Molecular Dynamics Simulation on the Separation of Ethanol/Water in the New 6FDA/mODMS Membranes

Wei Zhao[1,a], Wensheng Deng[2,a], Zhipeng Zhao[3,a], Miyi Li[4,b], Zhiping Zhao[5,a]

[a]Beijing Institute of Technology, Beijing 100081, China

Abstract. It is well known that 4,4'- hexafluoro isopropylidene-phthalic anhydride(FDA) has higher permeability and selectivity. It is contributed to –CF group contained in polyimide structure material. In this study, the diffusion properties of a,w-bis(3-aminopropyldimethyl) oligodimethylsiloxane (ODMS) fragment impact on 6FDA were studied. Molecular simulation techniques and Grand canonical Monte Carlo(GCMC)calculations were adopted for predicting the permeability of C_2H_5OH and H_2O in the three new polymers membranes. The membranes considered in this work were synthesized from 6FDA and ODMS. The sorption and diffusion properties of C_2H_5OH and H_2O were calculated. The results show that the 6FDA/6ODMS presents higher permeability than 6FDA/2ODMS and 6FDA/4ODMS. With the longer of ODMS segments in the repeat units, the permeability and selectivity of C_2H_5OH/H_2O increase in the order of 6FDA/2ODMS< 6FDA/4ODMS< 6FDA/6ODMS. The length of molecular chains becomes longer with the ODMS fragments increased, which leads to the gap between the molecular chains becoming larger. Due to the free volume in the system increases, it is more conducive to the larger molecular volume through the membrane. Hence, it can be predicted that the 6FDA/6ODMS is the best for the separation of C_2H_5OH/H_2O.

1 Introduction

Computer modeling of molecular systems at atomistic level has become a high-efficiency tool which is applied to study the membrane separation process [1-4]. Molecular dynamics (MD) simulation is an effective investigation approach for calculating the properties of polymeric microstructures [5-9] after dynamic and equilibrium. Meanwhile, MD simulation has previously been used to study the membranes' permeability of gaseous mixture and organic liquid mixture. Liu et al.[10] investigated the CO_2/CH_4 permeabilities in polyamide-imide isomers by molecular simulation. They found the 6FDA/12p exhibited higher diffusivity and permselectivity which were close to the reported experimental data. They also discussed the transport behavior of oxygen and nitrogen through organasilicon-containing polystyrenes by molecular simulation[11]. Zhou et al.[12] studied the separation of water/ethanol azeotropic mixture in poly (vinyl alcohol) membrane by molecular simulation. For PVA membrane, they found that the conditions of room temperature and high pressure were favorable for separation. Finally, they concluded that the separation factor of PVA membrane with polymerization degree of 1000 can ensure the concentration of ethanol reaching 99.96 wt % under 298 K and 101.325 Kpa. Kuhn et al.[13] investigated the adsorption and diffusion of water, methanol and ethanol in all-silica DD3R membrane. The simulated results were well agreement with the experimental data, too.

In order to make sure that using the molecular simulation method to calculate the diffusion coefficient is reliable, we repeated the work of Liu et al.[10,14], at first. The diffusivity of O_2 through the PDMS membrane was calculated by using Molecular dynamics (MD) simulation. Fortunately, the calculated value was well agreement with the experiment data[15,16]. In addition, the calculated value of solubility of CO_2 in 6FDA/8m membrane was well agreement with the experiment data[17]. Therefore, it can be concluded that the MD simulation method was reasonable to predict the penetration behavior of

molecules in membranes. The Molecular dynamics (MD) simulations are performed in this work to predict the permselectivity of C_2H_5OH/H_2O in three new polymer membranes which are based on 6FDA/mODMS (m=2, 4, 6). The Solubility and Diffusivity of the membranes were calculated and compared. Finally, the membrane composition will be found which is the most suitable for the separation of ethanol and water.

2 Methodology

The solution-diffusion mechanism[14] is used to describe the permeation of small penetrant through nonporous polymeric membranes. It is worth to note that the permeability is the product of the diffusion coefficient *(D)* and solubility coefficient *(S)* which can be described as

$$a_{A/B} = a_d \times a_s = (D_A/D_B) * (S_A/S_B) \qquad (1)$$

2.1 Solubility

The solubility coefficients of the penetrant molecules can be determined from the Grand Canonical Monte Carlo (GCMC) method. In addition, the concentration probability of penetrant in the membrane is determined by the energy change between the new configuration and the previous configuration. In this procedure, a Metropolis algorithm was used to decide on sorbate insertion and deletion as well as the acceptance or rejection of configurational moves (rotation and translation of the sorbate molecules)[15].

The dual-mode sorption model was illustrated to study the penetrant sorption behaviors from lower to higher pressure in this work, as the following equations[16-18] described:

$$C = k_D P + \frac{c_H bP}{1+bP} \qquad (2)$$

$$S = \frac{c}{p} = k_D + \frac{c_H b}{1+bP} \qquad (3)$$

Where C is the total penetrant concentration in a glassy polymer; k_D is the Henry's law coefficient; C_H and b are the capacity parameter and the Langmuir hole affinity parameter, respectively; S is the solubility of penetrant.

2.2 Diffusion

Diffusion coefficient is calculated by the Einstein's relationship[19]:

$$D = \lim_{t\to\infty} \frac{\langle |r(t) - r(0)|^2 \rangle}{6t} \quad (4)$$

Where D is the self-diffusion coefficient, and $r(0)$ is an initial position vector of the penetrant molecules at time 0, $r(t)$ is the position vectors of the penetrant molecule at time t. $\langle |r(t) - r(0)|^2 \rangle$ represents the ensemble average of the mean-square displacement (MSD) of the inserted penetrant molecules.

3 Models And Simulation Details

3.1 Models building

The simulations were performed using Material Studio (MS) software 6.0 (Accelrys Inc., San Diego). The chemical structures of 6FDA and ODMS were constructed by the Amorphous Cell module showed in **Fig.1**. One polymer chain was folded in the amorphous cell under periodic boundary conditions at 318K to get 10 independent configurations. Then, the configuration with lowest energy was selected for energy minimization. This task employed both steepest descent and conjugate gradient algorithms with the convergence level setting to $0.001 \text{kcal} \cdot \text{mol}^{-1} \cdot \text{Å}^{-1}$. In order to reach the equilibration, these structures were subjected to anneal simulation with the NPT ensemble at 1 atm. The cells were heated from 200 K to 800 K and then cooled down from 800 K to 200 K with the gradient of 50 K. At each step, 120 ps NPT MD simulation were carried out. After that, 150 ps NPT MD simulation were performed to further optimize the structures. Finally, 1.5 ns NVT MD simulation were performed for analyzing the properties of the membranes.
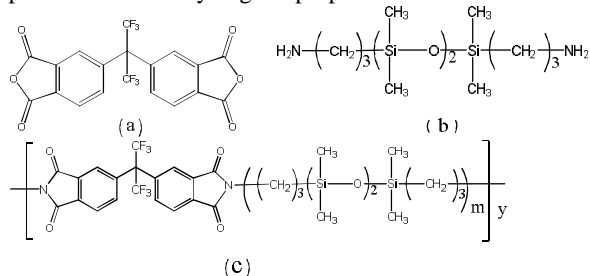
Figure 1. Represents the repeat units of the polymers used in this study, (a):6FDA, (b): OMDS, (c) the repeat unit of product, m=2,4,6.

In this study the COMPASS force field[20-22] was used which shows efficient in reproducing density-related properties in polymers[23]. The non-bonded interactions were calculated by using the Van der Waals and Coulombic interactions. The "atom based" method[24] was used with a cutoff distance of 9.5Å. The spine width and

buffer width were 1.00 Å and 0.5 Å, respectively. All the procedures were given the same step of 1 fs. The Andersen thermostat was used for temperature and the Bendersen was used for pressure control. In order to avoid packing algorithm related catenations and spearing of aromatic units it was necessary to start with a low initial packing density (typically 0.1 g/cc[25]).

3.2 Simulation of solubility and diffusivity

The solubility of H_2O and C_2H_5OH were calculated by using the GCMC (Grand Canonical Monte Carlo) method[26,27]. The sorption isotherm was obtained by using Sorption modules over a pressure range 10-500 KPa. At each pressure, 1000000 steps of GCMC calculations were performed by using an initial equilibration period of 100000 steps.

Diffusivities were obtained by the addition of 20 water and 1 ethanol molecules into each independently equilibrated configuration to form a new simulation cell at 318K. Then, the same procedure that described in Section 3.1 was used after each configuration equilibrated. The diffusion simulations were performed for 3.5 ns under the NVT ensemble. Finally, an average value of D was obtained from the independent states.

4 Results And Discussion

There are two empirical standards can prove the final equilibrium structures are obtained, that is the variation magnitude of temperature with time within 10%, the same as the energy. As can be seen from the **Fig.2**, both the ranges of change of the temperature and the energy are within 5%. Therefore, the final structures obtained after MD simulation were effective when they were used to analyze the data.
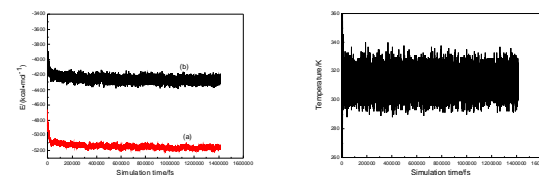
Figure 2. Energy vs. simulation time(a)Nonbond energy; (b)Potential energy,and Temperature vs. simulation time.

4.1 Solubility

The sorption isotherms of the 6FDA/2ODMS, 6FDA/4ODMS and 6FDA/6ODMS are shown in **Fig.3**. With the help of Eq. (2) and Eq. (3), the water solubility and ethanol solubility of the polymers can calculate. All the results are listed in **Table 1**. By the Eq. (1), the solubility selectivity can be obtained. According to **Table 1**, it is found that there is no significant difference among the water solubility in each polymer. The values of ethanol solubility in 6FDA/2ODMS and 6FDA/4ODMS are almost same, but the ethanol solubility in 6FDA/6ODMS is higher than these two.
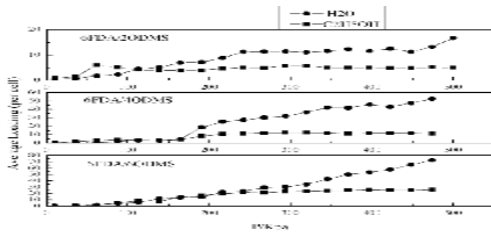
Figure 3. Represents the sorption isotherm of C_2H_5OH and H_2O in 6FDA/mODMS(m=2,4,6).

4.2 Diffusivity

All the results of diffusion coefficients are listed in **Table 1**. The log (MSD) dependence of log (time) of C_2H_5OH and H_2O molecules in 6FDA/2ODMS, 6FDA/4ODMS and 6FDA/6ODMS are presented in **Fig.4**. The criterion for a model system reaching the normal diffusion regime is that the slope of log (MSD) vs. log (t) approaches unity[28-30]. Note that the slope of the log (MSD) vs. log (t) curve increases approximately after1500 ps for H_2O and C_2H_5OH in 6FDA/2ODMS, after 800 ps for H_2O and C_2H_5OH in 6FDA/4ODMS, after 1000 ps for H_2O and C_2H_5OH in 6FDA/6ODMS, respectively. In **Fig.5**, the Mean-square displacements of H_2O and C_2H_5OH in 6FDA/2ODMS, 6FDA/4ODMS, 6FDA/6ODMS are listed in **Table 1**.
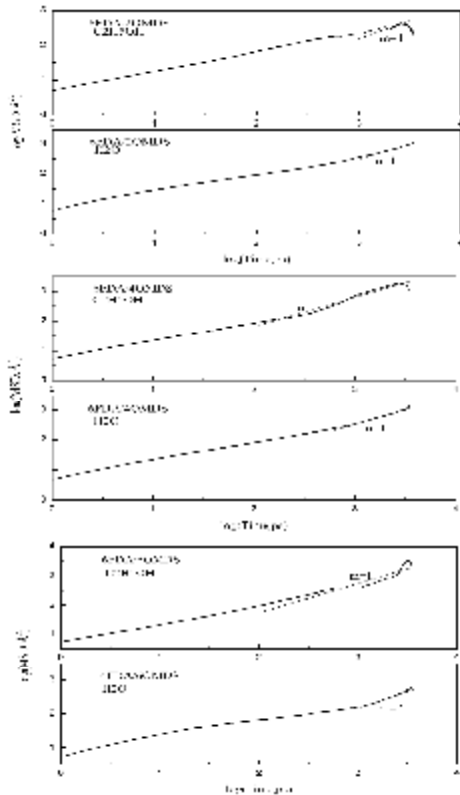
Figure 4. Log (MSD) vs. log (t) plots for the diffusion of C_2H_5OH and H_2O in the 6FDA/mODMS(m=2,4,6).
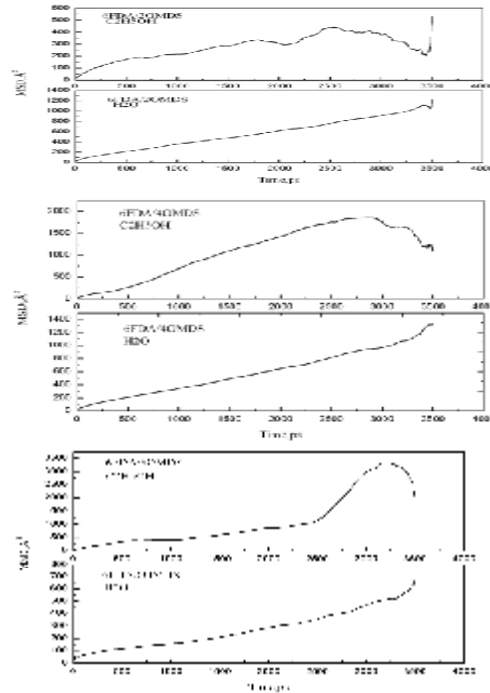
Figure 5. Represents the MSD of C_2H_5OH and H_2O in the 6FDA/mODMS(m=2,4,6).

According to **Table 1**, viewed that there is no significant difference between the water diffusivity in 6FDA/2ODMS and 6FDA/4ODMS, however, the water diffusivity in 6FDA/6ODMS is smaller than these two. It is found that the diffusivity of C_2H_5OH in the polymers increases in the order of 6FDA/2ODMS< 6FDA/4ODMS<6FDA/6ODMS. Absolutely, the diffusion selectivity of 6FDA/6ODMS is the largest.
The permselectivity can be calculated with Eq. (1), as listed in **Table 1**. It is found that the higher permselectivity of 6FDA/6ODMS is mainly due to its higher diffusivity selectivity. Also it can be found that with the increasing of ODMS segments in the repeat units, the $\alpha_{C_2H_5OH/H_2O}$ for the polymers increase in the order of 6FDA/2ODMS<6FDA/4ODMS<6FDA/6ODMS. The permeability in the polymers has relationship with the molecular dimension of penetrant and the free volume of the polymers. As we known, C_2H_5OH has larger dimension and smaller free volume than H_2O. With the increasing of ODMS segment in the repeat units, the free volume of the polymers increase, which lead to the permeability of C_2H_5OH in the polymer becoming larger. As the results shown in **Table 1**, the polymer 6FDA/6ODMS has the best permselectivity.

Table 1. solubility, diffusivity and selectivity values for C_2H_5OH and H_2O in 6FDA/2ODMS, 6FDA/4ODMS and 6FDA/6ODMS at 318K. (A and B respectively represent C_2H_5OH and H_2O).

	6FDA/2ODMS	6FDA/4ODMS	6FDA/6ODMS
$S_A*10^2/(cm^3(STP)\cdot cm^{-3}\cdot atm^{-1})$	2.6470	2.6040	6.1180
$S_B*10^2/(cm^3(STP)\cdot cm^{-3}\cdot atm^{-1})$	0.8586	0.9310	0.7596
$\alpha_s=S_A/S_B$	3.08	2.80	8.05
$D_A*10^6/(cm^2\cdot s^{-1})$	2.937	8.983	14.756
$D_B*10^6/(cm^2\cdot s^{-1})$	5.218	5.74	2.295
$\alpha_d=D_A/D_B$	0.563	1.57	6.43
$\alpha_{A/B}=\alpha_s\cdot\alpha_d$	1.73	4.40	51.7

5 Conclusions

Molecular dynamics simulations based on the COMPASS forcefield have been performed to study the permeability of C_2H_5OH/ H_2O in 6FDA/2ODMS, 6FDA/4ODMS and 6FDA/6ODMS. The sorption and diffusion properties of C_2H_5OH/ H_2O in the polymers are investigated. It is found that the solubility and diffusivity of H_2O in 6FDA/6ODMS have smaller values than the other two, and the solubility and diffusivity C_2H_5OH in 6FDA/6ODMS have greater values than the other two. Therefore, it can be obtained that the polymer 6FDA/6ODMS has the greater permselectivity of C_2H_5OH/ H_2O which is good for the separation of C_2H_5OH and H_2O.

Acknowledgment

References

[1] F.S Pan, J. Ma, L. Cui, Z.Y Jiang, *Chem. Eng. Sci.* 64(2009) 5192-5197.

[2] J.Y Wu, Q.L Liu, Y. Xiong, A.M Zhu, Y. Chen, *J. Phys. Chem. B*. 113(2009) 4267-4274.

[3] T. Pramananda Perumal, V. Sridhar, K.P.N. Murthy, K.S. Easwarakumar, S. Ramasamy, *Comp. Mater. Sci.* 38(2007) 865-872.

[4] C.H Lu, S.J Ni, W.K Chen, J.S Liao, C.J Zhang, *Comp. Mater. Sci.* 49(2010) 565-569.

[5] Wolfgang Paul, *Polymer*, 45(2004) 3901-3905.

[6] K.S Chang, Z.C Wu, S. Kim, K.L Tung, *J. Membr. Sci.* 454(2014) 1-11.

[7] M. Rahmati, H. Modarress, Reza Gooya, *Polymer.* 53(2012) 1939-1950.

[8] L.H Zhao, F.H Tian, X.B Wang, W.W Zhao, A.P Fu, Y.Y Shen, S.G Chen, S.Q Yu, *Comp. Mater. Sci.* 79(2013) 691-697.

[9] S.X Pan, Y.F Hu, Q. Li, *Comp. Mater. Sci.* 79(2013) 611-618.

[10] Y. Chen, Q.L Liu, A.M Zhu, Q.G Zhang, J.Y Wu, *J. Membr. Sci.* 348(2010) 204-212.

[11] Q.L Liu, Y. Huang, *J. Phys. Chem.* B. 110 (2006) 17375-17328.

[12] Z.W Qiao, Y.L Wu, X.W Li, J. Zhou, *Fluid Phase Equilibr.* 302(2011) 14-20.

[13] J. Kuhn, J. Gascon, S. Calero, J. Gross, *J. Phys. Chem. C.* 113(2009) 14290-14301.

[14] Y. Huang, Q.L Liu, *Journal of Xiamen University (Natural Science)*. 45(2006) 664-669.

[15] S.G Charati, S.A Stern, Macromolecules. 31(1998) 5529-5535.

[16] Stern S.A, *J. Membr. Sci.* 94(1994) 1-65.

[17] Z.K Xu, M. Böhning, J. Springer, *Polymer.* 38(1997) 581-588.

[18] R.W. Baker, *John Wiley & Sons, Ltd*. CA, (2004) 491-522.

[19] N. Metropolis, A.W. Resenbluth, M.N. Rosenbluth, A.H. Teller, E. Teller, *J. Chem. Phys.* 21 (1953) 1087–1109.

[20] W.R. Vieth, K.J. Sladek, *J. Colloid Sci.* 20 (1965) 1014–1033.

[21] D.R. Paul, W.J. Koros, *J. Polym. Sci. Polym. Phys. Ed.* 14(1976) 675-685.

[22] S. Kanehashi, K. Nagai, *J. Membr. Sci.* 253(2005)117–138.

[23] X.Y. Wang, A.J. Hill, B.D. Freeman, I.C. Sanchez, *J. Membr. Sci.* 314 (2008) 15–23.

[24] H. Sun, *J. Phys. Chem.* B 102 (1998) 7338–7364.

[25] H. Sun, *J. Comput. Chem.* 15 (1995) 752–768.

[26] H. Sun, P. Ren, J.R. Fried, *Comput. Theor. Polym. Sci.* 8 (1998) 229–246.

[27] M. Heuchel, D. Hofmann, P. Pullumbi, *Macromolecules.* 37 (2004) 201–214.

[28] P.V.K. Pant, R.H. Boyd, *Macromolecules.* 25 (1992) 494–495.

[29] Takeuchi H, *J. Chem. Phys.* 1990; 93:2062-2067.

[30] T. Liang, X. Zhang, *J. Polym. Sci. Part B: Polym. Phys.* 39(2001) 2243-2251.