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Investigation of the Structure and CO_2/N_2 Separation Performance of PEBA Membrane by Molecular Simulation Study

Mahdi Elyasi Kojabad[1,*], Haniyeh Golizadeh kahnamouei[1], Ali Akbar Babaluo[2]

[1] Faculty of Engineering, Behbahan Khatam Alanbia University of Technology, Behbahan, Iran
[2] Faculty of Chemical Engineering, Sahand University of Technology, Tabriz, Iran

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ABSTRACT

In this work, the structure of a poly ether block amide (PEBA) polymeric membrane was investigated using molecular simulation study. This membrane performance for the separation of CO_2 from N_2 was evaluated. In this regard, the density and fractional free volume (FFV) for this membrane were calculated and compared with experimental data. The results showed the conformity of the molecular simulation results with experimental work results. In addition, the mobility of PEBA chains and its polyether and polyamide parts were measured on a molecular scale which cannot be measured on a laboratory scale. Then the diffusion and solubility coefficients of gases were determined for this membrane and the permeability of CO_2 and CO_2/N_2 selectivity were calculated. The performance properties of the simulated membrane showed that, solubility has a greater role in CO_2/N_2 selectivity than diffusivity in this membrane, so that CO_2 permeability and CO_2/N_2 selectivity were 116.9 and 130 Barrer, respectively.

1. 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 [1]. There are different methods such as absorption, adsorption and membrane process for the separation and removal of CO_2 [2]. 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 [3, 4]. Among the polymer materials, polyether block amide (PEBA) is an

Corresponding author. Tel.: +0098-61-52721191.
E-mail address: m.elyasi@bkatu.ac.ir (M.E. Kojabad)

attractive copolymer for separating sour gases, or in other words, polar molecules from non-polar ones [5]. This high performance block copolymer containing soft polyether (PE) blocks that provides high permeability and hard polyamide (PA) blocks that gives mechanical strength [6]. 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 [7]. Different grades of PEBA can be tailored by adjusting the segment ratio of PA over PE to obtain optimal CO_2/N_2 selectivity [8]. PEBA 1657 is constituted by 40 wt% amide groups and 60 wt% ether linkages. This copolymer has high polar/nonpolar (e.g., CO_2/CH_4, and CO_2/N_2) selectivity relative to the other grades due to high polarity of PE and PA segments [9]. Several studies are available in the literature on the preparation of PEBA 1657 membranes for CO_2 separation. Ren et al. fabricated a PEBA 1657on polyetherimide (PEI) support for CO_2 separation [10]. Moreover, Wang et al. prepared PEBA 1657 layer on poly acrylonitrile (PAN) for CO_2 separation that perform as the support layer and PEBA 1657 was the main selective layer [11]. Although extensive laboratory studies have been performed in the field of gas separation, but this type of study is a costly and time consuming method, so using a method that requires less time and imposes less cost can be necessary.

Molecular simulation is a low-cost and efficient method that is used to investigate the structural properties and function of membranes [12]. Molecular simulation can determine the effect of each membrane component in gas separation with high accuracy [13]. Since the PE and PA parts of the PEBA 1657 shows a certain feature in membrane separation performance, evaluating the mobility of these chains can be of considerable importance. Disclosing the role of polyether and polyamide parts in CO_2 separation and also the tendency of each of these parts to this gas can be important. In addition, determining the values related to solubility and diffusivity coefficients can play a big role in the analysis of membrane separation performance. Therefore, in this study, first the PEBA 1657 polymer membrane was made using molecular simulation and then its separation performance and structural properties were investigated on a molecular scale.

2. Molecular simulation details

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. Fig. 1 shows the structure of the constructed membrane cell.

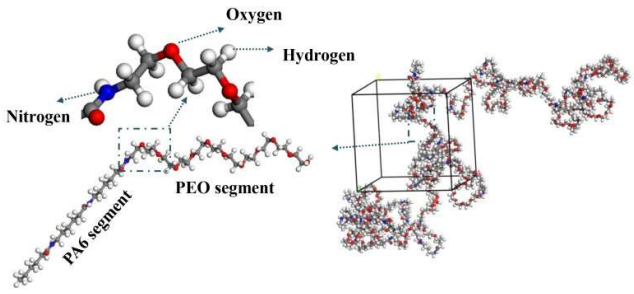


Fig.1. Constructed PEBA 1657 membrane cell

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).

In membranes with a solution-diffusion mechanism, permeability is defined as the product of the solubility coefficient multiplied by the diffusion coefficient (Eq. 1) [14].

$$P = S \times D \tag{1}$$

D is the diffusion coefficient and S is the solubility coefficient in the membrane. Selectivity ($\alpha_{A/B}$) for gases A and B is defined as the following equation [15].

$$\alpha_{A/B} = \frac{P_A}{P_B} \tag{2}$$

To calculate the solution and diffusion coefficients of gases, Equations 3 and 4 were used respectively [16].

$$S = \underset{P \to 0}{Lim} \left(\frac{C}{P} \right) \tag{3}$$

$$MSD = (2dD)\, t^n \tag{4}$$

In the mentioned equations, C is the gas concentration and P is the pressure in the system. D is the diffusion coefficient, t is the simulation time, d is the number of dimensions in which the diffusion is carried out, n is the slope of the MSD diagram in terms of time, and the MSD is the mean square displacement, which is calculated from the following equation [17].

$$MSD = \langle |r_i(t) - r_i(0)|^2 \rangle \tag{5}$$

$r_i(0)$ and $r_i(t)$ are the initial and final location vectors of molecule i, respectively. The radial distribution function (RDF)) describes the probability of an atom or a molecule existence relative to reference atom or molecule. The average RDF for CO_2 with different atoms is the number of atoms in the desired spherical surface relative to the number of CO_2 molecules and the number of used simulation frames.

3. Results and discussion

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.

Table 1. The average density and FFV of simulated membranes

Constructed membranes	FFV	Density (g/cm^3)
PEBA 1657	0.115 (0.113 [18])	1.11 (1.14[19])

The results of calculating the diffusivity and solubility coefficients are given in Table 2. According to this table, CO_2 gas has a significant solubility compared to N_2 gas. This high solubility, which is caused by the interaction between CO_2 gas and the ether group of PEBA 1657, has caused the high selectivity of CO_2/N_2 (130). As mentioned in the previous section, the CO_2/N_2 selectivity was obtained from the permeability ratio of CO_2 to N_2 (116.9/0.9). The diffusion coefficient of different parts of the PEBA polymer chains was calculated and results are given in Table 3. It is clear that the mobility of the PE part of PEBA is higher compared to its PA part, which is due to its softness. Radial distribution function (RDF) of CO_2 gas around different parts of the polymer chain is plotted and shown in Fig. 2. Based on this figure, the peak related to the interaction of CO_2 gas with the PE part of the PEBA 1657 chain is more intensive than that of the PA part, which can be a reason for the strong interaction of the PE part with CO_2 gas compared to the PA part. This behavior shows that the PE part has a great tendency to CO_2 due to the

ether groups in its structure and has a lot of interaction with this gas. Ether groups have the ability to create a momentary dipole-quadruple interaction with the CO_2 and hence they can facilitate the passage of this gas across the membrane.

Table 2. The solubility and diffusivity coefficients and permeability of CO_2 and N_2 in simulated membranes

Tested gas	S ($\times 10^{-4}$ cm^3 (STP) cm^{-3} (polymer) $cmHg^{-1}$)	D ($\times 10^{-6} cm^2/s$)	P (Barrer)
CO_2	167.00	0.70	116.90
N_2	2.80	0.31	0.90

Table 3. The diffusivity coefficients of different parts of PEBA 1657 polymer chains

Membrane	D ($\times 10^{-6} cm^2/s$)
PEBA 1657	0.050
Polyether	0.053
Polyamide	0.028

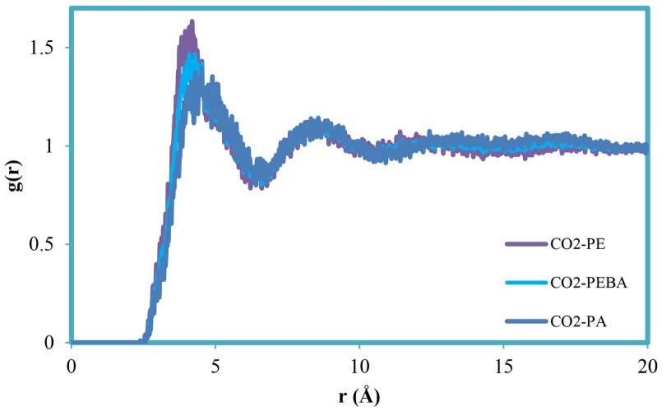


Fig. 2. RDF of CO_2 around different parts of PEBA 1657

3. Conclusion

The calculated structural properties showed that the density and FFV of the simulated membrane had a good approximation with the experimental values, which indicated the high accuracy of the simulation. In addition, based on the RDF results, the interaction of CO_2 gas with the polyether part is more than the polyamide part of the PEBA 1657 polymer chain. Comparing the mobility of different parts of the polymer chain showed that the polyether part had more mobility than the other part of the PEBA 1657 due to its softness. The performance properties of the simulated membrane showed that, solubility has a greater role in CO_2/N_2 selectivity than diffusivity in this membrane, so that CO_2 permeability and CO_2/N_2 selectivity were 116.9 and 130 Barrer, respectively.

Nomenclature

PA	Polyamide	FFV	Fractional free volume
PAN	Polyacrylonitrile	D	Diffusivity coefficient
PEI	Polyethylenimine	S	Solubility coefficient
PE	Polyether	P	Permeability
PEBA	Poly ether block amide	α	Selectivity
RDF	Radial distribution function	MSD	Mean square displacement

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