

## Membrane Simulation in Room Temperature Ionic Liquid and Oil using Molecular Dynamics

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### ABSTRACT

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The polyvinylidene fluoride (PVDF) membrane has been a popular material in membrane separation process. In this work, molecular dynamic (MD) simulation was done on the PVDF membrane with 100 wt% water, 100 wt% 1,3-dialkylimidazolium bromide ([C2bim]Br) ionic liquid (IL), 100 wt% heptane and 50 wt% IL at GROningen MAchine for Chemical Simulations (GROMACS). The results were evaluated based on potential energy, root mean square deviation (RMSD), root mean square fluctuation (RMSF), radial distribution function (RDF) and contact angle. The stability and interaction of PVDF were evaluated. Results reveal that PVDF has a stronger interaction to [C2bim]<sup>+</sup> cation compared to water, heptane and bromine anion. At high concentration of IL, potential energy and RMSD were lower. RDF reveals that [C2bim]<sup>+</sup> cation is dominant at short distance (less than 1 nm), indicating that strong interaction of cation with PVDF. Contact angle analysis proved that PVDF membrane is a hydrophobic and oleophilic membrane. IL has a good wettability characteristic on PVDF at high concentration and vice versa. Molecular dynamics (MD) simulation is an effective tool whose results can be used as reference prior to further experimental approach.

#### Keywords:

Molecular dynamics, polyvinylidene difluoride, ionic liquids, membrane

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## 1. Introduction

Membrane technologies had been received great interest in the field of wastewater separation process in the past there decades [1]. Several important processes have been developed in large scale membrane production such as ultrafiltration, microfiltration, reverse osmosis and gas separation [2]. These methods have high efficiency to be able to treat the wastewater to a very low level of soluble and insoluble solutes.

Polyvinylidene difluoride (PVDF) is semicrystalline polymer which is partially fluorinated [3]. PVDF attracts the interest of the industry due to some superior properties such as high mechanical strength, good thermal stability and chemical resistance and also great aging resistance. PVDF is

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mainly applied in the water treatment industry. The application of PVDF in wastewater treatment plant can be characterize into microfiltration, ultrafiltration, membrane bioreactor, etc. PVDF is also used as the material for membrane contactor. The membrane acts as a barrier between 2 phases. Research has been done on PVDF as membrane contactor due to the high hydrophobicity. These properties are the key feature of a good separation membrane in contactor application. There have been numbers of studies on the application field of the PVDF membrane [4-8].

Ionic liquids (ILs) are salts that appears to be liquids at ambient temperature [9]. ILs are the liquids which are only or almost completely composed of ions. The liquid presents properties of ionic conductivity. Today, ILs have a large variety of applications in the industry due to their superior properties over traditional solvent [10]. The first publication of ILs in the scientific literature was done by Walden in 1914, describing the IL ethylammonium nitrate which melts at 12.5°C [9]. The discovery is recognized as the first room temperature ionic liquid. ILs have advantage over normal organic solvent as the liquid is less volatile as compared to organic solvent. The absence of vapor reduces the risk of air pollution. Slight modification by varying the cations and anions can make ILs more versatile and useful for variety of applications. ILs have variety of application in chemistry and biochemistry. ILs are used in enzyme-catalysed reaction [11], electrolyte materials for double layer capacitors additives in HPLC [12], liquid-liquid extraction [13] etc.

Molecular dynamic (MD) is an effective tool in the theoretical studies of both simple liquid and biochemical molecules such as lipids and proteins [14]. Molecular dynamics can be categorize into many types. GROningen MACHine for Chemical Simulations (GROMACS) is a molecular simulation package which primarily developed for biochemical molecules but also non-biological system such as polymers due to its efficient calculation on non-bonded interaction [15]. The package applies traditional molecular mechanic where Newtonian physics is used to model the motions of atoms. Force field is applied to describe the characteristic of a system such as electrostatic, van der Waals radii, bonds, angles, torsion etc. The major application of this method is with non-bonded interaction especially with van der Waals and electrostatics. This method makes the calculation cheap and simple. Recent research focus on composite membrane of PVDF to investigate the possibility of increasing the performance of the material in term of reliability and anti-erosion properties [4, 16-20].

Many experimental studies and improvements have been done to PVDF membrane. This includes chemical crafting, physical blending and surface modifying [21]. Experimental method is somehow limited as it is unable to capture the chemical structure stability when small modification is done. Molecular dynamic simulation is capable of providing a minimal insight into the interaction between imidazolium ILs and PVDF membrane. Understanding PVDF structure at molecular level enables the application of PVDF to be safer and more effective.

This paper presents the fundamental understanding of the behaviour of simple model of polymer membrane by introducing imidazolium-based ILs into a model of polymer membrane. While the variety of polymer membrane is vast, we focus our simulation into PVDF, a polymer widely applied in ultrafiltration and microfiltration for general separation process. Observation on the disruption of the structure and the integrity of the PVDF membrane can be an indicator of the loss of functionality of the polymer membrane.

## 2. Experimental Study

The force field and bonding properties such as angle, distance and torsion of the PVDF and ionic liquid were found from the reliable source. PVDF molecules used in this simulation consists of 7

monomers [22]. 1,3-dialkylimidazolium bromide IL was selected as the simulation ILs [23]. The structure of water can be found in the library of GROMACS package. All the structures of the molecules were visualized using PYMOL package [24].

The initial condition of the basic configuration of the system is composed of a flat surface of PVDF and a cubic box of the fluid (water, ILs or water/ILs mixture) located over and below the PVDF layer. The molecules which have the primarily optimized geometry structure were put in a simulation box. The cations and anions were randomly placed in a cubic cell system with certain dimension using Packmol [25]. Moreover, water also packed in another simulation, acting as a constant. The size of the simulation box is set as  $60 \times 60 \times 60 \text{ \AA}^3$ . In the simulation box, the number of PVDF was 98 molecules. The numbers of water and IL required in the simulation box were determined based on the percentage weight of IL over the weight of water (% w/w). Table 1 shows the numbers of water and ILs in the simulation box.

**Table 1**  
Amount of water and ILs in the simulation box by mass fraction method

[C <sub>2</sub> BIM]Br:H <sub>2</sub> O (%WT/WT)	AVERAGE NUMBER OF MOLECULES		
	CATION	ANION	H <sub>2</sub> O
0:100	0	0	5776
50:50	224	224	2888
100:0	448	448	0

Energy minimization was done such that the orientation of all ILs molecules in the system is optimal, in which the force field is lowest. To ensure an efficient minimization, several steps were performed. Steepest descent method was first used with 50000 steps due to the fast calculation time. Firstly, heavy atoms of the PVDF were restrained at position by using force constant of  $106 \text{ kJ mol}^{-1} \text{ nm}^{-2}$ . The next steps was to apply the same minimization to the PVDF main chains atom with the same force constant. The last step was running the energy minimization without any position restraint to the whole system. Conjugate gradient with 50000 steps was performed after steepest descent by repeating the steps before.

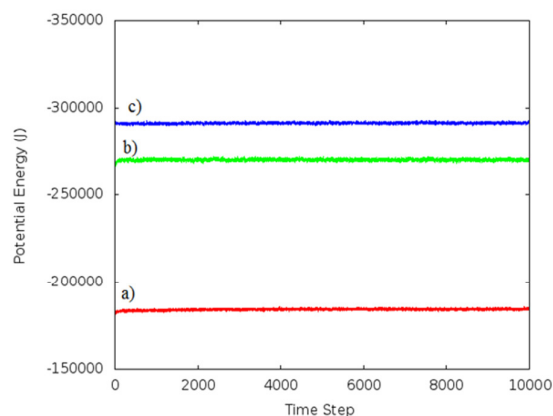
The production run was run at several parameters. The distance for non-bonded interactions calculations was up to 1.2 nm. Particle-Mesh Ewald (PME) electrostatics were applied to calculate the long-range electrostatic interactions with fourth order interpolation, 0.12 nm grid spacing. [26, 27] LINCS was used to constraint the bond lengths [28]. Neighbor searching was performed up to 1.2 nm and updated every 10 steps. Berendsen thermostat and Berendsen barostat were used to control the temperature and pressure respectively [29]. The reference pressure was set at 1 atm with relaxation time of 2 ps. Pressure control were performed at isothermal compressibility of  $4.5 \times 10^{-5} \text{ bar}^{-1}$ .

A pre-run with a single integration step before the production run was applied for proper and efficient pre-equilibration as final checking before the real simulation. All the simulation were performed in the NVT ensemble for  $10 \times 10^6$  integration steps wherein each time steps was 1fs. The simulation were conducted under ambient temperature of 25°C and pressure of 1 atm.

### 3. Results and Discussions

The potential energy after performing energy minimization should be negative. The potential energy of the system after performing energy minimization can be seen in Fig. 1. All three systems have negative values of potential energy and remain constant over the simulation. This indicates

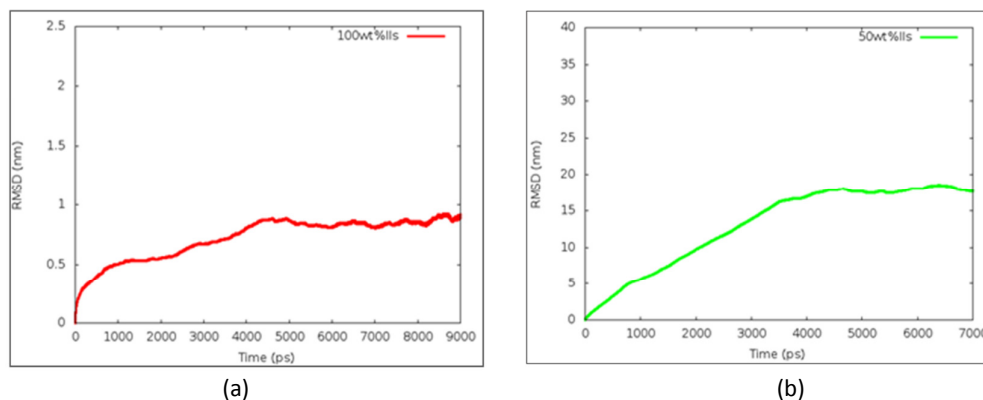
that there is no net repulsive forces within the system. Increasing the IL wt% may decrease the repulsive force within the system and lower the potential energy.



**Fig. 1.** Potential energy of system if PVDF in a) 100 wt% IL, b) 50 wt% IL, c) 100 wt% water

To evaluate the structural stability of system when running the simulation, root mean square deviation (RMSD) of PVDF was performed. Figure 2 shows the RMSD values of PVDF relative to the initial position of the molecules. Increasing the IL wt% seems to increase the RMSD of PVDF. This indicates that the IL is capable of maintaining the stability of PVDF.

Radial distribution function (RDF) analysis is shown Fig. 3 in for the  $[C_2bim]^+$  cation, bromine anion and water molecule to the PVDF. In Fig. 3a, sharp peaks were observed for both PVDF- $[C_2bim]^+$  cation and PVDF-bromine anion at a distance of 2.9 nm and a value of 1.0. This indicates that interaction of both the IL ions to PVDF are equally dominate at long distance. At short distance which is less than 1 nm, bromine anion shows higher curve compared to  $[C_2bim]^+$  cation. The curve signifies that the anions are placed closer to the surface of PVDF compared to the cations. The anion possesses strong interaction on the PVDF surface at high concentration. In Fig. 3b, similar peaks were observed for PVDF- $[C_2bim]^+$  cation, PVDF-bromine anion and PVDF-water molecule at a distance of 2.9 nm and value of 1.0. At short distance less than 1 nm,  $[C_2bim]^+$  cation shows highest curve, followed by water and finally bromine anion. This can be concluded that  $[C_2bim]^+$  cation is dominant at short distance. Water possesses stronger interaction to PVDF than bromine anion due to the hydrogen bonding between PVDF and oxygen atom of water.



**Fig. 2.** RMSD (nm) of PVDF simulated in a) 100 wt% IL and b) 50 wt% IL

The stability of the structure of PVDF can also be observed by presenting the final structure under Pymol. Figure 4 shows all the species of molecules demonstrated in Pymol. Figures 5a and 6a show that the PVDF layer after is thicker after the simulation. Both  $[C_2bim]^+$  cations and water are very close to the PVDF layer where water is dominant at medium distance while cation is dominant at short distance. Fig. 5b and 6b show that the distance between IL and PVDF are closer after the simulation. String interaction between ILs and PVDF exists. Bromine anion has a minor interaction to PVDF as compared  $[C_2bim]^+$  cation and water.

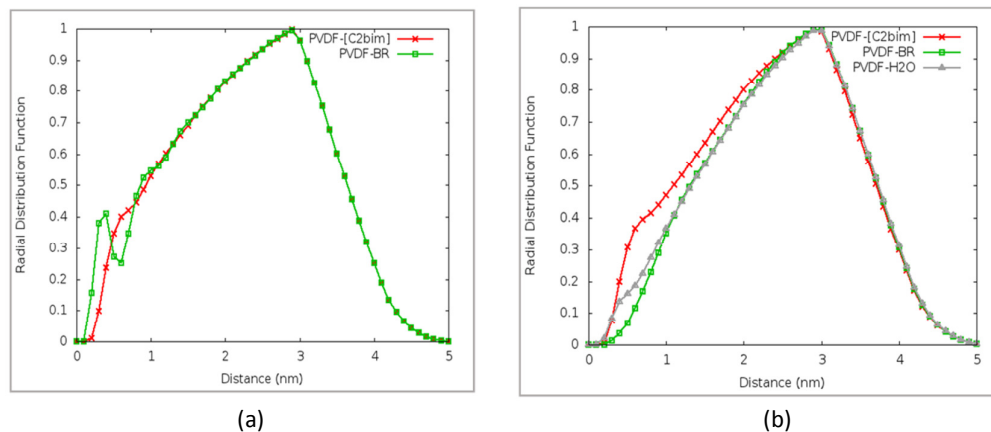


Fig. 3. RDF of PVDF simulated in a) 100 wt% IL and b) 50 wt% IL

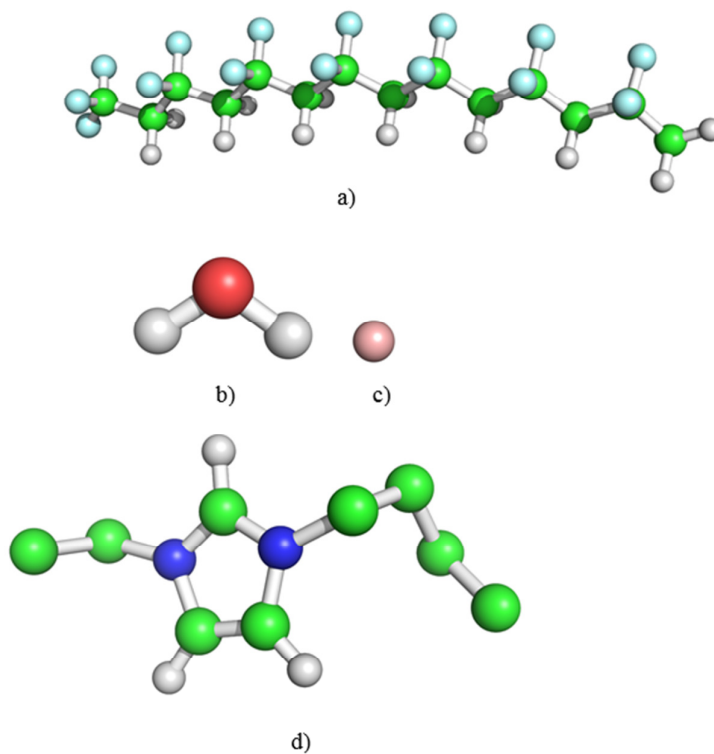
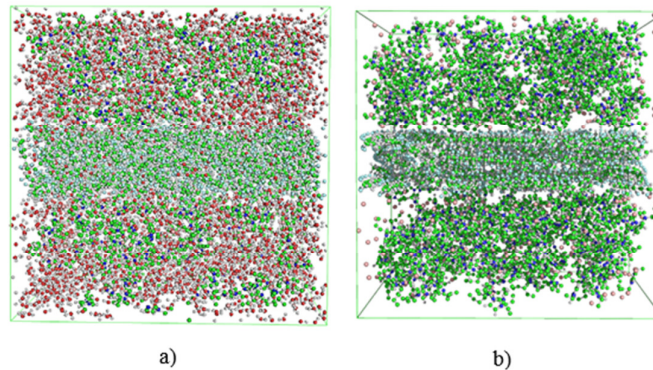
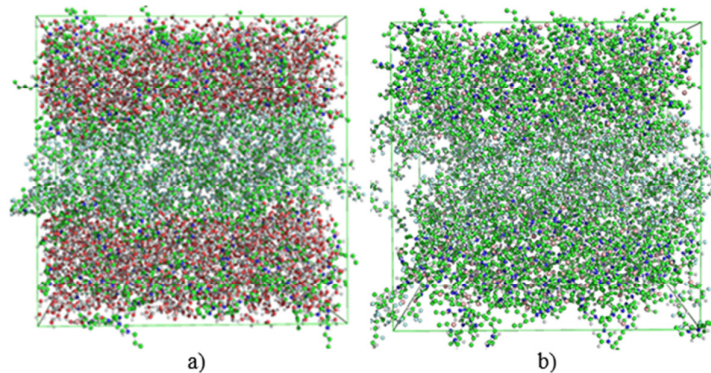


Fig. 4. Molecular structure of a) PVDF, b) water, c) bromine anion and d)  $[C_2bim]^+$  cation



**Fig. 5.** Side view of a) PVDF-50 wt% IL and b) PVDF-100wt% IL before simulation



**Fig. 6.** Side view of a) PVDF-50 wt% IL and b) PVDF-100wt% IL after simulation

#### 4. Conclusion

The structural stability and the interaction of PVDF in IL were discussed by referring to the results from MD simulations. Pure ILs and mixture of IL with water molecules were used to study the effect of cation and anion on the stability of PVDF. Low root mean square deviation was found when PVDF was simulated in pure IL. This indicates that IL is able to maintain and stabilize the structure of PVDF membrane. Energy minimization also presents that the potential is lowest when using pure ILs, showing that the IL is able to lower the net repulsive force within the system. The modelling of system in Pymol after simulation shows that the interaction of  $[C2bim]^+$  cation is strongest followed by water and bromine anion.

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