Influence of toluene on CO_2 and CH_4 gas transport properties in thermally rearranged (TR) 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

Separation of complex gas mixtures, such as natural gas using polymer membranes, often involves components with a wide range of condensabilities and propensity to interact with the polymer, potentially changing the transport properties of all components. There are few studies of such phenomena in the open literature. Here, the influence of toluene, a surrogate aromatic contaminant in natural gas, on pure and mixed CO_2 and CH_4 gas transport properties at 35 °C was investigated for a thermally rearranged (TR) polymer prepared from a polyimide precursor based on 3,3′-dihydroxy-4,4′-diamino-biphenyl (HAB) and 2,2′-bis-(3,4-dicarboxy-phenyl) hexafluoropropane dianhydride (6FDA). As the polymer was exposed to CO_2, CH_4, and their equimolar mixture, at a toluene activity of about 0.3, CO_2 and CH_4 permeability coefficients decreased by more than 90% relative to their respective pre-exposure values due to antiplastization and competitive sorption. CO_2/CH_4 selectivity went through a maximum as toluene activity increased, reflecting the interplay between competitive sorption, antiplasticization, and plasticization. The recovery of gas permeation properties was explored by measuring CO_2 and CH_4 permeabilities after removing toluene from the feed. These effects were largely reversed when toluene was removed from the feed gas mixture. Toluene vapor sorption was determined as a function of toluene activity, and the sorption data were used to help rationalize the changes in CO_2 and CH_4 gas permeability coefficients in the presence of toluene. A qualitative assessment of antiplasticization and competitive sorption effects was provided using the partial-immobilization dual mode model.

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1. Introduction

Contaminants and impurities, such as heavy aliphatic hydrocarbons, water, aromatics, and H_2S, are often present in natural gas streams. Raw natural gas, for example, can contain 5–15% C2-C6 aliphatic hydrocarbons [1,2]. In addition, up to 1000 ppm of water and 500 ppm of BTEX aromatics (benzene, toluene, ethylbenzene, and xylene) can be present in such streams [1]. With typical natural gas operating conditions at 50 °C and 20–60 bar, these impurities can approach unit activity and even condense onto the membrane surface [1].

The presence of such contaminants may have deleterious effects on polymer gas transport properties [3]. Tanihara et al. [4] reported that after 1600–7600 ppm of toluene was introduced to an equimolar H_2/CH_4 feed gas mixture at 10 atm and 50 °C, a polyimide hollow fiber experienced a ~60% loss in H_2 permeance and an ~84% loss in H_2/CH_4 selectivity. Omole et al. [5] observed that as toluene concentration increased in a CO_2/CH_4 mixture feed stream, CO_2 permeance in a crosslinked polyimide hollow fiber decreased by as much as 80%, and CO_2/CH_4 selectivity initially increased from ~37 to ~39 at low toluene concentration (50 ppm) before decreasing to ~31 at higher toluene concentration (1000 ppm). Additionally, different contaminants may have different effects on light gas (e.g., H_2, CO_2 and CH_4) permeation properties. For example, White et al. [6] studied the influence of various contaminants on mixed gas transport properties of a proprietary polyimide film. Naphthalene immediately decreased gas flux through the membrane (> 50% decrease) but had little

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effect on CO_2/CH_4 selectivity; toluene significantly decreased the CO_2/CH_4 selectivity ($\sim$ 34% decrease) but had little effect on CO_2 permeability; and n-hexane increased CO_2 permeability ($\sim$55% increase) and decreased CO_2/CH_4 selectivity ($\sim$42% decrease) [6]. Such different effects on permeation performance demonstrate the difficulty in generalizing/predicting trends in gas transport properties in the presence of contaminants and highlight the necessity of studying specific polymer/contaminant combinations of interest.

The impact of contaminants on gas separation performance has been attributed generally to three factors: antiplasticization, plasticization and competitive sorption [7–13]. When certain low-molecular-weight compounds are incorporated into a polymer matrix, the compounds may increase polymer modulus and strength, while decreasing elongation at break and impact resistance, a phenomenon called antiplasticization [14–18]. In gas separation applications, the presence of such compounds, including toluene at low activity, may significantly decrease gas permeability [8,9,14–21]. For example, Maeda et al. studied the effects of low concentrations of various additives, such as tricresyl phosphate (TCP), N-phenyl-2-naphthylamine (PNA), and 4,4'-dichlorodiphenyl sulfone (DDS) on gas transport properties of polysulfone (PSF) and poly(phenylene oxide) (PPO) [14, 16–18]. After incorporating 30 wt% PNA into PSF, CO_2 permeability decreased from 5.82 Barrer to 0.22 Barrer [14]. Such permeability decreases were accompanied by either an increase or decrease in gas selectivity. For example, as the concentration of Kronitex 50, an aromatic additive, in PPO increased, CO_2/CH_4 selectivity initially increased from 15.6 to 16.8 at low additive concentrations and then decreased to 14.8 at higher additive concentrations [17]. Additionally, Maeda et al. concluded that the addition of these additives decreased gas solubility, but the major contribution to permeability reductions was a reduction in polymer free volume that led to a decrease in penetrant diffusion coefficients in the polymer matrix [18].

As contaminant concentration sorbed in a polymer increases, it may induce swelling of the polymer matrix, which increases polymer inter-chain spacing and may increase polymer segmental mobility, thereby increasing penetrant diffusion coefficients, lowering the polymer's size-sieving ability and decreasing gas selectivity. This phenomenon is called plasticization [22–26]. For glassy polymers, even after plasticizers are removed, the dilated polymer matrix may not immediately relax to its pre-swollen state. Consequently, the polymer may retain additional free volume long after exposure to such contaminants, a phenomenon known as conditioning [27,28].

For glassy polymers, more condensable contaminants, such as toluene and higher hydrocarbons, typically have a higher affinity for Langmuir sites in the polymer matrix than less condensable penetrants, such as CO_2 and CH_4. Preferential sorption of more condensable components can decrease solubility of less condensable penetrants, leading, in some cases, to lower gas permeability and higher selectivity [29]. This phenomenon is called competitive sorption.

This study explores the influence of toluene, a surrogate aromatic contaminant in natural gas, on CO_2 and CH_4 pure and mixed gas permeation properties of a thermally rearranged (TR) polymer prepared from a polyimide precursor based on 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB) and 2,2'-bis-(3,4-dicarboxy-phenyl) hexafluoropropane dianhydride (6FDA). TR polymers are a relatively recent class of materials that, due in part to high free volume and favorable free volume distribution, has interesting gas separation performance [30,31]. TR polymers are generally prepared by thermally treating a polyimide precursor in an inert atmosphere to rearrange the polymer structure to a more open and highly chemically and thermally stable poly(benzoxazole)-type

structure. Several studies have reported structure-property relationships [32–35] and free volume distribution [36–38] of these materials. However, most TR polymer gas transport studies are based on pure gas experiments. There are few reports of mixed gas permeation properties of TR polymers [31,39,40], and to the best of our knowledge, there are no reports of the influence of aromatic contaminants on mixed gas permeation properties of TR polymers.

Pure gas permeation, diffusion, and sorption properties of HAB-6FDA and its TR analogs have been reported elsewhere [30,41]. Recently, we reported mixed gas CO_2/CH_4 transport properties of HAB-6FDA and its TR analogs [39]. At low CH_4 fugacity ($< \sim$10 atm), mixed gas CH_4 permeability was depressed relative to pure gas transport properties due to competitive sorption, leading to an increase in CO_2/CH_4 selectivity. In this study, we seek to elucidate the influence of toluene on both pure and mixed gas CO_2/CH_4 permeation properties of a TR polymer prepared from HAB-6FDA. Toluene sorption and desorption was investigated, and the dual mode sorption model was used to interpret the sorption isotherms. Additionally, the partial-immobilization dual mode model was used to provide a qualitative assessment of anti-plasticization and competitive sorption effects.

2. Experimental

2.1. Materials

A polyimide precursor based on 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB) and 2,2'-bis-(3,4-dicarboxy-phenyl) hexa-fluoropropane dianhydride (6FDA) was synthesized via chemical imidization as described previously [30]. HAB was purchased from Chriskev (Lenexa, KS, USA), and 6FDA was purchased from Alfa Aesar (Ward Hill, MA, USA). Prior to synthesis, HAB was dehydrated by heating it at 50 °C under full vacuum for 12 h. To prevent possible photo-degradation of HAB, the monomer container and the vacuum oven window were covered with aluminum foil. 6FDA was heated at 200 °C under partial vacuum for 6 h and then maintained at 120 °C under full vacuum for 12 h to remove any water arising from closure of any hydrolyzed dianhydride rings. N-methyl-2-pyrrolidinone (NMP, anhydrous), pyridine (purity $\sim$99.9%), acetic anhydride (purity $\sim$99.5%), and dimethylaceta-mide (DMAc, anhydrous) were purchased from Sigma Aldrich (St. Louis, MO, USA) and used as received.

2.2. Polymer synthesis and casting

HAB-6FDA polyimide was synthesized via condensation polymerization of diamine and dianhydride followed by chemical imidization [30,42]. A detailed synthesis procedure was presented earlier [41], so only a brief summary is provided here. A poly(amic acid) was formed by reacting equimolar amounts of HAB and 6FDA in NMP at 0 °C for 24 h. Afterwards, the polyimide was obtained via chemical imidization by adding excess acetic anhydride and pyridine (8 mol of acetic anhydride and 8 mol of pyridine per mole of HAB) to the mixture at 60 °C and stirring for 1 h. The resulting polymer was precipitated in about 2 L of pure methanol and heated under vacuum at 100 °C for 24 h, 150 °C for 24 h, and 200 °C for 48 h to remove solvent. The chemical structures of the monomers and polyimide are presented in Fig. 1.

Polyimide films, about 6–8 μm thick, were prepared via solution casting. A solution containing 4 g polymer per 100 mL of solvent was prepared by dissolving HAB-6FDA in DMAc. After vigorous stirring, the solution was first filtered through a 5.0 μm Millex-LS PTFE filter (Part# SLLS025NS, Millipore, Billerica, MA, USA) to remove any dust or particles and then cast onto a clean, flat, and level glass plate. The casting solution was heated at 80 °C