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# Pure- and mixed-gas permeation of CO<sub>2</sub> and CH<sub>4</sub> 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 CO<sub>2</sub>, pure CH<sub>4</sub>, and CO<sub>2</sub>/CH<sub>4</sub> mixtures containing 50% CO<sub>2</sub> 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 CO<sub>2</sub> and CH<sub>4</sub> increased as the degree of TR conversion increased. For example, CO<sub>2</sub> 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, CO<sub>2</sub> 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 CH<sub>4</sub> permeability, with very little change in CO<sub>2</sub> permeability. In addition, plasticization by CO<sub>2</sub> was evident in the CH<sub>4</sub> mixed-gas permeability trends, but its impact was small in contrast with dual-mode competitive effects. Consequently, CO<sub>2</sub>/CH<sub>4</sub> 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 CO<sub>2</sub>-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.

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## 1. Introduction

A substantial effort has been expended in the search for superior polymeric materials for CO<sub>2</sub> removal from natural gas [1,2]. Very often, these studies focus on permeability measurements of pure CO<sub>2</sub> and pure CH<sub>4</sub> 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 CO<sub>2</sub> and CH<sub>4</sub> in cellulose acetate. Ideal CO<sub>2</sub>/CH<sub>4</sub> 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 CO<sub>2</sub>/CH<sub>4</sub> selectivity was 76,

but for a 70.6% CO<sub>2</sub>/CH<sub>4</sub> mixture, the selectivity was only 20. In the presence of CO<sub>2</sub>, the permeability of CH<sub>4</sub> increased dramatically, which translated to decreased selectivity. Results like these are commonly reported for polymers that plasticize. At elevated partial pressures, sorbed CO<sub>2</sub> 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 CO<sub>2</sub>/CH<sub>4</sub> permeation in cellulose acetate [9,10], polyimides [11–14], and styrene/methyl methacrylate copolymers [15].

For separations involving CO<sub>2</sub>, 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, CO<sub>2</sub> permeability at 15 atm decreases from its pure-gas value of 0.68 Barrer to 0.42 Barrer for a CO<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> mixture containing 50% CO<sub>2</sub>. This decrease in CO<sub>2</sub> permeability is attributed to competitive

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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 CO<sub>2</sub>-containing mixtures that mixed-gas selectivity is always lower than ideal selectivity. However, this is not true. While plasticization is usually detrimental to CO<sub>2</sub>/CH<sub>4</sub> selectivity, it can in fact be beneficial in other separations. Lin et al. [19] studied CO<sub>2</sub>/H<sub>2</sub> separation in crosslinked poly(ethylene glycol)-based membranes. These materials are reverse-selective for this gas pair, since they preferentially permeate the larger CO<sub>2</sub> molecule. The basis for selectivity in these materials is rooted in the high solubility of CO<sub>2</sub> compared with H<sub>2</sub>. Diffusivity selectivity, on the other hand, favors H<sub>2</sub> over CO<sub>2</sub>, and acts to lower the overall CO<sub>2</sub>/H<sub>2</sub> selectivity. Since plasticization diminishes diffusivity selectivity, it improves the overall selectivity for mixtures.

Because CO<sub>2</sub> is more condensable than CH<sub>4</sub>, dual-mode competitive sorption can act to improve selectivity for CO<sub>2</sub>/CH<sub>4</sub> mixtures, although this effect may be overwhelmed if substantial plasticization is present. For example, Hillock and Koros [20] crosslinked polyimide films to harden them against plasticization. Mixtures of CO<sub>2</sub>/CH<sub>4</sub> containing 10% CO<sub>2</sub> at 4.4 atm total pressure gave a selectivity of 44.8 versus a pure-gas selectivity of 37.1. Because CO<sub>2</sub> has a higher affinity for the Langmuir sites in the polymer, sorption of CH<sub>4</sub> was presumably suppressed in the presence of CO<sub>2</sub>, thereby reducing methane transport and improving selectivity. Similar results were reported by Visser et al. [8] for asymmetric membranes made from Matrimid<sup>®</sup> 5218 blends. For Matrimid blended with the polyimide P84, CO<sub>2</sub>/CH<sub>4</sub> mixtures containing 50% CO<sub>2</sub> at 8 atm fugacity had a mixed-gas selectivity of 36 versus a pure-gas selectivity of 29. Raharjo et al. [21] measured pure- and mixed-gas permeability and sorption of CH<sub>4</sub> and *n*-C<sub>4</sub>H<sub>10</sub> in poly(1-trimethylsilyl-1-propyne) (PTMSP) and found that *n*-C<sub>4</sub>H<sub>10</sub>/CH<sub>4</sub> mixed-gas permeability selectivity was as much as 30 times higher than the ideal (i.e., pure gas) selectivity. Competitive sorption was partially responsible for the higher selectivity, but CH<sub>4</sub> diffusivity was also reduced in the presence of *n*-C<sub>4</sub>H<sub>10</sub>. The reduction in diffusivity was attributed to blocking of interconnected free-volume elements by *n*-C<sub>4</sub>H<sub>10</sub>, which hinders CH<sub>4</sub> transport and further increases selectivity.

Recently, thermally rearranged (TR) polymers have emerged as promising materials for CO<sub>2</sub>/CH<sub>4</sub> separations [22,23]. TR polymers are polybenzoxazoles (PBOs), polybenzimidazoles (PBI), 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 CO<sub>2</sub>/CH<sub>4</sub> and other gas mixtures. They are highly chemically-resistant and are generally insoluble. They are resistant to plasticization by CO<sub>2</sub>, 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 CO<sub>2</sub> and pure CH<sub>4</sub>. 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 CH<sub>4</sub> permeability when CO<sub>2</sub> 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, CO<sub>2</sub> 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]:

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

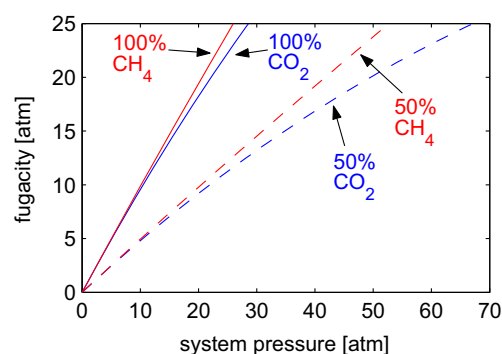


Fig. 1. Relationship between fugacity and total pressure, calculated using the SRK equation of state [32]. The solid lines show fugacities of pure CO<sub>2</sub> and CH<sub>4</sub>. The dashed lines show fugacities of each gas in a 50% CO<sub>2</sub>/CH<sub>4</sub> mixture.

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