Temperature dependence of gas transport and sorption in carbon molecular sieve membranes derived from four 6FDA based polyimides: entropic selectivity evaluation

Shilu Fu ^a, Edgar S. Sanders ^b, Sudhir S. Kulkarni ^b, Graham B. Wenz ^a, William J. Koros^{a,*}

^a School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, 311 Ferst Drive, Atlanta, GA 30332-0100, United States

^b Air Liquide, Delaware Research and Technology Center, 200 GBC Drive, Newark, DE 19702, United States

Abstract

Temperature dependences of gas transport and sorption properties on four previously isothermally studied 6FDA based carbon molecular sieve (CMS) membranes: 6FDA/DETDA, 6FDA:BPDA(1:1)/DETDA, 6FDA/DETDA:DABA(3:2) and 6FDA/1,5-ND:ODA(1:1), were examined over the temperature range from 35 °C to 50 °C. The permeability, sorption and diffusivity of these materials are reported, and activation energies of permeation and diffusion as well as heats of sorption for gases CO₂, CH₄, O₂, and N₂ of these materials are compared. Permselectivity of these materials at 35 °C was probed for three gas pairs: CO₂/CH₄, O₂/N₂, and N₂/CH₄, and results show that diffusion selectivity is the dominant factor in providing permselectivity. Diffusion selectivity can be factored further into an energetic selectivity and an entropic selectivity. The temperature dependence of both energetic and entropic selectivity and their contributions to overall diffusion selectivity are discussed in detail in this study. All four CMS membranes showed larger than unity entropic selectivity discriminations. 6FDA/DETDA derived CMS membrane, with the most compact structure, showed the largest entropic selectivity for CO₂/CH₄, O₂/N₂, and N₂/CH₄ as about 7.40, 4.24, and 2.17 respectively. Analysis of the

selectivity factors provides insights into the effects of polymer precursor backbone structures on key transport and sorption properties in CMS materials.

1. Introduction

During the last two decades, gas separation membrane processes have progressed remarkably [1-3]. Comparing with conventional techniques like cryogenic distillation and amine adsorption, membrane based devices offer higher energy efficiency, lower operational cost and smaller footprint [4-6]. Membranes have been widely explored for application in fields such as: natural gas treatments, landfill gas recovery, olefin-paraffin separation, air separation, and hydrogen recovery [7-9]. Among the various membrane materials, polymer membranes are attractive for some cases because of economical processability into hollow fibers modules with high surface area per unit volume [10]. Despite many advantages, solution processable polymer membranes face an “upper bound” limitation, showing a trade-off between gas productivity and separation efficiency [11]. Additionally, polymeric membranes face plasticization issues in aggressive streams [12-14]. With response to the limitations of polymeric membranes, inorganic membranes, such as carbon molecular sieves (CMS) membranes and zeolites, have been identified as alternative materials [15].

CMS membranes are formed by thermal decomposition of precursor polymers [16]. Their porous nature, resulting from the chain packing imperfection during thermal decomposition, leads to high productivity. On the other hand, the co-existing molecular sieving morphology provides CMS membranes with effective size and shape discrimination between gas penetrants [17]. With this unique pore morphology, CMS membranes often show gas separation properties exceeding the polymeric upper bound [18]. In many studies, carbon molecular sieve (CMS) membranes have shown attractive gas separation performance for challenging gas pairs, including CO_2/CH_4 , O_2/N_2 , $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$, and $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ [1, 19]. In addition, CMS fiber

membranes can maintain stability under high pressure up to 1000 psi without undergoing plasticization [20-22].

Numerous studies have characterized temperature dependence of permeability and selectivity for polymeric membranes [23-26]; however, temperature effects on CMS membranes need more systematic investigations. In this study, CMS membranes derived from four novel in-house synthesized 6FDA-based precursor polyimides: 6FDA/DETDA, 6FDA:BPDA(1:1)/DETDA, 6FDA/DETDA:DABA(3:2), and 6FDA/1,5-ND:ODA(1:1) are considered. The structures, physical and transport properties at 35 °C of these polyimides were considered in a previous study [27]. Here we seek to provide a more in-depth understanding of the complex separation process by studying the sorptive and diffusive contributions and their fundamental contributions to permeation and permselectivity over a certain range of temperature. Analysis of activation energies of permeation and diffusion as well as heats of sorption for CO₂, CH₄, O₂, and N₂ in four CMS materials derived from the above-mentioned precursors provides insights regarding the permeability and selectivity changes associated with increased operating temperature. In addition, the study of these related CMS materials provides a tool to identify structural characteristics that affect permeability and selectivity. Finally, the diffusion selectivity is factored into “energetic” and “entropic” selectivity contributions to clarify the importance of entropic factors as tools to tailor membrane performance.

2. Theory and background

2.1 Pore structure of CMS membranes

CMS materials are formed by thermal decomposition of a precursor polymer under controlled atmosphere and temperature conditions. An idealized pore structure, as shown in

Figure 1, can be described as “slit-like”, and can be represented by a bimodal pore size distribution with larger micropores ($\sim 7\text{-}20\text{ \AA}$) connected by smaller ultramicropores ($< 7\text{ \AA}$) [16, 28-30]. Micropores provide sorption sites, while ultramicropores enable molecular sieving, thereby making CMS materials both highly permeable and highly selective, with properties lying above the upper-bound limit of polymers [28, 31].

Fig. 1. i) A simplified idealized slit-like pore structures in CMS membranes. (a): micropores with sizes of 7-20 Å; (b): ultramicropores with sizes $< 7\text{ \AA}$; ii) bimodal distribution of pores.

2.2 Transport in CMS membranes

Intrinsic membrane productivity for a penetrant i is characterized by permeability, which equals the pressure and thickness normalized steady-state flux of the penetrant, viz.,

$$P_i = \frac{N_i \cdot l}{\Delta p_i} \quad (1)$$

where N_i is the penetrant flux through the membrane of thickness (l) under a transmembrane partial pressure difference of Δp_i . The commonly used unit for permeability, Barrer, is defined as below:

$$\text{Barrer} = 10^{-10} \frac{\text{cc(STP)} \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}} \quad (2)$$

Gas transport through molecular sieves follow a “sorption-diffusion” mechanism. Permeability can also be expressed as the product of an average sorption coefficient S_i and an average diffusion coefficient D_i :

$$P_i = S_i \cdot D_i \quad (3)$$

The sorption coefficient S_i is a thermodynamic term governed primarily by the condensability of a gas penetrant and the extent of polymer-penetrant interaction. The diffusion coefficient D_i is a kinetic term related to the ability of a gas molecule to execute jumps within the selective matrix. The diffusion coefficient can be calculated using the experimental values of permeability and [sorption coefficients](#) according to Eq. (3). Sorption in CMS membranes is commonly described by Langmuir isotherm as shown below:

$$S_A = \frac{C_i}{p_i} = \frac{C'_{\text{Hi}} b_i}{1 + b_i p_i} \quad (4)$$

where C'_{Hi} is the Langmuir hole filling capacity and b_i is the Langmuir affinity constant.

[The average diffusion coefficient has been widely used to characterize CMS membranes in literature \[32-35\];](#) however, it can be highly dependent on concentration. In some cases, especially when highly adsorbing gases are considered, a thermodynamically corrected diffusivity – Maxwell-Stefan diffusivity is useful. This refinement is reserved for discussion in Appendix A, and the directly measurable average diffusivity is considered here, since the trends seen in both the average and Maxwell-Stefan diffusion coefficients tend to be similar.

The separation factor, characterizes a membrane's ability to distinguish between different penetrants, and is equal to the ratio of the upstream and downstream mole fraction of two components. When the downstream pressure is negligible, as in this study, one can write:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \left(\frac{D_A}{D_B} \right) \left(\frac{S_A}{S_B} \right) \quad (5)$$

Gas permeation and diffusion through membranes are typically activated processes, and an Arrhenius relationship describes the temperature dependence of gas permeation and diffusion [36, 37], viz.,

$$P_i = P_{0i} \exp\left(\frac{-E_{Pi}}{RT}\right) \quad (6)$$

$$D_i = D_{0i} \exp\left(\frac{-E_{Di}}{RT}\right) \quad (7)$$

On the other hand, a van't Hoff expression describes gas sorption in membranes:

$$S_i = S_{0i} \exp\left(\frac{-H_{Si}}{RT}\right) \quad (8)$$

where P_{0i} , D_{0i} and S_{0i} are pre-exponential factors, E_{Pi} is the activation energy for permeation, E_{Di} is the activation energy for diffusion, and H_{Si} is the heat of sorption. R is the universal gas constant, and T is the absolute temperature.

Combination of Eqs. (3) and (6)-(8) states that permeation activation energy is the sum of diffusion activation energy and heat of sorption, so it is a more complex parameter than either of the individual energetic factors.

$$E_{Pi} = E_{Di} + H_{Si} \quad (9)$$

Moreover, the pre-exponential factors can be arranged to yield:

$$P_{0i} = D_{0i} * S_{0i} \quad (10)$$

3. Experimental

3.1 Materials

The synthesis, characterization, and isothermal gas separation performance of the resulting CMS membranes based on the four precursor polyimides, whose repeat units are shown in Table 1 and which are the focus of this study, have been discussed in detail in the authors' previous study [27]. The pure gases used in this study are CO₂, CH₄, O₂, and N₂, which were purchased from Praxair, Inc. with purity higher than 99.97%. The kinetic diameters and critical temperatures of these gases are shown in Table 2 [38, 39].

Table 1. Chemical structures of the polyimides discussed in this study.

Polymer	Chemical structure
6FDA/DETDA	
6FDA:BPDA(1:1)/DETDA	
6FDA/DETDA:DABA(3:2)	
6FDA/1:5-ND:ODA(1:1)	

Table 2. Kinetic diameters and critical temperatures of gases studied.

Gases	Kinetic diameter(Å)	Critical temperature (K)
CO ₂	3.30	304
CH ₄	3.80	191
O ₂	3.46	155
N ₂	3.64	126

Former studies have shown that the polymer precursor has significant effects on the separation performance of the resulting CMS membrane [40-42]. The authors' previous work [27] has reported the permeability order of the CMS membranes derived from four precursors to fall in the following order: 6FDA/DETDA < 6FDA:BPDA(1:1)/DETDA < 6FDA/1,5-ND:ODA(1:1) < 6FDA/DETDA:DABA(3:2) as shown in Table 3. The significantly higher permeability of 6FDA/DETDA:DABA(3:2) derived CMS membranes (above 20,000 Barrer for CO₂ and above 4000 Barrer for O₂ at 35°C) is due to the carboxylic group in DABA, which provides possible crosslinking positions [43]. The permeability order suggests information about the general pore structures of these carbon membrane materials. Specifically, a higher permeability implies a more open pore structure in the material. Thus, based on the permeability data, the pore structure of the 6FDA/DETDA:DABA(3:2) derived carbon is presumed to be more open compared with 6FDA/1,5-ND:ODA(1:1), followed by 6FDA:BPDA(1:1)/DETDA, and 6FDA/DETDA derived carbon, which has the most compact pore structure. In fact, we proved this statement to be true by CO₂ uptake measurements shown in the later results section.

Table 3. Pure gas permeation and separation properties measured at 35 °C and ~207 kPa (30 psia) of CMS membranes pyrolyzed under inert Argon atmosphere with the final temperature as 550 °C[27].

Polymer	Permeability (Barrer)				Selectivity	
	CO ₂	CH ₄	O ₂	N ₂	CO ₂ /CH ₄	O ₂ /N ₂
6FDA/DETDA	2779	60	663	91	46.3	7.3
6FDA:BPDA(1:1)/DETDA	4663	194	1074	229	24.0	4.7
6FDA/1,5-ND:ODA(1:1)	9791	217	2038	337	45.1	6.0
6FDA/DETDA:DABA(3:2)	21740	723	4293	868	30.1	4.9

$$1 \text{ Barrer} = 10^{-10} \frac{\text{cc(STP)} \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}}$$

3.2 Formation of polymeric and CMS dense films

As has been described in detail in our previous paper, a solution casting method was used to fabricate polymeric dense films [27]. A homogeneous 3-5wt% polymer solution was prepared with pre-dried polymer powder, and poured onto a Teflon[®] casting dish based on a previously reported method [44]. After 3-5 days of slow evaporation, a polymeric dense film was formed and annealed at 210 °C to remove residual solvent.

CMS dense films were formed by pyrolyzing the corresponding precursor polymeric films. The entire pyrolysis setup is shown in Figure 2[45].

Fig.2. Schematic representation of the pyrolysis system used in this study[45].

In this study, all CMS dense films were prepared under inert Argon atmosphere with the final temperature as 550 °C, and the heating protocol is listed as below:

- 1) 50-250 °C at a ramp rate of 13.3 °C /min.
- 2) 250°C-535°C ($T_{\text{max}} - 15$) at a ramp rate of 3.85 °C /min.
- 3) 535°C-550°C at a ramp rate of 0.25 °C /min.
- 4) Soak for 2 hours at 550 °C.

3.3 Equipment

Pore distribution analysis from CO₂ sorption

Surface area, micropore volume and micropore distribution were determined by CO₂ uptake measurements done with a Micromeritics ASAP 2020. CO₂ at 0 °C was used to probe the pore structure. A software based on the concept of density functional theory was then used to analyze the pore size distribution of the CMS membranes. The carbon dense film was first formed, crushed and then loaded into the system.

Permeation measurements

CMS dense films were masked by sandwiching between impermeable aluminum tapes with a known area ($\sim 1\text{cm}^2$) exposed for permeation. A constant-volume permeation system was used in this study [10]. Both upstream and downstream cell chambers were evacuated until the outgassing rate was less than 1% of the test gas permeate rate. Then the upstream was pressurized with the test gas, and the pressure rise in the downstream was recorded using LabView (National Instruments, Austin, TX, USA) until steady state was achieved. All pure gas permeabilities were measured at $\sim 207\text{ kPa}$ (30 psia).

Sorption measurement

Sorption was measured with a pressure decay sorption system [46]. To start, the entire system was degassed overnight. The reservoir cell was filled with a known amount of test gas and equilibrated thermally for 10 to 15 minutes. The valve between the reservoir and sample cell was then opened to charge the sample cell with gas, and LabView recorded the pressure decay in both cells. Once the pressure reached equilibrium, the run was stopped and the amount of sorbed

gas was calculated based on a mole balance [46]. All sorption isotherms were measured in a pressure range from ~69 kPa (10 psia) to ~1100 kPa (160 psia).

Limitations on the epoxy used for permeation measurements in this study restricted the highest temperature to be 50 °C. As a result, pure gas permeation and sorption measurements at 35 °C, 42.5 °C, and 50 °C on CMS membranes were examined to evaluate temperature dependence.

To avoid complications due to physical aging, which was discussed in detail in previous work [27], CMS membrane samples were replaced after testing each gas pair at each temperature. For example, one CMS dense film was used to complete the measurements of CO₂/CH₄ permeability at 35 °C, and then it was replaced by another freshly-pyrolyzed dense film to test CO₂/CH₄ permeability at 42.5 °C. Sorption tests followed the same procedure as well. *Duplicate or triplicate* samples were characterized for each condition, so considerable experimental effort was involved in obtaining the data discussed below.

4. Results and discussion

4.1 CMS dense films characterization

Prior to discussing the main transport and sorption properties of these carbon membranes, it is useful to probe the difference in their pore structures. In this study, we used sorption-based micropore distribution analysis to provide insight in the pore morphologies of these materials.

The pore distributions (Fig. 3) of CMS membranes pyrolyzed at 550 °C under UHP Argon were achieved based on the CO₂ sorption uptakes analyzed in terms of density functional theory[18, 28]. Figure 3 indicates the presence of a bimodal pore distribution as the authors have

noted in the theory and background section. In both micropore and ultramicropore regions, there is no clear pattern observable about the peaks of the pore width distributions of the four membranes. As a matter of fact, the critical molecular sieving ultramicropores are expected to be smaller than 4 Å (in the range of gas kinetic diameters as listed in Table 2). Thus, the permeability-selectivity trends cannot be conclusively determined based on pore size distributions obtained from CO₂ sorption measurement.

Fig.3. Pore distributions of CMS membranes derived from 6FDA/DETDA, 6FDA:BPDA(1:1)/DETDA, 6FDA/1, 5-ND: ODA(1:1) and 6FDA/DETDA:DABA(3:2) from CO₂ sorption.

Table 4 lists the total pore volume and total surface area per gram of CMS samples, which as well correlates very well with gas permeability, i.e., membrane with higher gas permeabilities showed larger pore volume and surface area, indicating a more open porous structure. It is not

surprising to see the much larger pore volume and surface area in 6FDA/DETDA:DABA(3:2) CMS membranes considering its extremely high gas permeabilities.

For a comparison purpose, the total pore volume and total surface area of 550 °C pyrolyzed Matrimid[®] are also listed in Table 4[18]. As can be seen, the total pore volume and surface area of Matrimid carbon membrane are noticeably smaller than 6FDA- containing polymer derived carbon membranes. This comparison proves that 6FDA- containing polymers derived carbon membranes have more open structures compared with Matrimid[®] derived ones. It is believed that the inhibited chain packing introduced by the bulky 6F group provides higher free volume in the precursor, which carries over to much higher gas permeabilities observed in 6FDA- carbon than Matrimid[®] carbon.

Table 4. Total pore volume and surface area of CMS films derived from 6FDA/DETDA, 6FDA:BPDA(1:1)/DETDA, 6FDA/1, 5-ND: ODA(1:1) and 6FDA/DETDA:DABA(3:2). The data for Matrimid[®] is also listed for comparison purpose.

	Total pore volume ≤ 10.8 (cm ³ /g)	Total surface area (m ² /g)
6FDA/DETDA	0.1342	570.3
6FDA:BPDA(1:1)/DETDA	0.1385	598.0
6FDA/1,5-ND:ODA(1:1)	0.1898	804.5
6FDA/DETDA:DABA(3:2)	0.2458	1060.3
Matrimid [®]	0.1041	478.1[18]

4.2 Temperature dependence of permeability

In this study, CO₂, CH₄, O₂, and N₂ permeability of CMS membranes derived from 6FDA/DETDA, 6FDA:BPDA(1:1)/DETDA, 6FDA/DETDA:DABA(3:2), and 6FDA/1,5-

ND:ODA(1:1) were obtained at ~207 kPa (30 psia) and 35 °C, 42.5 °C, and 50 °C. Measurements at higher temperatures were avoided to prevent artifacts due to possible degradation of the adhesive on the foil used to define the permeation area.

Figure 4 shows least squares fit of the permeability of four gases versus inverse absolute temperature for four CMS materials. As with studies on polymeric membranes [26, 47], the gas permeability of CMS membranes increases with temperature. According to Eq. (3), the permeability temperature dependence is a combination of diffusion and sorption coefficient temperature dependencies. Diffusion coefficients increase with temperature, because of positive diffusion activation energies, while sorption coefficients decrease due to typical negative heats of sorption. The change in diffusion coefficients usually outweighs the change in sorption coefficients as has been proven in literature [19, 45] and can be seen in the later section, as a result, permeability generally increases with temperature. The detailed temperature dependence of diffusion and sorption coefficients will be discussed in later sections.

Fig. 4. Temperature dependence of permeability for various gases in CMS membranes derived from 6FDA/DETDA, 6FDA:BPDA(1:1)/DETDA, 6FDA/DETDA:DABA(3:2), and 6FDA/1,5-ND:ODA(1:1) at ~207 kPa (30 psia) in the temperature range from 35 °C to 50 °C. (All data points are presented with error bars, some of the error bars are too small to be seen)

The permeation activation energies and the corresponding permeation pre-exponential factors for CO_2 , CH_4 , O_2 , and N_2 of the four CMS materials are tabulated in Table 5 and Table 6. Clearly, permeation activation energy depends on both penetrant sizes and CMS types. The permeation activation energies increase with penetrant size in the order $CO_2 < O_2 < N_2 < CH_4$. On

the other hand, it is noted that the CMS membrane with higher permeabilities possesses lower gas permeation activation energies for all gases. As shown in Table 3, the permeability order of the four CMS membranes at 35 °C to be: 6FDA/DETDA < 6FDA:BPDA(1:1)/DETDA < 6FDA/1,5-ND:ODA(1:1) < 6FDA/DETDA:DABA(3:2), while Table 5 shows a reverse order for permeation activation energy order. More specifically, 6FDA/DETDA CMS has the highest permeation activation energies for all gases and 6FDA/DETDA:DABA(3:2) CMS has the lowest. Since permeation activation energy is the sum of diffusion activation energy and heat of sorption, a detailed analysis of these factors will be pursued in the following sections.

Table 5. Permeation activation energies of four gases for CMS membranes derived from 6FDA/DETDA, 6FDA:BPDA(1:1)/DETDA, 6FDA/DETDA:DABA(3:2), and 6FDA/1,5-ND:ODA(1:1) at ~207 kPa (30 psia) in the temperature range from 35 °C to 50 °C.

CMS membrane	E _p [kJ/mol]			
	CO ₂	CH ₄	O ₂	N ₂
6FDA/DETDA	8.8	11.7	10.8	11.5
6FDA:BPDA(1:1)/DETDA	8.3	11.5	10.3	11.3
6FDA/1,5-ND:ODA(1:1)	7.9	11.0	9.5	10.5
6FDA/DETDA:DABA(3:2)	7.1	10.8	8.4	10.4

Table 6. Permeation pre-exponential factors of four gases for CMS membranes derived from 6FDA/DETDA, 6FDA:BPDA(1:1)/DETDA, 6FDA/DETDA:DABA(3:2), and 6FDA/1,5-ND:ODA(1:1) at ~207 kPa (30 psia) in the temperature range from 35 °C to 50 °C.

CMS membrane	P _o [Barrers]			
	CO ₂	CH ₄	O ₂	N ₂
6FDA/DETDA	8.7*10 ⁴	5.7*10 ³	4.4*10 ⁴	8.1*10 ³
6FDA:BPDA(1:1)/DETDA	1.2*10 ⁵	1.7*10 ⁴	6.0*10 ⁴	1.9*10 ⁴
6FDA/1,5-ND:ODA(1:1)	2.1*10 ⁵	1.6*10 ⁴	8.2*10 ⁴	2.1*10 ⁴
6FDA/DETDA:DABA(3:2)	3.5*10 ⁵	5.0*10 ⁴	1.1*10 ⁵	5.0*10 ⁴

The permeability pre-exponential factors correspond to the hypothetical intercepts at infinite temperature, so it has a complex physical interpretation associated with the combined nature of the parameters in Eq. (10).

4.3 Temperature dependence of sorption coefficients

CO₂, CH₄, O₂, and N₂ sorption measurements of CMS membranes derived from 6FDA/DETDA, 6FDA:BPDA(1:1)/DETDA, 6FDA/DETDA:DABA(3:2), and 6FDA/1,5-ND:ODA(1:1) were obtained at 35 °C, 42.5 °C, and 50 °C. The sorption coefficient, $S = C/P$, can be determined as the secant slope of the isotherm at a given pressure. Figure 5 shows the CO₂, CH₄, O₂, and N₂ sorption isotherms of 6FDA/DETDA:DABA(3:2) CMS membrane at the three temperatures along with the Langmuir mode fitting, and the fitted parameters are listed in Table 7. These isotherms are representative of those obtained for the other three CMS membranes studied here, which, along with the Langmuir mode fitting parameters, are provided in appendix B due to space limitation. The non-linear nature of Langmuir mode determines that the sorption coefficient varies somewhat with pressure. For consistency, the sorption coefficients reported here correspond to a sorption pressure of ~207 kPa (30 psia), equals to the permeation feed pressure reported earlier.

Fig. 5. CO₂, CH₄, O₂, and N₂ sorption isotherms of 6FDA/DETDA:DABA(3:2) CMS membrane at 35 °C, 42.5 °C, and 50 °C.

Table 7. CO₂, CH₄, O₂, and N₂ Langmuir mode parameters of 6FDA/DETDA:DABA(3:2) CMS membrane at 35 °C, 42.5 °C, and 50 °C.

6FDA/DETDA:DABA(3:2)						
	35 °C		42.5 °C		50 °C	
	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄
C _H [cm ³ (STP)/cm ³]	172.2	114.3	168.8	96.6	157.0	92.8
b [1/kPa]	0.0057	0.0020	0.0051	0.0020	0.0051	0.0020
	O ₂	N ₂	O ₂	N ₂	O ₂	N ₂
	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄
C _H [cm ³ (STP)/cm ³]	108.3	65.2	100.8	63.1	98.5	58.1
b [1/ kPa]	0.0010	0.0013	0.0010	0.0012	0.0010	0.0012

As expected, the Langmuir capacity associated with filling of the microvoids in the CMS increases with gas critical temperature in the order: N₂ < O₂ < CH₄ < CO₂, and decreases as

temperature increases. The drop of C'_H is primarily caused by decreased density of sorbed penetrants at higher temperature at saturation of the CMS microvoids [48].

Van't Hoff relationships (Eq. (8)) describe the temperature dependence of sorption coefficients, and Figure 6 shows the least squares fit of sorption coefficients of four gases versus inverse absolute temperature for the four CMS materials. The apparent heats of sorption and the corresponding sorption pre-exponential factors for CO₂, CH₄, O₂, and N₂ of the four CMS materials are tabulated in Table 8 and Table 9. As expected, sorption coefficients of all gases decrease with increasing temperature, reflecting a negative heat of sorption. In flexible polymers, the heat of sorption reflects the sum of two energetic contributions: one part represents the enthalpy change when a gas molecule transfers from the gas phase into a more stabilized sorbed state. This enthalpy change is mainly governed by the gas critical temperature, which measures the tendency of the molecule to exist in the sorbed state. The other energetic contribution represents the combination of formation of a sorption site and the energy of mixing the sorbed molecule with the formed site [49, 50]. In rigid porous CMS media, the need to form a sorption site is absent. Table 8 shows the relationship between gas condensability and the sorption heat. The heat of sorption increases in the order: N₂ < O₂ < CH₄ < CO₂ for the four CMS materials, which follows the order of gas critical temperature listed in Table 2. This general trend is consistent with expectation that the first factor, related to condensability, is dominant for these CMS materials. Table 8 also shows only moderate differences in the sorption enthalpy between CMS samples, probably showing similar intrinsic micropore natures of the different CMS materials.

Fig. 6. Temperature dependence of sorption coefficients for various gases in CMS membranes derived from 6FDA/DETDA, 6FDA:BPDA(1:1)/DETDA, 6FDA/DETDA:DABA(3:2), and 6FDA/1,5-ND:ODA(1:1) at ~207 kPa (30 psia) in the temperature range from 35 °C to 50 °C.

Table 8. Apparent heats of sorption of four gases for CMS membranes derived from 6FDA/DETDA, 6FDA:BPDA(1:1)/DETDA, 6FDA/DETDA:DABA(3:2), and 6FDA/1,5-ND:ODA(1:1) at ~207 kPa (30 psia) in the temperature range from 35 °C to 50 °C.

CMS membrane	H_s [kJ/mol]			
	CO ₂	CH ₄	O ₂	N ₂
6FDA/DETDA	-8.7	-8.1	-7.1	-6.9
6FDA:BPDA(1:1)/DETDA	-9.1	-8.2	-7.2	-7.1
6FDA/1,5-ND:ODA(1:1)	-8.8	-8.1	-7.9	-7.7
6FDA/DETDA:DABA(3:2)	-7.7	-7.6	-7.3	-7.1

Table 9. Sorption pre-exponential factors of four gases for CMS membranes derived from 6FDA/DETDA, 6FDA:BPDA(1:1)/DETDA, 6FDA/DETDA:DABA(3:2), and 6FDA/1,5-ND:ODA(1:1) at ~207 kPa (30 psia) in the temperature range from 35 °C to 50 °C.

CMS membrane	S_0 [cc(STP)/cm ³ /kPa]			
	CO ₂	CH ₄	O ₂	N ₂
6FDA/DETDA	0.0127	0.0061	0.0045	0.0039
6FDA:BPDA(1:1)/DETDA	0.0105	0.0056	0.0051	0.0044
6FDA/1,5-ND:ODA(1:1)	0.0146	0.0075	0.0051	0.0042
6FDA/DETDA:DABA(3:2)	0.0219	0.0083	0.0052	0.0040

4.4 Temperature dependence of diffusion coefficients

Average diffusion coefficients of CO₂, CH₄, O₂, and N₂ at 35 °C, 42.5 °C, and 50 °C were calculated from the permeability and sorption coefficients according to Eq. (3). Maxwell-Stefan diffusion coefficients were also studied and are discussed in Appendix A. Similar to permeability, temperature dependence of diffusion coefficients follows an Arrhenius relationship. Figure 7 illustrates the least squares fit of the diffusion coefficients for the four gases versus inverse absolute temperature for four CMS materials. The activation energies of diffusion and the corresponding diffusion pre-exponential factors are calculated according to Eq. (9) and Eq. (10), and are tabulated in Table 10 and Table 11.

Fig. 7. Temperature dependence of diffusion coefficients for various gases in CMS membranes derived from 6FDA/DETDA, 6FDA:BPDA(1:1)/DETDA, 6FDA/DETDA:DABA(3:2), and 6FDA/1,5-ND:ODA(1:1) at ~207 kPa (30 psia) in the temperature range from 35 °C to 50 °C. (All data points are presented with error bars, some of the error bars are too small to be seen)

Table 10. Diffusion activation energies of four gases for CMS membranes derived from 6FDA/DETDA, 6FDA:BPDA(1:1)/DETDA, 6FDA/DETDA:DABA(3:2), and 6FDA/1,5-ND:ODA(1:1) at ~207 kPa (30 psia) in the temperature range from 35 °C to 50 °C.

CMS membrane	E_D [kJ/mol]			
	CO ₂	CH ₄	O ₂	N ₂
6FDA/DETDA	17.6	19.8	17.9	18.4
6FDA:BPDA(1:1)/DETDA	17.4	19.7	17.5	18.4
6FDA/1,5-ND:ODA(1:1)	16.7	19.1	17.4	18.2
6FDA/DETDA:DABA(3:2)	14.8	18.4	15.7	17.6

Table 11. Diffusion pre-exponential factors of four gases for CMS membranes derived from 6FDA/DETDA, 6FDA:BPDA(1:1)/DETDA, 6FDA/DETDA:DABA(3:2), and 6FDA/1,5-ND:ODA(1:1) at ~207 kPa (30 psia) in the temperature range from 35 °C to 50 °C.

CMS membrane	D_0 [cm ² /s]			
	CO ₂	CH ₄	O ₂	N ₂
6FDA/DETDA	5.1×10^{-4}	7.0×10^{-5}	7.4×10^{-4}	1.6×10^{-4}
6FDA:BPDA(1:1)/DETDA	8.7×10^{-4}	2.3×10^{-4}	8.8×10^{-4}	3.3×10^{-4}
6FDA/1,5-ND:ODA(1:1)	1.1×10^{-3}	1.6×10^{-4}	1.2×10^{-3}	3.7×10^{-4}
6FDA/DETDA:DABA(3:2)	1.2×10^{-3}	4.5×10^{-4}	1.7×10^{-3}	9.3×10^{-4}

Diffusion coefficients increase with temperature (Figure 7), reflecting a positive activation energy for diffusion. Diffusion activation energy measures the minimum energy required for a penetrant to make a diffusive jump from one equilibrium site to another, and depends on CMS packing of the matrix, and the penetrant size. Larger penetrants require higher diffusion activation energy to enable passage through the size discriminating ultramicropores responsible for diffusive selectivity. This critical difference between the activation step in rigid CMS vs. flexible polymeric matrices, which relies upon motion of the membrane matrix, is fundamentally related to the higher selectivities achievable in CMS materials vs. flexible polymers. As expected, the diffusion coefficients of a larger penetrant exhibit greater temperature dependence than a smaller penetrant. Our previous statement that diffusion activation energy is expected to

outweigh the heat of sorption in affecting permeation activation energy is validated by comparing Table 8 and Table 10. The increase in diffusion coefficient outweighs the decrease in sorption coefficient, thereby resulting in an increase of permeability with temperature. Clearly, the increase in permeability is lower than that of diffusivity, due to the decreasing tendency of the sorption coefficient in Eq (10).

Table 10 shows that, similar to the trend observed in permeability activation energy, for 6FDA/DETDA:DABA(3:2) CMS membrane, which showed highest permeability and most open pore structure (as shown in Fig. 3) among the four, shows the lowest diffusion activation energy, while 6FDA/DETDA CMS membrane with the lowest permeability and most compact pore structure, shows the highest diffusion activation energy for all gases. These results, combined with the pore structures discussed in section 4.1, indicate that tighter 6FDA/DETDA CMS hindered the ability of all molecules to make a diffusive jump, while in an open structure like 6FDA/DETDA:DABA(3:2) CMS, effective diffusive jumps are easily executed.

4.5 Selectivity considerations

The permselectivity in Eq. (5) emphasizes the combined diffusion selectivity and sorption selectivity. Table 12 lists at 35 °C and ~207 kPa (30 psia), the overall membrane permselectivity

$\alpha_{A/B}$, the sorption selectivity $\frac{S_A}{S_B}$, and the diffusion selectivity $\frac{D_A}{D_B}$ of three gas pairs CO₂/CH₄,

O₂/N₂, and N₂/CH₄ for four CMS materials. The $\alpha_{A/B}$ and $\frac{S_A}{S_B}$ are determined using the

permeation measurements and sorption measurements, while $\frac{D_A}{D_B}$ is calculated according to Eq.

(5). Clearly for all three gas pairs, diffusion selectivity is the dominant contributor to the overall

permselectivity, with sorption selectivity for CO₂/CH₄, O₂/N₂ separation is only contributing around 2.7 and 1.4 respectively, regardless of the different CMS structures. For N₂/CH₄ separation, sorption selectivity is even less than unity due to the higher condensability of CH₄ vs.

N₂ reflected by the large difference in $\frac{(T_C)_{CH_4}}{(T_C)_{N_2}}$. The preceding factors show that to achieve

higher separation efficiency, tuning of diffusion selectivity is the key tool to improve separation performance of CMS membranes.

Table 12. The overall membrane permselectivity $\alpha_{A/B}$, the sorption selectivity $\frac{S_A}{S_B}$, and the diffusion selectivity $\frac{D_A}{D_B}$ of gas pairs CO₂/CH₄, O₂/N₂, and N₂/CH₄ for four CMS materials at 35 °C and ~207 kPa (30 psia).

CMS membrane	α_{CO_2/CH_4}	$\frac{S_{CO_2}}{S_{CH_4}}$	$\frac{D_{CO_2}}{D_{CH_4}}$
6FDA/DETDA	46.7	2.7	17.6
6FDA:BPDA(1:1)/DETDA	24.9	2.8	9.0
6FDA/1,5-ND:ODA(1:1)	45.1	2.6	17.1
6FDA/DETDA:DABA(3:2)	30.1	2.8	10.7
CMS membrane	α_{O_2/N_2}	$\frac{S_{O_2}}{S_{N_2}}$	$\frac{D_{O_2}}{D_{N_2}}$
6FDA/DETDA	7.3	1.2	5.9
6FDA:BPDA(1:1)/DETDA	4.7	1.2	3.8
6FDA/1,5-ND:ODA(1:1)	6.0	1.3	4.5
6FDA/DETDA:DABA(3:2)	4.9	1.4	3.6
CMS membrane	α_{N_2/CH_4}	$\frac{S_{N_2}}{S_{CH_4}}$	$\frac{D_{N_2}}{D_{CH_4}}$
6FDA/DETDA	1.5	0.4	3.4
6FDA:BPDA(1:1)/DETDA	1.2	0.5	2.3
6FDA/1,5-ND:ODA(1:1)	1.6	0.5	3.3
6FDA/DETDA:DABA(3:2)	1.2	0.4	2.9

To further pursue this issue, one can probe deeper into the source of the diffusion selectivity. According to transition state theory [51], D_{0i} in Eq. (7) can be written as:

$$D_{0i} = e\lambda^2 \frac{kT}{h} \exp\left(\frac{S_D}{R}\right) \quad (11)$$

where λ is the average diffusive jump length in the diffusion medium, S_D is the activation entropy of diffusion, k is Boltzmann's constant, and h is Planck's constant [17]. For gas pairs concerned in this study, λ may be considered equivalent since the average distance between equilibrium micropores should be same. The diffusion selectivity then becomes:

$$\frac{D_A}{D_B} = \frac{D_{0A}}{D_{0B}} \exp\left(-\frac{E_{DA} - E_{DB}}{RT}\right) = \underbrace{\left[\exp\left(\frac{S_{DA} - S_{DB}}{R}\right) \right]}_{\substack{\uparrow \\ \text{Entropic} \\ \text{selectivity}}} \underbrace{\left[\exp\left(-\frac{E_{DA} - E_{DB}}{RT}\right) \right]}_{\substack{\uparrow \\ \text{Energetic} \\ \text{selectivity}}} \quad (12)$$

Eq. (12) shows clearly that the diffusion selectivity can be factored into an “energetic selectivity” and an “entropic selectivity”. Energetic selectivity stems from the difference in the diffusion activation energies of the two penetrants, while entropic selectivity primarily reflects the difference in the diffusion activation entropies of the two penetrants. Singh and Koros [17] have discussed the significance of entropic selectivity in molecular sieving materials for the O_2/N_2 pair. They also showed that in polymeric membranes, entropic selectivity is close to unity, while in CMS membranes, a much higher entropic selectivity is observed. The high entropic selectivity in CMS membrane is enabled by the rigid CMS pore structures, which polymer membrane lacks. This fundamental fact is the main reason for CMS and zeolite membranes to

surpass the polymeric upper bound. Entropic selectivity reflects differences in penetrant shape and subtle configurational differences experienced by penetrants transversing the diffusion-limiting ultramicropores. This entropic configurational control can be engineered by controlling differences in rotational and internal vibrational degrees of freedom between the diffusing components.

Table 13 summarizes at ~207 kPa (30 psia) and in the temperature range from 35 °C to 50 °C, the energetic and entropic selectivities of gas pairs CO₂/CH₄, O₂/N₂, and N₂/CH₄ for four CMS membranes. Energetically for each gas pair, 6FDA/DETDA, 6FDA:BPDA(1:1)/DETDA and 6FDA/1,5-ND:ODA(1:1) CMS membranes showed similar discriminating ability. Based on Eq.(12), the energetic selectivity shows a small change over the temperature range studied; however, using the average over this range is convenient for discussion purposes. The energetic selectivities for these materials for CO₂/CH₄, O₂/N₂, and N₂/CH₄ are all about 2.4, 1.3 and 1.5 respectively. 6FDA/DETDA:DABA(3:2) CMS membrane showed somewhat higher CO₂/CH₄, O₂/N₂ energetic selectivities as about 4.0 and 2.0. On the other hand, entropically, all four CMS membranes showed larger than unity entropic discriminations for these gas pairs, illustrating that rigid CMS materials are capable of discrimination between different molecular configurations. The degree of discrimination must depend highly on the limiting pore size distribution of the CMS materials. The three DETDA-based CMS membranes possessed increasing entropic selectivity for all gas pairs following the order: 6FDA/DETDA:DABA(3:2) < 6FDA:BPDA(1:1)/DETDA < 6FDA/DETDA, which is the opposite of their permeability and pore volume order for the various penetrants. Such a trend for CMS derived from related precursor may arise from progressive tightening of the ultramicropore distribution leading to lower permeability and systematically higher shape and configurational discrimination between

different penetrants. Somewhat surprisingly, CMS membranes derived from 6FDA/1,5-ND:ODA(1:1) showed the second highest permeability but also comparable entropic selectivity to the 6FDA/DETDA derived CMS. As noted in our previous paper, the 6FDA/1,5-ND:ODA(1:1) polymer precursor contains a stiff structure of 1,5-ND connected with a flexible structure of ODA. While this combination of features may provide an additional tool to provide CMS materials with both high permeability and high entropic discrimination, the basis for such an effect is not clear at this point, but deserves further exploration with other stiff-flexible pair combinations

Table 13. Summary of energetic and entropic selectivities of gas pairs CO₂/CH₄, O₂/N₂, and N₂/CH₄ for four CMS materials at ~207 kPa (30 psia) in the temperature range from 35 °C to 50 °C.

CMS membrane	Energetic selectivity		
	CO ₂ /CH ₄	O ₂ /N ₂	N ₂ /CH ₄
6FDA/DETDA	2.38-2.28	1.22-1.21	1.71-1.67
6FDA:BPDA(1:1)/DETDA	2.43-2.33	1.38-1.36	1.67-1.63
6FDA/1,5-ND:ODA(1:1)	2.48-2.38	1.38-1.36	1.41-1.39
6FDA/DETDA:DABA(3:2)	4.03-3.78	2.02-1.95	1.41-1.39
CMS membrane	Entropic selectivity		
	CO ₂ /CH ₄	O ₂ /N ₂	N ₂ /CH ₄
6FDA/DETDA	7.27±0.13	4.80±0.00	2.20±0.03
6FDA:BPDA(1:1)/DETDA	3.70±0.00	2.70±0.01	1.38±0.00
6FDA/1,5-ND:ODA(1:1)	6.90±0.00	3.24±0.03	2.34±0.02
6FDA/DETDA:DABA(3:2)	2.65±0.00	1.77±0.00	2.08±0.00

As discussed by Rungta [44], the final pyrolysis temperature is a useful tool in tuning the CMS material pore structure for CMS samples, and as a result, the entropic discrimination abilities. This time consuming study is underway and will be probed in a future study.

5. Conclusion

The effects of testing temperature on gas permeation, sorption, and diffusion were analyzed to provide insights into the factors governing gas separation properties in CMS membrane materials. As expected, an increase in permeability as well as diffusivity and a decrease in sorption occur with increasing testing temperature. The temperature dependence study was also shown to be not only practically important, but also fundamentally valuable in evaluating the transport trends based on different CMS precursor structures. This study also clearly emphasizes the significance of entropic selectivity in CMS membranes for gas separation.

Acknowledgement

The authors acknowledge the support from American Air Liquide and DOE for the funding of this project.

Reference

- [1] Saufi SM, Ismail AF. Fabrication of carbon membranes for gas separation—a review. *Carbon*. 2004;42(2):241-59.
- [2] Jeazet HB, Staudt C, Janiak C. A method for increasing permeability in O₂/N₂ separation with mixed-matrix membranes made of water-stable MIL-101 and polysulfone. *Chem Commun*. 2012;48(15):2140-2.
- [3] Mehran G, Sedigh, Lifang Xu, Theodore T. Tsotsis, Sahimi M. Transport and Morphological Characteristics of Polyetherimide-Based Carbon Molecular Sieve Membranes. *Ind Eng Chem Res*. 1999;38(9):3367-80.
- [4] Baker RW, Lokhandwala K. Natural Gas Processing with Membranes: An Overview. *Ind Eng Chem Res*. 2008;47(7):2109-21.
- [5] Baker RW. Future directions of membrane gas separation technology. *Ind Eng Chem Res*. 2002;41(6):1393-411.
- [6] Sim YH, Wang H, Li FY, Chua ML, Chung T-S, Toriida M, et al. High performance carbon molecular sieve membranes derived from hyperbranched polyimide precursors for improved gas separation applications. *Carbon*. 2013;53:101-11.
- [7] Tseng H-H, Itta AK. Modification of carbon molecular sieve membrane structure by self-assisted deposition carbon segment for gas separation. *Journal of Membrane Science*. 2012;389:223-33.
- [8] Xu L, Rungta M, Koros WJ. Matrimid® derived carbon molecular sieve hollow fiber membranes for ethylene/ethane separation. *J Membr Sci*. 2011;380(1-2):138-47.

- [9] Barsema JN, Vegt NFAvd, Koops GH, Wessling M. Carbon molecular sieve membranes prepared from porous fiber precursor. *J Membr Sci.* 2002;205(1-2):239-46.
- [10] Kiyono M, Williams PJ, Koros WJ. Effect of pyrolysis atmosphere on separation performance of carbon molecular sieve membranes. *J Membr Sci.* 2010;359(1-2):2-10.
- [11] Robeson LM. The upper bound revisited. *J Membr Sci.* 2008;320(1-2):390-400.
- [12] Omole IC, Adams RT, Miller SJ, Koros WJ. Effects of CO₂ on a High Performance Hollow-Fiber Membrane for Natural Gas Purification. *Ind Eng Chem Res.* 2010;49:4887-96.
- [13] Vaughn JT, Koros WJ, Johnson JR, Karvan O. Effect of thermal annealing on a novel polyamide-imide polymer membrane for aggressive acid gas separations. *J Membr Sci.* 2012;401-402:163-74.
- [14] Tin PS, Chung T-S, Liu Y, Wang R. Separation of CO₂/CH₄ through carbon molecular sieve membranes derived from P84 polyimide. *Carbon.* 2004;42(15):3123-31.
- [15] Wind JD, Staudt-Bickel C, Paul DR, Koros WJ. The Effects of Crosslinking Chemistry on CO₂ Plasticization of Polyimide Gas Separation Membranes. *Ind Eng Chem Res.* 2002;41(24):6139-48.
- [16] Suda H, Haraya K. Gas permeation through micropores of carbon molecular sieve membranes derived from Kapton polyimide. *J Phys Chem B.* 1997;101:3988-94.
- [17] Singh A, Koros WJ. Significance of entropic selectivity for advanced gas separation membranes. *Ind Eng Chem Res.* 1996;35(4):1231-4.
- [18] Rungta M, Xu L, Koros WJ. Structure-performance characterization for carbon molecular sieve membranes using molecular scale gas probes. *Carbon.* 2015;85:429-42.
- [19] Rungta M, Xu L, Koros WJ. Carbon molecular sieve dense film membranes derived from Matrimid® for ethylene/ethane separation. *Carbon.* 2012;50(4):1488-502.
- [20] Xu L, Rungta M, Brayden MK, Martinez MV, Stears BA, Barbay GA, et al. Olefins-selective asymmetric carbon molecular sieve hollow fiber membranes for hybrid membrane-distillation processes for olefin/paraffin separations. *J Membr Sci.* 2012;423-424:314-23.
- [21] Vu DQ, Koros WJ, Miller SJ. High pressure CO₂/CH₄ separation using carbon molecular sieve hollow fiber membranes. *Ind Eng Chem Res.* 2002;41(3):367-80.
- [22] Tanihara N, Shimazaki H, Hirayama Y, Nakanishi S, Yoshinaga T, Kusuki Y. Gas permeation properties of asymmetric carbon hollow fiber membranes prepared from asymmetric polyimide hollow fiber. *J Membr Sci.* 1999;160(2): 179-86.
- [23] Costello LM, Walker DRB, Koros WJ. Analysis of a thermally stable polypyrrolone for high temperature membrane-based gas separations. *J Membr Sci.* 1994;90(1-2):117-30.
- [24] Costello LM, Koros WJ. Thermally stable polyimide isomers for membrane based gas separations at elevated temperatures. *J Polym Sci Polym Phys Ed.* 1995;33(1):135-46.
- [25] Costello LM, Koros WJ. Effect of structure on the temperature dependence of gas transport and sorption in a series of polycarbonates. *J Polym Sci Polym Phys Ed.* 1994;32(4):701-13.
- [26] Zimmerman CM, Koros WJ. Polypyrrolones for membrane gas separations. II. activation energies and heats of sorption. *J Polym Sci Polym Phys Ed.* 1999;37(12):1251-65.
- [27] Fu S, Sanders ES, Kulkarni SS, Koros WJ. Carbon molecular sieve membrane structure-property relationships for four novel 6FDA based polyimide precursors. *J Membr Sci.* 2015;487:60-73.
- [28] Steel KM, Koros WJ. Investigation of porosity of carbon materials and related effects on gas separation properties. *Carbon.* 2003;41:253-66.
- [29] Xiao Y, Chung T-S, Chng ML, Tamai S, Yamaguchi A. Structure and properties relationships for aromatic polyimides and their derived carbon membranes: Experimental and simulation approaches. *J Phys Chem B.* 2005;109(40):18741-8.
- [30] Shao L, Chung T, Wensley G, Goh S, Pramoda K. Casting solvent effects on morphologies, gas transport properties of a novel 6FDA/PMDA/TMMDA copolyimide membrane and its derived carbon membranes. *Journal of Membrane Science.* 2004;244(1-2):77-87.

- [31] Das M, Perry JD, Koros WJ. Gas-Transport-Property Performance of Hybrid Carbon Molecular Sieve-Polymer Materials. *Ind Eng Chem Res.* 2010;49:9310-21.
- [32] Chen YD, Yang RT. Preparation of Carbon Molecular Sieve Membrane and Diffusion of Binary Mixtures in the Membrane. *Ind Eng Chem Res.* 1994;33(12):3146-53.
- [33] Wang K, Suda H, Haraya K. Permeation Time Lag and the Concentration Dependence of the Diffusion Coefficient of CO₂ in a Carbon Molecular Sieve Membrane. *Ind Eng Chem Res.* 2001;40(13):2942-6.
- [34] Su J, Lua AC. Experimental and theoretical studies on gas permeation through carbon molecular sieve membranes. *Sep Purif Technol.* 2009;69(2):161-7.
- [35] Lagorsse S. Carbon molecular sieve membranes Sorption, kinetic and structural characterization. *Journal of Membrane Science.* 2004;241(2):275-87.
- [36] Van Amerongen GJ. The permeability of different rubbers to gases and its relation to diffusivity and solubility. *J Appl Phys.* 1946;17(11):972-85.
- [37] Koros WJ. Barrier polymers and structures. Washington DC: American Chemical Society; 1990.
- [38] Breck DW. Zeolite Molecular Sieves, Structure, Chemistry and Use. New York, London, Sydney, Toronto: John Wiley & Sons; 1974.
- [39] Lide DR. Handbook of Chemistry and Physics. 71st ed. Boca Raton, FL: CRC Press; 1980.
- [40] Kim YK, Lee JM, Park HB, Lee YM. The gas separation properties of carbon molecular sieve membranes derived from polyimides having carboxylic acid groups. *J Membr Sci.* 2004;235(1-2):139-46.
- [41] Park HB, Kim YK, Lee JM, Lee SY, Lee YM. Relationship between chemical structure of aromatic polyimides and gas permeation properties of their carbon molecular sieve membranes. *J Membr Sci.* 2004;229(1-2):117-27.
- [42] Kiyono M, Williams PJ, Koros WJ. Effect of polymer precursors on carbon molecular sieve structure and separation performance properties. *Carbon.* 2010;48(15):4432-41.
- [43] Kratochvil AM, Koros WJ. Decarboxylation-Induced Cross-Linking of a Polyimide for Enhanced CO₂ Plasticization Resistance. *Macromolecules.* 2008;41(21):7920-7.
- [44] Rungta M. Carbon molecular sieve dense film membranes for ethylene/ethane separations. Georgia Institute of Technology, PhD, 2012.
- [45] Ning X, Koros WJ. Carbon molecular sieve membranes derived from Matrimid[®] polyimide for nitrogen/methane separation. *Carbon.* 2014;66:511-22.
- [46] Koros WJ, Paul DR. Design considerations for measurement of gas sorption in polymers by pressure decay. *J Polym Sci Polym Phys Ed.* 1976;14(10):1903-7.
- [47] Costello LM, Koros WJ. Temperature dependence of gas sorption and transport properties in polymers: measurement and applications. *Ind Eng Chem Res.* 1992;31(12):2708-14.
- [48] Koros WJ, Paul DR. CO₂ sorption in poly(ethylene terephthalate) above and below the glass transition. *J Polym Sci Polym Phys Ed.* 1978;37(12):1251-65.
- [49] Van Amerongen GJ. Diffusion in elastomers. *Rubber Chem Technol.* 1964;37(5):1065-152.
- [50] Koros WJ. Simplified analysis of gas/polymer selective solubility behavior. *J Polym Sci Polym Phys Ed.* 1985;23(8):1611-28.
- [51] Glasstone S, Laidler KJ, Eyring H. The Theory of Rate Processes. 1st ed. New York: McGraw-Hill Book Co., Inc.; 1941.
- [52] Karger J, Ruthven DM. Diffusion in zeolites and other microporous solids. New York, USA: John Wiley; 1992.

Appendix A. Calculations based on Maxwell-Stefan diffusivity

Unlike the conventional Fickian transport diffusivity D_f , the Maxwell-Stefan diffusivity $\mathfrak{D}$ accounts for the amount of gas taken up by the media [38, 52] in its interpretation. The two coefficients can be mathematically related as Eq. (A.1):

$$\mathfrak{D} = D_f \frac{d \ln C(p)}{d \ln p} \quad (\text{A.1})$$

where p is the single component gas phase equilibrium pressure and $C(p)$ is the gas absorbed by the media at equilibrium pressure of p . In combination with a Langmuir isotherm model shown in Eq. (4), for gas i , one finds:

$$\mathfrak{D}_i = D_{fi} (1 - \theta_i) \quad (\text{A.2})$$

where θ_i is the fractional site saturation factor defined as below:

$$\theta_i = \frac{b_i p_i}{1 + b_i p_i} \quad (\text{A.3})$$

The average diffusivity can be calculated by integrating the local Fickian diffusivity between a given upstream and downstream (vacuum in this study) concentration in the membrane. Thus, from Eqs. (A.1-3), one finds:

$$D_i = \frac{\int_{C_i}^0 D_f dC_i}{\int_{C_i}^0 dC_i} \approx \frac{\int_{\theta_i}^0 \frac{\mathfrak{D}_i}{(1 - \theta_i)} d\theta_i}{\int_{\theta_i}^0 d\theta_i} = \frac{\mathfrak{D}_i}{\theta_i} \ln \left(\frac{1}{1 - \theta_i} \right) \quad (\text{A.4})$$

Eq. (A.4) provides a bridge to connect the average diffusivity, which can be easily obtained from permeation and sorption measurements, to the Maxwell-Stefan diffusivity.

Fig. A.1. Temperature dependence of Maxwell-Stefan diffusivities for various gases in CMS membranes derived from 6FDA/DETDA, 6FDA:BPDA(1:1)/DETDA, 6FDA/DETDA:DABA(3:2), and 6FDA/1,5-ND:ODA(1:1) at ~207 kPa (30 psia) in the temperature range from 35 °C to 50 °C. (In accordance with Figure 7). (All data points are presented with error bars, some of the error bars are too small to be seen)

Table A.1. Diffusion activation energies, based on Maxwell-Stefan diffusivity, of four gases for CMS membranes derived from 6FDA/DETDA, 6FDA:BPDA(1:1)/DETDA, 6FDA/DETDA:DABA(3:2), and 6FDA/1,5-ND:ODA(1:1) at ~207 kPa (30 psia) in the temperature range from 35 °C to 50 °C. (In accordance with Table 10).

CMS membrane	E_D [kJ/mol]			
	CO ₂	CH ₄	O ₂	N ₂
6FDA/DETDA	17.6	18.9	18.2	18.8
6FDA:BPDA(1:1)/DETDA	17.8	18.5	17.5	17.8
6FDA/1,5-ND:ODA(1:1)	17.3	18.5	17.0	18.1
6FDA/DETDA:DABA(3:2)	16.3	18.4	16.0	17.8

Table A.2. Diffusion pre-exponential factors, based on Maxwell-Stefan diffusivity, of four gases for CMS membranes derived from 6FDA/DETDA, 6FDA:BPDA(1:1)/DETDA, 6FDA/DETDA:DABA(3:2), and 6FDA/1,5-ND:ODA(1:1) at ~207 kPa (30 psia) in the temperature range from 35 °C to 50 °C. (In accordance with Table 11).

CMS membrane	D_0 [cm ² /s]			
	CO ₂	CH ₄	O ₂	N ₂
6FDA/DETDA	3.7*10 ⁻⁴	4.3*10 ⁻⁵	7.6*10 ⁻⁴	1.6*10 ⁻⁴
6FDA:BPDA(1:1)/DETDA	6.9*10 ⁻⁴	1.3*10 ⁻⁴	8.1*10 ⁻⁴	2.3*10 ⁻⁴
6FDA/1,5-ND:ODA(1:1)	9.2*10 ⁻⁴	1.1*10 ⁻⁴	9.6*10 ⁻⁴	3.4*10 ⁻⁴
6FDA/DETDA:DABA(3:2)	1.5*10 ⁻³	9.3*10 ⁻⁴	1.7*10 ⁻³	3.8*10 ⁻⁴

Table A.3. Summary of energetic and entropic selectivities of gas pairs CO₂/CH₄, O₂/N₂, and N₂/CH₄ for four CMS materials at ~207 kPa (30 psia) in the temperature range from 35 °C to 50 °C, based on Maxwell-Stefan diffusivity. (In accordance with Table 13).

CMS membrane	Energetic selectivity		
	CO ₂ /CH ₄	O ₂ /N ₂	N ₂ /CH ₄
6FDA/DETDA	1.72-1.67	1.27-1.26	1.06-1.05
6FDA:BPDA(1:1)/DETDA	1.34-1.32	1.09-1.09	1.35-1.34
6FDA/1,5-ND:ODA(1:1)	1.62-1.58	1.59-1.55	1.14-1.13
6FDA/DETDA:DABA(3:2)	2.27-2.19	2.03-1.96	1.27-1.25
CMS membrane	Entropic selectivity		
	CO ₂ /CH ₄	O ₂ /N ₂	N ₂ /CH ₄
6FDA/DETDA	8.46±0.12	4.66±0.00	3.78±0.04
6FDA:BPDA(1:1)/DETDA	5.32±0.01	3.48±0.00	1.79±0.01
6FDA/1,5-ND:ODA(1:1)	8.69±0.01	2.77±0.02	3.25±0.03
6FDA/DETDA:DABA(3:2)	3.89±0.03	1.78±0.01	2.44±0.00

Figure A.1 shows the temperature dependence of Maxwell-Stefan diffusivities for various gases of the four CMS membranes at ~207 kPa (30 psia) and in the temperature range from 35 °C to 50 °C.

Table A.1 and Table A.2 tabulate the Maxwell-Stefan diffusion activation energies and the corresponding Maxwell-Stefan diffusion pre-exponential factors for various gas of the four CMS membranes at ~207 kPa (30 psia) and in the temperature range from 35 °C to 50 °C.

Table A.3 summarizes at ~207 kPa (30 psia) and in the temperature range from 35 °C to 50 °C, the energetic and entropic selectivities of gas pairs CO₂/CH₄, O₂/N₂, and N₂/CH₄ for the four CMS membranes calculated based on Maxwell-Stefan diffusivity.

The general trends we observed from the results based on average diffusion coefficients are also valid for Maxwell-Stefan diffusion coefficients with only minor differences. By comparing Figure A.1 and Figure 7, clearly, as for the average diffusivities (Fig.7), the Maxwell-Stefan diffusivities increase with temperature. Table A.1 shows that, similar to the trend observed in average diffusion activation energy, the 6FDA/DETDA:DABA(3:2) CMS membrane, which shows the highest permeabilities (Table 3) among the four, shows the lowest Maxwell-Stefan diffusion activation energy. Also as expected, the energetic and entropic selectivities of gas pairs CO₂/CH₄, O₂/N₂, and N₂/CH₄ for the four CMS membranes calculated based on Maxwell-Stefan diffusivity shows consistent trends as obtained from calculation based on average diffusivity.

Essentially, Maxwell-Stefan diffusivities represent the diffusivity at zero loading. The more condensable the gas is, the more different the Maxwell-Stefan diffusivity is from the average diffusivity due to the concentration in Eq. (A.2). In this case, the results related with CO₂ were altered the most compared to the case with other less condensable gases.

Appendix B. Supplementary figures and tables

Fig. B.1. CO₂, CH₄, O₂, and N₂ sorption isotherms of 6FDA/DETDA CMS membrane at 35 °C, 42.5 °C, and 50 °C.

Table B.1. CO₂, CH₄, O₂, and N₂ Langmuir mode parameters of 6FDA/DETDA CMS membrane at 35 °C, 42.5 °C, and 50 °C.

6FDA/DETDA						
	35 °C		42.5 °C		50 °C	
	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄
C _H [cm ³ (STP) /cm ³]	155.5	107.3	145.5	90.9	132.5	85.1
b [1/kPa]	0.0051	0.0019	0.0051	0.0022	0.0051	0.0022
	O ₂	N ₂	O ₂	N ₂	O ₂	N ₂
	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄
C _H [cm ³ (STP) /cm ³]	90.1	64.4	84.9	61.1	83.9	60.8
b [1/kPa]	0.0010	0.0012	0.0010	0.0012	0.0087	0.0010

Fig. B.2. CO₂, CH₄, O₂, and N₂ sorption isotherms of 6FDA:BPDA(1:1)/DETDA CMS membrane at 35 °C, 42.5 °C, and 50 °C.

Table B.2. CO₂, CH₄, O₂, and N₂ Langmuir mode parameters of 6FDA:BPDA(1:1)/DETDA CMS membrane at 35 °C, 42.5 °C, and 50 °C.

6FDA:BPDA(1:1)/DETDA						
	35 °C		42.5 °C		50 °C	
	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄
C _H [cm ³ (STP) /cm ³]	127.0	94.4	121.7	88.2	113.1	81.8
b [1/kPa]	0.0068	0.0020	0.0062	0.0020	0.0061	0.0020
	O ₂	N ₂	O ₂	N ₂	O ₂	N ₂
	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄
C _H [cm ³ (STP) /cm ³]	107.5	73.0	101.0	63.2	95.4	56.9
b [1/kPa]	0.0010	0.0012	0.0010	0.0013	0.0010	0.0013

Fig. B.3. CO₂, CH₄, O₂, and N₂ sorption isotherms of 6FDA/1,5-ND:ODA(1:1) CMS membrane at 35 °C, 42.5 °C, and 50 °C.

Table B.3. CO₂, CH₄, O₂, and N₂ Langmuir mode parameters of 6FDA/1,5-ND:ODA(1:1) CMS membrane at 35 °C, 42.5 °C, and 50 °C.

6FDA/1,5-ND:ODA(1:1)						
	35 °C		42.5 °C		50 °C	
	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄
C _H [cm ³ (STP)/cm ³]	158.9	103.2	152.3	94.3	143.3	92.9
b [1/kPa]	0.0072	0.0026	0.0064	0.0026	0.0062	0.0024
	O ₂	N ₂	O ₂	N ₂	O ₂	N ₂
	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄
C _H [cm ³ (STP)/cm ³]	125.2	112.1	114.3	101.9	99.4	95.9
b [1/kPa]	0.0010	0.0009	0.0012	0.0009	0.0012	0.0009