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Research Paper

Molecular investigation of the effect of Tween surfactant on PEBA membrane in CO_2 separation process

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1. ABSTRACT

Environmental problems and global warming have led to the growth of research on the separation of CO_2 from natural gas and flue gas. In this research, membrane separation method using molecular simulation was used to CO_2 separation from N_2. In this regard, pure polyether block amide (PEBA) membrane and PEBA membrane containing tween surfactant were made using molecular simulation and analyzed from a molecular point of view. In order to investigate the structure of the membranes, their density and free fraction volume were calculated. Also, the radial distribution function was plotted in order to investigate the interaction of CO_2 gas with PEBA polymer chains and tween molecules, and the permeability and solubility coefficients against CO_2 and N_2 gases were obtained. Moreover, the selectivity of CO_2 over N_2 was calculated for the membranes. The molecular simulation results showed an increase in the solubility and diffusion coefficients of CO_2, followed by an increase in the permeability of this gas by adding tween to the polymer matrix, while the selectivity of the membrane containing tween decreased due to the increase in the diffusion coefficient of N_2 in this membrane compared to the pure membrane. The reason for this behavior is the softening of the polymer chains by the surfactant.

Keywords: Membrane, Polyether Block Amide, Surfactant, Tween, Molecular Simulation.

2. INTRODUCTION

Environmental problems and global warming have led to the growth of research on the separation of CO_2 from natural gas and flue gas. There are different methods such as absorption, adsorption and membrane process for the separation and removal of CO_2 [1]. Membrane technology is a widely used method for CO_2 separation due to its simplicity and low energy consumption. A wide variety of materials have been used as membrane such as polymers, ceramics or metals for CO_2 separation. Polymeric membranes are the most popular membranes in this field due to their ease of preparation and processing. Among the polymer materials, polyether block amide (PEBA) is an attractive copolymer for separating sour gases, or in other words, polar molecules from non-polar ones [2]. This high performance block copolymer containing soft polyether (PE) blocks that provides high permeability and hard polyamide (PA) blocks that gives mechanical strength. The transport mechanism in these membranes is solution-diffusion type so that CO_2 molecules are first dissolved on the surface of the membrane and then diffuse towards the passing stream. The main problem of this type of membrane is the low permeability of CO_2, which prevents the widespread use of this membrane in the separation industry. Today's research has been done with the aim of discovering and introducing different methods to overcome this limitation [3].

Molecular simulation is a low-cost and efficient method that is used to investigate the structural properties and function of membranes. Molecular simulation can determine the effect of each membrane component in gas separation with high accuracy [4]. The use of molecular simulation in order to design different polymer membranes is one of the important methods in order to investigate the functioning and behavior of membranes on a molecular scale. Since the investigation of membranes from a molecular point of view provides a better view of the functioning of various components in the membrane structure and the behavioral changes of the membranes can be easily justified, therefore, in this research, using materials studio software to simulate The pure membrane and the membrane containing surfactant were discussed and their structure and performance were investigated from a molecular point of view [5].

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3. MATERIALS AND METHODS

All simulations were carried out by using Materials Studio 2017R2 molecular simulation software (BIOVIA, San Diego). PEBA 1657 monomers were made by build module. Then polymer chains containing these monomers were simulated. These chains were used to make a polymer membrane (Figure 1). The constructed membrane cell were geometry optimized and energy minimized by COMPASSII force field with the smart minimizer method which is a part of the Amorphous Cell module of Materials Studio software and combines the steepest descent, conjugate gradient and newton methods to ensure that they are in their lowest level of energy and the most stable equilibrium state. Then the membrane cell subjected to 1000 ps under NPT conditions (constant number of particles, pressure and temperature) and then 3000 ps under NVT conditions (constant number of particles, volume and temperature).

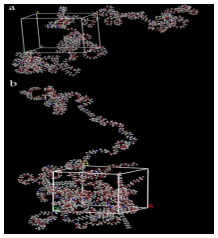

Figure 1. Structure of simulated membrane cells: a) P and b) PT

4. RESULTS AND DISCUSSION

4.1 Density and fractional free volume (FFV)

The density and fractional free volume (FFV) for the constructed membrane are given in Table 1. According to this table, the density and FFV of the pure membrane have a suitable approximation with the laboratory values, which shows that the method used to simulate the membranes is the correct method. In addition, it is clear that the density and FFF of the membrane containing tween is lower than that of the pure membrane. A view of the free volume between the polymer chains is shown in Figure 2.

Table 1. The average density and FFV of simulated membranes

Constructed membranes	FFV	density (g/cm^3)
P	0.12 (0.113)	1.12 (1.14)
PT	0.11	1.11

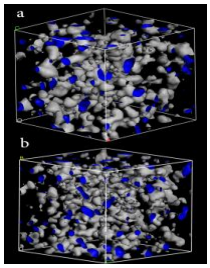

Figure 2. Structure of membrane cells: a) P and b) PT

4.2. Radial Distribution Function (RDF)

In order to investigate the interaction of carbon dioxide with polyether block amide and tween, the RDF was calculated and shown in Figure 3. The intense peak related to the RDF of CO_2 around the tween shows the high interaction of this gas with the tween. This high interaction shows the strong affinity of tween to CO_2. A schematic of the interaction of CO_2 gas and ether tween groups is shown in Figure 4.

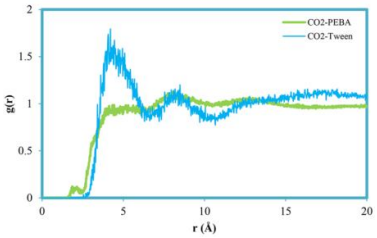

Figure 3. RDF related CO_2 around PEBA and tween.

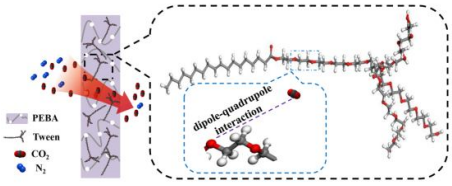

Figure 4. Schematic of the interaction of carbon dioxide gas and ether tween groups.

4.3. Solubility, diffusion and permeability coefficients along with CO_2/N_2 selectivity

Tables 2-4 show the solubility, diffusion and permeability coefficients along with permeability and selectivity of the simulated membranes, respectively. It is clear from these tables that the solubility of CO_2 in the membrane increased by adding tween, which had a great effect on increasing the permeability of this gas. Although, due to the softening of the

polymer matrix, the membrane containing tween has high N_2 permeability and its selectivity has decreased. It should be noted that the mean square displacement (MSD) of CO_2 and N_2 in the pure membrane and the membrane containing tween is shown in Figure 5.

Table 2. The solubility coefficients of CO_2 and N_2.

Tested gas	S_{CO2} ($\times 10^{-4}$ cm^3 (STP) cm^{-3} (polymer) $cmHg^{-1}$)	S_{N2} ($\times 10^{-4}$ cm^3 (STP) cm^{-3} (polymer) $cmHg^{-1}$)	Solubility selectivity
P	167.0	2.8	59.6
PT	203.4	2.0	101.7

Table 3. The diffusion coefficients of CO_2 and N_2.

Tested gas	D_{CO2} ($\times 10^{-6} cm^2/s$)	D_{N2} ($\times 10^{-6} cm^2/s$)	Diffusivity selectivity
P	70.3	31	2.3
PT	74.3	129	0.6

Table 4. The CO_2 permeability coefficients and CO_2/ N_2 selectivity.

Tested gas	P_{CO2} ($\times 10^{-6} cm^2/s$)	CO_2/N_2 Selectivity
P	117.4	137.1
PT	151.1	61.0

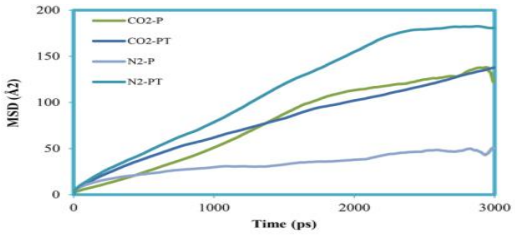

Figure 5. MSD of CO_2 and N_2 in the pure membrane and the membrane containing tween

5. CONCLUSION

In this research, the pure PEBA membrane and the membrane containing tween surfactant were made using molecular simulation and their performance was evaluated from a molecular point of view. Based on the results of the simulation, the density and the FFV of the PEBA membrane decreased with the addition of tween. The investigation of the RDF of CO_2 around PEBA chains and tween showed that this gas had a high interaction with tween compared to polyether block amide, which indicated the high ability of tween to dissolve CO_2. By calculating the solubility and diffusion coefficients, it was determined that since the diffusion and solubility coefficients both play a role in the permeability coefficient, by increasing the solubility and permeability coefficients for CO_2 gas in the membrane containing tween, the permeability of this gas has also increased. This is despite the fact that the reduction of diffusion selectivity and its dominance over the increase of solubility selectivity has led to the decrease of total CO_2/N_2 selectivity.

6. REFERENCES

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