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Pure- and Mixed-gas Permeation of CO₂ and CH₄ in Thermally Rearranged Polymers Based on 3,3'-dihydroxy-4,4'-diamino- biphenyl (HAB) and 2,2'-bis-(3,4-dicarboxyphenyl) Hexafluoropropane Dianhydride (6FDA)

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Abstract

Permeability coefficients for pure CO₂, pure CH₄, and CO₂/CH₄ mixtures containing 50% CO₂ are reported for a polyimide synthesized from 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB) and 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and for three thermally-rearranged (TR) derivatives thereof. Permeability measurements were made at 35 °C for fugacities ranging from 4 to 25 atm. The permeability of CO₂ and CH₄ increased as the degree of TR conversion increased. For example, CO₂ permeability at 10 atm increased by a factor of 30 between the unconverted polyimide and its TR analog converted at 450 °C. In pure-gas experiments, CO₂ was observed to plasticize the unconverted polyimide, but it did not appear to plasticize the TR polymers. In mixed-gas experiments, dual-mode competitive sorption caused a depression in CH₄ permeability, with very little change in CO₂ permeability. In addition, plasticization by CO₂ was evident in the CH₄ mixed-gas permeability trends, but its impact was small in contrast with dual-mode competitive effects. Consequently, CO₂/CH₄ mixed-gas permeability selectivity was higher than the ideal selectivity, calculated as the ratio of pure gas permeability coefficients. The dual-mode sorption and permeation model was fit to the experimental data. Dual-mode model parameters and model predictions are reported, along with their confidence intervals. By comparing the dual-mode model predictions with the experimental mixed-gas data, the degree of CO₂-induced plasticization was observed to decrease as the degree of TR conversion increased and was completely absent (within experimental uncertainty) for the TR polymer converted at 450 °C.

1. Introduction

A substantial effort has been expended in the search for superior polymeric materials for CO₂ removal from natural gas [1-2]. Very often, these studies focus on permeability measurements of pure CO₂ and pure CH₄ in candidate materials. Reports of experiments involving gas mixtures are rare by comparison, and when they are performed, permeability and selectivity for gas mixtures can often differ significantly from those of pure gases. The presence of one gas in a mixture may have a strong influence on the transport of other gases. For example, Lee et al. [3-4] compared pure- and mixed-gas permeation of CO₂ and CH₄ in cellulose acetate. Ideal CO₂/CH₄ selectivity values exhibited an increasing trend with increasing feed pressure. However, in mixed-gas experiments, the opposite trend was observed. At about 10 atm, the ideal CO₂/CH₄ selectivity was 76, but for a 70.6% CO₂/CH₄ mixture, the selectivity was only 20. In the presence of CO₂, the permeability of CH₄ increased dramatically, which translated to decreased selectivity. Results like these are commonly reported for polymers that plasticize. At elevated partial pressures, sorbed CO₂ swells the polymer, which leads to increased segmental mobility and reduced glass transition temperatures [5]. In the plasticized film, mobility increases for all penetrant species, but to a greater extent for larger molecules. As a result, the size-sieving capacity of the material is compromised, and diffusivity selectivity is reduced [6-8]. Similar findings have been reported in other studies of CO₂/CH₄ permeation in cellulose acetate [9-10], polyimides [11-14], and styrene/methyl methacrylate copolymers [15].

For separations involving CO₂, reductions in selectivity for mixed-gas compared to pure-gas experiments are often attributed to plasticization. However, other physical phenomena also play important roles. Sanders et al. [16] found that, in poly(methyl

methacrylate) films, CO₂ permeability at 15 atm decreases from its pure-gas value of 0.68 Barrer to 0.42 Barrer for a CO₂/C₂H₄ mixture containing 50% CO₂. This decrease in CO₂ permeability is attributed to competitive sorption, which, in addition to plasticization, contributes significantly to differences in selectivity for mixtures. Competitive sorption arises as a consequence of dual-mode sorption in glassy polymers [17-18]. The dual-mode theory postulates two distinct mechanisms for penetrant sorption: one mode follows Henry's law, which is analogous to dissolution of gas in a liquid, and the other mode follows the form of a Langmuir isotherm. The Langmuir mode behaves as if sorption occurs at a finite number of fixed sites, i.e., microvoids frozen in the polymer matrix due to the non-equilibrium nature of glassy polymers. Sorption into the Langmuir mode gives rise to the competitive effect. Since the number of Langmuir sites is fixed, species compete to occupy them. Thus, the presence of one gas reduces sorption, and hence permeability, of others. Affinity for the Langmuir sites generally increases with increasing penetrant condensability (e.g., as measured by critical temperature). When the condensabilities of species in a mixture are substantially different, the more condensable species tend to dominate the Langmuir sites and can strongly reduce permeability of the less condensable species.

Based on the aforementioned examples, one might conclude for CO₂-containing mixtures that mixed-gas selectivity is always lower than ideal selectivity. However, this is not true. While plasticization is usually detrimental to CO₂/CH₄ selectivity, it can in fact be beneficial in other separations. Lin et al. [19] studied CO₂/H₂ separation in crosslinked poly(ethylene glycol)-based membranes. These materials are reverse-selective for this gas pair, since they preferentially permeate the larger CO₂ molecule. The basis for selectivity in these materials is rooted in the high solubility of CO₂ compared with H₂. Diffusivity

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4 selectivity, on the other hand, favors H₂ over CO₂, and acts to lower the overall CO₂/H₂
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6 selectivity. Since plasticization diminishes diffusivity selectivity, it improves the overall
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8 selectivity for mixtures.
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11 Because CO₂ is more condensable than CH₄, dual-mode competitive sorption can act
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13 to improve selectivity for CO₂/CH₄ mixtures, although this effect may be overwhelmed if
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15 substantial plasticization is present. For example, Hillock and Koros [20] crosslinked
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17 polyimide films to harden them against plasticization. Mixtures of CO₂/CH₄ containing
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19 10% CO₂ at 4.4 atm total pressure gave a selectivity of 44.8 versus a pure-gas selectivity of
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21 37.1. Because CO₂ has a higher affinity for the Langmuir sites in the polymer, sorption of
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23 CH₄ was presumably suppressed in the presence of CO₂, thereby reducing methane
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25 transport and improving selectivity. Similar results were reported by Visser et al. [8] for
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27 asymmetric membranes made from Matrimid® 5218 blends. For Matrimid blended with
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29 the polyimide P84, CO₂/CH₄ mixtures containing 50% CO₂ at 8 atm fugacity had a mixed-
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31 gas selectivity of 36 versus a pure-gas selectivity of 29. Raharjo et al. [21] measured pure-
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33 and mixed-gas permeability and sorption of CH₄ and *n*-C₄H₁₀ in poly(1-trimethylsilyl-1-
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35 propyne) (PTMSP) and found that *n*-C₄H₁₀/CH₄ mixed-gas permeability selectivity was as
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37 much as 30 times higher than the ideal (i.e., pure gas) selectivity. Competitive sorption was
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39 partially responsible for the higher selectivity, but CH₄ diffusivity was also reduced in the
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41 presence of *n*-C₄H₁₀. The reduction in diffusivity was attributed to blocking of
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43 interconnected free-volume elements by *n*-C₄H₁₀, which hinders CH₄ transport and further
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45 increases selectivity.
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57 Recently, thermally rearranged (TR) polymers have emerged as promising materials
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59 for CO₂/CH₄ separations [22-23]. TR polymers are polybenzoxazoles (PBOs),
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polybenzimidazoles (PBIs), or polybenzothiazoles (PBTs) formed in a thermally induced solid-state reaction of an ortho-functional polyimide or polyamide precursor [23-25].

Owing to their unique free volume distribution and rigid structure, these materials exhibit very high separation performance for CO₂/CH₄ and other gas mixtures. They are highly chemically-resistant and are generally insoluble. They are resistant to plasticization by CO₂, possibly due in part to crosslinking occurring during thermal rearrangement [26]. In our previous work [27-28], we reported the permeation, diffusion, and sorption properties for pure gases in TR polymers based on 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB) and 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA). In the present study, we present mixed-gas permeation results at 35 °C for HAB-6FDA polyimide films and their TR derivatives. These results are presented alongside permeation results for pure CO₂ and pure CH₄. Plasticization in these materials decreases as the degree of conversion from polyimide to PBO increases. Selectivity in the mixed-gas experiments is higher than the ideal selectivity, owing to a decrease in CH₄ permeability when CO₂ is present. The impact of plasticization and dual-mode competitive sorption on permeability is discussed, and model parameters are extracted by fitting the experimental data. Our results illustrate a balance between plasticization and competitive sorption in mixed-gas performance and the necessity of mixed-gas studies to thoroughly elucidate the relative contributions of these processes.

2. Background

2.1. Solution-diffusion Model

Permeability is defined as the steady state flux normalized by the trans-membrane driving force and membrane thickness. We have adopted the following definition for permeability P_A of gas species A [29]:

$$P_A = \frac{N_A l}{f_{A,2} - f_{A,1}} \quad (1)$$

where N_A is the steady-state flux of species A, l is the thickness of the film, and $f_{A,1}$ and $f_{A,2}$ are the downstream and upstream fugacities of species A, respectively. Because the driving force for permeation is rooted in a chemical potential difference [30], fugacity is used rather than partial pressure in Eq. 1 [31]. For experiments involving gases that are effectively ideal, fugacity may be replaced by partial pressure. In the present work, compared to partial pressure, CO₂ fugacity is up to 14% lower in pure-gas experiments and up to 26% lower in mixed-gas experiments. If partial pressure were used in place of fugacity in Eq. 1, permeability values would be similarly affected, resulting in a discrepancy between pure- and mixed-gas results that might be falsely attributed to an interaction between the gases and the polymer. In this study, fugacity values were computed from pressure using the Soave-Redlich-Kwong (SRK) equation of state [32]. A comparison between fugacity and pressure is presented in Fig. 1.

According to the solution-diffusion model, the permeability of species A is given by [29]:

$$P_A = \bar{D}_A \frac{C_{A,2} - C_{A,1}}{f_{A,2} - f_{A,1}} \quad (2)$$

where $\bar{D}_A$ is the concentration-averaged effective diffusion coefficient of species A, and $C_{A,1}$ and $C_{A,2}$ are the concentrations of species A at the downstream and upstream faces of the polymer, respectively. When $f_{A,1} \ll f_{A,2}$ and $C_{A,1} \ll C_{A,2}$, Eq. 2 can be written:

$$P_A = \bar{D}_A S_A \quad (3)$$

where the solubility coefficient S_A is defined as $S_A = C_{A,2}/f_{A,2}$.

The selectivity $\alpha_{A/B}$ of a membrane for species A over species B is defined as the ratio of permeabilities, and in light of Eq. 3, may be expressed as the product of diffusivity selectivity and solubility selectivity:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{\bar{D}_A}{\bar{D}_B} \cdot \frac{S_A}{S_B} \quad (4)$$

Because Eq. 4 has been defined in terms of fugacity, selectivity is not equivalent to the separation factor. When $f_{A,1} \ll f_{A,2}$, the separation factor $\alpha_{A/B}^*$ is related to the selectivity by [6]:

$$\alpha_{A/B}^* = \frac{y_A/y_B}{x_A/x_B} = \alpha_{A/B} \frac{f_A/f_B}{x_A/x_B} \quad (5)$$

where y_A and y_B are the downstream mol fractions of species A and B, respectively, and x_A and x_B are the upstream mol fractions.

2.2. Dual-mode Model

Permeation in glassy polymers often obeys the dual-mode sorption and transport models. According to the dual-sorption model, sorption of gas A, C_A , may be decomposed

into two terms, C_{D_A} , the Henry's law concentration term, and C_{H_A} , the Langmuir-type concentration term [17]:

$$C_A = C_{D_A} + C_{H_A} = k_{D_A} f_A + C'_{H_A} \frac{b_A f_A}{1 + b_A f_A} \quad (6)$$

where k_{D_A} is the Henry's law partition coefficient for species A, C'_{H_A} is the Langmuir capacity coefficient, and b_A is the Langmuir affinity coefficient. Koros [33] extended the model to multi-component mixtures. For a mixture of two gases, A and B:

$$C_A = k_{D_A} f_A + C'_{H_A} \frac{b_A f_A}{1 + b_A f_A + b_B f_B} \quad (7)$$

Thus, the equilibrium concentration of species A in the polymer is reduced in the presence of species B. The affinity coefficients b_A and b_B determine the balance of gases A and B in the Langmuir sites. If $b_A f_A \gg b_B f_B$, the mixed-gas and pure-gas sorption of A are nearly equal. On the other hand, if $b_A f_A \ll b_B f_B$, species A will be excluded from the Langmuir sites and its mixed-gas sorption will be reduced by a value as high as C'_{H_A} .

Permeability in the dual-mode transport model is described by the so-called partial-immobilization concept, in terms of two diffusion coefficients D_{D_A} and D_{H_A} associated with the Henry's law and Langmuir modes, respectively [18]. For pure gases:

$$P_A = k_{D_A} \bar{D}_{D_A} + C'_{H_A} \bar{D}_{H_A} \frac{b_A}{1 + b_A f_A} \quad (8)$$

and for binary mixtures:

$$P_A = k_{D_A} \bar{D}_{D_A} + C'_{H_A} \bar{D}_{H_A} \frac{b_A}{1 + b_A f_A + b_B f_B} \quad (9)$$

If the dual-mode parameter values are known from pure-gas measurements, Eq. 9 may be used to predict mixed-gas permeability (provided that plasticization and other phenomena do not interfere). Determining all five parameters requires measurements of both sorption and permeation as a function of fugacity. When only permeation data are available, three parameters can be extracted from Eq. 8: the product $k_{D_A} \bar{D}_{D_A}$, the product $C'_{H_A} \bar{D}_{H_A}$, and b_A .

In the simplest form of the model, the dual-mode parameters are constants (i.e., they do not depend on the concentration of either gas in the polymer). The validity of this assumption with respect to the present study is discussed in section 4.2.

3. Experimental

3.1. Materials

3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB, >99% purity) was supplied by Wakayama Seika Kogyo Co., Ltd. (Wakayama City, Wakayama Prefecture, Japan) and was dried under vacuum at 50 °C for 24 hours before use while shielding it from light. 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA, 99% purity) was purchased from Sigma Aldrich (St. Louis, MO, USA). The 6FDA powder was dried initially under vacuum at room temperature for about 30 minutes. To dehydrate anhydride rings which may have hydrolyzed during storage, the 6FDA was then dried under -10 inHg vacuum at 200 °C for 6 hours and finally under full vacuum at 120 °C for 12 hours. 1-methyl-2-pyrrolidinone (NMP, 99% purity) was purchased from Sigma Aldrich and was purified by distillation immediately before use. Acetic anhydride (99.5% purity), pyridine (99.9% purity), and dimethylacetamide (DMAc, 99% purity) were purchased from Sigma Aldrich

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4 and used as received. Methane and carbon dioxide (research grade) were purchased from
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6 AirGas (Radnor, PA, USA) and used as received.
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9 10 **3.2. Polymer Synthesis and Film Preparation**

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12 The procedures for preparing film samples for permeation tests are described in
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14 detail in our previous work [28]. These procedures are summarized here only briefly.
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16 Equimolar amounts of HAB and 6FDA were dissolved in NMP to make a 15% (g/ml)
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18 solution and allowed to react at 0 °C to form a poly(amic acid). The poly(amic acid) was
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20 converted to polyimide (Fig. 2) via chemical imidization by adding acetic anhydride and
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22 pyridine to the solution. The polyimide was precipitated in methanol and then dried over
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24 the course of several days under vacuum at increasing temperatures up to 200 °C. The
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26 polyimide chemical structure was confirmed by ¹H NMR.
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33 In order to cast films, the polyimide was dissolved in DMAc to form a 2% (g/ml)
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35 solution. This solution was filtered using a 5.0 µm Millex-LS PTFE syringe filter (Millipore,
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37 SLLS025NS) and dispensed onto a glass casting plate. The bulk of the solvent was removed
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39 slowly under partial vacuum at 80 °C for 24 h in a vacuum oven. Once solid films had
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41 formed, the remaining solvent was removed under full vacuum at 200 °C for 24 h. The
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43 resulting films were nominally 40 µm thick. No detectable levels of solvent were observed
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45 by thermogravimetric analysis (TGA).
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51 Polyimide films were converted to polybenzoxazole (PBO) (Fig. 3) by heating under
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53 flowing N₂ in a tube furnace. Three heating protocols were followed, which are shown in
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55 Fig. 4 and Table 1. The heating protocol consists of an initial 60 minute treatment at 300 °C
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57 to ensure that all of the imide rings were closed followed by a 30-60 minute treatment at
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the final conversion temperature. As the thermal treatment temperature increases, so does the degree of conversion to PBO. We define percent conversion as the ratio of the actual mass loss during thermal treatment to the theoretical mass loss associated with stoichiometric conversion of the polyimide structure to PBO. The actual mass loss for films converted according to each protocol was measured by TGA. Estimating the percent conversion in this way does not discriminate between mass loss due to PBO conversion and mass loss through other processes (e.g., thermal degradation) [34]. Byproducts of the thermal conversion process were characterized using TGA mass-spectrometry by Smith et al. [28]. At temperatures up to 450 °C, the reaction byproducts were consistent with the polyimide to PBO conversion; only at higher temperatures were measurable quantities of degradation byproducts observed.

3.3. Pure- and Mixed-gas Permeation

To ascertain the impact of PBO conversion on basic transport properties, dual-mode behavior, and plasticization, a systematic permeation study of the HAB-6FDA polyimide and several TR derivatives was conducted. Measurements were made at 35 °C for pure CO₂, pure CH₄, and a CO₂/CH₄ mixture containing 50% CO₂. Pure-gas permeability was determined at feed pressures ranging from 4 to 28 atm. Mixed-gas permeability was determined at total feed pressures ranging from 8 to 55 atm. Results are reported for the unconverted polyimide and three TR derivatives, which were converted at increasing temperatures and, consequently, increasing percent conversion to PBO (cf., Table 1). The TR conversion protocols were chosen to match our prior studies [27-28].

The apparatus for making permeability measurements is illustrated in Fig. 5. This system bears many similarities to a system design reported by O'Brien et al. [35].

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4 The upstream challenge gas mixture was supplied by a pair of mass flow controllers
5 (MFCs) (Model F-231M, Bronkhorst USA, Bethlehem, PA, USA). Measurements of pure
6 gases were performed using a single MFC. Upstream pressure was monitored using a 1000
7 psig (69 atm) diaphragm strain-gauge pressure transducer (Model STJE, Honeywell
8 Sensotec, Columbus, OH, USA). A proportional solenoid valve (Model F-011A, Bronkhorst
9 USA), labeled V4 in Fig. 5, was wired in a feedback loop with the pressure transducer to
10 regulate the upstream pressure within 1% of the desired setpoint.
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22 Total membrane flux was measured using the constant-volume, variable pressure
23 method [35-36]. Initially, the membrane sample was degassed for at least 16 hours by
24 holding both upstream and downstream under vacuum with valves V1, V2, V4, and V6
25 closed and V3, V5, V7, and V8 open. Depending on the expected flux, V7 may be closed to
26 select a small downstream volume or opened to select a large volume. The system leak rate
27 was determined by closing V5 for at least one hour and measuring the rate of downstream
28 pressure rise. Next, the upstream was pressurized by enabling the MFCs, opening V1
29 and/or V2, closing V3, and placing V4 into feedback mode. V5 remained closed throughout
30 the pressurization process and until permeation reached steady-state. While V5 was
31 closed, permeating gas expanded into the downstream volume. The downstream pressure
32 was recorded at a rate of 1 Hz using a 10 Torr capacitance manometer (Baratron 626A,
33 MKS Instruments, Andover, MA, USA). The lag time, θ , for pure gases was calculated by
34 analyzing the transient behavior of the downstream pressure [37]. To ensure steady-state
35 conditions, flux measurements were made after waiting a period of at least 6θ . For mixed-
36 gas measurements, 6θ was determined using the lag time of the slower pure gas. The ideal
37 gas law was used to calculate flux from the steady-state rate of pressure rise (after
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4 accounting for the leak rate), the volume of the downstream, and the area of film exposed
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6 to the challenge gas. After a measurement cycle was completed, V5 was opened for five
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8 minutes to evacuate the downstream volume and then measurements continued with the
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10 next pressure point.
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15 In mixed-gas experiments, gas chromatography (GC) was used to determine the
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17 individual gas concentrations in the retentate and permeate streams. Data from these
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19 measurements were used to confirm the composition of the upstream gas and to determine
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21 the fraction of membrane flux due to each species. Measurements were performed using
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23 an Agilent 6890 (Agilent Technologies, Santa Clara, CA, USA) equipped with a thermal
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25 conductivity detector (TCD) and a 30 m × 0.53 mm GS-Carbon PLOT capillary column
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27 (Agilent Technologies). Gas from the retentate stream was injected onto the column for
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29 analysis using a 6-port valve with a 50 µl sample loop. Measurement of the permeate was
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31 accomplished with a second 6-port valve with a 1000 µl sample loop, connected at one end
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33 to the downstream volume through V6, and at the other end through V8 to a vacuum pump.
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35 After making a flux measurement as described above, the downstream was evacuated by
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37 opening V5 for five minutes, closing V7, and then filling the downstream to a pressure of 10
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39 Torr with fresh permeate gas. The GC sample loop was held under vacuum with V8 open
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41 and V6 closed until the downstream volume was filled. Once the downstream volume was
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43 filled, V6 was opened, V8 was closed five seconds later, and V6 was held open for 60
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45 seconds to allow the downstream gas to expand into the sample loop. This sample was
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47 then injected onto the column. Four GC measurement cycles were performed at each feed
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49 pressure.
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Upstream gas flow rates in the mixed-gas experiments were chosen to be high enough to prevent concentration polarization at the upstream face of the film. When present, concentration polarization manifests itself as a dependence of permeate flux upon the upstream flow rate [38]. We tested for concentration polarization by making measurements at several upstream flow rates. For the permeation cell used in these experiments, which contains a flow distributor, concentration polarization effects were not present when the stage cut (i.e., the ratio of the upstream flow rate to the permeation rate) was less than about 1%. For the results presented in this study, the stage cut was less than 0.1%.

Carbon dioxide can have a long-term conditioning effect on many polymeric materials [39], which often results in higher permeability to all gases after exposure to CO₂. Precautions were taken to prevent CO₂-induced conditioning from affecting permeation measurements. Separate film samples were used for pure-gas and mixed-gas measurements. For pure-gas measurements, CH₄ was always tested before CO₂.

4. Results and Discussion

4.1. Pure- and Mixed-gas Permeation Measurements

Pure- and mixed-gas permeability measurements of CO₂ in the unconverted polyimide and the three TR derivatives are presented in Fig. 6. Across the fugacity range considered, pure-gas CO₂ permeability generally matches the mixed-gas permeability for all four polymers, although small deviations are present. Owing to the higher condensability of CO₂, it is expected to have a higher affinity for Langmuir sites than CH₄. As a consequence, CO₂ permeability is not expected to depend strongly on the amount of CH₄ present; any dual-mode competitive effects should cause mixed-gas CO₂ permeability

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4 to decrease only slightly relative to pure-gas values. The dual-mode model requires
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6 monotonically decreasing permeability as fugacity increases. For the polyimide (Fig. 6-A),
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8 the pure CO₂ permeation curve passes through a minimum at about 20 atm, and then
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10 begins to increase. Such a minimum is often referred to as the plasticization pressure
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12 point, below which the effects of plasticization are considered to be negligible [40]. Above
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14 the plasticization pressure, transport can no longer be described by the dual-mode model
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16 alone. Mixed-gas CO₂ permeability in the polyimide is slightly higher than for pure CO₂
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18 beyond the plasticization pressure. This difference is probably a consequence of the longer
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20 time required to make mixed-gas measurements compared with pure-gas measurements,
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22 during which time permeability increases slowly due to conditioning effects that often
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24 accompany plasticization [39]. For example, in pure CO₂ experiments, the polyimide
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26 sample was held at each pressure for a period of one hour; in mixed-gas experiments, the
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28 sample was held at each pressure for three to four hours to allow CH₄ to reach steady-state
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30 and to make the GC measurements. For the TR350, TR400, and TR450 polymers (Fig. 6-
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32 B, -C and -D, respectively), plasticization pressure points are not observed for CO₂ up to 25
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34 atm. Mixed-gas CO₂ permeability is slightly lower than for pure gas for all three TR
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36 polymers. Moreover, permeability increases systematically as a function of TR conversion.
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38 At 10 atm, CO₂ permeability is about 3 times higher for the TR-350 (36% conversion to
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40 PBO), 13 times higher for the TR-400 (59% conversion), and 30 times higher for the TR-
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42 450 (79% conversion) sample than for the unconverted polyimide.
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54 Permeability measurements for CH₄ are presented in Fig. 7. In contrast to CO₂, the
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56 mixed-gas permeability of CH₄ differs substantially from the corresponding pure gas
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58 measurements. At the low end of the fugacity range, CH₄ permeability is depressed for the
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4 mixed-gas case. For all four polymers, CH₄ mixed-gas permeability is approximately 20%
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6 lower at 10 atm than for the pure gas. Since CH₄ is less condensable than CO₂, CO₂ is
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8 expected to be favored over CH₄ in the Langmuir sites, and CH₄ mixed-gas permeability
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10 decreases as a result. None of the polymers have plasticization pressure points up to 28
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12 atm when exposed to pure CH₄. However, the plasticizing effect of CO₂ is evident in the CH₄
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14 mixed-gas permeability. The polyimide film (Fig. 7-A), which is the only material to exhibit
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16 a CO₂ plasticization pressure point, exhibits a mixed-gas CO₂ permeability minimum at 10
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18 atm. The minimum occurs at a lower point than the CO₂ plasticization point, and as
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20 fugacity increases, CH₄ permeability increases more than CO₂ permeability. Thus, CH₄ is a
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22 more sensitive probe for plasticization effects than CO₂, which is consistent with free-
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24 volume theory, where the mobility of the larger CH₄ molecule is more sensitive to changes
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26 in free volume than CO₂. If only the CO₂ data are considered, the three TR polymers do not
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28 show plasticization pressure points. However, the mixed-gas CH₄ permeability trends for
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30 the TR350 and the TR400 films (Fig. 7-B and -C) are consistent with plasticization
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32 occurring at about 10-15 atm. These permeability minima occur at higher fugacities than
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34 those of the polyimide, and, furthermore, the increase in permeability is less as a function
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36 of fugacity for the TR350 and TR400 than for the polyimide. Thus, the TR350 and TR400
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38 films are less susceptible to CO₂ plasticization than the unconverted polyimide. The TR450
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40 film (Fig. 7-D) does not exhibit a permeability minimum in the mixed-gas CH₄ data,
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42 suggesting the highest plasticization resistance of all samples considered. Thus, there
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44 exists a systematic relationship between the degree of TR conversion and plasticization
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46 resistance. Similar to the results for CO₂, CH₄ permeability increases with conversion. At
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48 10 atm, CH₄ pure-gas permeability is 2.8 times higher for the TR350, 16 times higher for
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the TR400, and 55 times higher for the TR450 than for the unconverted polyimide. CH₄ mixed-gas permeability at 10 atm scales in the same proportions as pure-gas permeability for the three TR polymers.

Pure and mixed-gas CO₂/CH₄ selectivities are presented in Fig. 8 as a function of CO₂ fugacity. For all four polymers, the mixed-gas selectivity is greater than the ideal selectivity for most of the fugacity range considered. The ideal and mixed-gas selectivity trends also have different shapes. For the polyimide (Fig. 8-A), mixed-gas selectivity is around 25% higher than ideal selectivity at lower CO₂ fugacities, which is primarily a consequence of the depressed CH₄ permeability caused by dual-mode competitive effects. Mixed-gas selectivity decreases steadily as fugacity increases, which is likely a result of two effects: plasticization and Langmuir capacity saturation. At the highest fugacity measured (CO₂ at 24 atm), mixed-gas selectivity decreases by 19% from its value at the lowest fugacity (CO₂ at 4 atm). Ideal selectivity passes through a minimum at 10-15 atm, and then begins to increase. This apparent increase is an artifact of pure-gas permeation tests for a film that plasticizes. Plasticization occurs during the pure CO₂ measurement, while the corresponding pure CH₄ measurements are unaffected by plasticization.

TR conversion initially causes a boost in selectivity. For the TR350 (Fig. 8-B), mixed-gas selectivity at 10 atm is 10% higher than for the unconverted polyimide, while under the same conditions, CO₂ permeability is about 300% higher. A similar observation based on pure-gas measurements was reported by Sanders et al. [27]. As the degree of conversion increases further for the TR400 and TR450 samples (Fig. 8-C and -D), there is a tradeoff of decreasing selectivity accompanied by increasing permeability. Selectivity at 10 atm is 25% lower for the TR400 and 47% lower for the TR450 than for the polyimide. Like

the polyimide, all three TR polymers exhibit higher mixed-gas selectivity than ideal selectivity at lower fugacities, presumably due to the dual-mode competitive transport effect. Additionally, as fugacity increases, mixed-gas selectivity decreases due to plasticization and dual-mode effects for all samples. At the highest fugacities considered, mixed-gas selectivity for the TR polymers decreases by 25-30% compared with the lowest fugacities. Nevertheless, mixed-gas selectivity values remain higher than ideal selectivity for all four polymers up to at least CO₂ fugacities of 20 atm.

In Fig. 9, pure- and mixed-gas selectivity measurements from the present study and four literature examples are presented together with Robeson's 1991 and 2008 upper bounds for CO₂/CH₄ [2, 41]. Experimental conditions for the measurements in Fig. 9 are recorded in Table 2. The HAB-6FDA polyimide performs substantially below the 1991 upper bound, but, for all three TR polymers, mixed-gas performance exceeds the 1991 upper bound. As the degree of TR conversion increases, mixed-gas selectivity decreases but performance improves relative to the upper bound. All four polymers show better mixed-gas selectivity than pure-gas selectivity. This is in contrast with several other studies from the literature presented in Fig. 9. Cellulose acetate mixed-gas selectivity is more than 40% lower than pure-gas selectivity, primarily due to plasticization [9]. For Matrimid® 5218, CO₂ permeability is 8% lower in mixed-gas measurements as a consequence of competitive sorption, and mixed-gas selectivity is 25% lower due to plasticization [14]. A similar result is observed for a 6FDA-6FpDA polyimide [13]. CO₂ permeability is 4% lower due to competitive sorption, and selectivity is 10% lower due to plasticization. Results for a crosslinked 6FDA-DAM-DABA polyimide are similar to what we have observed in this study. Plasticization was reduced as a result of crosslinking, and

mixed-gas selectivity was 20% higher due to a reduction in CH₄ permeability presumably caused by competitive sorption [20].

4.2. Comparison With the Dual-mode Model

In principle, Eqs. 8-9 provide a powerful framework for predicting permeability for gas mixtures solely based on pure-gas experimental data. By fitting pure-gas permeation data to Eq. 8, three independent parameters may be extracted for each gas and then used with Eq. 9 to predict permeabilities for the mixture. Fitting is a straightforward application of the method of maximum likelihood [42]. Given values for the adjustable parameters $k_D \bar{D}_D$, $C'_H \bar{D}_H$, and b for one gas and a set of experimental permeabilities, P_i , at fugacities, f_i , with uncertainties (i.e., standard deviations) of σ_i , the goodness of fit parameter is [42]:

$$\chi^2 = \sum_i \frac{1}{\sigma_i^2} \left[P_i - \left(k_D \bar{D}_D + C'_H \bar{D}_H \frac{b}{1 + b f_i} \right) \right]^2 \quad (10)$$

The optimum values of the adjustable parameters are obtained by minimizing Eq. 10 using an iterative technique. We initially tried this approach to fit the dual-mode model to our experimental data. Because plasticization is not encompassed in the dual-mode model, we restricted the CO₂ fit to fugacities below the plasticization pressure point for each polymer. Using the optimum values of the parameters, plotting Eq. 8 appears to produce an excellent fit for our experimental pure-gas data—all of the data points pass neatly through the resulting curve with very little scatter. On the other hand, plotting Eq. 9 superimposed with our mixed-gas data gives rather poor results, with the model prediction for CH₄ differing from the experimental data by 10% or more. Difficulties of obtaining dual-mode parameters by fitting sorption data have been documented in the past [43-44], and the same difficulties apply for this study. Owing to the form of Eq. 8, the parameters $C'_H \bar{D}_H$ and

b are strongly coupled and, thus, a large deviation in b may be offset by a corresponding large deviation in $C'_H \bar{D}_H$ with only a weak impact on the overall quality of the fit. This situation can be visualized by plotting a 1σ contour. The contour line is the locus of all points in $C'_H \bar{D}_H$ vs. b space for which $\chi^2 - \chi^2_{\min} = 1$. In order to account for coupling between *all* of the parameters, χ^2 is computed by fixing $C'_H \bar{D}_H$ and b and then minimizing Eq. 10 by adjusting the remaining parameters (in this case, one parameter: $k_D \bar{D}_D$). An example of such a plot, for CO₂ in the TR350 polymer, is given in Fig. 10. The estimate for b , within 1σ , is $1.1^{+8.9}_{-0.6}$ atm⁻¹. Because the uncertainty in b is so large, it is not surprising that the comparison between our mixed-gas measurements and the dual-mode model was poor.

A few different approaches are available to improve the precision of dual-mode parameter estimates. Koros et al. [43] recommend extending the measurement range to pressures where the Langmuir sites are nearly saturated. This approach was not possible in the present work due to constraints with the measurement system (also, we could not fit CO₂ data beyond the plasticization pressure). Imposing additional constraints on the parameters can also improve their precision. Smith et al. [28] constrained k_D and b to increase exponentially with the critical temperature of each gas, which follows trends observed for a number of other polymers. A different technique, if measurements are available at several temperatures, is to constrain k_D and b to follow an Arrhenius relation [45].

In the present work, we have improved the fit by simultaneously fitting pure- and mixed-gas data for both gases. The goodness of fit parameter for a pair of gases A and B is:

$$\chi^2 = \sum_i \frac{1}{\sigma_{A_i}^2} \left[P_{A_i} - \left(k_{D_A} \bar{D}_{D_A} + C'_{H_A} \bar{D}_{H_A} \frac{b_A f_{A_i}}{1 + b_A f_{A_i} + b_B f_{B_i}} \right) \right] + \sum_i \frac{1}{\sigma_{B_i}^2} \left[P_{B_i} - \left(k_{D_B} \bar{D}_{D_B} + C'_{H_B} \bar{D}_{H_B} \frac{b_B f_{B_i}}{1 + b_A f_{A_i} + b_B f_{B_i}} \right) \right] \quad (11)$$

where P_{A_i} is the permeability of gas A measured at fugacities f_{A_i} and f_{B_i} for gases A and B, respectively; σ_{A_i} is the uncertainty (standard deviation) of P_{A_i} . Similarly, P_{B_i} is the permeability of gas B with uncertainty σ_{B_i} . In contrast with Eq. 10, all six parameters (three for each gas) are determined simultaneously by minimizing Eq. 11. This enforces coupling of the parameters between the two gases without introducing additional assumptions about the nature of the model parameters. As a result, the uncertainty in the model parameters is reduced, as is the uncertainty in the model predictions.

Care must be taken when estimating σ_{A_i} and σ_{B_i} , as overestimating these uncertainties will, in turn, cause overestimation of the uncertainties in the model parameters. For pure-gas measurements, the sources of uncertainty are membrane geometry (thickness and area), downstream volume, temperature, challenge gas pressure, and the rate of pressure rise in the downstream volume. For mixed-gas measurements, there are also the uncertainties in the upstream and downstream gas compositions. For a series of measurements made using the same film and the same measurement system, uncertainties in membrane geometry, downstream volume, and temperature are all systematic within that data set and should not be included in σ_{A_i} or σ_{B_i} . Rather, these sources of uncertainty should be propagated to $k_D \bar{D}_D$ and $C'_H \bar{D}_H$ after fitting [42]. Mixed-gas measurements were made using a different film sample than pure-gas measurements, and as a result, uncertainty in the membrane geometry is not systematic for the mixed-gas

data relative to the pure-gas data. We have addressed this by including uncertainties in membrane geometry in σ_{A_i} and σ_{B_i} for mixed-gas measurements.

Because plasticization is not described by the dual-mode model, we restricted the experimental data used to minimize Eq. 11. All of the CH₄ pure-gas data were used while CO₂ pure-gas data were restricted to fugacities below 15 atm in the unconverted polyimide; all of the CO₂ pure-gas data for the three TR polymers were used. The CO₂ and CH₄ mixed-gas data were restricted to fugacities below 8 atm (i.e., the two lowest fugacities) for all four polymers. Using these data points, minimization of Eq. 11 yields the dual-mode parameter values listed in Table 3. To account for coupling, uncertainties in Table 3 were computed by systematically varying the parameter of interest while allowing the remaining parameters to adjust to their optimal values; the confidence interval is bounded by the points where $\chi^2 - \chi_{\min}^2 = 1$. The uncertainties are still quite large, but they have improved significantly from the pure-gas-only fit described above. The improvement in precision is exemplified in Fig. 10, in which 1σ contours in $C'_H \bar{D}_H$ vs. b space for the two fitting methods are compared: the estimate for b (for CO₂ in the TR350 polymer) has improved from $1.1^{+8.9}_{-0.6} \text{ atm}^{-1}$ to $0.95^{+0.79}_{-0.36} \text{ atm}^{-1}$. While the uncertainties in the dual-mode *parameter* estimates are large, perhaps too large to make meaningful arguments about the physical significance of the parameters themselves, the dual-mode model *predictions* are reasonably precise. Model predictions, with 1σ confidence bands, are plotted together with our experimental data in Fig. 6-7. The confidence bands were constructed using a Monte Carlo technique, using 5,000 randomly chosen sets of the six dual-mode parameters for which $\chi^2 - \chi_{\min}^2 \leq 1$ [46].

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4 The dual-mode sorption model shares a common parameter, b , with the dual-mode
5 permeation model. However, estimates for b in the present study do not agree with our
6 previous estimates for b based on sorption measurements [28]. The discrepancies may be
7 due in part to differences in the model fitting technique and the use of pressure rather than
8 fugacity in the calculations. We attempted to reconcile these differences by simultaneously
9 fitting the permeation data from the present study and the sorption data from Ref. 28. The
10 quality of this fit was very poor. Values for b do not exist which satisfactorily fit both
11 permeation and sorption data. The reason is not fully understood. It is possible that the
12 polymer samples in the present study differ from those used in Ref. 28, owing to
13 differences in preparation techniques. It is also possible that the dual-mode model does
14 not fully capture the physics of the combined data sets. In any event, such discrepancies
15 represent areas for potential future study.

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17 Because only two data points from the mixed-gas experiments were used in the
18 dual-mode fit, it is possible to use the model as a backdrop to more closely analyze our
19 mixed-gas experimental results beyond the fitting region. Plasticization effects are
20 apparent where mixed-gas permeability data are higher than the dual-mode prediction.
21 For the unconverted polyimide, at 22 atm (CO_2 fugacity), CO_2 mixed-gas permeability is 6%
22 higher than the model prediction, and CH_4 mixed-gas permeability is 19% higher. For the
23 TR polymers, measurable plasticization is indicated only in the CH_4 mixed-gas results. The
24 discrepancy between the model and the mixed-gas CH_4 permeability decreases
25 systematically as the degree of TR conversion increases. At 22 atm, CH_4 permeability is
26 11% higher for the TR350, 9% for the TR400, and 3% for the TR450.

The CO₂ permeability trends for the three TR polymers do not indicate any plasticization. Instead, CO₂ mixed-gas permeability is slightly lower than the model predicts, by 5% for the TR350, 10% for the TR400, and 6% for the TR450. For the results to fit perfectly within the dual-mode framework, a slight modification of the model is necessary: some (or all) of the CO₂ dual-mode parameters, which are assumed to be constants, would need to be modified to be functions of CH₄ concentration. The possibility of such a modification was anticipated early in the development of the model [18], and has been demonstrated for the blocking effect in PTMSP [21] where the dual-mode diffusion coefficients were found to depend on *n*-C₄H₁₀ concentration. Additional data (e.g., mixed-gas sorption measurements) would be necessary to determine which of the CO₂ dual-mode parameters are affected by CH₄ concentration. Even if this data were available, the analysis would be complicated by plasticization in the TR350 and TR400 polymers.

At pressures for which plasticization is minimal, the extracted dual-mode parameters may be used to predict mixed-gas permeability and selectivity for mixture concentrations other than 50% CO₂. At CO₂ concentrations above about 20%, CO₂ and CH₄ permeability values predicted by Eq. 9 depend primarily on CO₂ fugacity; the values depend only weakly on CH₄ fugacity. Therefore, as a function of CO₂ fugacity, the selectivity for mixtures containing more than 20% CO₂ should be near the values presented in Fig. 8. For example, selectivity for the TR450 at 10 atm (CO₂ fugacity) is 25 for a 20% CO₂ mixture and 26 for an 80% CO₂ mixture.

5. Conclusions

Pure- and mixed-gas permeability measurements for CO₂ and CH₄ have been presented for an HAB-6FDA polyimide and three TR derivatives with increasing degrees of

conversion. CH₄ permeability is depressed in mixed-gas experiments as a consequence of competitive sorption, which contributes to higher CO₂/CH₄ selectivity for gas mixtures compared with ideal (i.e., pure-gas) selectivity. CO₂ permeability for the unconverted polyimide passes through a minimum at about 20 atm, indicating plasticization, but such minima are absent for the three TR polymers. Nevertheless, CH₄ mixed-gas permeability trends reveal that mild plasticization is occurring in the TR350 and TR400 polymers. The experimental results were fit to the dual-mode permeation model. The impact of plasticization in mixed-gas experiments was compared quantitatively against the dual-mode model predictions (which do not reflect plasticization) and was found to decrease systematically as the degree of TR conversion increased. For the TR450 polymer, plasticization was absent within the experimental uncertainty. Small discrepancies between the dual-mode model and the experimental data were also observed for mixed-gas CO₂ permeability measurements in the TR polymers; these differences suggest that the presence of CH₄ has a small but measureable impact upon CO₂ permeability beyond what would be expected based on the dual-mode model alone.

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Tables

Table 1. Thermal rearrangement conditions for samples, and degree of conversion to PBO.

Name	Conversion temperature, T_c [°C]	Conversion time, t_c [min]	Percent conversion
TR350	350	60	36%
TR400	400	60	59%
TR450	450	30	79%

Table 2. Experimental conditions for measurements presented in Fig. 9.

	Polymer	Temp. [°C]	CO ₂ fugacity [atm]		CO ₂ mixture mol %	Ref.
			pure-gas	mixed-gas		
A	HAB-6FDA polyimide	35	10	10	50	this work
B	TR350	35	10	10	50	this work
C	TR400	35	10	10	50	this work
D	TR450	35	10	10	50	this work
E	cellulose acetate	30	10*	10*	50	[9]
F	Matrimid® 5218	35	6.0*	6.0*	40	[14]
G	6FDA-6FpDA polyimide	35	10*	10*	50	[13]
H	crosslinked 6FDA-DAM-DABA polyimide	35	4.4*	0.44*	10	[20]

* CO₂ pressure or partial pressure

Table 3. Dual-mode parameters fit to gas permeation data.

Gas	Polymer	$k_D \bar{D}_D$ [Barrer]	$C'_H \bar{D}_H$ [Barrer·atm]	b [atm ⁻¹]
CO ₂	HAB-6FDA polyimide	$10.9^{+0.3}_{-0.5}$	26^{+13}_{-7}	$0.30^{+0.25}_{-0.13}$
	TR350	$36.1^{+0.3}_{-0.3}$	56^{+7}_{-6}	$0.95^{+0.79}_{-0.36}$
	TR400	$135^{+1.4}_{-1.6}$	330^{+50}_{-40}	$0.50^{+0.25}_{-0.15}$
	TR450	280^{+6}_{-7}	1600^{+300}_{-200}	$0.21^{+0.06}_{-0.04}$
CH ₄	HAB-6FDA polyimide	$0.22^{+0.02}_{-0.03}$	$4.3^{+2.8}_{-1.4}$	$0.035^{+0.014}_{-0.011}$
	TR350	$0.70^{+0.02}_{-0.03}$	$5.4^{+1.8}_{-1.3}$	$0.078^{+0.028}_{-0.020}$
	TR400	$4.0^{+0.14}_{-0.18}$	34^{+13}_{-9}	$0.056^{+0.019}_{-0.014}$
	TR450	$12.8^{+0.7}_{-1.0}$	160^{+90}_{-50}	$0.043^{+0.018}_{-0.012}$

Figures

Fig. 1. Relationship between fugacity and total pressure, calculated using the SRK equation of state [32]. The solid lines show fugacities of pure CO_2 and CH_4 . The dashed lines show fugacities of each gas in a 50% CO_2/CH_4 mixture.

Fig. 2. Structure of the HAB-6FDA polyimide precursor.

Fig. 3. Structure of the polybenzoxazole formed by thermal rearrangement of polyimide films.

Fig. 4. Thermal protocol for converting polyimide films to PBO.

Fig. 5. Schematic of the permeation system used for measurement of pure- and mixed-gas permeability.

Fig. 6. Pure- and mixed-gas permeability of CO₂ for A) unconverted polyimide, B) TR350, C) TR400, and D) TR450. Symbols represent experimental measurements: ○ pure-gas, ◻ mixed-gas. The dashed blue line indicates the dual-mode model prediction for pure CO₂, with the 1σ confidence band indicated by dotted blue lines. The solid red line indicates the dual-mode prediction for a 50% CO₂/CH₄ mixture, with the 1σ confidence band indicated by the shaded red region.

Fig. 7. Pure- and mixed-gas permeability of CH₄ for A) unconverted polyimide, B) TR350, C) TR400, and D) TR450. Symbols represent experimental measurements: $\circ$ pure-gas, $\square$ mixed-gas. The dashed blue line indicates the dual-mode model prediction for pure CO₂, with the 1 σ confidence band indicated by dotted blue lines. The solid red line indicates the dual-mode prediction for a 50% CO₂/CH₄ mixture, with the 1 σ confidence band indicated by the shaded red region.

Fig. 8. CO_2/CH_4 selectivity for A) unconverted polyimide, B) TR350, C) TR400, and D) TR450. $\circ$ ideal selectivity calculated from pure-gas measurements. $\square$ mixed-gas selectivity.

Fig. 9. Relationship between pure-gas (open symbols) and mixed-gas transport properties (filled symbols) for A) unconverted HAB-6FDA polyimide, B) TR350, C) TR400, D) TR450, E) cellulose acetate [9], F) Matrimid® 5218 [14], G) 6FDA-6FpDA polyimide [13], and H) crosslinked 6FDA-DAM-DABA polyimide [20].

Fig. 10. Example 1 σ contour plots illustrating the coupling between dual-mode parameters, b and $C'_H \bar{D}_H$, for CO₂ in the TR350 polymer. $\times$ indicates the best fit to the pure-gas data, with the region enclosed by the blue dashed line encompassing parameter values within one standard deviation. $\circ$ indicates the best fit when mixed-gas data are included in the fit, with the shaded red region encompassing parameter values within one standard deviation.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6-A

Figure 6-B

Figure 6-C

Figure 6-D

Figure 7-A

Figure 7-B

Figure 7-C

Figure 7-D

Figure 8-A

Figure 8-B

Figure 8-C

Figure 8-D

Figure 9

Figure 10