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Comparison of Hydrogen Sulfide Transport Properties in Fluorinated and Nonfluorinated Polymers

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ABSTRACT: Permeability coefficients of hydrogen sulfide in fluorinated polymers are anomalously low when compared to its permeability in nonfluorinated polymers. As a result, fluoropolymer membranes have unusual selectivities for gas pairs involving H_2S. For example, while the mixture CO_2/H_2S selectivity is 0.66 for nonfluorinated, rubbery poly(dimethylsiloxane), this selectivity is 8.0 for a fluoroelastomer composed of tetrafluoroethylene, perfluoromethyl vinyl ether, and perfluoro-8-cyano-5-methyl-3,6-dioxa-1-octene (TFE/PMVE/8CNVE) and 27 for a glassy, cyclic perfluoroether (Cytop) under similar test conditions. The low H_2S permeability in fluoropolymers is caused primarily by unexpectedly low H_2S solubility in the fluorinated polymer matrices. For instance, H_2S solubility in a Teflon AF copolymer of tetrafluoroethylene and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole is approximately 5 times lower than the value predicted by a correlation of solubility with gas critical temperature. This low solubility is not related to penetrant size or condensability effects but rather is caused by unfavorable molecular interactions between H_2S and fluoropolymers. As a result of this unusual solubility behavior, fluorinated glassy polymers are more resistant to H_2S-induced plasticization than nonfluorinated glasses. These findings may prove useful in emerging membrane applications that involve H_2S, such as natural gas treatment.

Introduction

Ever since the discovery of poly(tetrafluoroethylene) (PTFE) in 1938,[1] fluoropolymers have been recognized as materials with exceptional thermal and chemical stability. They tend to be resistant to common organic solvents, typically dissolving only in fluorinated liquids.[2] This stability makes fluoropolymers useful for challenging industrial applications, such as in the aerospace and chemical industries where they are used in O-rings and seals that are exposed to high temperatures and aggressive chemicals.[2] Traditionally, fluoropolymers have not been employed as membrane materials due to their high cost, processing difficulties, and low permeability.[3] Their relative impermeability is partially ascribed to the semicrystalline nature of common fluoropolymers, such as PTFE. In addition to imparting low permeability, crystallinity also renders fluoropolymers insoluble in all solvents, preventing membrane fabrication by the common solution-casting method. In the past decade, however, the discovery of soluble, amorphous perfluorinated polymers[4−8] that are highly permeable has rekindled interest in their use as membrane materials. Amorphous perfluoropolymers, such as Teflon AF (DuPont), Hyflon AD (Solvay Solexis), and Cytop (Asahi Glass), can be dissolved in selected perfluorinated solvents and fabricated into thin-film composite membranes via solution-casting techniques. Recent work with these fluorinated polymers has demonstrated that they have some unusual transport properties, such as very low sorption of hydrocarbon gases and vapors.[9−12] This attribute has been utilized to develop plasticization-resistant composite membranes for use in petrochemical applications where hydrocarbon vapors have a detrimental effect on conventional membrane performance.[13,14]

In light of their excellent chemical stability, fluorinated polymers are being examined as gas separation membrane materials in chemically demanding industrial environments. One promising area where polymer membranes have made significant inroads is in commercial natural gas treatment.[15,16] In this application, the gas mixture to be processed by membranes typically contains H_2S and other acid gases. Another important industrial operation that involves H_2S and for which membranes may prove useful is the desulfurization of coal-derived syngas.[17] If polymer membranes are to be properly designed to operate in these applications, it is necessary to have accurate H_2S transport property information. However, there are relatively few studies of H_2S transport properties in polymer membranes due, in part, to the difficulty in handling this toxic compound.

Much of the available literature data for H_2S transport in polymer films comes from studies performed in the 1950s and 1960s. This work was focused primarily on packaging and other barrier applications because membrane gas separation was in its infancy at this time and not practiced industrially. The earliest of these studies was that of Simril and Hershberger, who reported H_2S permeability coefficients in regenerated cellulose, polyethylene, poly(vinyl alcohol), and a poly(vinyl butyral/vinyl alcohol) copolymer.[18] The authors found H_2S to be relatively permeable compared to light gases, especially in rubbers or plasticized cellulose. Stannett and co-workers conducted probably the most complete examination of H_2S transport in polymers in this same time frame.[19,20] They reported permeability, solubility, and diffusion coefficients for H_2S in a variety of polymers that were commercially available at the time, including nylon-6 (polyamide), Mylar [poly(terephthalic ester)], Saran [poly(vinylidene chloride)], cellulose acetate, ethyl cellulose, and polyethylene. These fundamental studies showed H_2S to be relatively permeable, more so than light gases or even CO_2, consistent with hydrogen sulfide's comparatively high condensability and, thus, high solubility in the polymers. Braunisch and Lenhart, while also investigating materials for packaging applications, reported H_2S and NH_3 permeability coefficients in a variety of polymer films, including polyethylene, polypropylene, poly(vinyl chloride), and cellulosics.[21]

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They found polar H_2S and NH_3 to be generally more permeable than nonpolar, light gases such as nitrogen and oxygen.

More recent studies have described H_2S transport properties in polymers being evaluated as materials for membrane-based gas separation applications. Robb[22] reported the pure-gas H_2S permeability coefficient in poly(dimethylsiloxane) [PDMS] at 25 °C, while Stern and Bhide[23] reported pure-gas permeability coefficients of H_2S in several silicone polymers, including PDMS, from 10 to 55 °C. These authors found H_2S to be relatively permeable compared to light gases, consistent with the results of Stannett et al. Heyd and McCandless[24] reported H_2S/N_2 separation factors for a number of commercial polymers over a wide range of temperatures. They observed room-temperature selectivities of up to 12.7 for polysulfone and suggested that membranes may be useful for removing H_2S from coal gas. In the course of evaluating materials for natural gas conditioning applications, Chatterjee et al.[25] reported mixed-gas H_2S permeability coefficients in poly(ether urethanes), poly(ether urethane ureas), and polyamide−polyether block copolymers and found H_2S/CH_4 selectivities as high as 106 at 20 °C in poly(ether urethane ureas) films. In the patent literature, Blume and Pinnau[26] reported high H_2S/H_2 selectivities at 20 °C in a series of composite membranes containing polyamide-polyether block copolymer separating layers. For example, using a membrane composed of a Pebax 4011 separating layer coated on a silicone rubber sealing layer with a porous polysulfone support, they measured an H_2S/H_2 selectivity of 97 at 20 °C.[26] Similarly, Kulprathipanja and Kulkarni[27] reported excellent H_2S/H_2 separation properties at room temperature for composite membranes of a poly(ethylene glycol)/PDMS blend deposited on a porous polysulfone support. In each of these examples, H_2S was found to be very permeable relative to light gases, such as H_2, and even more permeable than small, quadrapolar CO_2.

Recently, we have discovered that fluorinated polymer membranes display unusual H_2S transport behavior.[28] Whereas many polymer membranes are selective for H_2S over CO_2, fluoropolymers exhibit unusually low H_2S permeability, rendering them CO_2-selective. In this work, permeation and sorption data are used to probe the anomalous nature of H_2S transport in fluoropolymers. These results are compared with similar data collected for nonfluorinated polymers to highlight the strikingly different fluoropolymer behavior.

Background

Gas and vapor permeation through nonporous polymer membranes is usually rationalized by the solution−diffusion model.[29] In simple cases where Fick's law applies, this leads to the equation

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

where P is the gas permeability coefficient, a thickness- and pressure-normalized gas flux; S is the gas solubility coefficient; and D is the penetrant diffusion coefficient. The solubility coefficient is equal to the concentration, C, of gas sorbed in a polymer divided by the pressure, p, of the contiguous gas phase (i.e., $S = C/p$).

Gas solubility in a polymer typically scales with measures of gas condensability, such as normal boiling point or critical temperature (T_C); in the absence of specific interactions, the more condensable a species is, the higher is its solubility. Gas diffusion coefficients in a polymer scale with measures of molecular size, such as kinetic diameter or critical volume (V_C); the larger a molecule is, the lower is its diffusion coefficient. In light of eq 1, the selectivity of a membrane for component A over component B, $\alpha_{A/B}$, can be expressed as the product of solubility selectivity and diffusivity selectivity:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{S_A}{S_B} \times \frac{D_A}{D_B} \tag{2}$$

The transport properties of hydrogen sulfide are compared with those of carbon dioxide in this study to emphasize differences in behavior between fluorinated and nonfluorinated polymers. Hydrogen sulfide molecules ($V_C = 98.6$ cm^3/mol) are slightly larger than those of carbon dioxide ($V_C = 93.9$ cm^3/mol).[30] Consequently, CO_2 diffuses through polymers faster than H_2S. However, hydrogen sulfide ($T_C = 373.2$ K) is significantly more condensable than carbon dioxide ($T_C = 304.1$ K).[30] As a result, H_2S is generally more soluble in polymers than CO_2. These molecular property differences result in many conventional polymer membranes being modestly selective for H_2S over CO_2.[3]

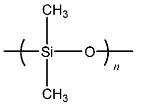
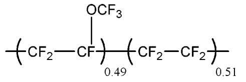
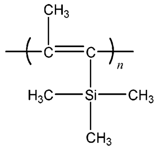
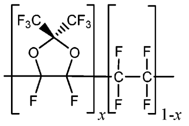
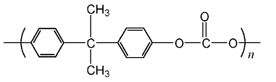
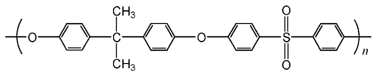
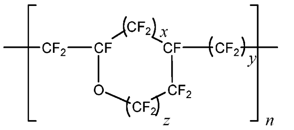
Typically, when strong polymer−penetrant chemical interactions are absent, solubility selectivity varies only a small amount among different polymers. In contrast, diffusivity selectivity can vary by orders of magnitude, depending on the polymer structure. This variation in diffusivity selectivity is largely determined by polymer chain mobility, as characterized by glass transition temperature (T_g), and polymer chain spacing, as measured by fractional free volume (FFV). Polymers that are rubbery at experimental conditions have high chain mobility, which allows permeant molecules to diffuse through them relatively indiscriminately. Consequently, rubbers tend to be weakly size-sieving and have low diffusivity selectivity. In these materials, CO_2 diffuses faster than larger H_2S, but the difference in diffusion coefficients is small. As a result, the higher solubility of H_2S in rubbery polymers dominates over diffusivity differences, causing most of these materials to be selective for H_2S over CO_2.

Compared to rubbers, glassy polymers are typically more size-sieving because of limited chain mobility. A small number of glasses have large chain spacing that yields materials with high FFV (up to 0.32). Such high-free-volume glassy materials, like rubbers, do not discriminate well between molecules of different sizes and, thus, have relatively low diffusivity selectivity. These glasses typically behave like rubbers and are expected to be more permeable to H_2S than to CO_2. The majority of glassy polymers, however, have smaller chain spacing and, hence, lower FFV values in the range of 0.15 to 0.21. These conventional-free-volume glasses are much more effective as molecular filters and can have very high diffusivity selectivities for molecules of different sizes. Smaller CO_2 is expected to diffuse substantially faster than larger H_2S in these materials. Consequently, particularly at low pressures where polymer swelling is not a factor, conventional-free-volume glasses should be selective for CO_2 over H_2S.

Experimental Section

Materials. Experimental gas permeation and sorption data were measured in a number of different fluorinated and nonfluorinated polymers. For each class of polymer (fluorinated or nonfluorinated), a representative rubber, high-free-volume glass, and conventional-free-volume glass were selected for examination. This sampling of polymers allows an investigation of the impact of polymer structure on H_2S transport properties. A summary of the polymers studied and their relevant properties are shown in Table 1.

Table 1. Chemical Structure and Relevant Properties of Polymers Studied

polymer	chemical structure	density (g/cm^3)	T_g (°C)	FFV[a]	N_2 permeability[b] (barrer)
	Rubbery Polymers				
PDMS	 $-\!\!\left(\mathrm{Si(CH_3)_2}-\mathrm{O}\right)_n\!\!-$	0.98	–123	0.18	400
TFE/PMVE49	 $-\!\left(\mathrm{CF_2}-\mathrm{CF(OCF_3)}\right)_{0.49}\!-\!\left(\mathrm{CF_2}-\mathrm{CF_2}\right)_{0.51}\!-$	2.0	–8	0.22	7.8
	High-Free-Volume, Glassy Polymers				
PTMSP	 $-\!\left(\mathrm{C(CH_3)}{=}\mathrm{C(Si(CH_3)_3)}\right)_n\!-$	0.75	>250	0.28	6000
Teflon AF 2400[c]		1.74	240	0.32	480[10]
	Conventional-Free-Volume, Glassy Polymers				
PC		1.1	150	0.16	0.29
PSf		1.24	190	0.14	0.24[48]
Cytop		2.03	108	0.21	5.0[43]

[a] FFV values computed from polymer density and group contribution methods.[47] [b] N_2 permeability values at room temperature. [c] In the chemical formula, $x = 0.87$ for Teflon AF 2400.

The nonfluorinated polymers studied were rubbery, cross-linked PDMS, high-free-volume, glassy poly(1-trimethylsilyl-1-propyne) [PTMSP], and two conventional-free-volume glasses, polycarbonate (PC) and polysulfone (PSf). Filler-free, 200-μm-thick PDMS films for sorption and permeation studies were prepared from an isooctane solution of 40 wt % Dehesive 940A silicone (Wacker Chemical Corporation, Adrian, MI) containing the manufacturer's proprietary cross-linker/catalyst system. The PDMS solution was cast onto glass plates with a Teflon FEP-coated surface. After drying slowly at ambient conditions for 2 days, the cast PDMS films were placed in a 110 °C oven for 20−30 min to remove residual solvent and to fully cross-link the polymer. PTMSP polymer was kindly supplied by Dr. J. J. Burke of Permea, Inc. (St. Louis, MO). PTMSP films with a thickness of 100 μm were cast from a 2 wt % toluene solution as described previously.[31] Due to the known physical aging properties of PTMSP,[32] sorption and permeation studies were conducted on these films over a period of several hours during which transport properties were stable within experimental uncertainty. PC films with thicknesses of 40 and 125 μm were supplied by Dr. Benny Freeman's polymer laboratory (currently at The University of Texas at Austin but formerly at North Carolina State University) and were used as received. PSf polymer (Aldrich Chemical Co., Milwaukee, WI) was cast into a film from a 4 wt % tetrahydrofuran solution. After drying at room temperature for 24 h, the cast PSf film was put in a 120 °C oven to completely remove residual solvent. The resulting PSf film tested had a thickness of 30 μm.

The fluorinated polymers studied for H_2S sorption and transport were two rubbery perfluoroelastomers designated as TFE/PMVE49 and TFE/PMVE/8CNVE, two high-free-volume, glassy polymers with the trade name Teflon AF, and a conventional-free-volume, perfluorinated glassy polymer with the trade name Cytop. Rubbery TFE/PMVE49 and TFE/PMVE/8CNVE are random copolymers of tetrafluoroethylene (TFE) and perfluoromethyl vinyl ether (PMVE) and were kindly supplied by Dupont Dow Elastomers, L.L.C. (Wilmington, DE). On a mole basis, TFE/PMVE49 is composed of 50.7% TFE and 49.3% PMVE, while TFE/PMVE/8CNVE consists of 47.5% TFE, 51.8% PMVE, and 0.7% perfluoro-8-cyano-5-methyl-3,6-dioxa-1-octene (8CNVE). Isotropic films of these materials were prepared by solution-casting from 2 wt % polymer solutions in PF-5060, a perfluorinated solvent supplied by 3M (St. Paul, MN). The cast films were dried at ambient conditions. Teflon AF 1600 and Teflon AF 2400 (DuPont, Wilmington, DE), the two grades of high-free-volume, fluorinated glasses examined in this study, are random copolymers of TFE and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (PDD). Teflon AF 1600 is composed of 35 mol % TFE and 65 mol % PDD; Teflon AF 2400 is 13 mol % TFE and 87 mol % PDD. Films of these materials were prepared by solution-casting as described previously.[10] Film thicknesses were 30 μm for Teflon AF 1600 and 20 μm for Teflon AF 2400.

Conventional-free-volume, glassy Cytop was purchased from Asahi Glass Company (Tokyo, Japan). A film of this amorphous, perfluorinated polymer was solution-cast from PF-5060, dried at ambient conditions for 3 days until a nascent film was formed, and then further dried in a vacuum oven at 80 °C for 2 h to remove residual solvent. Thickness of the Cytop film tested was 55 μm.

For sorption experiments, high-purity carbon dioxide from National Specialty Gases (Durham, NC) and high-purity hydrogen sulfide from Matheson Tri-Gas (Newark, CA) were used. For gas permeation studies, three gas mixtures were obtained (composition on a mole basis): (i) a four-component syngas mixture containing 0.7% H_2S, 11.7% CO_2, 36.5% CO, and 51.1% H_2; (ii) a second syngas mixture composed of 1.5% H_2S, 10.5% CO_2, 46% CO, and 42% H_2; and (iii) a binary mixture containing 15% H_2S in nitrogen. High-purity carbon dioxide and nitrogen were also used to measure pure-gas permeabilities of some polymer films. The three H_2S-containing mixtures and both pure gases were supplied by National Specialty Gases. All gases were used as received.

Sorption Measurements. The solubility of gases in the polymers examined was measured with a high-pressure barometric sorption apparatus.[33] Initially, a polymer film was placed in a sample chamber and exposed to vacuum overnight to outgas. Penetrant gas was then introduced into the chamber and allowed to equilibrate. Once the chamber pressure was constant, additional penetrant was introduced, and equilibrium was reestablished. In this incremental manner, penetrant uptake was measured as a function of penetrant pressure. Sorption equilibrium for all gases was reached within, at most, a few hours. The experimental temperature was ambient (21 ± 1 °C) in these studies.

Permeation Measurements. Permeation properties were determined utilizing a modified constant-pressure/variable-volume apparatus that had been described previously.[17] The current incarnation of this system uses a Millipore stainless steel filter holder with an effective membrane surface area of 13.8 cm^2. The filter holder has been modified to include an inlet port on the low-pressure side to allow for a sweep stream, an outlet port on the high-pressure side to allow for a residue (nonpermeate) stream, and a thermocouple near the film surface for accurate temperature measurement. Gas stream compositions were measured by two gas chromatographs (GCs) connected in series. The first GC is equipped with two thermal conductivity detectors (TCDs) and is used for measuring the concentration of non-sulfur gases. The second GC, operating in sulfur mode, is outfitted with a flame photometric detector to detect H_2S concentrations less than 1% and a TCD to detect H_2S concentrations greater than 1%. A detailed description of this gas analysis setup is available elsewhere.[17]

When steady-state transmembrane flux was reached and the feed flow rate was much greater than the gas flux through the polymer film (i.e., stage-cut, which equals permeate flux divided by feed flux, < 1%), the following expression was used to evaluate permeability:

$$P_i = \left(\frac{x_i^P H l}{x_{He}^P A \Delta p_i}\right)\left(\frac{273.15 p_a}{76 T}\right) \tag{3}$$

where P_i is the permeability coefficient of component i, H is the helium sweep gas flow rate, x_i^P is the mole fraction of component i in the permeate stream, x_{He}^P is the mole fraction of sweep helium in the permeate stream, l is the film thickness, A is the film area available for permeation, Δp_i is the partial pressure difference across the film for component i, T is the experimental temperature, and p_a is atmospheric pressure. All permeability coefficients are reported in units of barrers, where 1 barrer = 10^{-10} $cm^3(STP)\cdot cm/(cm^2\cdot s\cdot cmHg)$.

Results and Discussion

Solubility. Figure 1 presents CO_2 and H_2S sorption isotherms in TFE/PMVE49 and PDMS, a fluorinated and nonfluorinated rubber, respectively. In both polymers, the sorption isotherms are linear or slightly convex to the pressure axis, behavior that is typical for gas sorption in rubbers. In PDMS, H_2S is substantially more soluble than CO_2 (Figure 1a). For instance, at 80 psia, PDMS sorbs almost 4 times as much H_2S as it does CO_2 (33 vs 8.5 $cm^3(STP)/cm^3$). In contrast, at the same pressure, TFE/PMVE49 sorbs more CO_2 (6.7 $cm^3(STP)/cm^3$) than H_2S (4.8 $cm^3(STP)/cm^3$) (Figure 1b). This result for the fluoropolymer is quite unusual because it is well-known that solubility typically increases with gas critical temperature and H_2S (373.2 K) has a higher T_C than CO_2 (304.1 K).

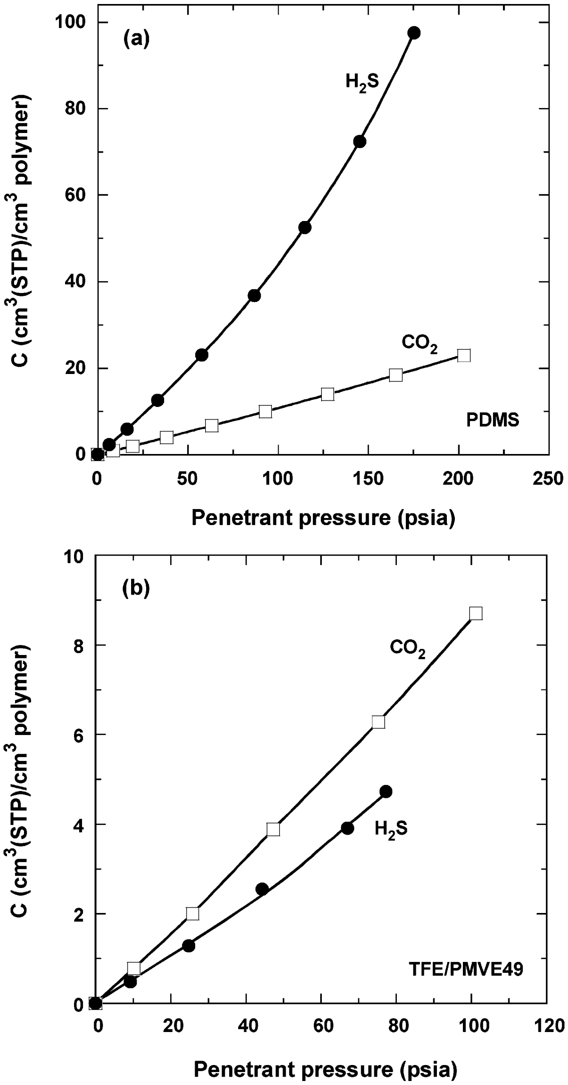


Figure 1. CO_2 and H_2S sorption isotherms in two rubbery polymers at 21 °C: (a) nonfluorinated PDMS and (b) fluorinated TFE/PMVE49.

The generality of this unusual fluoropolymer sorption behavior is illustrated in Figures 2 and 3, which present CO_2 and H_2S sorption isotherms in fluorinated and nonfluorinated, high-free-volume and conventional-free-volume glassy polymers, respectively. For each of these polymers, the sorption isotherms are slightly concave to the pressure axis, which is typical behavior for gas and vapor sorption in glassy materials. Teflon AF 2400 and PTMSP possess the highest free volumes of all known fluorinated and nonfluorinated polymers, respectively. Similar to the sorption results in the rubbery polymers, H_2S is significantly more soluble than CO_2 in PTMSP (Figure 2a), whereas fluorinated Teflon AF 2400 sorbs more CO_2 than H_2S

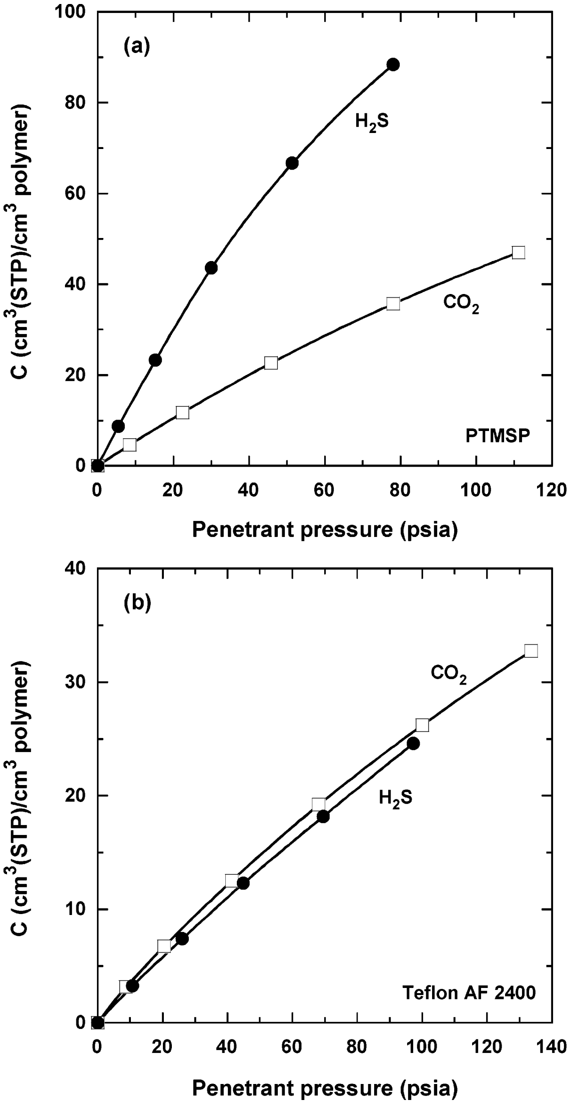


Figure 2. CO_2 and H_2S sorption isotherms in two high-free-volume, glassy polymers at 21 °C: (a) nonfluorinated PTMSP and (b) fluorinated Teflon AF 2400.

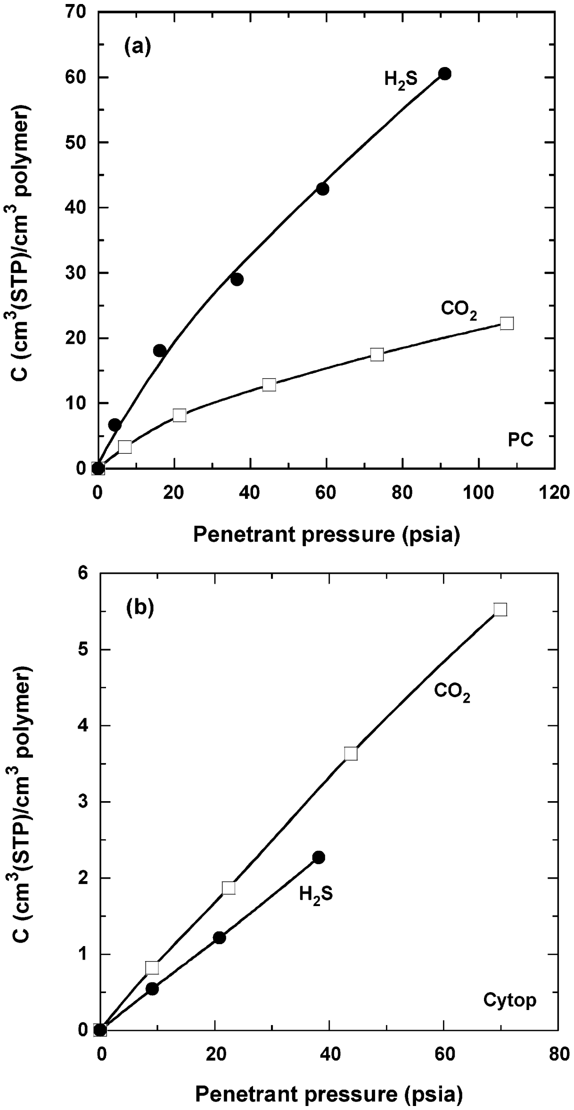


Figure 3. CO_2 and H_2S sorption isotherms in two conventional-free-volume, glassy polymers at 21 °C: (a) nonfluorinated PC and (b) fluorinated Cytop.

(Figure 2b). As demonstrated in Figure 3, the relative solubilities follow the same trend in the two conventional-free-volume glasses, PC and Cytop. These results indicate that, independent of the state of the polymer (rubbery or glassy) or the relative free volume of the polymer, there are large differences in the CO_2 and H_2S relative solubilities in fluorinated polymers as compared to that in nonfluorinated polymers. As will be shown in the following discussion, this difference is caused by unusually low H_2S solubility in fluoropolymers.

Previous results indicate that gas solubility in polymers generally scales with a measure of penetrant condensability such as T_C or $(T_C/T)^2$.[10,12,34,35] Figures 4a and 4b present gas solubilities as a function of $(T_C/T)^2$ for PDMS and Teflon AF 2400, respectively. $(T_C/T)^2$ has been used as the correlating parameter for solubility in Figure 4 because it incorporates the temperature dependence of solubility and, thus, allows the data in the present work to be compared to prior results obtained for these polymers at different experimental temperatures. For both polymers, the logarithm of penetrant solubility generally increases linearly with $(T_C/T)^2$. The N_2, CO_2, and H_2S solubility coefficients measured for PDMS in this study lie near the trend line through the previous data. This result indicates that, in nonfluorinated PDMS, the solubility of H_2S is consistent with what would be anticipated on the basis of this penetrant's molecular properties (i.e., T_C). In contrast, while the N_2 and CO_2 solubility coefficients in Teflon AF 2400 are in agreement with prior results, the H_2S solubility in this fluorinated glass falls significantly below the trend line through the other penetrants. In fact, the actual value is approximately 5 times lower than the H_2S solubility anticipated from the correlation line. This result clearly illustrates anomalously low H_2S solubility in fluorinated Teflon AF 2400 and suggests that understanding H_2S solubility in fluoropolymers requires factors other than simply penetrant condensability be taken into account.

Sorption of penetrant molecules into a polymer matrix can be considered a two-step thermodynamic process consisting of (i) condensation of penetrant molecules from the gas phase followed by (ii) mixing of condensed penetrant with polymer chains. The first step of this process depends on the penetrant condensability at the experimental temperature, while the second stage depends on polymer−penetrant interactions.[36] Previously, it was shown that multiplying the gas solubility coefficient with the associated penetrant saturation vapor pressure, p_{sat}, at the experimental temperature normalizes for differences in penetrant condensability.[9,37] Comparison of the resulting activity-basis solubility, S^a, allows a direct examination of polymer−penetrant

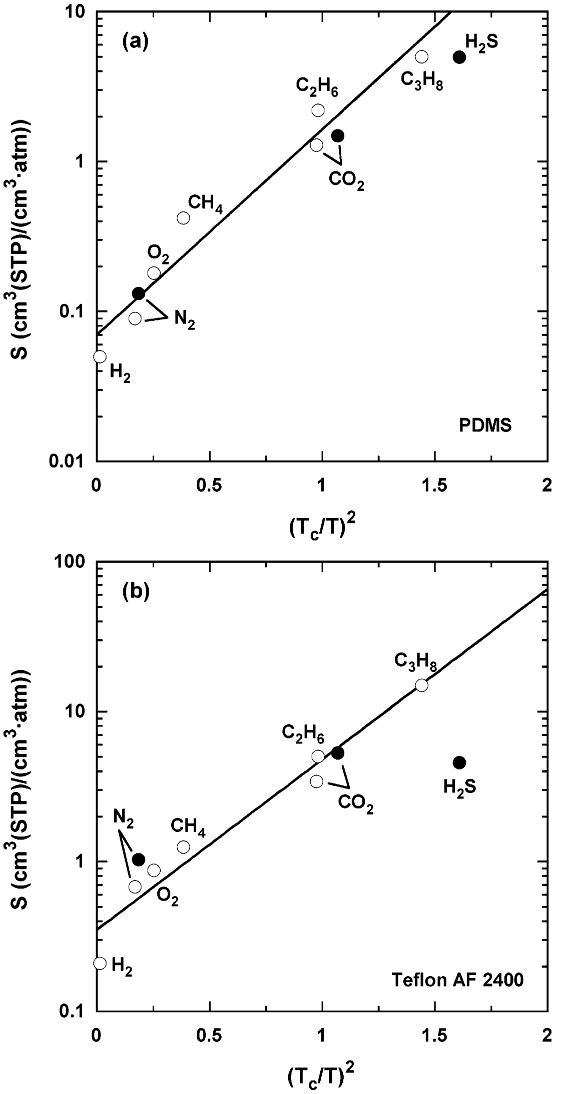


Figure 4. Penetrant infinite-dilution solubility in (a) nonfluorinated PDMS and (b) fluorinated Teflon AF 2400 as a function of $(T_C/T)^2$. Open symbols represent data from previous studies at 35 °C,[10,39] and solid symbols are for data measured at 21 °C in this work.

interaction effects on solubility. Activity-basis solubility may be expressed as

$$S^a = Sp_{sat} = \left(\frac{C}{p}\right)p_{sat} \tag{4}$$

Figure 5 compares the ratio of CO_2 to H_2S activity-basis solubility coefficients for each of the six polymers examined in Figures 1-3. The S^a values were calculated as the product of the infinite-dilution solubilities extracted from the sorption isotherms and the penetrant saturation vapor pressures at 21 °C. For the nonfluorinated polymers, the H_2S activity-basis solubility is nearly equivalent or slightly lower than that for CO_2. Previously, activity-basis solubility was shown to be a weak function of penetrant size, with larger penetrants having lower solubility due to the greater energy required to create an opening in the polymer matrix to accommodate them relative to smaller species.[9] Because H_2S is slightly larger than CO_2, it is reasonable that the CO_2 activity-basis solubility in a polymer could be somewhat higher than that of H_2S. For example, the activity-basis solubility of CO_2 is 9−10% higher than the value for H_2S in PTMSP. Nevertheless, aside from these small differences, the solubility results for the nonfluorinated polymers are consistent with a sorption process that depends primarily on penetrant condensability with little influence of polymer−penetrant interactions. For the fluoropolymers, however, H_2S activity-basis solubility is significantly lower than that of CO_2. In Cytop, for example, the activity-basis solubility is nearly 5 times lower for H_2S than for CO_2. Such a large difference in solubility values that have been normalized for penetrant condensability variations suggests a significant influence of polymer−penetrant interactions in this system. The low H_2S activity-basis solubility in Cytop and the other fluoropolymers indicates unfavorable interactions between this penetrant and fluoropolymers relative to the interactions between CO_2 and these polymers. This unfavorable H_2S-fluoropolymer interaction is responsible for the observed low H_2S solubility in fluoropolymers.

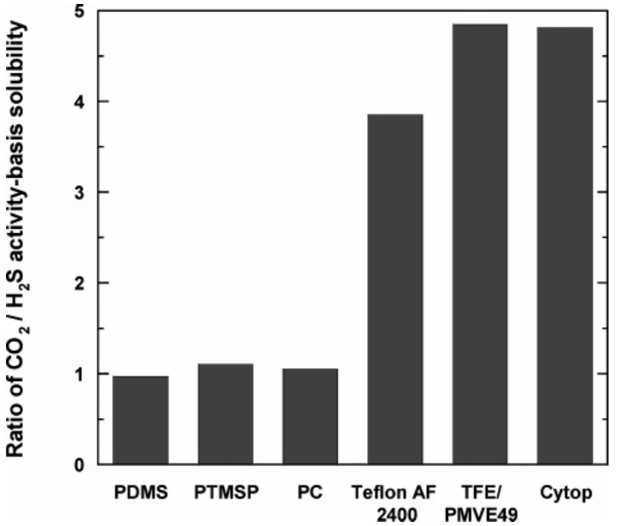


Figure 5. Ratio of CO_2 to H_2S activity-basis solubility coefficients for six different polymers. Calculated saturation vapor pressures at 21 °C: 59.5 atm for CO_2 and 18.5 atm for H_2S.[30]

Several recent studies[10−12] have shown that unusually low hydrocarbon gas solubility in fluorinated polymers parallels gas−liquid and liquid−liquid solubility behavior for hydrocarbon−fluorocarbon mixtures. This comparison was made possible by the existence of hydrocarbon solubility data in fluorinated liquids. However, for the present case, the authors are not aware of any published data describing hydrogen sulfide solubility in fluorinated liquids. This limits our ability to make any generalizations about H_2S solubility in fluorinated media. The closest gas−liquid system for which solubility data exists is a compilation of H_2S solubility in halogenated liquid alkanes containing bromine, chlorine, or iodine.[38] These data show that, as the number of halogen atoms in the solvent molecule increases (and the number of hydrogen atoms decreases), H_2S solubility decreases. It has been suggested that this result indicates H_2S solubility in haloalkanes is influenced by hydrogen bond formation.[38] As the hydrogen content of the liquid alkane decreases, so does the capacity to form hydrogen bonds with H_2S; consequently, H_2S solubility decreases. This hypothesis is consistent with our data, which show that complete halogenation (with fluorine) of the sorbing polymer results in greatly reduced H_2S solubility relative to that in nonfluorinated polymers.

Recent efforts to describe hydrocarbon−fluorocarbon solubility data using regular solution theory,[39] modern equation-of-state approaches,[40,41] and state-of-the-art computer simulations[42] have failed to uncover the underlying molecular phenomena responsible for the observed anomalous sorption behavior. In

Table 2. Infinite-Dilution H_2S and CO_2 Solubilities and H_2S/CO_2 Solubility Selectivity in Nonfluorinated and Fluorinated Polymers

polymer	solubility[a] [$cm^3(STP)/(cm^3 \cdot atm)$] CO_2	solubility[a] [$cm^3(STP)/(cm^3 \cdot atm)$] H_2S	H_2S/CO_2 solubility selectivity[a]
Nonfluorinated Polymers			
PDMS	1.5	5.0	3.3
PTMSP	8.2	24	2.9
PC	7.5	23	3.1
predicted theoretical value[b]			3.2
Fluorinated Polymers			
TFE/PMVE49	1.1	0.73	0.66
Teflon AF 2400	5.5	4.6	0.83
Cytop	1.3	0.87	0.69

[a] Infinite-dilution values at 21 °C. [b] Estimated from eq 5 according to a classical thermodynamics theory for gas solubility in polymers.

each case, unusually low solubility was traced to unlike molecule interactions that are more unfavorable than predicted by conventional mixing rules.[43] It will be interesting to see whether any of these approaches might explain the anomalously low H_2S solubility in fluoropolymers described here.

The impact of low H_2S solubility on selectivity in fluoropolymers is illustrated in Table 2, which presents CO_2 and H_2S solubility coefficients and H_2S/CO_2 solubility selectivity values for several different fluorinated and nonfluorinated polymers. On the basis of a model developed from classical thermodynamics for gas solubility in polymers,[44] solubility scales exponentially with gas critical temperature in the absence of specific interactions. Consequently, a theoretical polymer H_2S/CO_2 solubility selectivity can be expressed as a function of gas critical temperatures in the following manner:

$$\frac{S_{H_2S}}{S_{CO_2}} = \exp[b(T_C^{H_2S} - T_C^{CO_2})] \tag{5}$$

where b is an empirical constant that has previously been reported to be 0.017 K^{-1} for a wide variety of polymers.[35] Given the respective critical temperatures of H_2S and CO_2, eq 5 predicts that the theoretical H_2S/CO_2 solubility selectivity in polymers is 3.2. For the nonfluorinated polymers (PDMS, PTMSP, and PC) examined, their measured H_2S/CO_2 solubility selectivity is close to this predicted theoretical value. However, as shown in Table 2, the measured H_2S/CO_2 solubility selectivity for the three fluoropolymers (TFE/PMVE49, Teflon AF 2400, and Cytop) is less than 1. This result again highlights the difference in H_2S sorption behavior between fluorinated and nonfluorinated polymers and demonstrates how solubility can affect overall membrane selectivity. In nonfluorinated polymers, H_2S enjoys a significant solubility advantage over CO_2, allowing larger H_2S to be more permeable than CO_2 in weakly size-sieving polymers while lowering the overall CO_2/H_2S permeability selectivity in more strongly size-selective materials. On the other hand, in fluoropolymers, the unfavorable interaction between H_2S and the fluorinated polymer matrix robs H_2S of its usual solubility advantage over CO_2, thereby maximizing the CO_2/H_2S permeability selectivity that can be achieved for a given diffusion selectivity. It is also interesting to note that, among the fluoropolymers studied, the H_2S/CO_2 solubility selectivity is slightly higher in high-free-volume Teflon AF 2400. This result may suggest that the unfavorable interaction causing low H_2S solubility in fluorinated polymers is amplified in lower-free-volume materials (e.g., Cytop, TFE/PMVE49) where penetrant molecules and polymer chains are forced into more intimate contact.

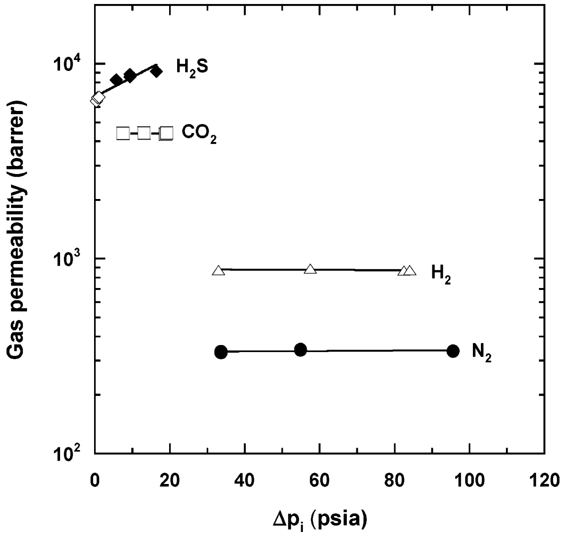


Figure 6. Mixed-gas permeability coefficients in PDMS at 21 °C as a function of gas partial pressure difference. Solid symbols represent data collected using a binary feed gas containing 15% H_2S in nitrogen. Open symbols are for data obtained using a syngas mixture containing 0.7% H_2S, 11.7% CO_2, 36.5% CO, and balance H_2.

Permeability. Figure 6 presents mixed-gas permeability coefficients of H_2, N_2, CO_2, and H_2S in PDMS as a function of gas partial pressure difference across the polymer film. Consistent with previous results for this nonfluorinated, rubbery polymer,[23] the H_2S permeability coefficient is higher than those of the light gases (H_2 and N_2) and even that of CO_2. For instance, at low pressure, PDMS is 1.5 times more permeable to H_2S than to CO_2. The H_2S permeability in PDMS is also strongly pressure-dependent, which is typical behavior for highly sorbing penetrants. Because H_2S permeability increases with pressure faster than CO_2, the mixed-gas H_2S/CO_2 selectivity increases to 2.1 at the maximum H_2S partial pressure examined (i.e., 16 psia). These PDMS results are consistent with the behavior of weakly size-sieving polymers in which solubility determines overall relative permeability and more condensable H_2S sorbs preferentially over CO_2.

In Figure 7, various gas permeability coefficients in perfluorinated Cytop are also plotted as a function of gas partial pressure difference. The relative permeability of H_2S in this glassy fluoropolymer is very different from that observed in rubbery PDMS. In Cytop, H_2S is much less permeable than CO_2, H_2, or N_2. Consequently, Cytop exhibits a very high CO_2/H_2S selectivity ranging from 20 to 27 depending on pressure. This result is partly due to (i) H_2S being larger than the light gases and (ii) Cytop being a size-sieving, glassy polymer in which relative permeability is governed by diffusion selectivity. However, based on the data in Table 2, abnormally low H_2S solubility in Cytop also significantly influences selectivities involving this gas. For example, CO_2/H_2S solubility selectivity in Cytop is approximately 4.5 times higher than that in common nonfluorinated polymers. Thus, relative to that of a hypothetical nonfluorinated polymer with equivalent diffusion selectivity, the overall CO_2/H_2S permeability selectivity of the Cytop membrane would be higher by a factor of 4.5 because of solubility effects.

A useful comparison is to contrast the permeation properties of Cytop with those of a nonfluorinated, conventional-free-volume glass such as PC. In Figure 8, the gas permeability coefficients in glassy PC are shown as a function of gas partial pressure difference. The H_2 and CO_2 permeabilities measured for PC in our study are similar to values reported by previous researchers. For example, at the slightly higher temperature of

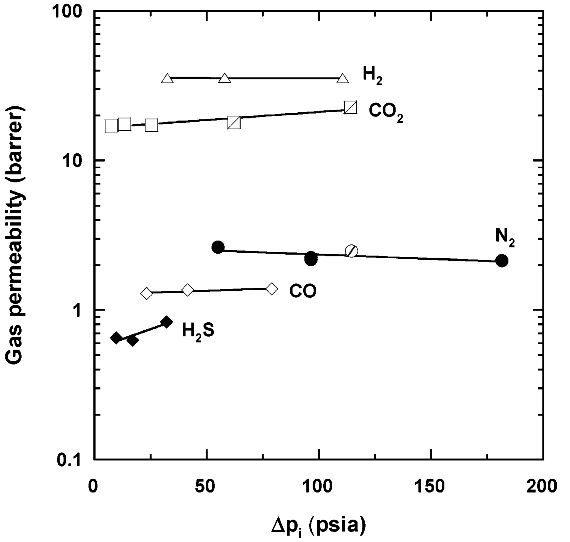


Figure 7. Gas permeability coefficients in Cytop at 21 °C as a function of gas partial pressure difference. Solid symbols represent mixed-gas data obtained with a 15% H_2S in nitrogen mixture. Open symbols are data collected with a syngas mixture containing 0.7% H_2S, 11.7% CO_2, 36.5% CO, and balance H_2. (It is noted that H_2S permeability was too low to be measured with the syngas mixture.) Open symbols with diagonal lines are pure-gas data points.

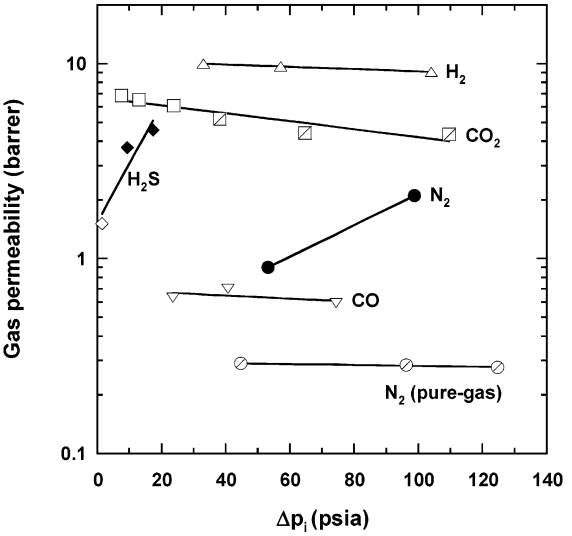


Figure 8. Gas permeability coefficients in PC at 21 °C as a function of gas partial pressure difference. Solid symbols represent mixed-gas data obtained with a 15% H_2S in nitrogen mixture. Open symbols are data collected with a syngas mixture containing 0.7% H_2S, 11.7% CO_2, 36.5% CO, and balance H_2. Open symbols with diagonal lines are pure-gas data points. Pure-gas N_2 data were determined at 35 °C.

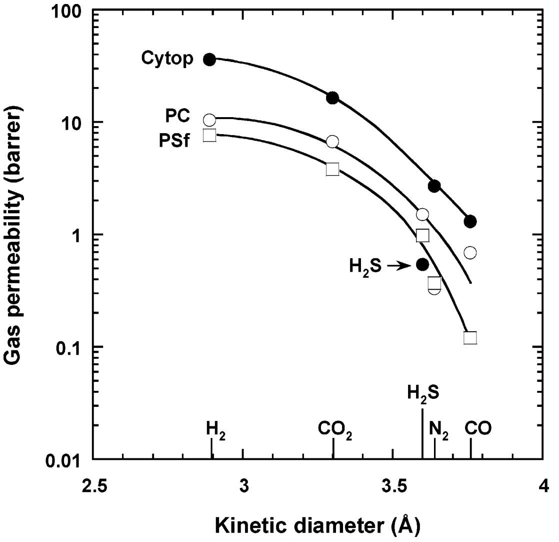


Figure 9. Gas permeability coefficients at $\Delta p_i = 0$ and 21 °C in fluorinated Cytop and nonfluorinated PC and PSf as a function of penetrant molecular size.

25 °C, Norton measured pure-gas permeabilities of 12 barrers for H_2 and 8.0 barrers for CO_2 in Lexan PC.[45] These literature values compare favorably with our low-pressure, mixed-gas H_2 and CO_2 permeabilities of 10 and 6.9 barrers for H_2 and CO_2, respectively. Like Cytop, PC is a conventional-free-volume, size-sieving polymer in which relative permeability is largely determined by diffusivity selectivity. Consequently, smaller CO_2 is more permeable than larger H_2S in PC. However, the difference in the permeabilities of these two gases is much smaller in PC than in Cytop. For example, at infinite dilution (i.e., $\Delta p_i = 0$), PC has a CO_2/H_2S selectivity of only 4.5, while Cytop shows a substantially higher selectivity of 30. Furthermore, the difference in CO_2/H_2S selectivity of these two polymers becomes even greater at higher H_2S partial pressures because H_2S permeability exhibits much stronger pressure dependence in PC than in Cytop. For example, over a similar H_2S partial pressure range, H_2S permeability increases by 200% in PC (Figure 8) but increases by only 28% in Cytop (Figure 7). The large H_2S permeability rise in PC suggests that this nonfluorinated, glassy polymer is strongly plasticized by H_2S. Plasticization of glassy polymers is a phenomenon whereby highly sorbing species cause polymer swelling that typically increases polymer free volume and polymer chain mobility. Thus, sorption-induced plasticization increases gas diffusion coefficients and, in turn, permeability coefficients.

Further evidence of H_2S-sorption-induced plasticization of PC is the high mixed-gas permeability coefficients measured for N_2 during its co-permeation with H_2S. At an H_2S partial pressure of 17.4 psia, PC has a mixed-gas N_2 permeability of 2.1 barrers, which is 7 times higher than its measured pure-gas N_2 permeability of 0.29 barrers (Figure 8). In contrast, for Cytop, the mixed-gas N_2 permeability measured during co-permeation with H_2S is essentially the same as the pure-gas value (Figure 7). This result suggests that low H_2S sorption in Cytop renders this perfluorinated polymer resistant to plasticization by H_2S, whereas nonfluorinated PC exhibits evidence of strong sorption-induced plasticization.

The effect of penetrant size on gas permeability coefficients in Cytop, PC, and PSf is shown in Figure 9. Typically, in conventional-free-volume, glassy polymers, gas permeability decreases regularly with increasing penetrant size, as characterized by critical volume or kinetic diameter. This is generally the case for permeabilities in Cytop, PC, and PSf. The primary deviation from this trend is the unusually low H_2S permeability in Cytop. As shown in Figure 9, the measured H_2S permeability in Cytop is about 6.5 times lower than the value expected on the basis of H_2S molecular size and the correlation line through the other penetrants. This low H_2S permeability in Cytop is a result of the aforementioned unfavorable interaction between H_2S and the fluorinated polymer matrix.

To highlight the unusual nature of the CO_2/H_2S selectivity exhibited by fluorinated materials, Table 3 compares the CO_2 and H_2S permeation properties measured for several fluorinated and nonfluorinated polymers. For nonfluorinated, rubbery polymers (PDMS and Pebax, a polyether-polyamide block copolymer) and a nonfluorinated, high-free-volume glass (PTMSP), H_2S is more permeable than CO_2. The nonfluorinated,

Table 3. Mixed-Gas CO_2 Permeability and CO_2/H_2S Selectivity for Various Nonfluorinated and Fluorinated Polymers

polymer	CO_2 permeability (barrer)	CO_2/H_2S selectivity	source
	Nonfluorinated Polymers		
PTMSP	18 000	0.85	this work[a]
PDMS	4400	0.66	this work[b]
Pebax 1657	69	0.27	this work[c]
Pebax 1074	122	0.22	this work[c]
PC	6.5	4.3	this work[b]
PSf	3.8	3.9	this work[c]
cellulose acetate	2.4	1.2	ref 25[d]
nylon-6	0.088	0.26	ref 19
	Fluorinated Polymers		
Cytop	17	27	this work[e]
TFE/PMVE/8CNVE	28	8.0	this work[f]
Teflon AF 1600	680	6.8	this work[a]
Teflon AF 2400	2300	5.6	this work[a]

[a] Feed gas mixture: 1.5% H_2S, 10.5% CO_2, 46% CO, and balance H_2; $T = 23$ °C; $\Delta p = 20$ psig [b] Feed gas mixture: 0.7% H_2S, 11.7% CO_2, 36.5% CO, and balance H_2; $T = 21$ °C; $\Delta p = 100$ psig. [c] Same feed mixture as footnote *b*, but $\Delta p = 190$ psig. [d] $T = 35$ °C; $\Delta p = 147$ psig. [e] CO_2 permeability was measured with the mixture given in footnote *b*, but H_2S permeability was too low to be measured with this feed composition. H_2S permeability was obtained using a binary 15% H_2S in nitrogen mixture. Experiments were conducted at $T = 21$ °C and $\Delta p = 100$ psig. [f] Same feed mixture as footnote *a*, except $T = 37$ °C and $\Delta p = 100$ psig.

conventional-free-volume, glassy polymers exhibit mixed behavior, with some glasses (PC, PSf, and cellulose acetate) being slightly CO_2-selective and one (nylon-6) being more permeable to H_2S. In contrast, all of the fluorinated polymers examined (a rubber as well as high- and conventional-free-volume glasses) are more permeable to CO_2 than to H_2S. According to the data in Table 3, CO_2/H_2S selectivity increases with decreasing fluoropolymer permeability. For example, at the test conditions examined, the CO_2/H_2S selectivity is as high as 27 for Cytop (CO_2 permeability ∼ 17 barrers) and only 5.6 for Teflon AF 2400 (CO_2 permeability ∼ 2300 barrers). This selectivity trend in the fluoropolymers is attributed to the following two factors:

(1) A lower-permeability polymer tends to be more size-sieving and, hence, will favor the transport of smaller CO_2 over that of larger H_2S. Consequently, Cytop, the least permeable fluoropolymer investigated, will have the highest CO_2/H_2S diffusion selectivity.

(2) A lower-permeability polymer typically has less free volume and, hence, higher density than a higher-permeability material. In a denser fluoropolymer structure, any unfavorable chemical interaction between H_2S and the fluorinated matrix will be amplified because the penetrant and polymer would be forced into more intimate contact. As a result, H_2S solubility will be suppressed to a greater extent in a fluoropolymer with lower free volume (e.g., Cytop) than in one with a higher free volume (e.g., Teflon AF 2400), yielding higher CO_2/H_2S solubility selectivity in the lower-free-volume material.

Figure 10 presents the data of Table 3 in the form of a selectivity–permeability tradeoff plot of the type popularized by Robeson.[46] For size-selective separations, these plots typically show that, as the permeability of polymer membranes increases, their size selectivity decreases and vice versa. Ideally, for separation applications, polymers with both high permeability and high selectivity are desired. Graphically, this desirable combination of transport properties corresponds to the upper right-hand quadrant of a tradeoff plot. Polymers with properties that fall closest to this region are termed "upper bound" materials. Figure 10 shows that fluoropolymers are clearly the upper bound materials for CO_2/H_2S membrane separations.

Decomposition of the overall CO_2/H_2S permeability selectivity into its respective solubility and diffusivity selectivity

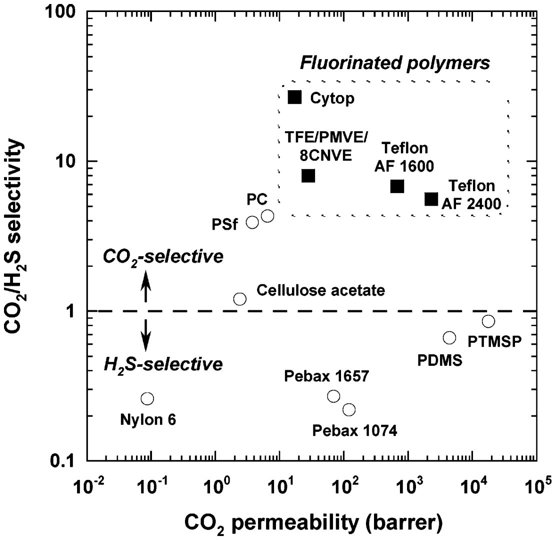


Figure 10. Membrane CO_2/H_2S selectivity as a function of CO_2 permeability for various fluorinated and nonfluorinated polymers.

Table 4. Infinite-Dilution Permeability, Solubility, and Diffusivity Selectivities for CO_2 over H_2S in Nonfluorinated and Fluorinated Polymers

polymer	P_{CO_2}/P_{H_2S}	S_{CO_2}/S_{H_2S}	D_{CO_2}/D_{H_2S}[a]
	Nonfluorinated Polymers		
PDMS	0.65	0.30	2.2
PTMSP	0.85	0.34	2.5
PC	4.5	0.32	14
	Fluorinated Polymers		
Teflon AF 2400	5.6	1.2	4.7
Cytop	30	1.5	20

[a] Diffusivity selectivities calculated from infinite-dilution permeability and solubility selectivities by using eq 2.

contributions is shown in Table 4 for several fluorinated and nonfluorinated polymers to quantitatively illustrate the effect of low H_2S solubility in fluoropolymers on membrane separation properties. In each of the polymers, CO_2 has a higher diffusion coefficient than H_2S, consistent with the smaller molecular size of CO_2. The order of CO_2/H_2S diffusivity selectivity in the polymers examined is Cytop > PC > Teflon AF 2400 > PTMSP > PDMS. This ranking is consistent with the known size-sieving capacity of these polymers, as deduced from their free volume and chain mobility.

For nonfluorinated PDMS and PTMSP, the transport advantage that CO_2 gains from the diffusion step is offset by the significantly higher solubility of H_2S relative to that of CO_2 in these polymers. As a result, PDMS and PTMSP are more permeable to H_2S than to CO_2 even though CO_2 diffuses faster in them. On the basis of the data in Table 3, this appears to be a rather common result for nonfluorinated polymers. For high-free-volume Teflon AF 2400, the unfavorable interaction of H_2S with the fluorinated matrix eliminates the usual H_2S solubility advantage. In fact, CO_2 both sorbs more and diffuses faster than H_2S in this fluoropolymer. Consequently, Teflon AF 2400 is significantly more permeable to CO_2 than to H_2S. For the two conventional-free-volume polymers, Cytop and PC, the CO_2/H_2S diffusivity selectivities are relatively high due to the stronger size-discriminating nature of these materials. For nonfluorinated PC, high H_2S solubility detracts from the overall CO_2/H_2S permeability selectivity, resulting in PC having lower CO_2/H_2S permeability selectivity than weakly size-sieving Teflon AF 2400. In contrast, both solubility selectivity and diffusivity selectivity favor CO_2 in fluorinated Cytop, resulting in the highest overall CO_2/H_2S permeability selectivity of the materials studied.

Conclusions

The permeability of fluoropolymer membranes to hydrogen sulfide is substantially lower than what would be expected on the basis of the molecular properties of this penetrant. In contrast, H_2S permeability in nonfluorinated polymers follows standard correlations of permeability with penetrant size. As a consequence, the selectivity of fluorinated membranes for separations involving H_2S is very different from that of nonfluorinated membranes. The anomalously low H_2S permeability in fluoropolymers is caused primarily by low H_2S solubility. This unexpected solubility behavior appears to be related to unfavorable interactions between H_2S and fluorinated polymers.

Generally speaking, the fact that a given fluoropolymer offers significantly greater resistance to H_2S transport than an analogous nonfluorinated polymer is an important material selection guideline. The extremely low H_2S solubility in fluoropolymers, in addition to imparting low permeability, also suggests that membranes fabricated from these materials will not be subject to H_2S-induced plasticization and consequent performance losses. This information should prove useful to process designers using fluorinated membranes for applications, such as natural gas treatment, in which H_2S is present.

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