturbation method in NEMD simulations using the Berendsen and velocity-rescale thermostats vary significantly with coupling time and system size. The Nose'-Hoover thermostat is found to be the most reliable choice for shear viscosity determination from NEMD simulations [201].



Chapter 7

Structure and dynamics of benzyl-NX₃ (X=Me, Et) trifluoromethanesulfonate ionic liquids

7.1 Introduction

ILs have attained popularity for various electrochemical applications (such as electrolyte in fuel cells, lithium ion batteries and solar cells) in the past decade due to high thermal stability and ionic conductivity [202–206]. Hu and Margulis [207, 208] investigated dynamic heterogeneity in ILs and showed that the cationic and anionic diffusivity were highly correlated. Maginn [209] demonstrated the effect of simulation time scale and force-field dependence on accurate determination of transport properties of ILs using atomistic simulations. Angell *et al.* [210] reviewed the physical properties of protic and aprotic ILs for energy applications. Lu *et al.* [211] showed improved synthesis, electro-activity and electrochemical properties with use of room-temperature imidazolium-based ILs in π -conjugated polymers. Schmidt *et al.* [39] studied a Nafion membrane impregnated with imidazolium based ionic liquids and observed less swelling of the membrane without reducing thermal stability. The authors also observed that doping of IL in dry Nafion leads to enhancement of ionic conductivities by 2 orders of magnitude. An application of IL as an electrolyte was also demonstrated by a single molecule electro-chemical gating experiment performed using methylimidazolium trifluoromethanesulfonate by Kay *et al.* [212]. Lu and Archer [213] investigated the potential use of ILs in secondary lithium–metal batteries as hybrid electrolytes.

The use of ammonium based protic and aprotic ILs are of interest as fuel cell electrolytes due to their easy preparation, low cost, performance, excellent thermal stability

and ionic conductivity [214–218]. Lee *et al.* [219] investigated protic ILs such as diethyl-methylammonium trifluoromethanesulfonate ($[\text{dema}^+][\text{TFA}^-]$) as a proton conductor in fuel cells and observed fast proton exchange occurs due to the ammonium cation. Di Noto *et al.* [220–222] studied the influence of anions on proton-conduction of Nafion 117 impregnated with a quaternary ammonium ion based IL. The authors chose tetraethylammonium methanesulfonate, triethylammonium $[\text{TEA}^+]$ methanesulfonate $[\text{TFA}^-]$ and triethylammonium $[\text{TEA}^+]$ perfluorobutanesulfonate $[\text{PFBu}^-]$ doped Nafion 117 membrane and observed a significant increase in proton conduction, thermal stability and mechanical properties of the membrane. Sood *et al.* [223] investigated membrane nanostructure and transport properties of IL $[\text{TEA}^+][\text{TFA}^-]$ doped Nafion membrane. The authors observed a substantial increase in anhydrous ionic conductivity with increase in IL concentration.

Chang *et al.* [224] employed MD simulations on neat and hydrated ($[\text{dema}^+][\text{TFA}^-]$) IL. The authors observed that hydration leads to enhanced vehicular ionic conductivity. Tsuzuki [225] concluded that cation–anion interaction, shape/symmetry or size of cation, conformational flexibility, and molecular mass play a key role in diffusion of ILs. Blanchard *et al.* [226] studied diffusion mechanism in triethylamine based protic ILs using pulse field gradient stimulated echo NMR spectroscopy. The authors did not find any evidence of Grotthuss mechanism and reported acidic proton diffusion in the presence of water.

While ammonium -based protic and aprotic ILs have been considered as fuel cell electrolytes, their studies have been limited only to room temperature. Further, these ILs have high miscibility with water and leaching even at room temperature that limits their application as dopant in solid polymer membrane electrolytes. To overcome these limitations, the benzyltrimethylammonium triflate (BzTMA-TFA) and benzyltriethylammonium triflate (BzTEA-TFA) ILs (see Figure 7.1) have been chosen in the present study of this chapter. These ILs are nontoxic [227], exist in solid form at room temperature, with a glass transition temperature $<80\text{ }^\circ\text{C}$ and show high thermal stability ($>300\text{ }^\circ\text{C}$) [228].

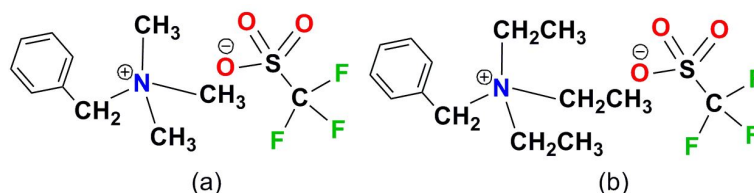


Figure 7.1: Chemical structure of a) BzTMA-TFA and b) BzTEA-TFA IL.

These ILs can offer better thermal stability, ionic conductivity, reduced IL leaching, and can enhance the fuel cell operation at higher temperature ($>140\text{ }^{\circ}\text{C}$) by reducing CO poisoning of the Pt catalyst. The details of MD simulations are presented in Section 7.2. The experimental details are shown in Section 7.3. The objective of this chapter is to elucidate a qualitative relationship between electrostatic, cation-phenyl [229, 230] (see Figure 7.2) and C-H/phenyl interactions with dynamics of BzTMA-TFA and BzTEA-TFA ILs, which is presented in Section 7.4. Further, influence of temperature (300, 318, 333 and 350 K) and Relative Humidity (RH = 0, 30, and 90%) on structure and dynamics is also examined. The self-diffusion coefficients of ILs are calculated using MD simulations and ionic conductivity is measured using electrochemical-impedance spectroscopy (EIS). A summary of the most important results concludes the chapter.

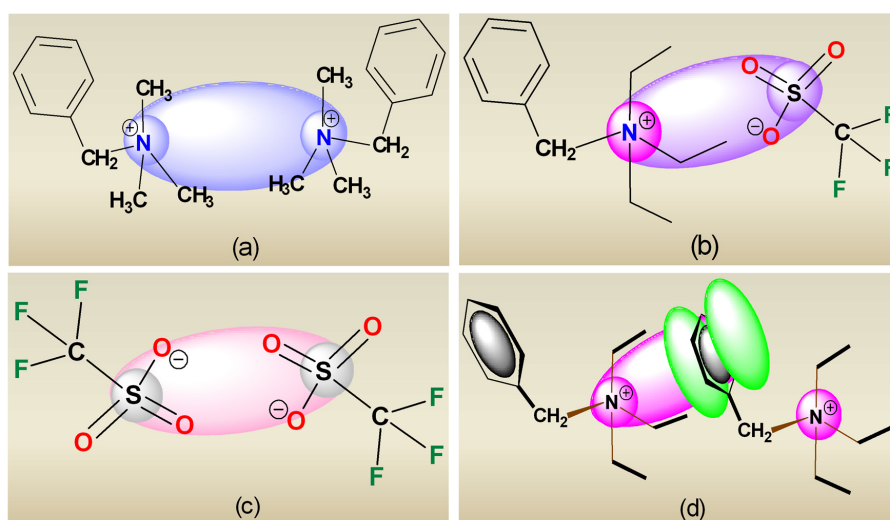


Figure 7.2: Schematic illustration of a) cation–cation, b) cation–anion, c) anion-anion and d) cation-phenyl interaction in ILs.

7.2 Computational details

7.2.1 Force-field

MD simulations were performed using the GROMACS [91] 4.5.4 program. All force-field parameters (except partial charges) of benzyl trimethyl ammonium cation (BzTMA^+) and benzytriethyl ammonium (BzTEA^+) cation were taken from the OPLS-AA force-field

database [72]. The partial charges of ammonium cations was calculated using CHELP [93] algorithm (MP2/6-31G** basis set) in the Gaussian 03 program [92]. The force-field parameters of triflate anion were taken from the work of Sunda *et al.* [123]

7.2.2 Simulation details

The input configurations for MD simulations were obtained as follows: An energy minimized BzTMA-TFA IL molecule was replicated to generate a cubic box of 64 IL molecules. The replicated configuration was heated from 300 to 1000 K and cooled back to 300 K with an annealing time of 6.75 ns. The final configuration from the annealing was used and replicated to generate a cubic box of 512 IL molecules. A similar procedure was applied for BzTEA-TFA IL and these replicated systems were now used as input for MD simulations. MD simulations were performed for BzTMA-TFA and BzTEA-TFA ILs at 300, 318, 333, and 353 K. The leapfrog algorithm [74] was chosen as an integrator with a time step of 1 fs. The cutoff for van der Waals and electrostatic interactions were chosen as 10 Å. The long-range electrostatic interactions were described by the PME method [98, 99]. The input configuration of each ionic IL was used for equilibration for 10 ns using the NPT ensemble with a 1 bar isotropic pressure and a Berendsen barostat [96]. The velocity-rescale thermostat [97] was used to maintain a constant temperature with a coupling time of 0.1 ps. The equilibrated structure were used to perform MD simulation for dry (neat) and aqueous (30 and 90 wt% water) ILs. The SPC/E [95] water model was used to create hydrated ILs. The number of water molecules, box length and density (calculated from equilibration) of ILs are shown in Table A7-1 (see Appendix A). As a benchmark, our simulated density of neat ILs (1.2 g cm^{-3} , 300 K) is in agreement with the experimental [228] density (1.2 g cm^{-3} , 298 K). Equilibration was followed by a 20 ns production run using the NVT ensemble. The Nosé-Hoover thermostat [191, 192] was used with a coupling time of 0.2 ps. The snapshots from the production run (RH=30 and RH=90% at 300 and 353 K) are shown in Figure B7-1 (see Appendix B). Trajectories generated from the production run were saved every 5 ps for calculation of structural (RDFs, clustering) and dynamical properties (MSDs, diffusion).

7.3 Experimental details

Benzyltrimethylammonium chloride, benzyltriethylammonium chloride, and triflic acid (from Aldrich) were used as received. IL synthesis was carried out by reaction of chloride

salt of respective cation with trifluoromethanesulfonic acid (with molar ratio $\text{BzNX}_3\text{Cl}/\text{TFA} = 1.05$; $\text{X}=\text{Methyl or Ethyl}$) in deionized water at room temperature in an ice bath (stir for 30-45 min). Subsequently, water was evaporated from the synthesized IL using a rotavap. After removal of water, methanol was added and stirred for 15-20 min followed by filtration to remove impurities or unreacted products. Methanol was evaporated followed by drying at 100 C under vacuum for 24 h. The synthesized IL was characterized by ^1H (see Figure 7.3), ^{13}C , ^{19}F NMR and characteristic NMR peaks were observed (see Figure B7-2). The characteristic $\pi \rightarrow \pi^*$ transition peak of the phenyl group of ILs at 240-275 nm wavelengths was observed in the UV visible spectrum (see Figure B7-2 of Appendix B). The thermal stability of ILs was examined by thermogravimetric analysis (TGA) analyzer where both ILs show thermal stability up to 600 K (see Figure B7-3 of Appendix B).

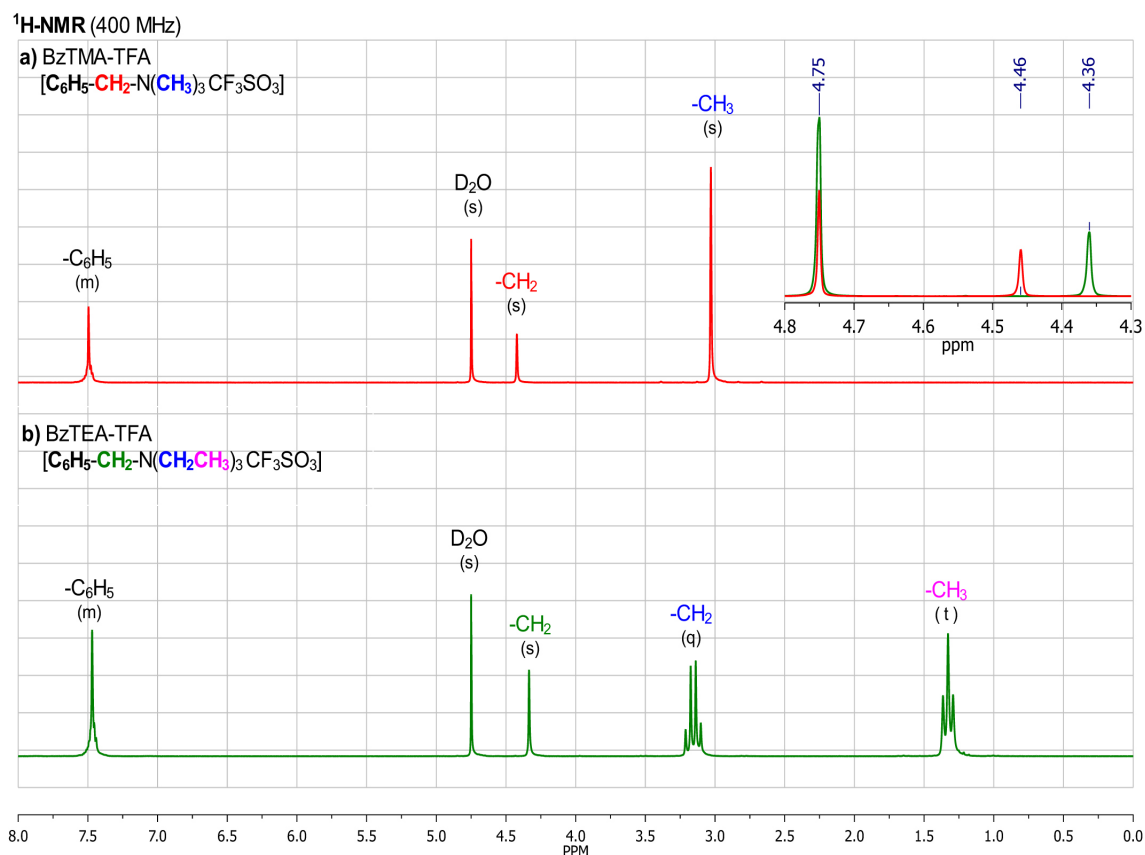


Figure 7.3: ^1H NMR chemical shift for BzTMA-TFA (red) and BzTEA-TFA IL (green).

7.4 Results and discussion

7.4.1 Interactions in BzTMA-TFA and BzTEA-TFA ILs

The structural influence of methyl or ethyl substituents attached to the quaternary nitrogen on various interactions between cation–cation and cation–anion is examined by RDFs (see Figure 7.4). The strong cation–cation and cation–anion interactions are observed from N-N and N-S RDFs in BzTMA-TFA IL respectively. The peak position of cation–cation interaction in N-N RDF (see Figure 7.4a) is shifted from 6.1 to 7.4 Å from methyl to the bulky ethyl substituted ammonium cation. The ethyl substituted ammonium cation shows larger solvation shell of ~ 9 Å compared to BzTMA-TFA IL (~ 8 Å). Similarly, cation–anion interactions characterized by N-S RDFs, shows a peak position in the N-S RDF at 4.75 Å in BzTMA-TFA compared to 5 Å in BzTEA-TFA IL (see Figure 7.4b). The N-S RDFs peak at ~ 5 Å is similar to cation–anion interactions in $[\text{dema}^+][\text{TFA}^-]$

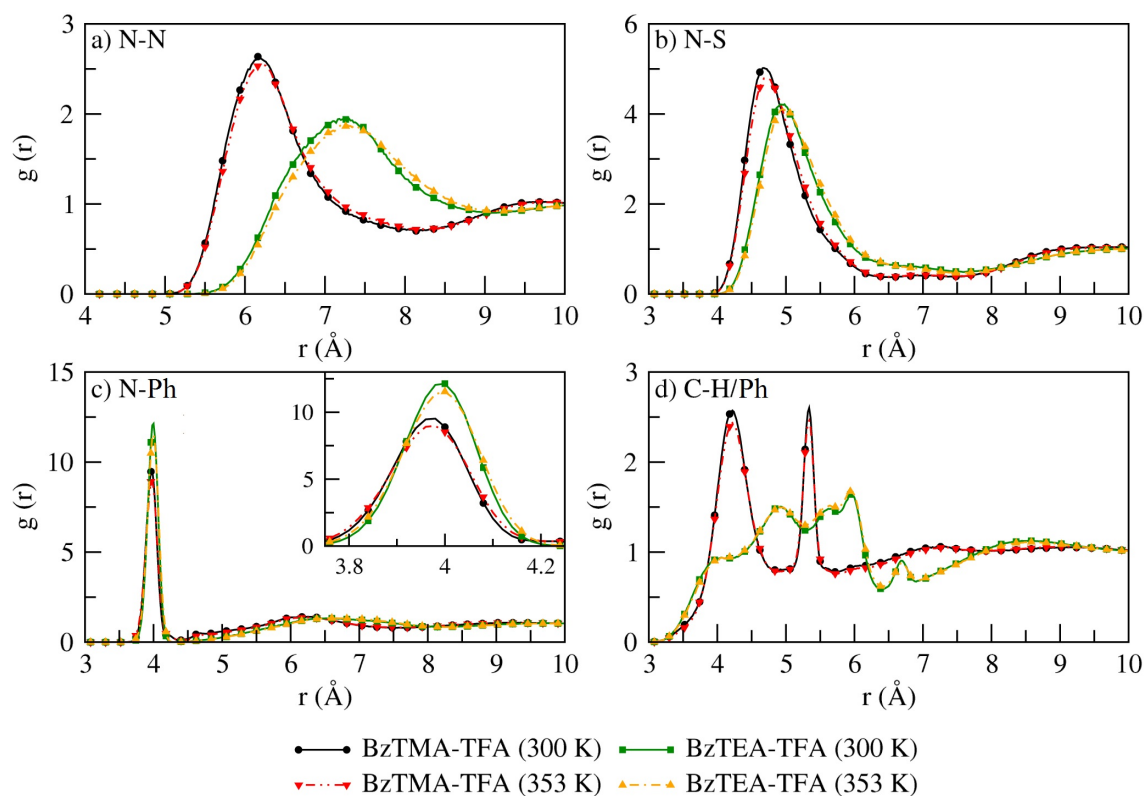


Figure 7.4: RDFs for a) N-N, b) N-S, c) N–Ph and d) C–H/Ph interactions in BzTMA-TFA and BzTEA-TFA IL.

as observed by Chang *et al.* [224]. The influence of aromatic ring (using center of mass of phenyl ring: Ph) on structure and cationic interactions is seen from the N-Ph and C-H/Ph

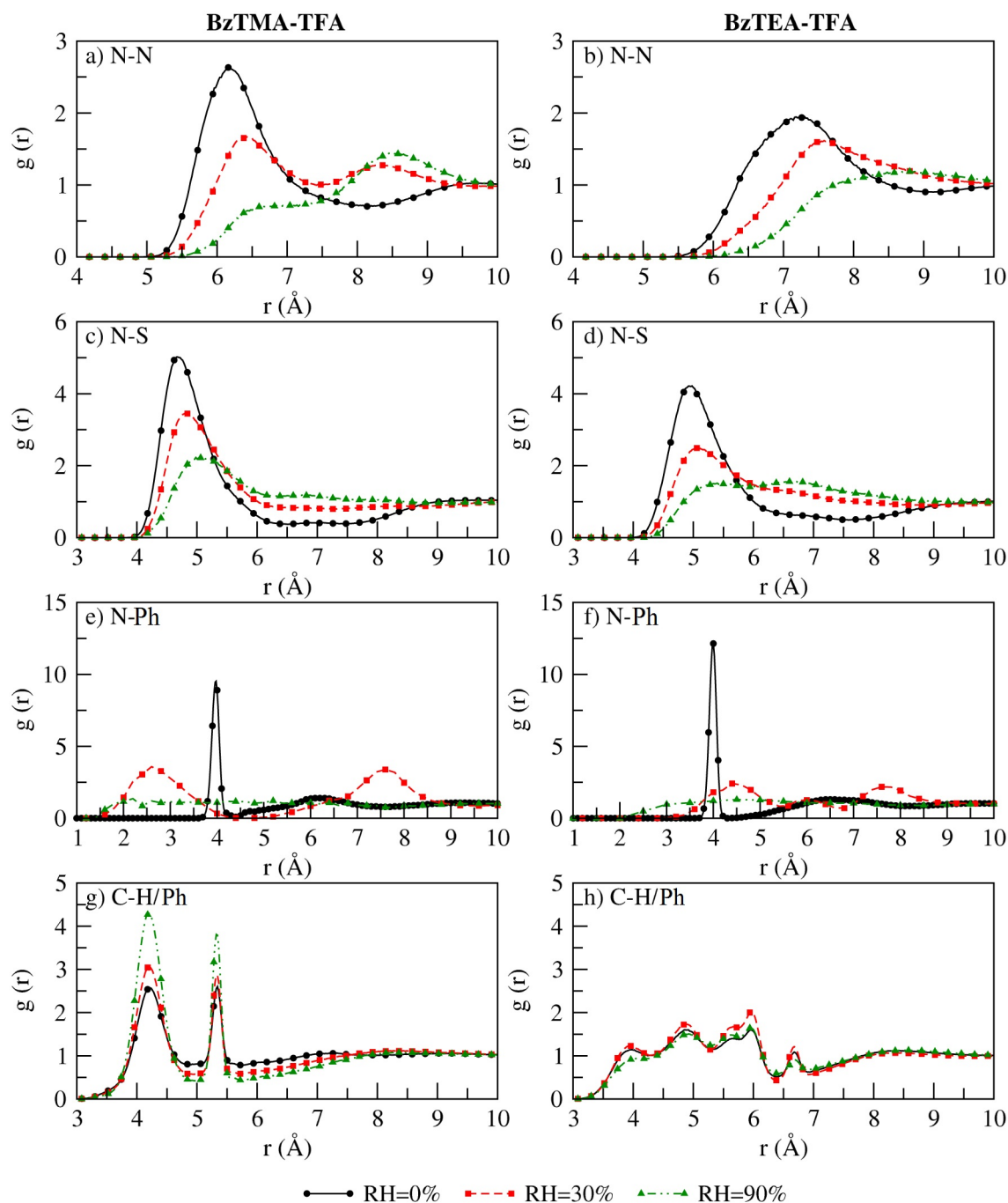


Figure 7.5: RDFs for (a, b) N-N, (c, d) N-S, (e, f) N-Ph and (g, h) C-H/ π interactions in BzTMA-TFA and BzTEA-TFA ILs at RH=0% (Neat), RH=30% and RH=90%.

RDFs. A sharp peak is seen from the N-Ph RDF (see Figure 7.4c) at 4 Å shows the presence of strong cation- π interactions [229, 231, 232]. The $d_{\text{N-Ph}}$ distance (4 Å) from the N-Ph RDF peak closely resembles the $d_{\text{N-Ph}}$ distance between the aromatic benzene ring and nitrogen atom of NMe_4^+ reported by Reddy and Sastry [233]. In BzTMA-TFA IL, a sharp intense peak at 4.2 Å (see Figure 7.4d) shows strong C-H/Ph interactions [234]. *Ab initio* calculations [235–238] have shown that dispersion contributes significantly to C-H/ π interactions. However, such interactions could not be seen in BzTEA cations due to less dispersion interactions between the terminal C-H of ethyl group and the phenyl ring. The C-H/Ph interactions completely diminish in BzTEA-TFA IL. This is because the ethyl group (compared to methyl) reduces the positive charge on the nitrogen atom. This is further examined from the inset of ^1H NMR spectra (see Figure 7.3), where the CH_2 proton of benzyl group is shielded by 0.1 δ ppm in BzTEA-TFA compare to BzTMA-TFA. For all RDF, the effect of temperature is also insignificant in both ILs. The effect of RH on anion–anion interaction is insignificant as seen from S-S RDFs (see Figure B7-5 of Appendix B). However, a significant effect of RH is observed (see Figure 7.5) for other interactions. For example, the cation–cation, cation–anion and cation–phenyl (N-Ph) interactions decrease significantly at RH=90% compared to neat RH=0% and RH=30% (see Figure 7.5a-d). The N-Ph interactions almost disappear at RH=30% and RH=90% (see Figure 7.5(e and f)). In contrast with other interactions, the effect of RH on C-H/Ph interactions shows the following trends: The peak intensity of C-H/Ph RDF increases with RH in BzTMA-TFA IL (see Figure 7.5g) which suggests hydration leads to an increase in C-H/Ph interactions. However, C-H/Ph interactions are absent at RH=90% in BzTEA-TFA IL (see Figure 7.5h).

7.4.2 C–H/Phenyl interaction and cluster analysis

The presence of C-H/Ph interactions in BzTMA-TFA IL is examined through a cluster analysis in neat IL (RH=0%). The clustering of cations and anions in IL is calculated with respect to the center of mass of a reference ion-pair using the Gromos algorithm [144] method with a cutoff distance of 10 Å. Because the neat system is completely homogeneous, the reference ion-pair can be chosen randomly from a box of ion-pairs. An orthographic view of a cluster of IL molecules is shown in Figure 7.6. A clear view of C-H/Ph interaction in BzTMA cations (see Figure 7.6), where the methyl group of other two neighboring molecules in the cluster shows weak intermolecular noncovalent interactions with the phenyl ring of center BzTMA-TFA IL molecule. As depicted in

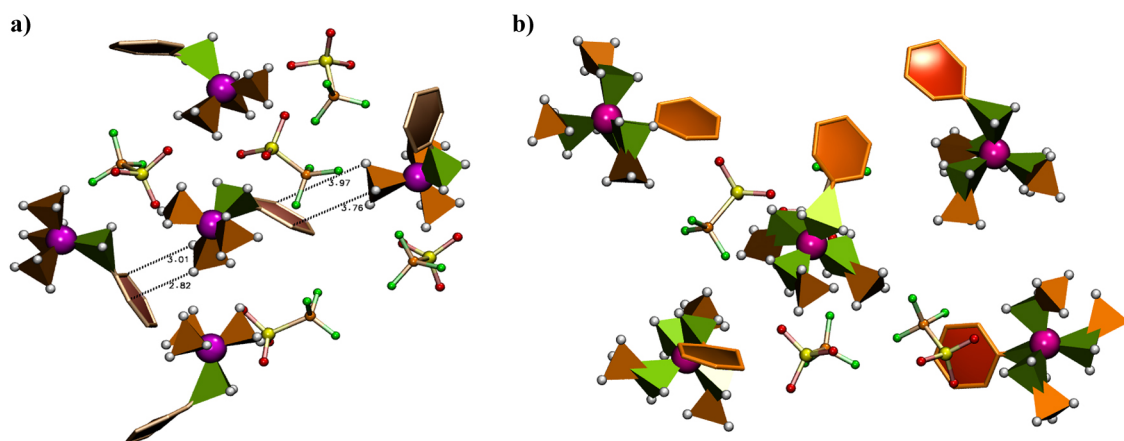


Figure 7.6: Cluster (orthographic view) of (a) BzTMA-TFA (illustrate C–H/ π interactions), and (b) BzTEA-TFA ILs respectively. [Nitrogen, CPK (magenta); CH₃, polyhedral (orange); CH₂ carbon, polyhedral (green); aliphatic hydrogen, CPK (white); aromatic ring paper chain and TFA, CPK (sulfur, yellow; oxygen, red; fluorine, green)].

7.6a, the distance between hydrogen atom of methyl group and carbon atoms of the plane of phenyl ring is less than 4 Å. However, such preferred alignment of terminal methyl group with phenyl ring is not seen in cluster of BzTEA-TFA IL (see Figure 7.6b).

The directionality and dynamic behavior of C–H/Ph interactions in the cluster of BzTMA-TFA IL is calculated from the final 0.5 ns trajectory of MD simulations at 300 K. To characterize these interactions, a second ion pair is chosen as an average structure that is system and time averaged (includes all ion pairs within the cutoff distance of 10 Å from the reference ion-pair generated by the cluster analysis described earlier). A schematic of C–H/Ph interaction in BzTMA cations between a reference ion-pair and the second ion-pair is shown in Figure 7.7a. The angle, ψ , denotes the angle formed between the plane of the phenyl ring with the H–C vector. The variation in C–H/Ph angle (ψ) and distances ($d_{\text{H-Ph}}$ and $d_{\text{C-Ph}}$) with time is shown in Figure 7.7b for three methyl hydrogen atoms (H_{a1} , H_{a2} , and H_{a3}) and methyl carbon, respectively. The $d_{\text{H-Ph}}$ distance is less than 4.0 Å for the two hydrogen atoms ($\psi = 90$ to 120°) and greater than 4.5 Å for the third hydrogen atom ($\psi < 60^\circ$) respectively. The variation in ψ and $d_{\text{H-Ph}}$ distance for methyl H-atom with time suggests that two hydrogen atoms of methyl group orient toward the phenyl ring at a time where the ψ changes with rotation of hydrogen atoms. As the angle decreases from 90 to 30° , the methyl hydrogen atom moves away from the plane of the aromatic ring. An average θ (angle between methyl carbon atom and vector perpendicular to the plane of phenyl ring) value is 35° . The average $d_{\text{C-Ph}}$ distance is 4.1 Å and is

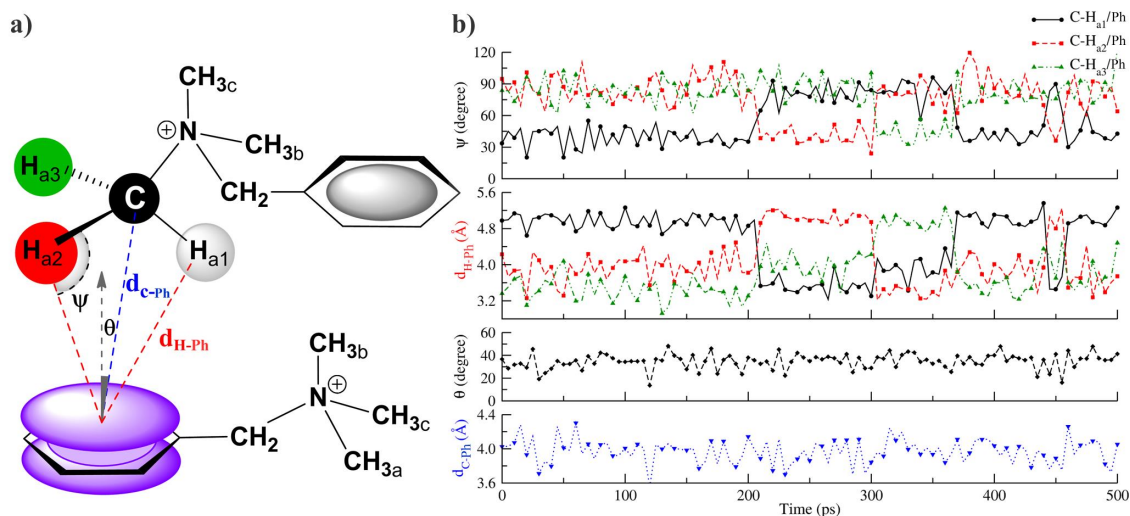


Figure 7.7: (a) Schematic representation of C–H/Ph interaction in BzTMA cations and (b) variation in C–H/Ph angle (ψ), θ and distances (d_{H-Ph} and d_{C-Ph}) calculated with time for three methyl hydrogen atoms (H_{a1} , H_{a2} and H_{a3}) and methyl carbon, respectively (where ψ , is the angle between plane of phenyl ring with the H–C vector; θ is angle between methyl carbon atom and vector perpendicular to the plane of phenyl ring).

in excellent agreement with the geometric criterion for C–H/ π interactions reported by Plevin *et al.* [234]. *Ab initio* calculations on C–H/ π interaction between hydrocarbon and benzene by Tsuzuki *et al.* [235–237] have shown that the interaction is strongest when a C–H bond of methyl group is pointing directly at the center of the π e^- cloud of aromatic ring ($\psi=180^\circ$). Plevin *et al.* [234] found that the deviation in ψ from 180° slightly reduces the interaction energy and the effect of lateral displacement of the donor group on interaction energy is minimal. The authors had concluded that a “classical XH/ π geometry ($\psi=180^\circ$) is favored”. However, the location of the carbon atom close to the π e^- cloud of phenyl ring determines the interaction energy rather than the location of the proton [234].

7.4.3 Nernst-Einstein ionic conductivity: MD Simulations

The ionic mobility of ILs (for RH = 30 and 90%) is determined from the MSD using Einstein relationship. A log MSD versus log time plot and its first derivative (denoted as β) is shown in Figure B7-6a to B7-6d of Appendix B). A value of $\beta \sim 1$ suggests diffusive behavior [207–209, 239, 240]. For all temperatures and RH = 30 and 90%, the β value is ~ 1 suggesting a diffusive regime (2 ns to 18 ns). The self-diffusion coefficients (D_A) are

calculated from the diffusive regime of MSD (see Figure B7-7 of Appendix B). However, at RH = 0%, the average β value deviates significantly from 1 and varies randomly and hence a diffusive behavior could not be achieved. In order to check if diffusive behavior exists, we performed 40 ns production run simulations at 353 K for both ILs. However, a diffusive regime could not be obtained and hence the diffusion coefficients for neat ILs cannot be calculated (see Figure B7-6e of Appendix B). The nondiffusive behavior could be due to the solid phase of the neat IL up to 353 K. At RH = 30 and 90%, the conductivity of IL is calculated from diffusion coefficient of cation and anion using Nernst-Einstein relation (see Figure 7.8). An examination of Nernst-Einstein conductivity (σ_{NE}) of IL at varying RH and temperature shows the following trends: For all temperature and RH, the σ_{NE} is slightly higher in BzTEA-TFA IL compared to BzTMA-TFA IL. For example, at 353 K and RH = 30%, the σ_{NE} of BzTEA-TFA IL is higher by a factor of 1.32 compared to the σ_{NE} of BzTMA-TFA IL. Similar trends are seen at RH = 90%. For both ILs, at all temperatures, an increase in σ_{NE} by an order of magnitude is seen from RH = 30 to 90% (see Figure 7.8). The cation–anion interactions decrease with RH and hence ionic mobility increases with RH. As expected, for all RH, the conductivity of ILs increase with temperature. The trends seen in σ_{NE} of ILs are compared by the measurement of ionic conductivity using electro-chemical impedance spectroscopy (EIS) as discussed in the next section.

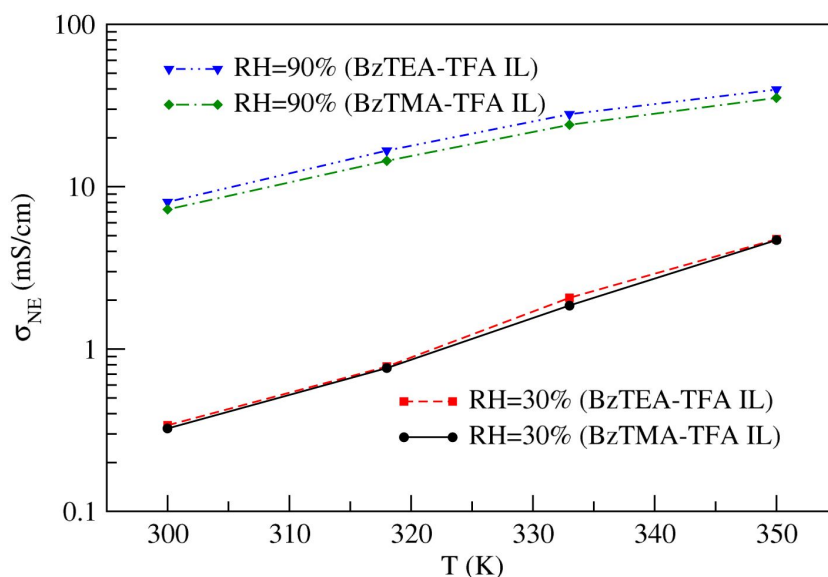


Figure 7.8: Nernst-Einstein conductivity from diffusion coefficient obtained for ammonium cation and triflate anion (at RH = 30 and 90%) of BzTMA-TFA and BzTEA-TFA ILs.

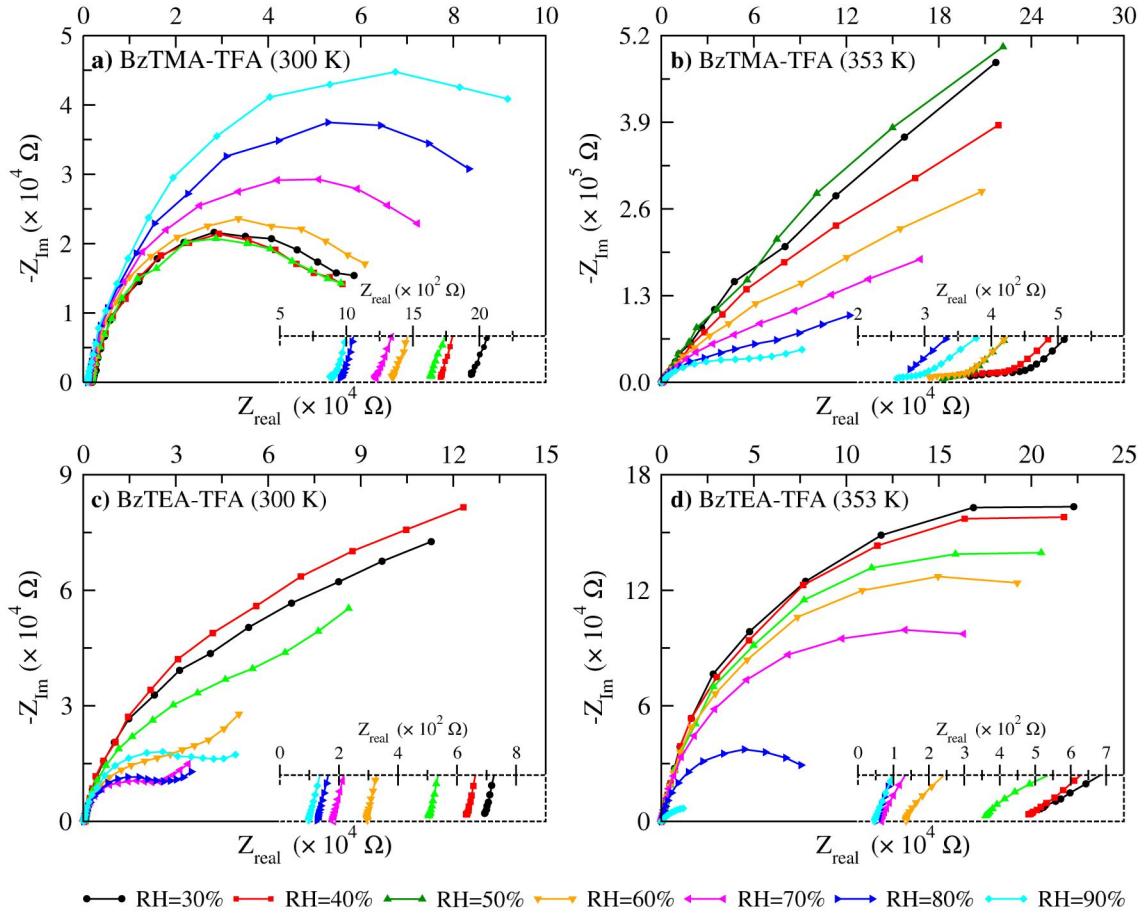


Figure 7.9: Nyquist plots for BzTMA-TFA IL at (a) 300 K, and (b) 353 K; for BzTEA-TFA IL at (c) 300 K and (d) 353 K.

7.4.4 Impedance and ionic conductivity: Electrochemical Impedance Spectroscopy

EIS measurements are performed in controlled temperature and humidity conditions. The AC impedance is measured at varying relative humidity (from 30 to 90%) and at four different temperatures 300, 318, 333, and 353 K. The frequency responses are analyzed by EC-lab software. The impedance response at 300 and 353 K for both ILs is shown as a Nyquist plot (see Figure 7.9). The Nyquist plots at 318 and 333 K are shown in Figure B7-8 of Appendix B. The obtained data from EIS closely resembles to Randles circuits of mixed kinetics and diffusion control model (see Figure 1.13b). The resistance of ILs decreases with increase in RH (RH = 30 to 90%) as seen from the high frequency intercept to the real axis of the Nyquist plot. The ionic conductivity (reciprocal of resistance) is

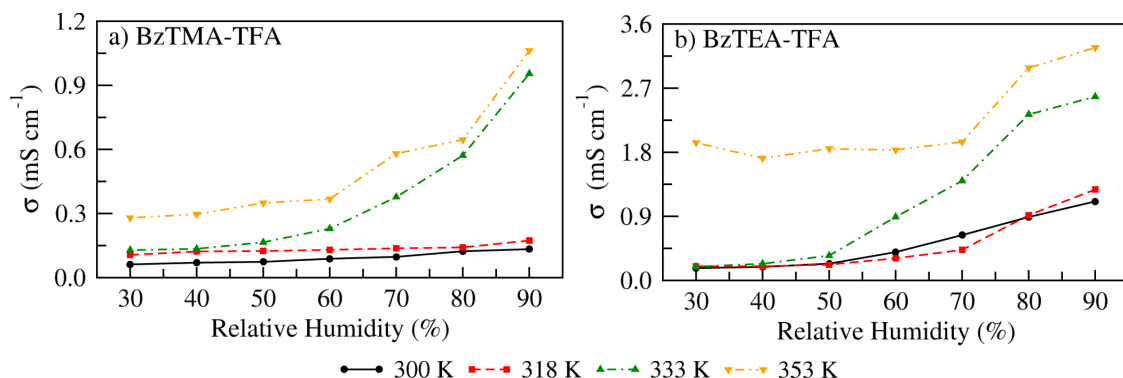


Figure 7.10: Ionic conductivity calculated from EIS for a) BzTMA-TFA and b) BzTEA-TFA ILs respectively at varying RH.

calculated from the high frequency intercept to the real axis of the Nyquist plot for each RH and temperature (see Figure 7.10). As seen, the ionic conductivity is relatively low at room temperature for both ILs. For example, the ionic conductivity is 0.06 and 0.17 mS cm⁻¹ for BzTMA-TFA and BzTEA-TFA ILs, respectively (T=300 K and RH=30%). The ionic conductivity increases with RH and temperature. At RH =90% and 353 K, the ionic conductivity of BzTEA-TFA IL is ~ 3 times higher compared to the BzTMA-TFA IL. At RH = 90%, electrostatic interactions and cationphenyl interactions are relatively very low. While, lower molecular mass should result in faster ionic diffusion in BzTMA-TFA ILs, the presence of strong CH/Ph interactions (see Figure 7.5g) in BzTMA-TFA IL limits the mobility of ions. This is consistent with the study of Tsuzuki [225] on factors controlling ionic diffusivity in ILs. For each temperature and RH, the ionic conductivity measured from EIS is lower by an order of magnitude compared to σ_{NE} from MD simulations. This could be due to solubility of solid IL with increase in RH in EIS electrode setup. The differences can also arise from the effect of partial charges on each atom in MD simulations as observed by Zhang and Maginn [78] for condensed phase simulations of ILs. The comparison of ionic conductivities and simulated diffusion coefficients is further examined from trends seen in the activation energy.

7.4.5 Activation energy

The activation energy (E_A) is calculated using an Arrhenius expression of Nernst-Einstein conductivity (σ_{NE} from simulation) and ionic conductivity (σ from EIS) (see Table 7.1). Results from MD simulations shows that increase in RH from 30 to 90% leads to a de-

Table 7.1: Activation Energy (E_A in kJ mol^{-1}) for BzTMA-TFA and BzTEA-TFA ILs, Respectively.

RH %	BzTMA-TFA		BzTEA-TFA	
	sim.	expt.	sim.	expt.
30	46.82	23.99	46.79	36.24
40		22.35		34.01
50		25.05		33.08
60		24.37		27.74
70		30.53		22.10
80		23.33		22.57
90	18.75	22.62	23.45	19.63

(see Figure B7-9 and Figure B7-10 of Appendix B)

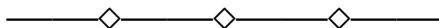
crease in E_A (σ_{NE}) by a factor of 2.4 and 2 for BzTMA-TFA and BzTEA-TFA IL, respectively. However, experiments show that the effect of RH on E_A (σ) is significant only for BzTEA-TFA IL compared to BzTMA-TFA IL. For example, the E_A (σ) of BzTEA-TFA IL decreases from $36.24 \text{ kJ mol}^{-1}$ (RH = 30%) to $19.63 \text{ kJ mol}^{-1}$ (RH = 90%). The lack of RH dependence on E_A (σ) in BzTMA-TFA IL could be due to the two probe EIS experimental setup where hydration of the solid IL may have not been uniform. However, for both ILs, at high RH (90%), the E_a from simulations and experiments are in excellent agreement (difference of $\sim 4 \text{ kJ mol}^{-1}$). However, at low RH, the differences in activation energy are significant. This difference could be due to a complex temperature dependence (solvation of cations, anions, water network formation) [241] of ion pair domain formation (between simulations and experiment) for each RH.

7.5 Conclusions

A molecular understanding of structural relation of electrostatic, cation–phenyl and the C–H/Ph interactions with dynamics in BzTMA-TFA and BzTEA-TFA ILs is presented in this chapter using MD simulation and electro-chemical impedance spectroscopy. In neat BzTMA-TFA IL, strong electrostatic (cation–cation, cation–anion and anion–anion) interactions are seen compared to BzTEA-TFA IL. The C–H/Ph interactions exist in BzTMA cation, where two hydrogen atoms of any CH_3 group weak noncovalent interaction with a phenyl ring. The C–H/Ph angle (ψ) fluctuates around 90 to 120° ($d_{\text{H-Ph}} < 4.0 \text{ \AA}$) for two hydrogen atoms and around 30° ($d_{\text{H-Ph}}$ distances $> 4.5 \text{ \AA}$) for third hydrogen where the ψ changes with rotation hydrogen atoms. As the angle varies from 30 to 90°

or higher, the methyl hydrogen atom in BzTMA moves closer to the aromatic ring. However, the C–H/Ph interactions diminish in the BzTEA-TFA IL completely due to the more positive-induced influence of ethyl group on the nitrogen atom. Except for C–H/Ph interaction, the cation–cation, cation–anion, anion–anion, and cation–phenyl interactions decrease with RH [242].

The TGA of BzTMA-TFA and BzTEA-TFA ILs shows thermal stability up to 600 K and is similar to the thermal stability study of [218] on trioctylammonium triflate or triphenylammonium triflate ILs. The EIS experiments show excellent ionic conductivity of 1.06 mS cm^{-1} (BzTMA-TFA) and 3.27 mS cm^{-1} (BzTEA-TFA), respectively ($T=353 \text{ K}$ for $\text{RH} = 90\%$). A molecular level understanding of structural and dynamical properties of these ILs from simulations and experiments can facilitate the design of novel protic and aprotic ILs for various technological applications. The role of cationic asymmetry and N–H or N–H/ π interactions in protic ILs can be the focus of future activities and is discussed in the next chapter.



Chapter 8

Summary

8.1 Conclusions

In this thesis, classical MD simulations were employed to characterize the nanostructure and dynamics of molecular transport in PFSA and ABPBI fuel cell membranes, and ammonium based aprotic ILs. The salient features of thesis are as follows:

- ❖ The sulfonate group (a functional group of PFSA membranes) plays a key role in proton conduction. The increase in hydration results in lower sulfonate-hydronium electrostatic interactions and increases water solvation around the triflate ions and hydronium ions. Thus increasing hydration leads to an increase in diffusion of triflate ions, hydronium ions and water molecules which shows that water molecules play a significant role in the mobility of triflate and hydronium ions.
- ❖ The elastic deformation due to pendant chain length contraction in the Nafion side chain pendant leads to a hydrosphere region at $\lambda \geq 9$. This is a spherical region of strongly bound hydronium ions and 5 to 6 water molecules. This form of the segregated nanostructure could disturb the connectivity of water nano-channels in Nafion pendant-water mixtures, which could affect proton conductivity at higher hydration.
- ❖ The presence of a rigid pendant side chain in Aciplex results in certain differences with the structure and dynamics of Nafion. The simulations shows the following differences:
 - The structural comparison (at 300 K and 350 K) shows that the influence of temperature is negligible on the pendant side chain nanostructure of the hydrated Aciplex membrane.

- The strong interactions between the sulfonate groups (within a large solvation shell of 4-8 Å) in Aciplex arise predominantly from inter-chain interactions.
 - A significant increase in the mobility of water molecules (at $\lambda \geq 9$) is observed in the Aciplex membrane due to enlarged hydrophobic domains assisted by the rigid pendant side chain of the Aciplex ionomer compared to Nafion.
- ❖ A molecular study of phosphoric acid and triflic acid doped hydrated ABPBI polymer membranes show that the interactions in the membrane remains invariant with hydration and choice of blend (ABPBI+PA, ABPBI+TFA and ABPBI+PA+TFA). The increase in interactions between the ABPBI membrane and water in the presence of TFA leads to a significant decrease in water mobility. The simulations predict ABPBI+PA+TFA blend to be a better choice in reducing the leaching of PA from the membrane.
 - ❖ The determination of shear viscosity of SPC/E water from EMD and NEMD simulations suggests that the shear viscosities calculated using the transverse current autocorrelation method from EMD simulations vary significantly with coupling time and system size. The Nose'-Hoover thermostat having excellent thermodynamic stability for NEMD simulations can be considered as a superior choice for accurate determination of shear viscosity.
 - ❖ An atomistic simulation and experimental study on BzTMA-TFA and BzTEA-TFA ILs shows that electrostatic, cation-phenyl and C-H/Ph interactions strongly influence the dynamics at varying RH and temperature. Except for C-H/Ph interaction, the cation-cation, cation-anion, cation-phenyl and anion-anion interactions decrease with RH. At RH=90%, the presence of strong inter-molecular C-H/Ph interaction results in lower ionic conductivity of BzTMA-TFA IL (MD simulations and EIS experiment) compared to BzTEA-TFA IL.

The structural and dynamical properties calculated from classical MD simulations (in this thesis) can validate existing experimental work and can inspire further experimental investigations on PEMs. The structural and dynamical properties (obtained from simulations) like RDFs, structure factors, scattering intensities, radius of gyration, water-acid clustering, diffusion coefficients and activation energy of PEMs provides a molecular level understanding and will be useful for the development of next generation PEMs. Finally, an application of *ab initio* MD [243] and reactive MD simulations [68, 130] will provide additional insights in the characterization of proton transport in PEMs and can be one of the focus of future activities.

8.2 Future directions

A molecular level understanding of structural and dynamical properties of IL doped polymer membranes from simulations and experiments can facilitate the development of non-aqueous composite PEM for high temperature fuel cell applications. For example, Nafion doped with proton-conducting ionic liquids (PCILs) have shown improved thermal and mechanical properties and an increased range of operating temperatures compared to Nafion 117 [220–223]. The proposed work aim to investigate the influence of fuel cell operating conditions on properties of ILs and IL doped polymer membrane. Specifically, the effect of cationic and anionic species of the ILs on structural property of the PEMs, electrode interface and proton transport will also be investigated. The objectives of proposed work are summarized as follows:

8.2.1 Cation asymmetry and N–H/ π interactions

Macfarlane *et al.* [202], Bai *et al.* [204] and Angell *et al.* [210] observed excellent proton conductivity in various PCILs. Among various PCILs, the ammonium based protic and aprotic ILs are considered as fuel cell electrolytes due to their easy preparation, low cost, performance, excellent thermal stability and ionic conductivity [214–217, 219]. The role of cationic asymmetry (see Figure 8.1) and N–H or N–H/ π interactions in protic ILs in the design of novel protic ILs for various technological applications (fuel cells, batteries etc.) can be the focus of future activities.

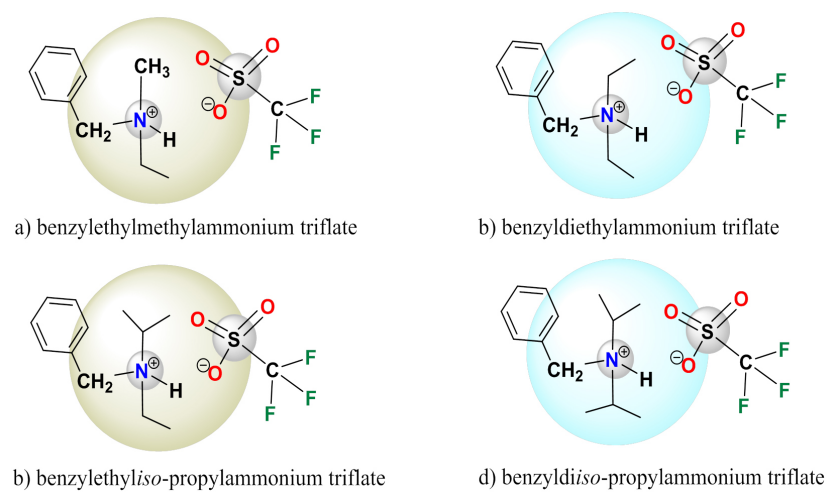


Figure 8.1: Asymmetric protic ILs of ammonium triflate.

8.2.2 Replacement of -N atom by -P atom

Luo *et al.* [218] examined proton conductivity of ammonium triflate and phosphonium triflate ILs using large bulky group on cation (trioctyl and triphenyl). The authors observed excellent thermal stability (>600 K) in all the ILs. The proton conductivity in phosphorus based cations is higher compared to ammonium based cations. The effect of replacement of -N atom by -P atom (see Figure 8.2) on proton transfer can be also investigated.

8.2.3 Replacement of -Ph by -BI unit

The replacement of phenyl group (-Ph) in the BzTEA⁺ cation by benzimidazole unit (see Figure 8.2) can be a possible proton conducting medium in PA doped PEMs. The proton transfer mechanism in such aprotic ILs can lead to development of high temperature PEM.

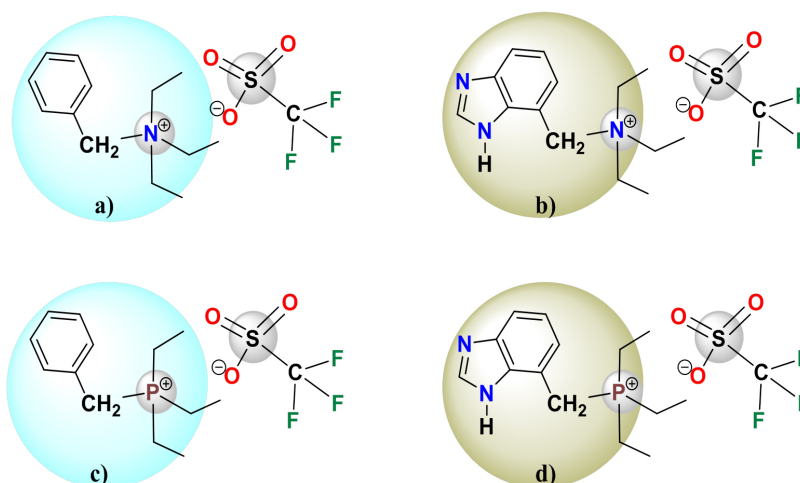


Figure 8.2: a, b) Ammonium triflate and c, d) phosphonium triflate ILs with phenyl and benzimidazole group.

The characterization of structural diffusion of protons in these ILs can be performed using AIMD methods. Such a study can provide further insights on the mechanism of proton transfer in IL and IL doped polymer membranes.

8.2.4 Interaction of ILs at electrode interface

A molecular understanding of the electro-catalytic processes such electro-oxidation of ammonia at the Pt(100), Pt(111) and Pt(110) in alkaline solution interface (see Figure

8.3) has been studied by Skachkov *et al.* [244]. The authors employed AIMD and DFT to probe the mechanistic details of ammonia electro-oxidation on the metal surface. The authors found that the strongly adsorbed $N_{\text{(hollow)}}$ (nitrogen atom without any hydrogen bonding with water molecules) leads to catalytic inactivity of the Pt(111) and Pt(110) surfaces. The hollow sites of both Pt(111) and Pt(110) surfaces strongly bind with the nitrogen atoms which results in high activation barrier for dimerization of $N_{\text{(hollow)}}$.

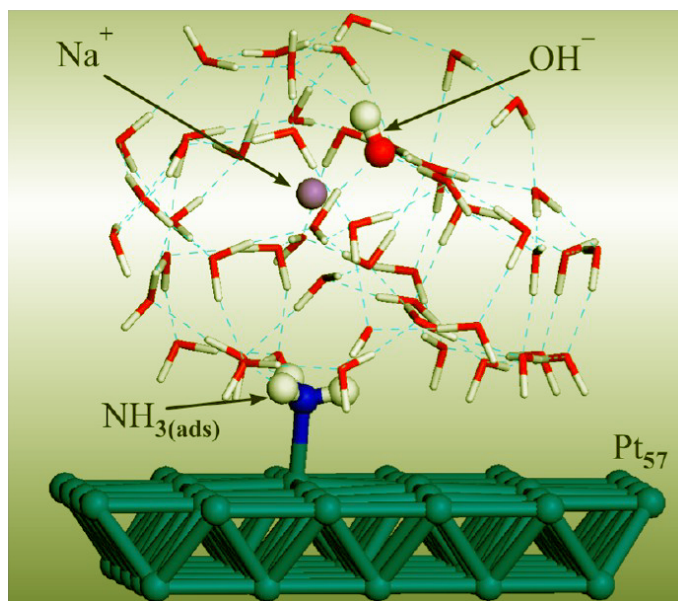
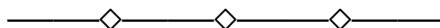


Figure 8.3: $Pt_{57}(100)$ cluster with adsorbed NH_3 in NaOH alkaline solution (Adapted from Skachkov *et al.* [244] Copyright 2013 American Chemical Society).

The interactions of various protic/aprotic ILs at the Pt electrode interface and influence on catalytic activity in the presence of IL have not been examined at a molecular level. Thus, a molecular understanding of various electro-catalytic processes at the electrode interface in the presence of ammonium/phosphonium based ILs is required to examine the metal surface catalytic activity and its relationship with proton transport in aqueous and non-aqueous medium.



Appendix A

Table A2-1: Force-field parameters of triflic acid.

Atom	q	σ (nm)	ε (kJ mol ⁻¹)			
C	+0.36 ^a	0.350	0.276144			
F	-0.12 ^a	0.295	0.221752			
S	+1.31 ^b	0.355	1.406000			
O _S	-0.58 ^b	0.300	0.711280			
H	+0.45 ^b	0.010	0.010000			
O _Y	-0.61 ^b	0.296	0.711280			
O _Y	-0.57 ^b	0.296	0.711280			
Bond ^a	r ₀ (nm)	k _b (kJ mol ⁻¹ nm ⁻²)				
C–F	0.1332	307105.6				
C–S	0.1810	185769.6				
S–O _S	0.1630	251040.0				
S–O _Y	0.1440	585760.0				
O _S –H	0.0945	462750.4				
Bond angle ^a	θ_0 (deg)	k $_{\theta}$ (kJ mol ⁻¹ rad ⁻²)				
F–C–F	109.1	644.336				
F–C–S	109.5	418.400				
C–S–O _S	98.9 (98.5 ^c)	619.232				
C–S–O _Y	108.9	619.232				
O _S –S–O _Y	119.0	870.272				
S–O _S –H	109.5	397.480				
Dihedral angle	Dihedral coefficients (kJ mol ⁻¹)					
	C ₀	C ₁	C ₂	C ₃	C ₄	C ₅
F–C–S–O _S ^d	0.2212	0.3525	0.1215	0.2976	13.7695	-12.5714
C–S–O _S –H ^e	22.5285	-8.5186	-32.1323	3.0103	15.1122	0.0

^aOPLS parameters, ^bCHELPG charges, ^cRef.: Gejji et al. [94], ^dDihedral function (see Eqn. 2.1), ^eRyckert-Bellemans function (see Eqn. 2.3)

Table A2-2: Force-field parameters of triflate ion.

Atom	q	σ (nm)	ε (kJ mol ⁻¹)			
C	+0.36 ^a	0.350	0.276144			
F	-0.12 ^a	0.295	0.221752			
S	+1.37 ^b	0.355	1.406000			
O _T	-0.79 ^b	0.296	0.711280			
Bond ^a	r ₀ (nm)	k _b (kJ mol ⁻¹ nm ⁻²)				
C–F	0.1332	307105.6				
C–S	0.1810	185769.6				
S–O _T	0.1440	585760.0				
Bond angle ^a	θ_0 (deg)	k _{θ} (kJ mol ⁻¹ rad ⁻²)				
F–C–F	109.1	644.336				
F–C–S	109.5	418.400				
C–S–O _T	119.0	870.272				
O _T –S–O _T	119.0	870.272				
S–O _S –H	119.0	870.272				
Dihedral angle	Dihedral coefficients (kJ mol ⁻¹)					
	C ₀	C ₁	C ₂	C ₃	C ₄	C ₅
F–C–S–O _T ^c	-0.1267	3.0979	-0.1352	0.6067	17.0603	-12.5664
^a OPLS parameters, ^b CHELP charges, and ^c Dihedral function (see Eqn. 2.1)						

^aOPLS parameters, ^bCHELPG charges, and ^cDihedral function (see Eqn. 2.1)

Table A3-1: Force-field parameters of side chain of PFSA polymer electrolyte membranes.

Atom	σ (nm)	ε (kJ mol ⁻¹)				
C	0.350	0.276144				
F	0.295	0.221752				
S	0.355	1.406000				
O	0.300	0.711280				
O	0.296	0.711280				
Bond	r_0 (nm)	k_b (kJ mol ⁻¹ nm ⁻²)				
C–F	0.1332	307105.6				
C–C	0.1529	224262.4				
C–O	0.1410	267776.0				
C–S	0.1810	185769.6				
S–O	0.1440	585760.0				
Bond angle	θ_0 (deg)	k_θ (kJ mol ⁻¹ rad ⁻²)				
F–C–F	109.1	644.336				
F–C–S	109.5	418.400				
F–C–C	109.5	418.400				
F–C–O	109.8	425.000				
C–C–C	112.5	488.273				
C–C–O	109.5	418.400				
C–O–C	116.9	694.544				
C–S–O	108.9	619.232				
O–S–O ^a	119.0	870.272				
Dihedral angle	Dihedral coefficients (kJ mol ⁻¹)					
	C ₀	C ₁	C ₂	C ₃	C ₄	C ₅
C–C–C–F ^b	0.2460	-0.3285	0.5831	1.8585	7.4668	0.3716
F–C–C–F ^b	0.7084	0.6226	0.9997	0.3564	14.9016	-6.1012
F–C–C–O ^b	0.1936	1.0729	0.6616	1.9442	12.1706	-6.6721
C–C–S–O ^b	-0.5741	1.0065	-0.5901	0.9551	11.2104	-0.0044
C–C–O–C ^c	47.1740	-44.0367	1.7176	-6.8656	0.0	0.0
F–C–O–C ^c	45.1736	46.0834	3.0942	-159.279	0.0	0.0
^a Sunda et al. [123], ^b Dihedral function (see Eqn. 3.1), ^c Dihedral function (see Eqn. 3.2)						

^aSunda et al. [123], ^bDihedral function (see Eqn. 3.1), ^cDihedral function (see Eqn. 3.2)

Table A3-2: Box length (l) and density (ρ) obtained from 10 ns equilibration of side chain pendant-water mixtures of Dow, Aciplex and Nafion at 300 K.

λ	Dow		Aciplex		Nafion	
	l (Å)	ρ (g cm ⁻³)	l (Å)	ρ (g cm ⁻³)	l (Å)	ρ (g cm ⁻³)
3	60.550	1.680	66.089	1.736	66.670	1.732
6	64.392	1.563	69.521	1.634	69.904	1.636
9	67.975	1.479	72.502	1.559	72.917	1.565
12	71.003	1.419	75.209	1.497	75.632	1.503
15	74.062	1.370	77.896	1.448	78.290	1.451

Table A3-3: Box length (l) and density (ρ) obtained from 10 ns equilibration of side chain pendant-water mixtures of Dow, Aciplex and Nafion at 350 K.

λ	Dow		Aciplex		Nafion	
	l (Å)	ρ (g cm ⁻³)	l (Å)	ρ (g cm ⁻³)	l (Å)	ρ (g cm ⁻³)
3	61.643	1.590	67.461	1.631	66.841	1.632
6	65.646	1.483	70.682	1.545	71.507	1.550
9	69.003	1.407	73.865	1.468	74.208	1.479
12	72.373	1.353	76.952	1.408	76.914	1.424
15	75.181	1.309	79.173	1.376	79.667	1.380

Table A3-4: Diffusion Coefficient ($D_A \times 10^{-5}$ cm² sec⁻¹) of H₃O⁺ obtained from 20 ns production run of side chain pendant-water mixtures.

Pendant	Temp. (K)	$\lambda=3$	$\lambda=3$	$\lambda=9$	$\lambda=12$	$\lambda=15$
Dow	300	0.0323	0.1303	0.2401	0.3570	0.4599
	320	0.0590	0.2632	0.4880	0.5764	0.6811
	335	0.1124	0.3265	0.5861	0.8042	1.0104
	350	0.1568	0.5141	0.8326	1.1348	1.1939
Aciplex	300	0.0175	0.0979	0.1824	0.2858	0.3193
	320	0.0339	0.1699	0.3196	0.4579	0.5662
	335	0.0548	0.2302	0.4456	0.6083	0.7930
	350	0.0988	0.3457	0.6385	0.8899	0.9414
Nafion	300	0.0180	0.0751	0.1430	0.2193	0.2275
	320	0.0361	0.1286	0.2470	0.3110	0.4674
	335	0.0537	0.2054	0.3720	0.4706	0.5298
	350	0.0774	0.2812	0.4665	0.5820	0.7540

Table A3-5: Diffusion Coefficient ($D_A \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$) of water molecules obtained from 20 ns production run of side chain pendant-water mixtures.

Pendant	Temp. (K)	$\lambda=3$	$\lambda=3$	$\lambda=9$	$\lambda=12$	$\lambda=15$
Dow	300	0.2097	0.5201	0.8542	1.0739	1.2662
	320	0.3580	0.8606	1.3120	1.6571	1.9425
	335	0.5562	1.2149	1.7907	2.2278	2.5225
	350	0.7354	1.6351	2.2614	2.8246	3.1875
Aciplex	300	0.1220	0.4545	0.7081	0.9467	1.1004
	320	0.2319	0.7165	1.1305	1.4255	1.7134
	335	0.3650	0.9167	1.4267	1.8755	2.2655
	350	0.5248	1.2890	1.8975	2.4173	2.8161
Nafion	300	0.1380	0.3978	0.6520	0.9626	1.1158
	320	0.2392	0.5713	1.0210	1.3198	1.6121
	335	0.3860	0.8935	1.4253	1.7164	2.0581
	350	0.5040	1.1295	1.8252	2.2710	2.5097

Table A3-6: Activation energy of diffusion (E_A in kJ mol^{-1}) calculated from diffusion coefficients in side chain pendant-water mixtures.

λ	E_A of H_3O^+			E_A of water		
	Dow	Aciplex	Nafion	Dow	Aciplex	Nafion
3	28.414	29.778	25.420	22.289	25.620	23.147
6	23.100	21.613	23.414	20.044	17.829	18.801
9	21.050	21.684	21.084	17.148	16.958	18.145
12	20.068	19.454	17.589	16.975	16.350	14.881
15	17.265	19.250	20.074	16.115	16.502	14.217

Table A5-1: The system size, No. of PA molecules (N_{PA}), No. of TFA molecules (N_{TFA}), No. of water molecules (N_{water}), Box length (l), average density (ρ), end-to-end polymer chain distance ($R_{\text{E-E}}$), radius of gyration (R_g) and Diffusion coefficients ($D_A \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$) of PA, hydronium ions, TFA and water molecules in hydrated ($\lambda=3$) ABPBI+PA+TFA blend.

System	[ABPBI+PA+TFA] ^a	[ABPBI+PA+TFA] ^b
Total No. of atoms	45568	91008
N_{PA}	1280	2560
N_{TFA}	1280	2560
N_{water}	3840	7680
l (Å)	80.5541	101.6332
ρ (g cm^{-3})	1.5369 ± 0.0022	1.5301 ± 0.0022
$R_{\text{E-E}}$ (Å)	29.1042 ± 11.2577	20.2490 ± 9.2409
R_g (Å)	11.8469 ± 1.9312	11.9717 ± 1.2403
$R_{\text{E-E}}/R_g$	2.45	1.69
D_A of PA	0.0217 ± 0.0002	0.0191 ± 0.0008
D_A of H_3O^+	0.0655 ± 0.0001	0.0767 ± 0.0005
D_A of TFA	0.0232 ± 0.0002	0.0267 ± 0.0017
D_A of water	0.2792 ± 0.0085	0.3098 ± 0.0133
^a (polymer chain from 10 monomers units), ^b (polymer chain from 20 monomers units)		

Table A5-2: Co-ordination number calculated using the first minima (in parenthesis) from interactions in hydrated ($\lambda=3$) ABPBI + PA + TFA blend.

Polymer chain length	N–N (5.8 Å)	N–N _H (3.6 Å)	N–H _N (3.2 Å)	H _N –O _w (2.6 Å)
n=10	2.56	0.41	0.41	0.22
n=20	2.60	0.39	0.39	0.24

Table A7-1: Number of water molecules (N_{water}), box length (l) and average density (ρ) of ILs (obtained from last 5 ns of equilibration of MD simulations).

RH		BzTMA-TFA		BzTEA-TFA	
(wt%)		300 K	350 K	300 K	350 K
0	N_{water}	-	-	-	-
	l (Å)	57.97	58.13	61.68	62.10
	ρ (g cm ⁻³)	1.295	1.283	1.237	1.211
30	N_{water}	2023	2039	2437	2487
	l (Å)	62.53	63.20	66.62	67.51
	ρ (g cm ⁻³)	1.282	1.245	1.218	1.181
90	N_{water}	6069	6118	7312	7460
	l (Å)	71.26	72.32	75.93	77.27
	ρ (g cm ⁻³)	1.202	1.147	1.162	1.111

Appendix B

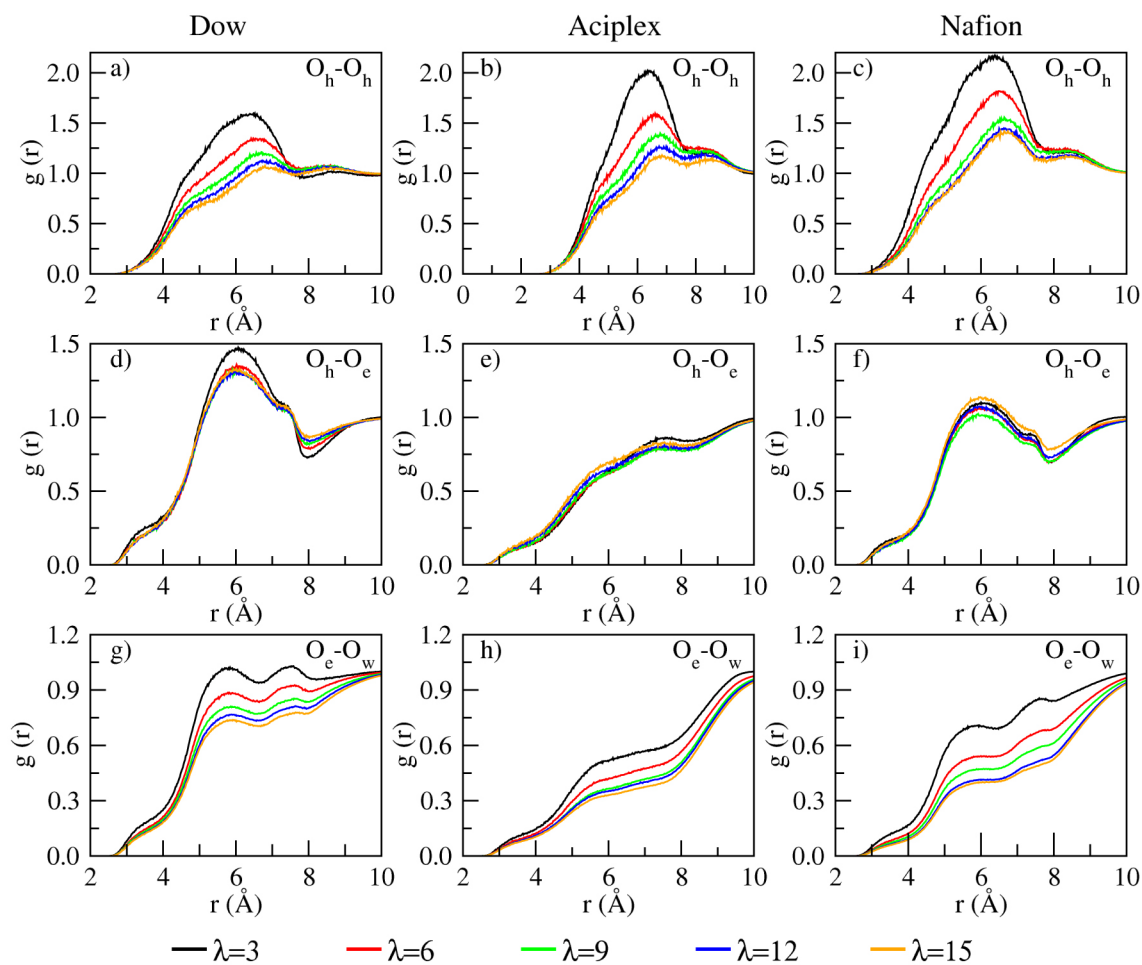


Figure B3-1: RDFs of side chain pendant-water mixtures for (a-c) O_h-O_h , (d-f) O_h-O_e and (g-i) O_e-O_w at 350 K.

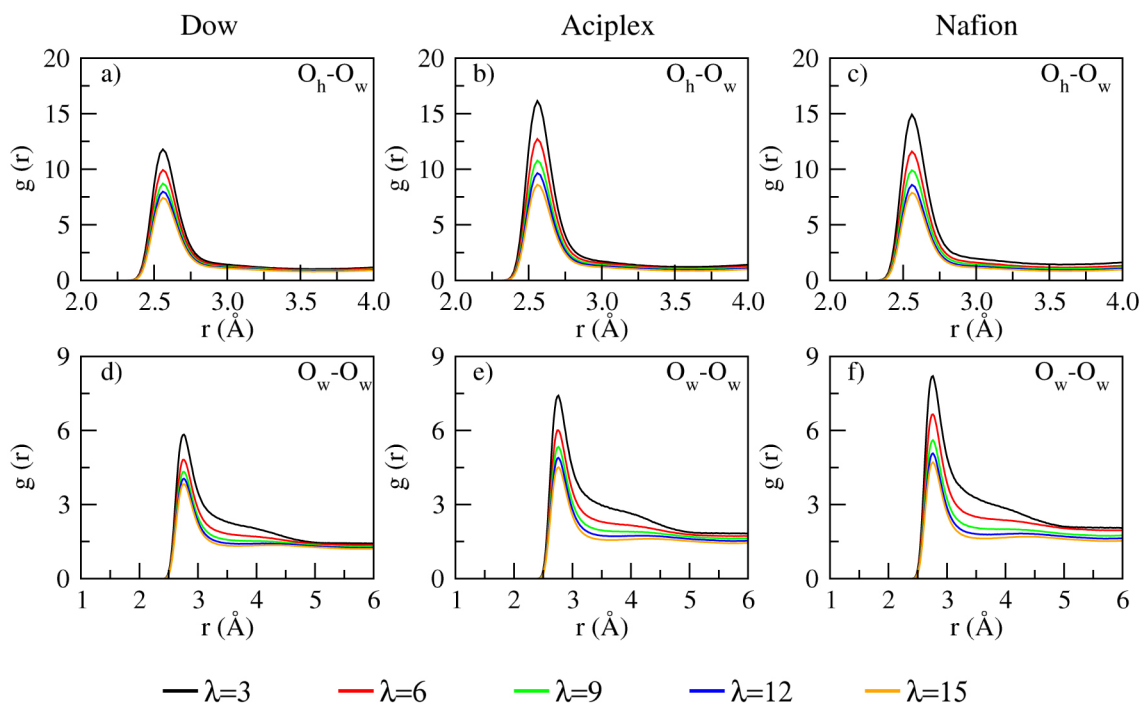


Figure B3-2: RDFs of side chain pendant-water mixtures for (a-c) O_h-O_w and (d-f) O_w-O_w at 350 K.

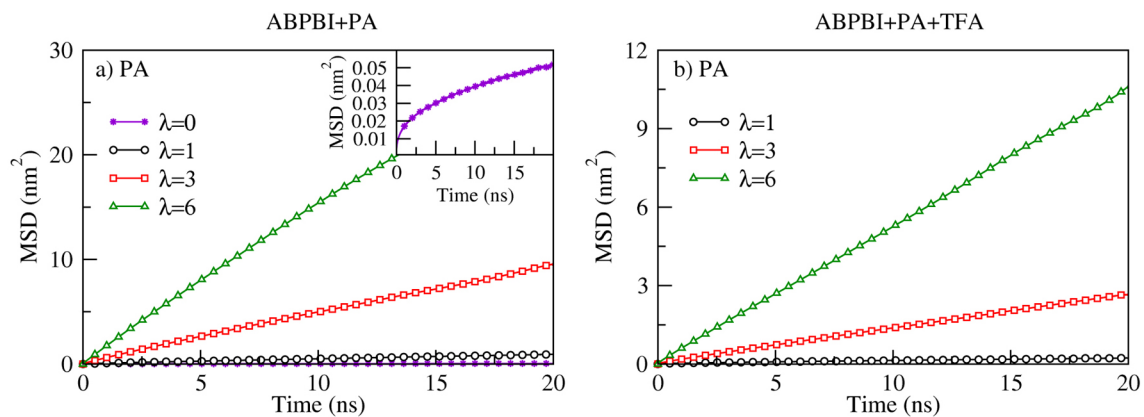


Figure B5-1: Mean Square Displacement of phosphoric acid(PA).

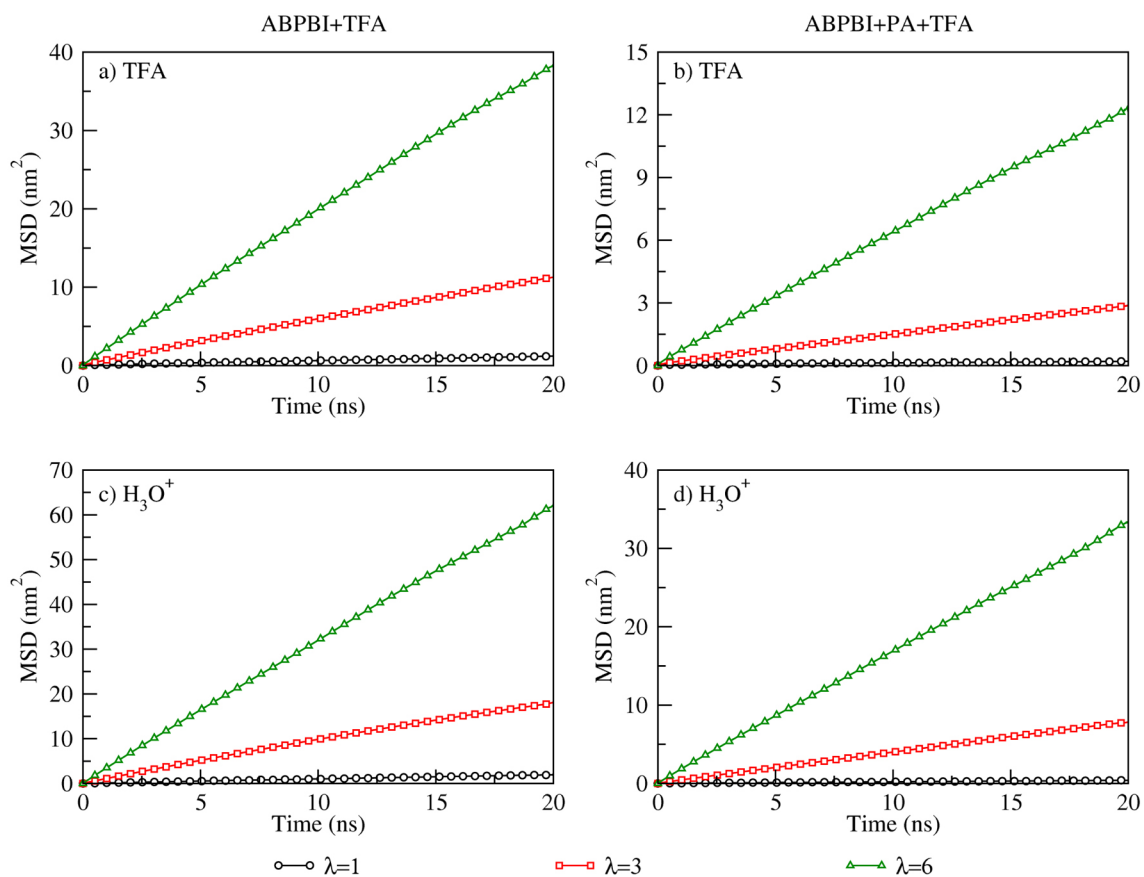


Figure B5-2: Mean Square Displacement of (a, b) TFA (CF_3SO_3^-) and (c, d) hydronium ions (H_3O^+).

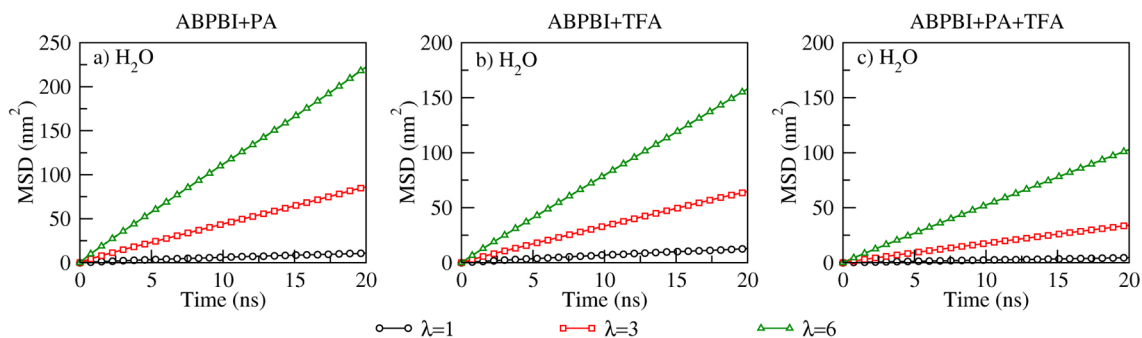


Figure B5-3: Mean Square Displacement of water molecules.

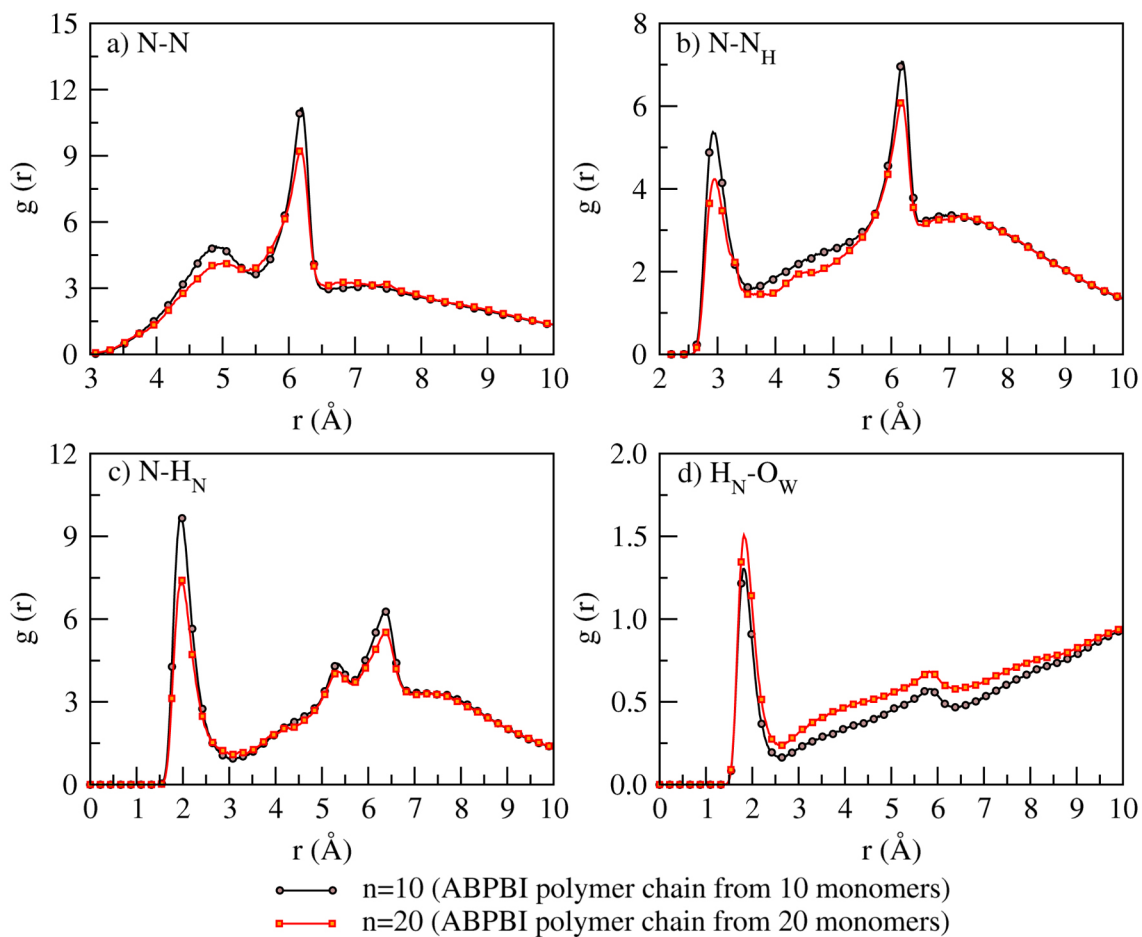


Figure B5-4: RDFs of a) N-N, b) N-N_H, c) N-H_N and d) H_N-O_w in hydrated ($\lambda=3$) ABPBI + PA + TFA blend.

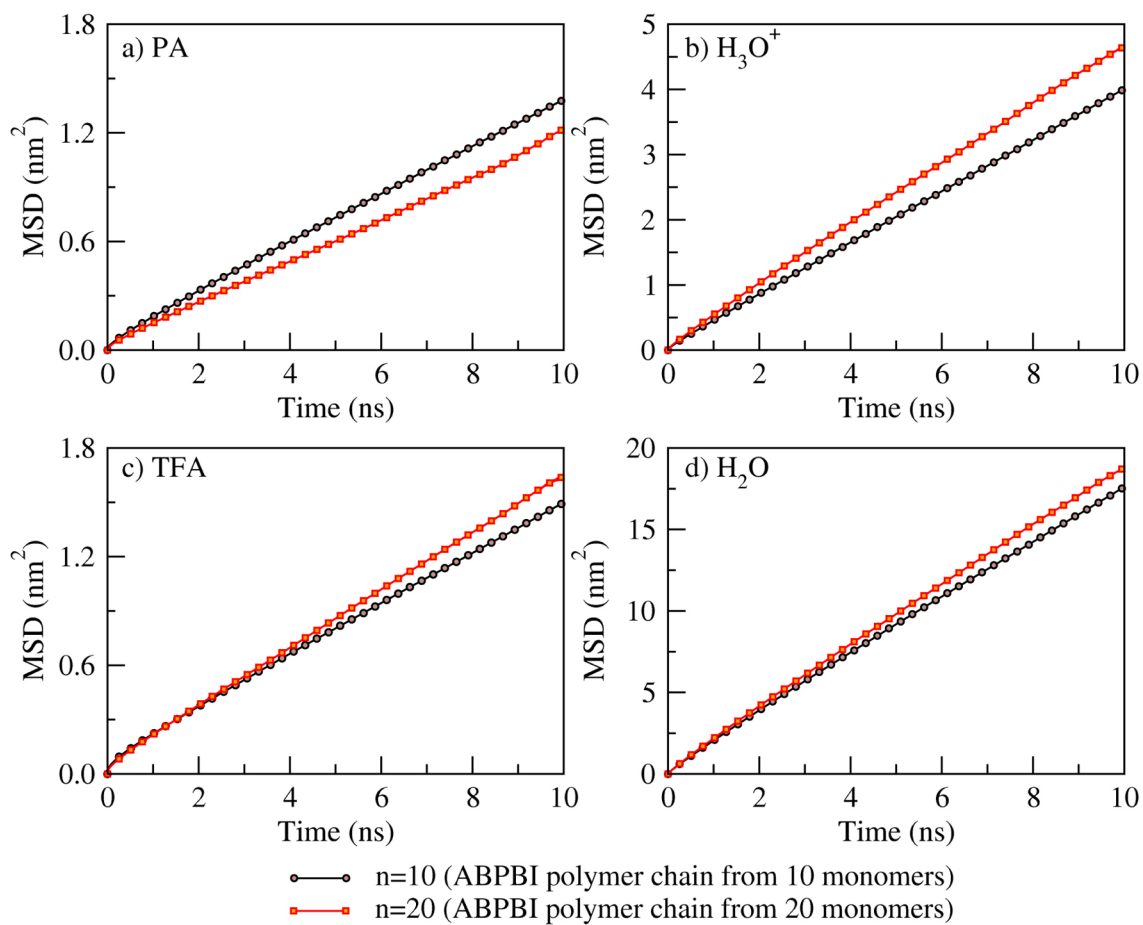


Figure B5-5: Mean Square Displacement of (a) PA, (b) hydronium ions, (c) TFA, and (d) water from hydrated ($\lambda=3$) ABPBI+ PA + TFA blend.

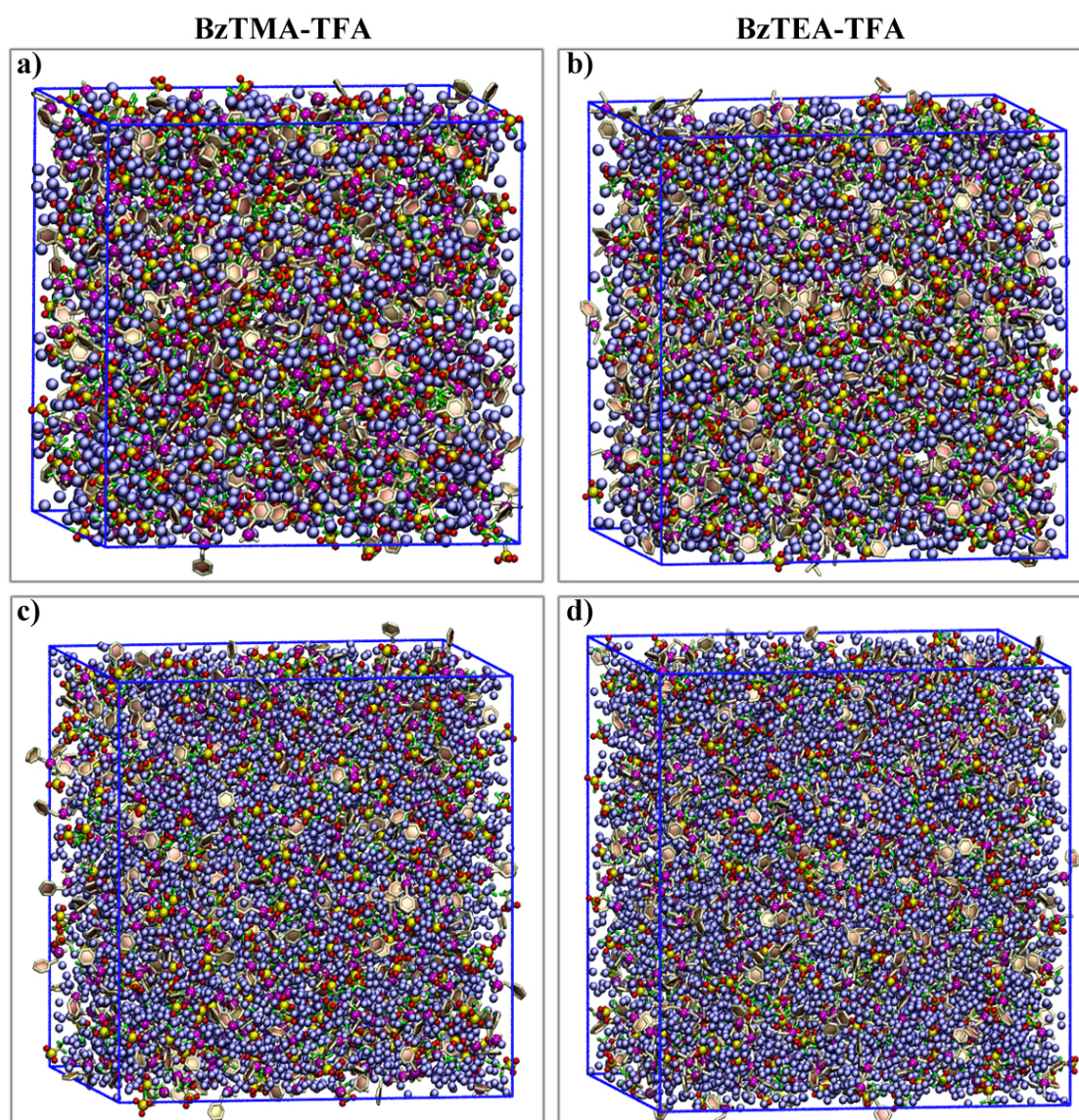


Figure B7-1: Snapshots of hydrated BzTMA-TFA and BzTEA-TFA ILs at (a and b) RH=30% and (c and d) RH=90% at 300 K. [Nitrogen: magenta (CPK); phenyl ring: white (paper chain); sulfonate group: yellow and red (CPK); fluorine: green (Licorice) and water molecules: blue beads]

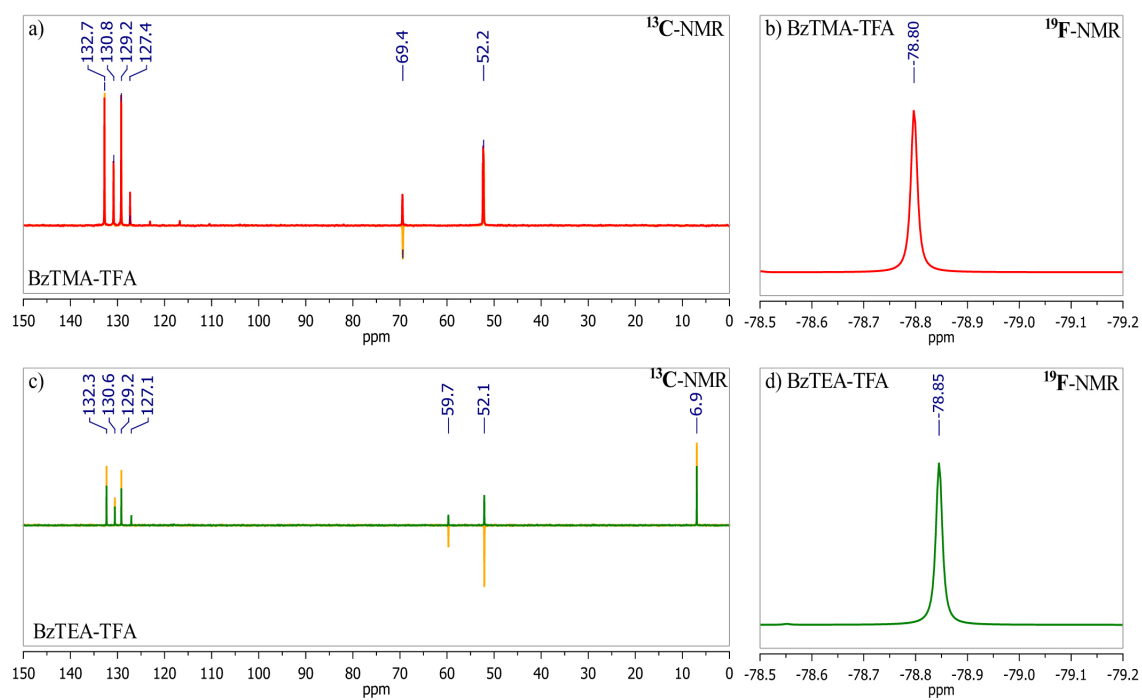


Figure B7-2: NMR spectra of BzTMA-TFA and BzTEA-TFA ILs in D_2O solvent ^{13}C -NMR (left) and ^{19}F -NMR (right). [Negative intensities in ^{13}C -NMR show CH_2 carbon peak from DEPT-NMR]

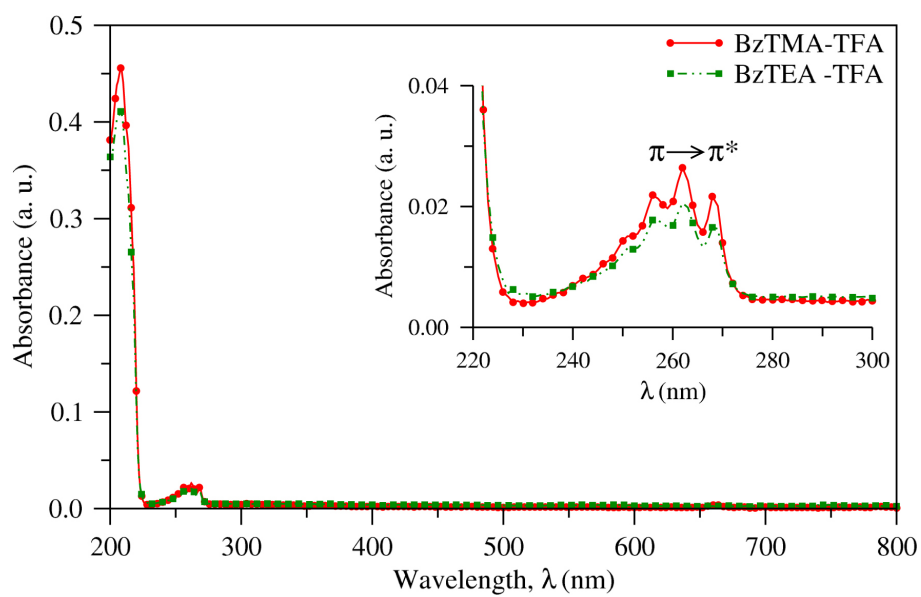


Figure B7-3: UV-Visible spectrum of BzTMA-TFA and BzTEA-TFA ILs.

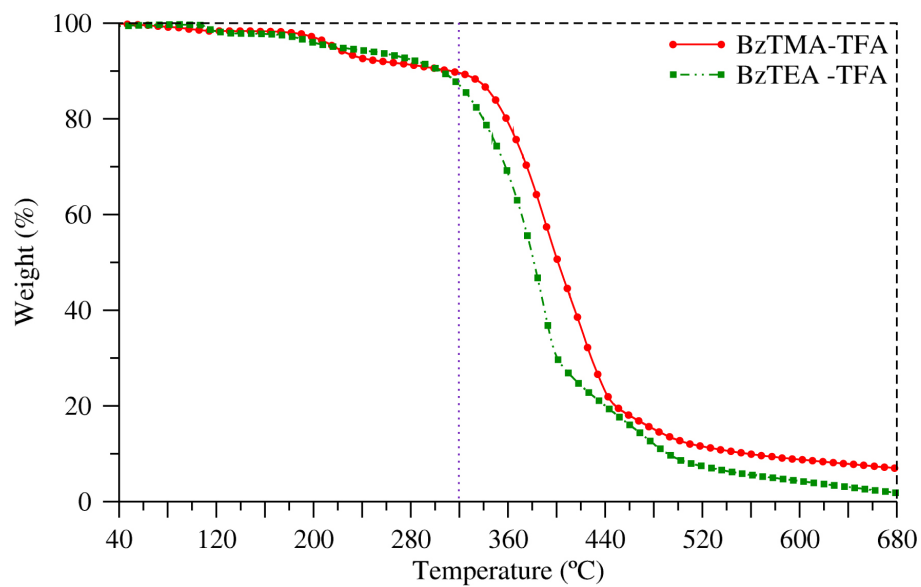


Figure B7-4: Thermogravimetric analysis of BzTMA-TFA and BzTEA-TFA ILs.

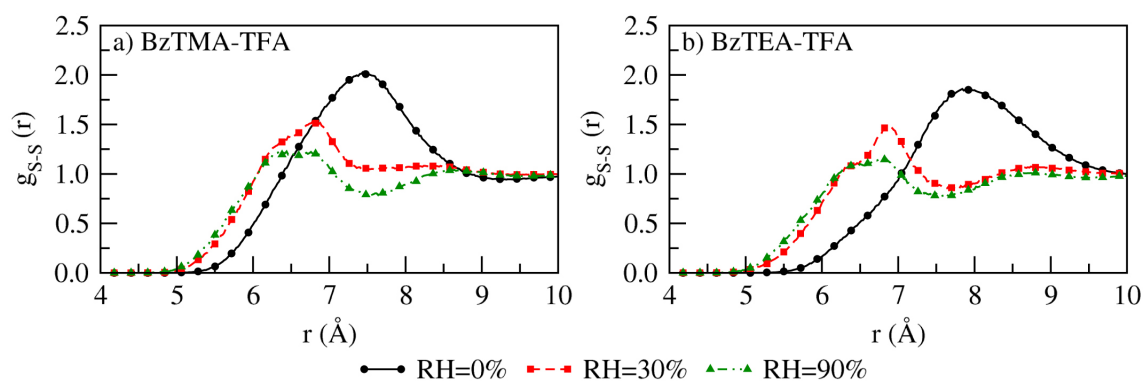


Figure B7-5: RDFs for anion-anion sulfonate (S-S) interactions in BzTMA-TFA and BzTEA-TFA ILs at RH=0% (Neat), RH=30% and RH=90%.

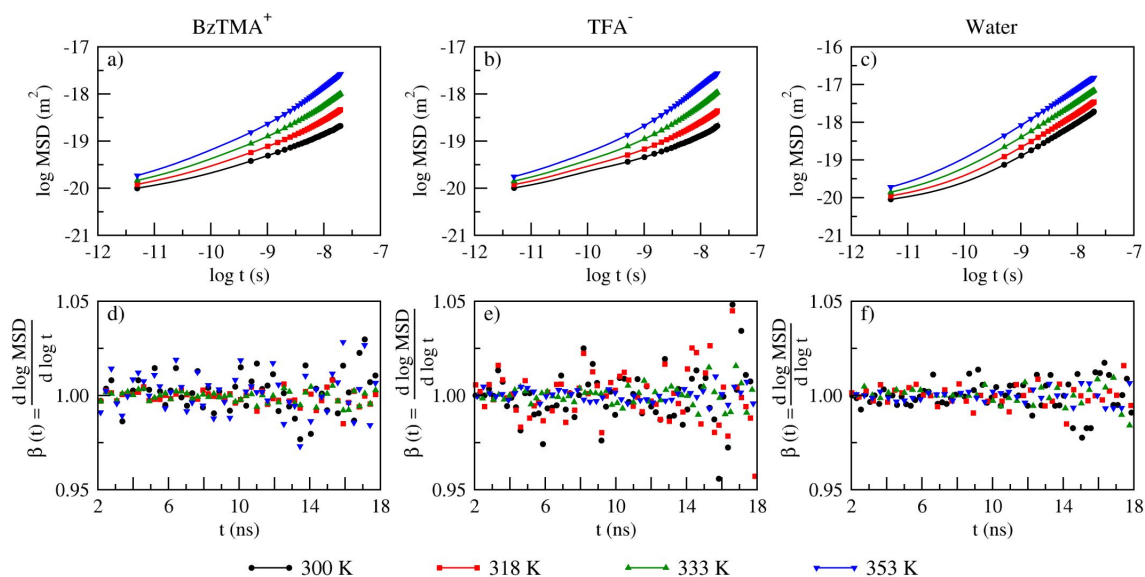


Figure B7-6a: A log MSD versus log time plot for BzTMA-TFA IL (RH=30%) and (d-f) its first derivative (β) plot for ammonium cation, TFA anion and water molecules.

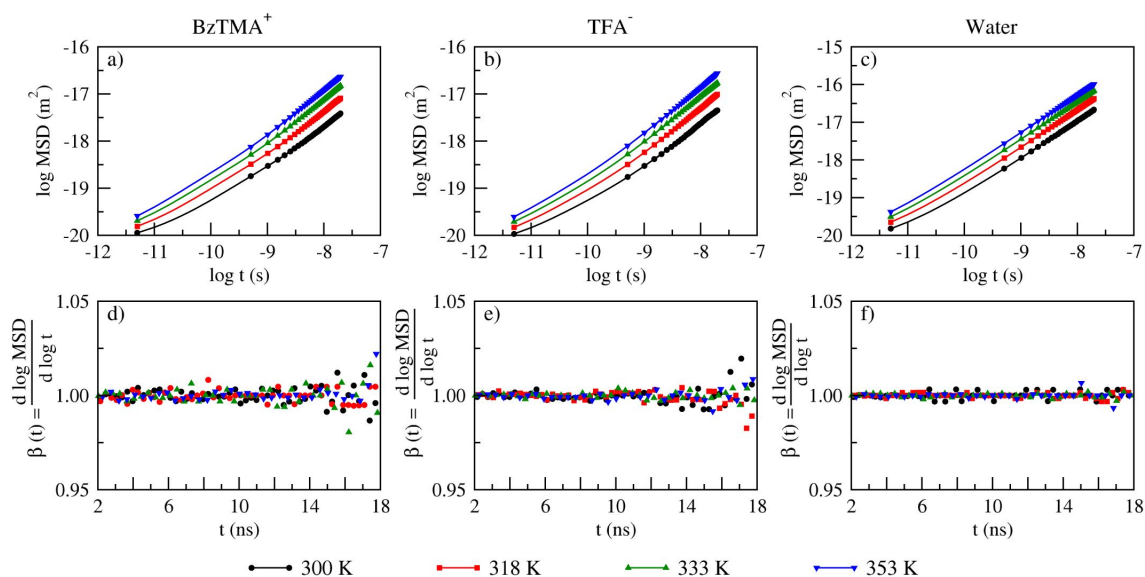


Figure B7-6b: A log MSD versus log time plot for BzTMA-TFA IL (RH=90%) and (d-f) its first derivative (β) plot for ammonium cation, TFA anion and water molecules.

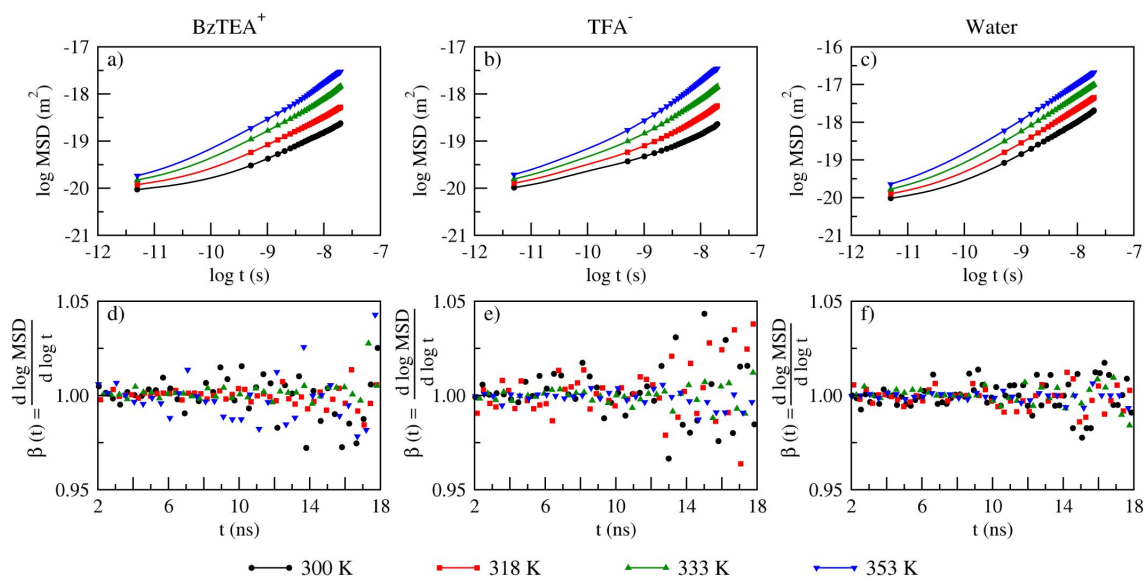


Figure B7-6c: A log MSD versus log time plot for BzTEA-TFA IL (RH=30%) and (d-f) its first derivative (β) plot for ammonium cation, TFA anion and water molecules.

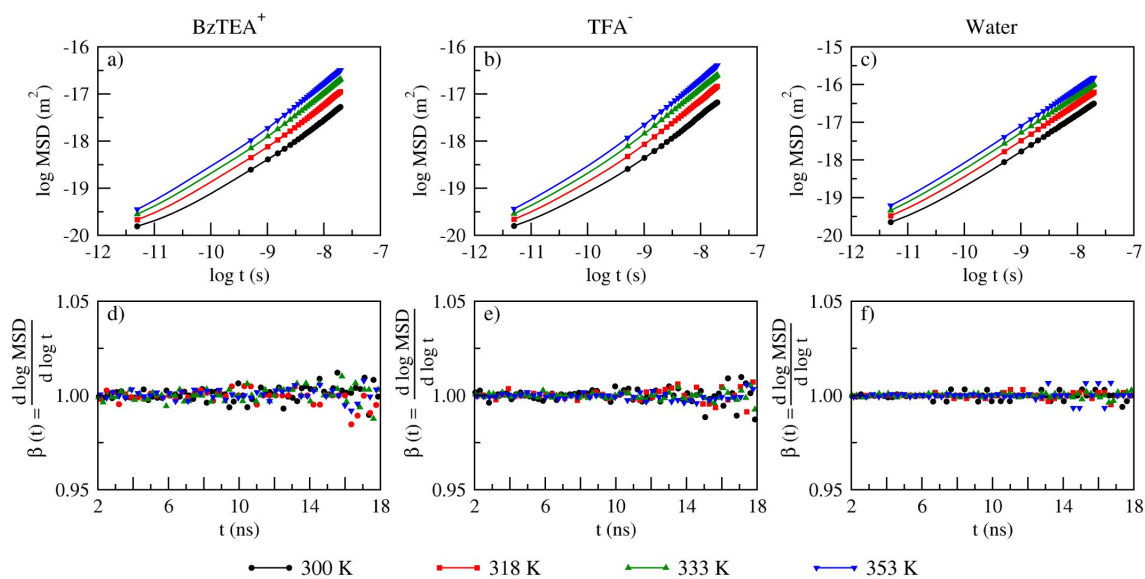


Figure B7-6d: A log MSD versus log time plot for BzTEA-TFA IL (RH=90%) and (d-f) its first derivative (β) plot for ammonium cation, TFA anion and water molecules.

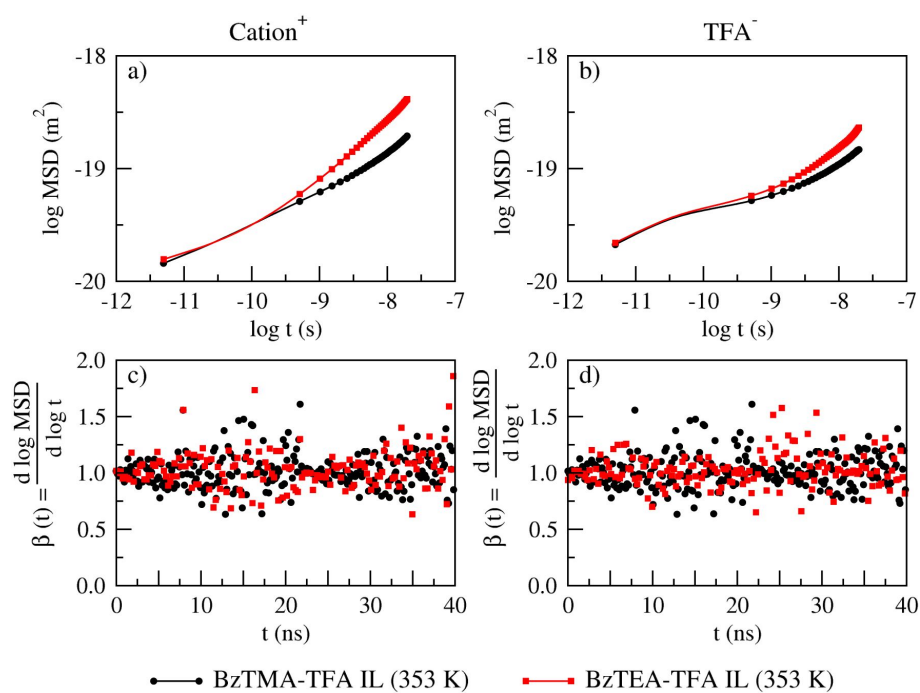


Figure B7-6e: (a and b) A log MSD versus log time plot for BzTMA-TFA and BzTEA-TFA ILs (RH=0% and T=353 K) and (c and d) its first derivative (β) plot for ammonium cation and TFA anion.

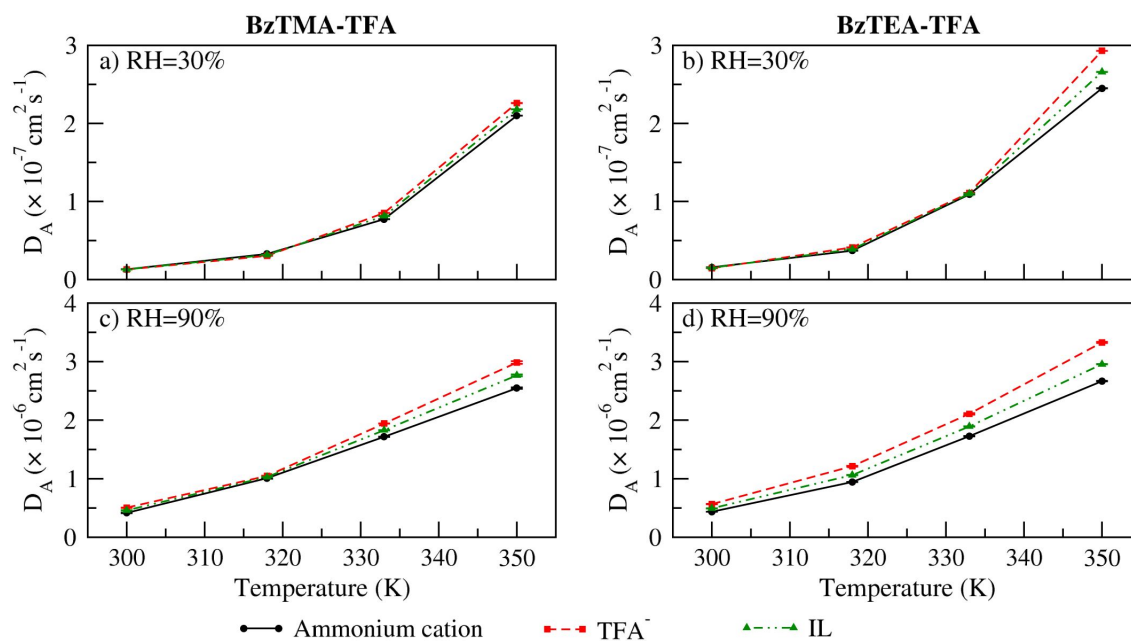


Figure B7-7: Diffusion coefficients (MD simulation) of ammonium cation, triflate anion and IL at a-b) RH = 30 % and c-d) RH = 90 % of BzTMA-TFA and BzTEA-TFA ILs (Error bar represents standard deviation).

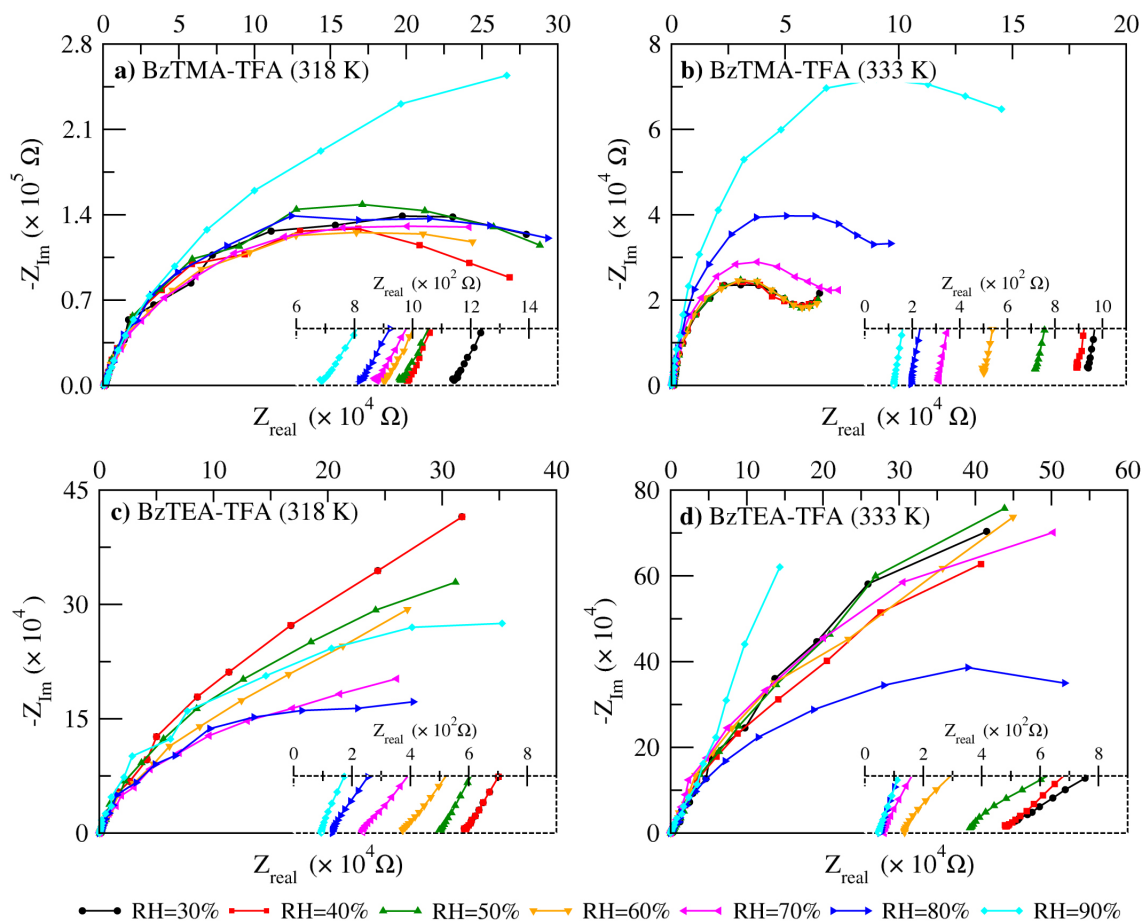


Figure B7-8: Nyquist plots for BzTMA-TFA IL at a) 318 K and b) 333 K; for BzTEA-TFA IL at c) 318 K and d) 333 K respectively.

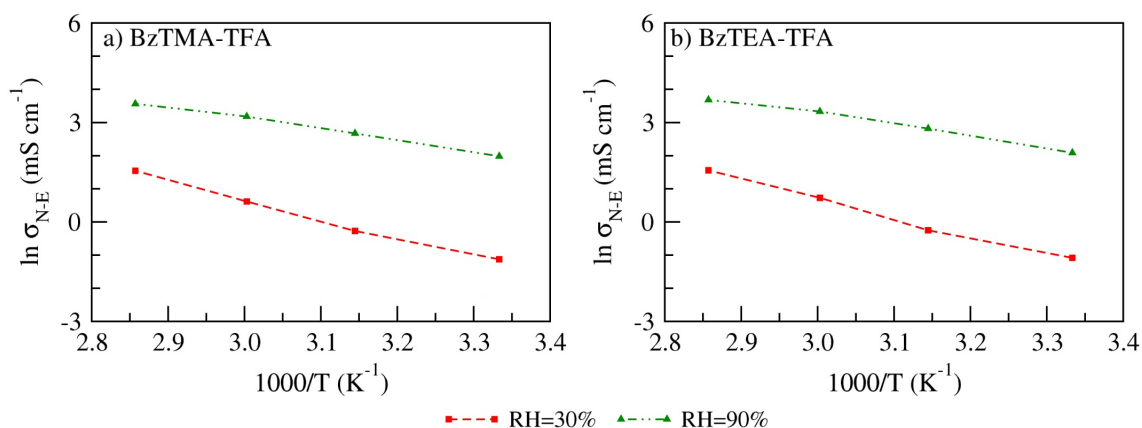


Figure B7-9: Arrhenius plot of Nernst-Einstein ionic conductivity (calculated from MD simulation) of a) BzTMA-TFA and b) BzTEA-TFA ILs.

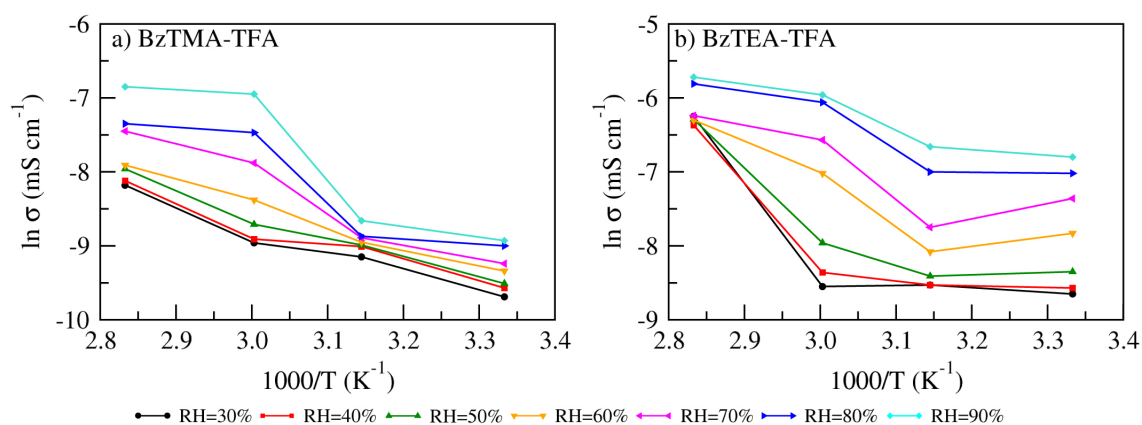


Figure B7-10: Arrhenius plot of ionic conductivity (calculated from the EIS) of a) BzTMA-TFA and b) BzTEA-TFA IL.

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Curriculum Vitae

Education

Master of Philosophy (MPhil, Energy) 2008-2009
Center for Non-conventional Energy Resources, (I div., 67.6%)
University of Rajasthan, Jaipur, India.

Master of Science (MSc, Physical Chemistry) 2006-2008
Department of Chemistry (I div., 68.3%)
University of Rajasthan, Jaipur, India.

Bachelor of Science (BSc, Chemistry) 2003-2006
University of Rajasthan, Jaipur, India. (I div., 78.1%)

Awards/Fellowships

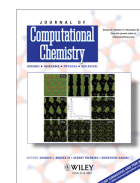
- UGC-Senior Research Fellowship (2012)
- Rajat Jayanti Science Communication Award (2011)
from National Council for Science and Technology Communication,
Department of Science and Technology, New-Delhi.
- II prize for Poster presentation in *Science Fest* at IISER-Pune (2011)
- UGC-Junior Research Fellowship (2010)
(CSIR-UGC NET Exam- Chemical Sciences: December-2009; Rank 314)
- GATE Fellowship (2009)
(GATE 2009 Exam-Chemical Sciences: 90.46 percentile score)

Teaching Assistantship

- Teaching Assistant for *CHM–436: Molecular Modelling and Simulation* course for the fourth year of BS-MS program and also attended by (Fall–2012 & Fall–2013) Integrated PhD and PhD students.
- Teaching Assistant for *CHM–201: Fundamentals of Spectroscopy* course for the second year of BS-MS program. (Spring–2011)
- Teaching Assistant for *CHM–101: Introductory Physical Chemistry* course for the first year of BS-MS program. (Fall–2010 & Fall–2011)

Publications

- ① **A. P. Sunda** and A. Venkatnathan; *Molecular Dynamics simulations of Triflic Acid and Triflate/water mixture: A potential electrolyte in fuel cells*, *J. Computational Chemistry* **2011**, Vol. 32, Issue 15, Page 3319–3328. [Featured on the cover]
- ② **A. P. Sunda** and A. Venkatnathan; *Atomistic simulations of structure and dynamics of hydrated Aciplex polymer electrolyte membrane*, *Soft Matter* **2012**, Vol. 8, Issue 42, Page 10827–10836.
- ③ **A. P. Sunda** and A. Venkatnathan; *Molecular Dynamics simulations of side chain pendant of PFSA polymer electrolyte membranes*, *J. Materials Chemistry A* **2013**, Vol. 1, Issue 3, Page 557–569.
- ④ **A. P. Sunda**, M. More and A. Venkatnathan; *A Molecular Investigation of structure and dynamics of the Phosphoric/Triflic acid blends of ABPBI (2,5-Benzimidazole) Polymer Electrolyte Membrane*, *Soft Matter* **2013**, Vol. 9, Issue 4, Page 1122–1131.
- ⑤ **A. P. Sunda** and A. Venkatnathan; *Parametric dependence on shear viscosity of SPC/E water from equilibrium and non-equilibrium molecular dynamics simulations*, *Molecular Simulation* **2013**, Vol. 39, Issue 9, Page 728–733.



- ⑥ **A. P. Sunda**, V. M. Dhavale, K. Sreekumar and A. Venkatnathan; *Structure and dynamics of benzyl-NX₃ (X=Methyl, Ethyl) trifluoromethanesulfonate ionic liquids*, *J. Phys. Chem. B* **2014** Vol. 118, Issue 7, Page 1831–1838.
- ⑦ M. More[†], **A. P. Sunda**[†], and A. Venkatnathan; *Polymer chain length, phosphoric acid doping and temperature dependence on structure and dynamics of ABPBI [poly(2,5-benzimidazole)] polymer electrolyte membrane*, *RSC Advances* **2014** Vol. 4, Issue 38, Page 19746–19755. ([†]Equal contribution)

Seminar/Conferences/Workshops

Invited Lectures:

- One Day Awareness workshop on Science Communication (organized by DST, New-Delhi), Visvaniketan's IMEET-Mumbai. (Sept.–2013)
- 7th *CRSI-RSC Symposium*, IIT BHU-Varanasi. (Jan.–2013)

Oral presentations:

- Chemical Constellation Cheminar-2012, NIT-Jalandhar. (Sept.–2012)
(An International Conference)
- 3rd Polymer Science Congress MACRO, IIT New-Delhi. (Dec.–2010)
(An International Conference)

Poster presentations:

- Science festival, IISER-Pune. (Feb.–2011 & Feb.–2013)
- Theoretical Chemistry Symposium, IIT–Guwahati. (Dec.–2012)
- International Symposium on Material Education, Yashada-Pune. (Mar.–2011)
- RSC West India PhD Symposium, University of Goa. (Sept.–2010)

Honorary work and workshops:

- Volunteer in 1st Indo-US Research Fellowship conclave at Pune. (Mar.–2013)
- Attended full agenda of ACS (American Chemical Society) on Campus event at National Chemical Laboratory–Pune. (Oct. 10, 2012)

