

Synthesis and Gas Permeation Properties of a Single Layer PDMS Membrane

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ABSTRACT: In this work, a new polydimethylsiloxane (PDMS) membrane was synthesized and its sorption, diffusion, and permeation properties were investigated using H₂, N₂, O₂, CH₄, CO₂, and C₃H₈ as a function of pressure at 35°C. PDMS, as a rubbery membrane, was confirmed to be more permeable to more condensable gases such as C₃H₈. The synthesized PDMS membrane showed much better gas permeation performance than others reported in the literature. Based on the sorption data of this study and other researchers' works, some valuable parameters such as Flory-Huggins (FH) interaction parameters, χ , etc., were calculated and discussed. The concentration-averaged FH interaction parameters of H₂, N₂, O₂, CH₄, CO₂, and C₃H₈ in the synthesized PDMS membrane were estimated to be 2.196, 0.678, 0.165, 0.139, 0.418, and 0.247, respectively. Chemical similarity of O₂, CH₄, and C₃H₈ with backbone

structure of PDMS led to lower χ values or more favorable interactions with polymer matrix, particularly for CH₄. Regular solution theory was applied to verify correctness of evaluated interaction parameters. Local effective diffusion coefficient of C₃H₈ and CO₂ increased with increasing penetrant concentration, which indicated the plasticization effect of these gases over the range of penetrant concentration studied. According to high C₃H₈/gas ideal selectivity values, the synthesized PDMS membrane is recommended as an efficient membrane for the separation of organic vapors from noncondensable gases. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 33–48, 2010

Key words: polydimethylsiloxane; gas sorption; permeability; solubility; diffusivity; ideal selectivity; Flory-Huggins interaction parameter

INTRODUCTION

The separation of gases by thin barriers termed as membranes is a dynamic and rapidly growing field. The membrane separation processes offer a number of advantages in terms of low energy consumptions and capital investments. The process also requires simple, easy to operate, and compact equipment. Hence, recently, the process has a significant role in the industry in terms of economical considerations.¹

The recovery of higher hydrocarbons such as liquefied petroleum gas, liquefied natural gas, and volatile organic compounds from gas streams is of great importance economically. When the rates of these gas streams are modest and higher hydrocarbons are the minor components of these streams, applying membrane gas separation process with rubbery membranes such as polydimethylsiloxane (PDMS) becomes rational.

PDMS is the most commonly used rubbery membrane material for the separation of higher hydrocarbons from permanent gases.² Many studies have been carried out on the transport properties of pure and mixed gas mixtures of O₂, N₂, H₂, CO, CO₂, CH₄, C₂–C₄ olefins, and paraffins using PDMS membranes.^{3–17}

Many researchers studied pure and mixed gas permeation through PDMS membranes and did not consider interaction of gas molecules with the polymer matrix.^{3,11–17} However, many of them reported the diffusion of gases in silicone polymers by molecular dynamics simulation methods.^{4–10}

Shah et al.⁴ measured solubility of CH₄, C₃H₈, and CO₂ in five silicone polymers including PDMS at 10, 35, and 55°C. They evaluated interaction parameter of these gases by two methods, (1) Flory–Huggins (FH) interaction parameter, where solubility coefficient was in the limit of zero (infinite solubility coefficient) and (2) regular solution theory. Interaction parameters derived from these methods were in the range of –0.13 to 1.4 and 0.14 to 2.3, respectively.

Fleming and Koros⁵ investigated sorption and desorption of CO₂ in silicone rubber as a function of pressure (0–900 psia) at 35°C. They compared the experimental sorption and desorption data with FH expression using CO₂ average interaction parameter of 0.75 and Henry's law.

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Merkel et al.^{6,7} and Prabhakar et al.⁹ focused on hydrocarbon and perfluorocarbons sorption in PDMS membranes. They also reported sorption and permeation of permanent gases (H_2 , O_2 , and N_2) in PDMS membranes. Perfluorocarbons solubility was found to be lower than that of their hydrocarbon analogs in PDMS due to less favorable polymer-perfluorocarbon interactions. Merkel et al. showed that permeability coefficients of perfluorinated penetrants (CF_4 , C_2F_6 , and C_3F_8) were approximately an order of magnitude lower than those of their hydrocarbon analogs (CH_4 , C_2H_6 , and C_3H_8). Perfluorocarbon permeabilities were even lower than that of permanent gas permeability coefficients. They attributed this result to very low perfluorocarbon solubilities in PDMS coupled with their low diffusion coefficients which is relative to those of their hydrocarbon analogs. The FH interaction parameters of N_2 , C_3H_8 , and C_3F_8 were calculated and plotted as a function penetrant concentration. They indicated that for PDMS/ C_3H_8 system, interaction parameter decreases as penetrant concentration increases. An inverse trend was observed for PDMS/ C_3F_8 .⁶

Raharjo et al.⁸ reported pure and mixed gas n - C_4H_{10} and CH_4 sorption and dilation properties in PDMS at temperatures ranging from -20 to $50^\circ C$. They did not focus on interaction of the penetrants with the polymer matrix.

Kamiya et al.¹⁰ determined Henry's law coefficients and partial molar volumes of 34 penetrants (5 inert gases, 6 inorganic gases, 17 hydrocarbon gases, 5 fluorinated gases, and CCl_4 vapor) dissolved in PDMS at $25^\circ C$ by measuring sorption of the gases and the concomitant dilation of the polymers. They estimated Flory-Huggins parameters for polymer/gas interactions from the Henry's law coefficients and the partial molar volumes.

In this study, a single layer PDMS membrane was synthesized and gas sorption, permeation, and diffusion in it were investigated and the results were compared with other researchers' works.³⁻¹⁰ Solubility, permeability, and diffusivity coefficients were correlated with pressure at constant temperature ($35^\circ C$). Strong correlation of these coefficients with critical properties of gases was also identified. FH interaction parameter of each gas with the polymer matrix was calculated, and this parameter was thoroughly discussed for PDMS/ C_3H_8 system. Regular solution theory was also applied to validate calculated interaction values. C_3H_8 sorption in the PDMS membrane was predicted using correlated values of PDMS/ C_3H_8 interaction parameters. Plasticization effects of gases were determined by estimating the local effective diffusion coefficients. C_3H_8 /gas solubility and diffusivity selectivities as well as ideal permeation selectivity were determined to assess the ability of the synthesized PDMS membrane for separation of organic vapors from permanent gases.

Unlike conventional glassy polymers used for permanent gas separations (e.g., O_2/N_2 , H_2/N_2 , N_2/CH_4 , CO_2/CH_4 , etc.), PDMS can be used for separation of many organic vapors, such as C_3H_8 , from supercritical gases, such as N_2 , O_2 , and H_2 .

THEORY

Gas transport in polymer membranes is widely modeled using the solution-diffusion mechanism and is expressed by a permeability coefficient, P , defined as follows:

$$P = \frac{Nl}{p_2 - p_1} \quad (1)$$

where N is the steady-state gas flux through a polymer membrane of thickness l due to a partial pressure difference ($p_2 - p_1$) across the film, p_1 is the permeate or downstream pressure and p_2 is the feed or upstream pressure. In the simplest case, penetrant diffusion is modeled using Fick's law of diffusion¹⁸:

$$N = -\frac{D_{loc}}{(1 - \omega)} \left(\frac{dC}{dx} \right) \quad (2)$$

where D_{loc} is the local concentration-dependent diffusion coefficient and ω is the penetrant mass fraction in the polymer at concentration C . Combining eqs. (1) and (2) and integrating across the film thickness yields:

$$P = \frac{1}{p_2 - p_1} \int_{C_1}^{C_2} D_{eff} dC \quad (3)$$

where C_2 and C_1 are the penetrant concentrations in the polymer at the upstream and downstream faces of the membrane, respectively, at a given temperature and D_{eff} is the local, effective diffusion coefficient, defined for convenience as $D_{eff} = D_{loc}/(1 - \omega)$. If the diffusion coefficient is not a function of concentration,

$$P = \frac{C_2 - C_1}{p_2 - p_1} D_{eff} \quad (4)$$

If the diffusion coefficient is dependent on concentration, D_{eff} is replaced with the concentration-averaged effective diffusivity \bar{D} . If the downstream pressure is negligible compared to the upstream pressure, eq. (4) can be simplified:

$$P = S D \quad (5)$$

where, D is D_{eff} or \bar{D} and the solubility coefficients, S , is defined as follows:

$$S = \frac{C}{p} \quad (6)$$

In eq. (6), S should be evaluated at the upstream conditions. Equation (5) is widely used to rationalize gas transport properties in polymer membranes.

The ideal selectivity, $\alpha_{A/B}$, of component A over B is a measure of the potential separation ability of the membrane material. It can be written as the ratio of the pure gas permeabilities¹⁹:

$$\alpha_{A/B} = \frac{P_A}{P_B} \quad (7)$$

When permeability is viewed as the product of solubility and diffusivity [eq. (5)], this expression may be rewritten as the product of two ratios:

$$\alpha_{A/B} = \left(\frac{S_A}{S_B} \right) \times \left(\frac{D_A}{D_B} \right) \quad (8)$$

where the first term is the solubility selectivity and the second is the diffusivity or mobility selectivity. In addition to operating conditions (i.e., temperature, pressure, and gas composition), penetrant solubility depends on condensability and polymer-penetrant interactions.¹⁹ In the absence of specific interactions (e.g., hydrogen bonding), the first effect is dominant, and solubility increases as penetrant condensability, characterized by critical temperature, normal boiling point or Lennard Jones force constant increases.¹⁹ Thus, solubility selectivity increases as the difference between condensability of two penetrants in a mixture increases. Often, larger penetrants are more condensable, and therefore, more soluble than smaller penetrants. The diffusion coefficient decreases as penetrant size increases, and therefore, diffusivity selectivity increases as the relative size difference between two penetrants increases, with the smaller penetrant having higher diffusivity.¹⁹ Thus, a tradeoff often exists between solubility selectivity and diffusivity selectivity, with the overall selectivity depending on the relative magnitudes of these two terms.

The concentration of sparingly soluble gases and vapors in rubbery polymers generally exhibits a linear dependence on penetrant pressure. This so-called Henry's law sorption isotherm is given by¹⁹:

$$C = k_d p \quad (9)$$

where C [cm^3 (STP) of penetrant sorbed per cm^3 of polymer] is the equilibrium penetrant concentration in the polymer at pressure p (atm) and k_d [$\text{cm}^3(\text{STP})/(\text{cm}^3 \text{ atm})$] is the Henry's law constant.

The uptake of more soluble vapors in uncrosslinked rubbery polymers is frequently described using the FH expression⁴⁻⁶:

$$\ln a = \ln \phi_2 + (1 - \phi_2) + \chi(1 - \phi_2)^2 \quad (10)$$

where a is penetrant activity in the vapor phase, ϕ_2 is the volume fraction of sorbed penetrant and χ is the FH interaction parameter. For crosslinked rubbery polymers, a modified form of the aforementioned equation, called the Flory–Rehner (FR) expression is often used^{6,9}:

$$\ln a = \ln \phi_2 + (1 - \phi_2) + \chi(1 - \phi_2)^2 + V_2 \left(\frac{v_e}{V_0} \right) \times \left[(1 - \phi_2)^{1/3} - \left(\frac{1 - \phi_2}{2} \right) \right] \quad (11)$$

where V_2 is the penetrant molar volume and v_e/V_0 is the effective number of crosslinks per unit volume of penetrant-free polymer (expressed in moles of crosslinks per unit volume of penetrant-free polymer). In this study, penetrant activity was set equal to the relative pressure, p/p_{sat} , where p_{sat} is the saturation vapor pressure of penetrant. The volume fraction of sorbed penetrant, ϕ_2 , is calculated from the equilibrium penetrant concentration in the polymer, C , as follows:

$$\phi_2 = \left[1 + \frac{22414}{C\bar{V}_2} \right]^{-1} \quad (12)$$

where \bar{V}_2 is the penetrant partial molar volume and is estimated as described by Merkel et al.⁶ In this equation, C and \bar{V}_2 have units of [cm^3 (STP)/ cm^3 polymer] and [cm^3/mol], respectively. 22,414 is a conversion factor [cm^3 (STP)/mol].

EXPERIMENTAL

Membrane preparation

PDMS films were prepared from toluene solution containing 55 wt % Dehesive 944 silicone (Wacker Silicones Corporation, Adrian, MI). As supplied by the manufacturer, Dehesive 944 is a solvent-based addition crosslinkable silicone. Before casting, the proprietary Crosslinker V24/Catalyst OL system provided by Wacker was added to the polymer solution. Films were prepared by pouring the polymer solution into a glassy casting die supported by a Teflon-based polymer. The cast films were dried slowly under ambient conditions for 48 h. They were then placed in an oven at 80°C for 2 h to remove residual solvent and to fully crosslink the polymer. After they were cooled to room temperature, the crosslinked films were easily removed from the Teflon-based polymer. Finally, the thin films were detached from the glassy die using a very sharp razor. The resulting PDMS films were transparent and not tacky. Thickness of the films was determined with a digital micrometer (Mitutoyo Model MDC-25SB)

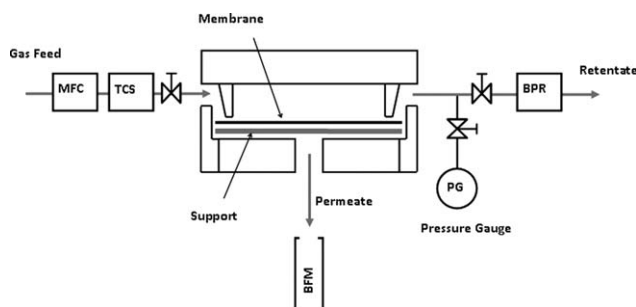


Figure 1 Schematic view of the gas permeation module.

readable to $\pm 1 \mu\text{m}$ and found to be $\sim 100 \mu\text{m}$. The synthesized membranes were housed in the gas permeation module. Sorption experiments were conducted with thicker films (about $300 \mu\text{m}$) of PDMS to monitor gas solubility more precisely. Crosslinking was achieved employing the same components and conditions as those used earlier. The crosslink density of the PDMS films used in the sorption and gas permeation experiments was estimated to be $1.5 \times 10^{-3} \text{ mol/cm}^3$. At first, sorption of a gas (C_3H_8 in the present work) in uncrosslinked silicone oil was measured ($58.3 \text{ cm}^3 \text{ gas/cm}^3 \text{ oil}$ at 4.3 atm and 25°C). Based on eq. (10), FH interaction parameter was calculated to be 0.175. C_3H_8 sorption in the crosslinked membrane was then obtained at the same pressure and temperature ($53.2 \text{ cm}^3 \text{ gas/cm}^3 \text{ polymer}$). Finally, crosslink density (v_c/V_0) was calculated with the aid of eq. (11). The crosslink density was measured at eight pressures and the average value was reported.

The crosslink density of membranes synthesized by Fleming and Koros,⁵ Merkel et al.,⁶ and Raharjo et al.⁸ were reported to be 1.24×10^{-4} , 7.8×10^{-5} , and $3.15 \pm 0.03 \times 10^{-4} \text{ mol/cm}^3$, respectively. Crosslink density and type of crosslinker are important parameters in determining mechanical and thermal properties of rubber products and consequently their life span.²⁰ As a general rule, the higher the crosslink density of a polymer network, the lower swelling capacity of the polymer.²¹ However, as mentioned later in this study, it does not mean that membranes with higher crosslink density have poor gas permeation properties. Crosslinking of the polymer matrix reduces swelling or diminishes plasticization effect (which decreases gas permeation) in one hand, but increases the membrane resistance to hydrostatic compression (which increases gas permeation) on the other hand. Meanwhile, gas permeation through a synthesized membrane is dependent on other synthesis parameters such as solvent and catalyst concentrations in the casting solution, type of solvent (or boiling point of solvent), and synthesis time (stirring time and curing time). It means that comparing gas permeation through different mem-

branes, which is only based on their crosslink density, is almost impossible.

Permeability measurement

A plate and frame module made from stainless steel (grade 316) was used to conduct the experiments (Fig. 1). The membrane was housed in the module that consisted of two detachable parts. The membrane had an effective area of $\sim 0.0024 \text{ m}^2$. Rubber O-rings were used to provide a pressure-tight seal between the membrane and the module. The physical dimensions of length, height, and width of the cell were 0.13, 0.06, and 0.09 m, respectively.

H_2 , N_2 , O_2 , CO_2 , and CH_4 gases with purity of 99.5% supplied by Technical Gas Services and C_3H_8 gas with purity of 99.9% supplied by Air Products and Chemicals were used as feed gases. The feed flow rate was controlled by Dwyer mass flow controllers, model GFC 2111 (0–15000 normal mL/min range). Gas temperature was set at 35°C using a P&ID temperature control system (TCS) model. Constant transmembrane pressure was controlled by a back pressure regulator, model 26.60 SCFBXE262C086. Permeate flow rates were measured using a bubble flow meter (BFM). In most of the experiments, a digital mass flow meter (MFM) was used instead of the BFM for convenience. The MFM was formerly calibrated by the BFM.

At steady state condition, gas permeability was calculated using the following equation:

$$P = \frac{22414}{A} \frac{l}{p_2 - p_1} \frac{p_1}{RT} \frac{dV}{dt} \quad (13)$$

where A is the membrane area (cm^2), R is the universal gas constant [$6236.56 \text{ cm}^3 \text{ cmHg}/(\text{mol K})$], T is the absolute temperature (K) and dV/dt is the volumetric displacement rate of the soap film in the BFM (cm^3/s).

Sorption measurement

Pure gas sorption measurements were carried out using a pressure decay module as shown in Figure 2. Gas sorption apparatus consisted of a stainless

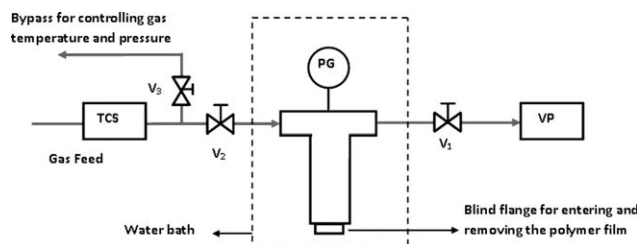


Figure 2 Schematic view of the gas sorption module.

module of known volume. The module was connected to vacuum pump and TCS by stainless steel valves. The gas pressure in this module was monitored using sensitive pressure transducers and recorded automatically by a data acquisition system employing LabTech software. TCS was employed to set the gas temperature at 35°C and a water bath was used to maintain the module at this temperature during the sorption process. The vacuum pump was connected to this apparatus to degas the module, whenever required.

Initially, a polymer film was placed in the sample cell and exposed to vacuum to remove sorbed gases from the polymer. Simultaneously, temperature set-point of TCS and water bath was scheduled at 35°C. When gas temperature and pressure were reached to target values, V_1 and V_3 were closed and the gas was introduced into the module by opening then closing V_2 , impulsively.

The number of moles of the gas introduced into the module could be calculated from the chamber pressure (initial pressure of the module), water bath temperature (35°C), and known chamber volume (290 cm³). Gas sorption into the polymer started exactly after opening V_2 and the pressure in the module decreased. When the system reached to equilibrium (sorption and desorption of gas molecules became equal), pressure reduction stopped. The difference between initial and final moles of gas in the module was the moles of gas sorbed into the polymer at the initial pressure in the module.

Concentration of the penetrant gas in the polymer at a given temperature and pressure was calculated from the following relation⁴:

$$C = \frac{22414}{RT} (p_i - p_f) \frac{V_m}{V_p} \quad (14)$$

where C is the uniform concentration of the dissolved penetrant at equilibrium state [cm³(STP)/cm³ polymer]; p_i and p_f designate, respectively, the initial and the final pressure in the module; V_m and V_p are the volumes of the module and the polymer sample (cm³), respectively and 22,414 is the number of cm³ (STP) of penetrant per mole.

Additional penetrant was then introduced into the module and the procedure was repeated. In this incremental manner, the penetrant uptake could be determined as a function of pressure.

RESULTS AND DISCUSSION

Solubility

Sorption isotherms for H₂, O₂, N₂, CH₄, CO₂, and C₃H₈ in the synthesized PDMS membrane at 35°C are presented in Figure 3. The isotherms for all pen-

etrants are linear (H₂, O₂, N₂, and CH₄) or nearly linear (CO₂ and C₃H₈), which is consistent with previously reported gas and vapor sorption isotherms in PDMS⁴⁻⁹ and in rubbery polymers in general.^{17,22}

As observed in Figure 3(a-d), the isotherms for the diatomic gases (H₂, O₂, and N₂) and CH₄ are linear and obey Henry's law [eq. (9)]. As the sorption ratio of gases is expected to be comparable among rubbery polymers and gases, one simple method for ensuring that the data obtained in this study are reasonable is to compare sorption ratio of the gases in the PDMS and some liquids. From Figure 3(a,b), the ratio of N₂ to H₂ sorption is approximately 1.37. The average values of this ratio in a specific pressure range were calculated to be 1.84 and 1.21, based on Merkel et al. and Prabhakar et al. studies, respectively.

PDMS is a rubbery polymer (its glass transition temperature, T_g , is -123°C), which offers a mobile, liquid-like environment to penetrant molecules. Hence, N₂/H₂ ratio is expected to be comparable among PDMS membrane and liquids.⁹ The value of this ratio in a wide variety of liquids lies between 1.2 and 2.2.⁹ For example, the N₂/H₂ sorption ratio is 1.4 in CS₂, around 1.7 in alcohols, and in the range of 1.9-2.2 in hydrocarbon liquids at 25°C and 1 atm.⁹ Thus, the N₂/H₂ solubility ratio lies in the same range as that in the literature.

CO₂ sorption isotherms in PDMS at 35°C [Fig. 3(e)], seems to be almost linear like the permanent gases. This result is in accordance with what Fleming and Koros observed at pressures lower than 300 psia (20.4 atm).⁵ They found out that, for pressures up to 300 psia, a Henry's law prediction appears to work quite well in describing the sorption data. Fleming and Koros reported Henry's law constant of 1.385 [cm³ (STP)/cm³ polymer atm] for CO₂ below 300 psia, which is in good agreement with that obtained in our experiments (1.795 below 22 atm).⁵

C₃H₈ sorption isotherm [Fig. 3(f)] is convex to the pressure axis, which is consistent with the behavior of highly sorbing penetrants in rubbery polymers.⁴⁻⁹ The concentration of C₃H₈ in the PDMS is 113.7, 93.3, 48.5, 20.8, and 5.7 times higher than that of H₂, N₂, O₂, CH₄, and CO₂ at 4 atm. The convex curvature of C₃H₈ sorption isotherms is due to the high levels of sorbed penetrants at high pressures and is similar to that reported for vapor/polymer systems.²²⁻²⁸

Such vapor/polymer systems are typically described by FH treatment [eq. (10)] for uncrosslinked polymers and FR treatment [eq. (11)] for crosslinked polymers. In a crosslinked polymer, as in this study, FR equation may be rearranged to solve for the χ parameter explicitly for a given sorption value. Since crosslink density is very low, the third term in the right hand side of FR equation

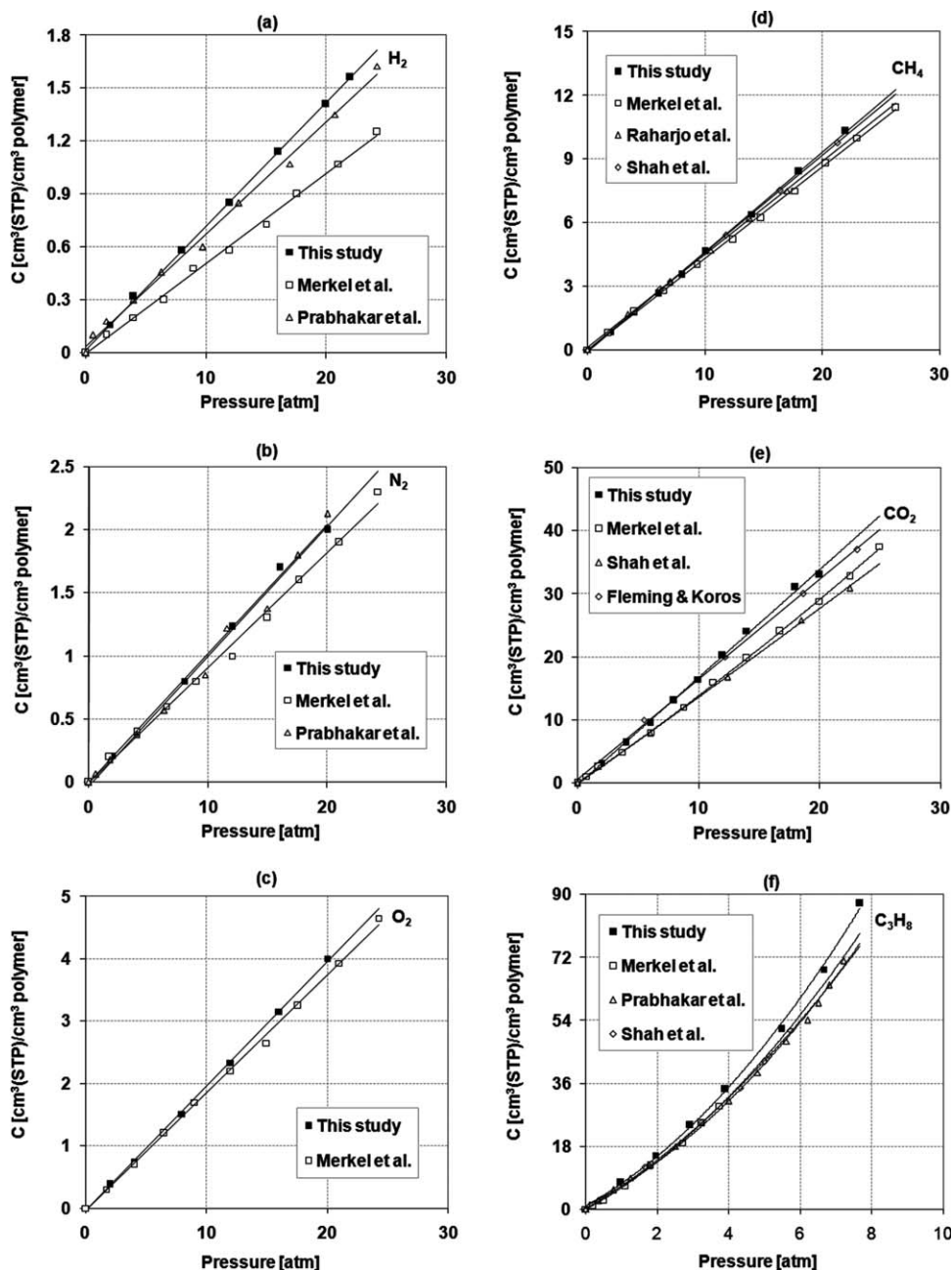


Figure 3 Sorption isotherms for gases in the synthesized PDMS membrane at 35°C, data obtained in this study are compared with Merkel et al.,⁶ Prabhakar et al.,⁹ Shah et al.,⁴ Raharjo et al.,⁸ and Fleming and Koros⁵ results.

becomes almost zero. In this case, similar χ values are evaluated using FH and FR equations.

To use these equations, penetrants critical properties, saturation vapor pressure at 35°C, partial molar volume, and molar volume should be determined (Table I). The critical temperature of all gases, except for C_3H_8 , is lower than the experimental temperature (35°C), so the values of saturation vapor pressure, p_{sat} are undefined at 35°C. Hypothetical values of p_{sat} can be estimated by a log-linear extrapolation of the vapor pressure curve to 35°C. In the case of CO_2 , since the critical temperature (31.2°C) is

slightly lower than the experimental temperature, this extrapolation provides a reasonable estimate of p_{sat} used in eqs. (10) and (11). The extrapolated value of CO_2 vapor pressure at 35°C is determined to be 80.6 atm, which is in good agreement with the corresponding values reported by Shah et al. (78 atm) and Merkel et al. (81.9 atm).^{5,6}

Among different methods for estimating and correlating the p_{sat} of pure species such as Antoine, Clausius–Clapeyron, Gomez and Thodos, Wagner and Lee–Kesler, Wagner method was recommended as the best method for extrapolating.²⁹

TABLE I
Penetrants Critical Properties, Saturation Vapor Pressure at 35°C, Partial Molar Volume, and Molar Volume at the Normal Boiling Point^{29,30}

Penetrant	T_c (K)	p_c (atm)	V_c (cm ³ /mol)	p_{sat} (atm)	\bar{V}_2 (cm ³ /mol)	V_2 (cm ³ /mol)
H ₂	33.2	12.9	64.3	314.8	40	28
O ₂	154.6	50.4	73.4	784.4	47	28
N ₂	126.2	33.9	89.8	865.3	48	35
CO ₂	304.1	73.8	93.9	80.58	45	46
CH ₄	190.5	46.0	99.2	354.0	46	38
C ₃ H ₈	369.8	42.5	203.0	12.3	80	76

It is also worthy to say that, at pressures lower than 25 atm, nonideal behavior of gases can be neglected and the expression for the activity, $a = f/f_{\text{sat}}$, is expressed as $a = p/p_{\text{sat}}$.⁵

Partial molar volumes were obtained based on Kamiya et al. studies.³⁰ They observed that the relationship between the partial molar volumes of C₁ to C₅ hydrocarbon gases dissolved in rubbery polymers and their van der Waals volumes is approximately the same as the relation between the partial molar and van der Waals volumes of liquid *n*-alkanes (C₅–C₂₄).

Values for the FH interaction parameter, χ , were determined for each sorption value of the gases. Figure 4 shows χ values of gases in the synthesized PDMS membrane as a function of upstream pressure. As can be seen, χ does not vary noticeably with pressure for all gases except for C₃H₈. Hence, it is logical to use an average value of χ for these gases at constant temperature and various pressures. For C₃H₈ a linear function of χ with pressure was used in FH equation.

Higher values of χ parameter exhibits less favorable interaction between gas and membrane. Typically, if the polymer matrix and the penetrant mole-

cules are chemically dissimilar, they do not have specific interaction with each other. In this case, interactions among the penetrant molecules are more favorable than those between the penetrant molecules and the polymer chains. Thus, according to Figure 4, it can be predicted that CH₄, O₂, and C₃H₈ are chemically more similar to PDMS than other gases.

FH interaction parameters of all gases with PDMS membrane were also determined using sorption data of other researchers' studies. Their concentration-averaged values are reported in Table II. Concentration-averaged interaction parameters, $\bar{\chi}$, were calculated as follows⁶:

$$\bar{\chi} = \frac{1}{\phi_{2,\text{max}}} \int_0^{\phi_{2,\text{max}}} \chi(\phi_2) d\phi_2 \quad (15)$$

where $\phi_{2,\text{max}}$ is the maximum penetrant volume fraction considered in this study. According to this table and Figure 4, it is realized that χ values of larger, more condensable gases are not always lower than those of smaller, permanent gases. As mentioned earlier, FH interaction parameter is largely affected by the similarity or dissimilarity of the penetrants with the polymer matrix. PDMS is a hydrocarbon-based polymer with a backbone structure of [SiO(CH₃)₂]_{*n*}. Obviously, oxygen, methyl groups, and Si are the building blocks of these types of polymers. Hence, low χ values of O₂ and CH₄ are rationalized.

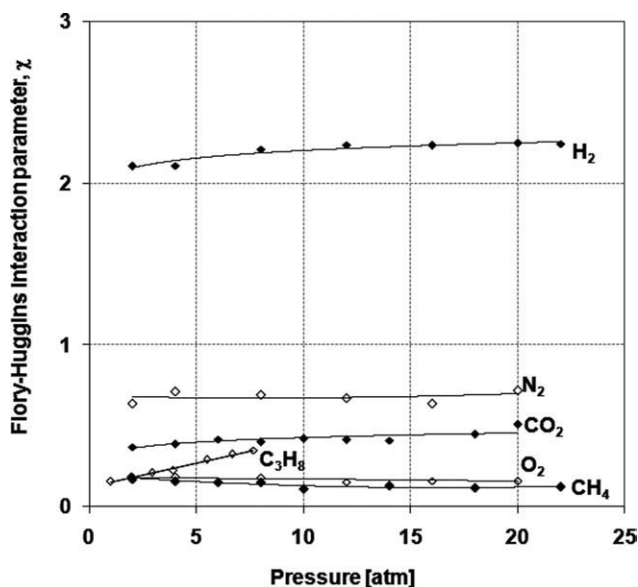


Figure 4 χ values of gases as a function of pressure.

TABLE II
Concentration-Averaged Interaction Parameters, $\bar{\chi}$, Calculated Using Sorption Data of This Study and Other Researchers' Works

Penetrant	This study	Merkel and coworkers ⁶	Shah et al. ⁴	Prabhakar et al. ⁹	Fleming and Koros ⁵
H ₂	2.196	2.563	–	2.139	–
O ₂	0.165	0.169	–	–	–
N ₂	0.678	0.743	–	0.684	–
CO ₂	0.418	0.585	0.643	–	0.450
CH ₄	0.139	0.196	0.138	0.132	–
C ₃ H ₈	0.247	0.386	0.275	0.239	–

It should be noted that penetrant solubility in a polymer is determined by both penetrant condensability (as characterized by saturation vapor pressure, critical temperature, normal boiling point, etc.) and by polymer-penetrant interaction (as characterized by χ values).⁶ The interplay between these two factors determines the overall solubility of a penetrant in a polymer. For example, as shown in Figure 3, C_3H_8 sorption in the PDMS membrane is higher than CH_4 and O_2 sorption more than 20 times, even though both CH_4 and O_2 have lower χ values than C_3H_8 (Fig. 4 and Table II). Solubility of C_3H_8 is higher than those of CH_4 and O_2 due to the much more condensable nature of C_3H_8 as indicated by its higher critical temperature and lower saturation vapor pressure (Table I).

Sorption is typically viewed as a two-step process involving penetrant condensation from a gas-like density to a liquid-like density (condensability as mentioned earlier) followed by mixing condensed penetrant molecules with polymer segments (related to interaction parameter). The enthalpy of sorption can be viewed as a sum of the enthalpy changes for these two steps^{9,31}:

$$\Delta H_s = \Delta H_{\text{cond}} + \Delta H_{\text{mix}} \quad (16)$$

where ΔH_{cond} and ΔH_{mix} are the enthalpy changes associated with penetrant condensation and mixing, respectively. ΔH_{cond} is only related to the physical properties of penetrants and can be extracted at each temperature from the literature.^{29,31} ΔH_{mix} is a function of FH interaction parameter, penetrant concentration in the polymer, and partial molar volume of penetrant as follows:

$$\Delta H_{\text{mix}} = RT\chi(1 - \phi_2) \quad (17)$$

Equations 15 and 16 confirm that gas solubility in the polymer is affected by its condensability as well as its interaction with the polymer chains, χ .

Figure 5 demonstrates the effect of penetrant concentration on the interaction parameter for C_3H_8 . For the permanent gases and CH_4 as a low solubility hydrocarbon, it was observed that χ is essentially independent of pressure and subsequently independent of concentration. For the more condensable gas, C_3H_8 , χ was found as a function of penetrant concentration. Only χ values calculated using sorption data of Merkel et al. decreases as penetrant concentration increases. Merkel et al. claimed that as C_3H_8 concentration in the polymer increases, the environment into which C_3H_8 is dissolving is becoming more like that of pure condensed penetrant, and hence, more compatible with C_3H_8 than the polymer alone. However, it should be noted that when the environment into which the penetrant is sorbing

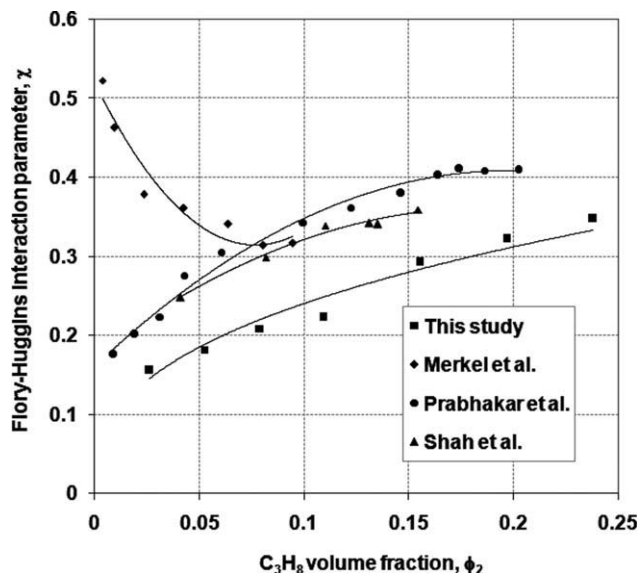


Figure 5 χ values of C_3H_8 in the synthesized PDMS membrane as a function of gas volume fraction, χ values are calculated based on sorption data of this study, Merkel et al.,⁶ Prabhakar et al.,⁹ and Shah et al.³ works.

becomes more like that of the penetrant, mixing process becomes more favorable or enthalpy of mixing, ΔH_{mix} , decreases. One cannot conclude that since ΔH_{mix} decreases FH interaction parameter decreases based on eq. (16). Rearranging eq. (17) to solve χ , it is observed that χ is also proportional to the gas concentration in the polymer. When the rate of $(1 - \phi_2)$ reduction in the denominator is greater than that of ΔH_{mix} in the nominator, χ increases.

In the present work, like Shah et al. and Prabhakar et al. studies, it was indicated that increasing concentration increases χ values. This is due to this fact that increasing C_3H_8 concentration causes interactions among penetrant molecules become more favorable than those between penetrant molecules and polymer chains. As a rule, the higher interaction parameter, the less positive interaction between penetrant and polymer.

The concentration dependence of the interaction parameter for C_3H_8 was modeled using the following empirical linear expression:

$$\chi = \chi_0 + \chi_1(1 - \phi_2) \quad (18)$$

where χ_0 and χ_1 are defined to be 1.072 and -0.940 , respectively, by plotting χ vs. $(1 - \phi_2)$. C_3H_8 χ values were also predictable excellently by an empirical equation proposed by Prabhakar et al.¹⁸:

$$\chi = \chi_a + \frac{\chi_b}{T} + \chi_c(1 - \phi_2) \quad (19)$$

where χ_a , χ_b and χ_c are -0.64 , 518 , and -0.97 , respectively.

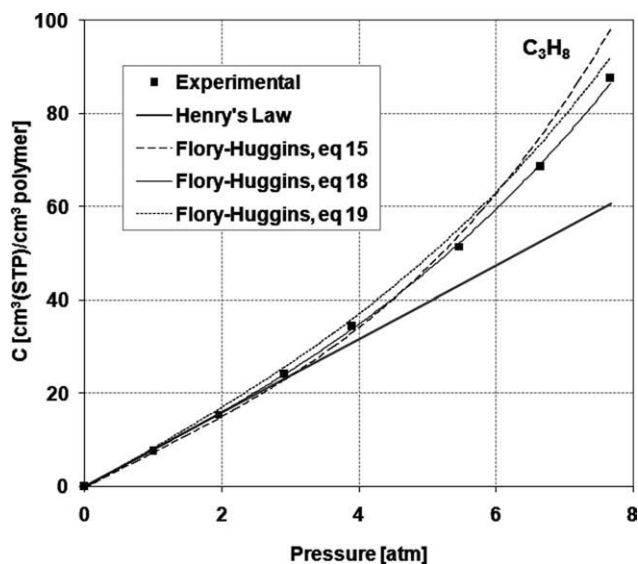


Figure 6 C_3H_8 sorption prediction using Henry's law and Flory-Huggins theory, χ values were calculated using eq. (15) (concentration-averaged χ parameter, $\bar{\chi}$) and eqs. (18) and (19) (linear expressions proposed by us and Prabhakar et al.,⁹ respectively).

Figure 6 shows the resulting sorption isotherms predicted for C_3H_8 based on Henry's law and FH theory using concentration-averaged χ parameter (0.247) and χ values estimated by eqs. (18) and (19). As observed, Henry's law cannot predict C_3H_8 sorption at higher pressures. Applying concentration-averaged χ parameter [eq. (15)] in the FH equation results in better responses especially at pressures lower than 5 atm. As expected, sorption results obtained using empirical expressions proposed by us and Prabhakar et al. (eqs. (18) and (19), respectively) are in excellent agreement with the experimental data.

The penetrant/polymer interaction parameter may be expressed in terms of solubility parameters applying regular solution theory^{6,32}:

$$\bar{\chi} = \frac{V_2}{RT} (\delta_2 - \delta_1)^2 \quad (20)$$

where δ_2 and δ_1 are the solubility parameters of penetrant and polymer, respectively. Utilizing this equation and concentration-averaged χ values measured by the sorption data of this study and other researchers' works (Table II), the quantity of $(\delta_2 - \delta_1)^2$, which is a measure of the mismatch in cohesive energy density between the penetrant and the polymer,⁶ was calculated for C_3H_8 in PDMS. $(\delta_2 - \delta_1)^2$ was also calculated using the literature values of penetrant and PDMS solubility parameters [$\delta_2 = 6.40$ ³³ and $\delta_1 = 7.30-7.58$ (cal/cm³)^{1/2}].^{4,33} These results are presented in Table III. As can be seen, calculated $(\delta_2 - \delta_1)^2$ values using $\bar{\chi}$ of this study and

TABLE III
Squares of the Solubility Parameters Difference for C_3H_8 in the Synthesized PDMS Membrane at 35°C (Kamiya et al. Worked at 25°C)

Reference	$\bar{\chi}$	Measured $(\delta_2 - \delta_1)^2$	Error $(\delta_2 = 7.58,^{33})$ Measured - predicted / Measured
This study	0.247	1.987	0.300
Merkel and coworkers ⁶	0.386	3.106	0.552
Shah et al. ⁴	0.275	2.213	0.371
Prabhakar et al. ⁹	0.239	1.932	0.276
Kamiya et al. ¹⁰	0.330	2.573	0.459

Measured values are compared with evaluated ones using literature values of polymer and C_3H_8 solubility parameters, $(\delta_2 - \delta_1)^2 = 1.39$ (cal/cm³)^{1/2,33}, $(\delta_2 - \delta_1)^2 = 0.81$ (cal/cm³)^{1/2,4}.

Prabhakar et al. work are much closer to the evaluated one. Hence, correctness of the sorption data obtained in the present work is verified.

From the sorption isotherms, the solubility of each penetrant was calculated using eq. (6). The values are presented as a function of pressure in Figure 7. As shown, in contrast to C_3H_8 that its solubility in PDMS increases largely with pressure, the solubility coefficients of other light gases are almost constant. However, solubility coefficient of all gases can be well represented by the following linear equation:

$$S = S^\infty + np \quad (21)$$

where S^∞ is the infinite dilution solubility which is defined as follows:

$$S^\infty = \lim_{p \rightarrow 0} (C/p) \quad (22)$$

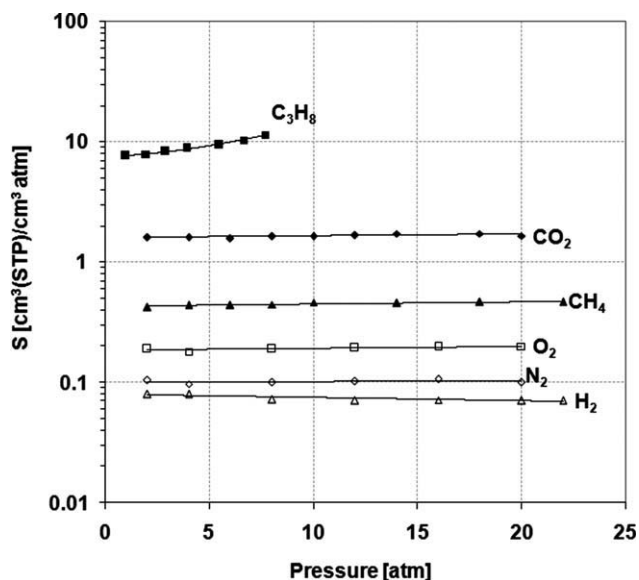


Figure 7 Penetrant solubility in the synthesized PDMS membrane as a function of pressure at 35°C.

TABLE IV
Experimental and Calculated (FH) Values of S^∞ [cm^3 (STP)/ cm^3 atm], n [cm^3 (STP)/ cm^3 atm²] and Infinite Solubility Selectivity of C_3H_8 to Other Gases at 35°C

Penetrant	S^∞ Experimental	S^∞ FH	$n \times 10^3$	Solubility selectivity ($S_{\text{C}_3\text{H}_8}/S_{\text{gas}}$)
H_2	0.0794 ± 0.002	0.0733	-0.50 ± 0.02	85.75 ± 7.2
O_2	0.1828 ± 0.01	0.1896	0.90 ± 0.03	37.25 ± 4.4
N_2	0.1013 ± 0.005	0.1007	0.06 ± 0.001	67.21 ± 7.5
CO_2	1.5821 ± 0.15	1.4970	6.40 ± 0.35	4.30 ± 0.7
CH_4	0.4288 ± 0.02	0.4402	2.10 ± 0.22	15.87 ± 1.74
C_3H_8	6.8093 ± 0.4	6.5457	542.51 ± 50	1.00 ± 0.0

S^∞ can be calculated theoretically using FH equation. In the limit of infinite dilution, this equation is reformulated as follows:

$$S^\infty p_{\text{sat}} = \frac{22414}{\bar{V}_2 \exp(1 + \chi)} \quad (23)$$

In eq. (21), n characterizes the pressure dependence of solubility. S^∞ (experimental results and values estimated by FH equation), n and solubility selectivity of C_3H_8 to other gases are presented in Table IV.

For the relatively low-sorbing penetrants such as H_2 , O_2 , N_2 , and CH_4 , the pressure dependence of solubility, n , is almost zero. Hence, as occurred before, the solubility of these penetrants in PDMS is essentially independent of penetrant pressure and is well-described by Henry's law, which is typical for the sorption of light gases in many polymers.^{3,6}

The more strongly sorbing penetrants, C_3H_8 and CO_2 , exhibit larger values of n , which confirms strong solubility dependence of these penetrants with pressure. This is also a typical behavior for many organic vapors in rubbery polymers.^{6,19}

In the absence of specific interactions between the penetrant molecules and the polymer matrix, gas solubility coefficients are usually scaled with measures of penetrant condensability such as critical temperature, T_c .^{6,9,19} To compare solubilities of penetrants on a consistent basis, solubility coefficient in the limit of zero pressure, S^∞ , is utilized. Figure 8 presents S^∞ , as a function of the penetrants critical temperature. Previous results indicate that the logarithm of gas solubility in polymers often increases linearly with penetrants' critical temperature. This trend is confirmed in Figure 8. Slope of the best-fit line in this figure is 0.013 compared with 0.017, 0.016, and 0.014 obtained by Van Amerongen, Michaels and Bixler, and Merkel et al., respectively.⁶

Permeability

The permeability of H_2 , O_2 , N_2 , CH_4 , CO_2 , and C_3H_8 at 35°C as a function of the pressure difference

across the PDMS membrane is presented in Figure 9. Figure 10 indicates that, the permanent gas and hydrocarbon permeability values are in good agreement with previously reported values.^{3,4,6,8,9} All researchers have found out that N_2 , O_2 , H_2 , and CH_4 exhibit constant or decreasing permeabilities at all upstream pressures tested [Fig. 10(a-d)], whereas permeabilities of CO_2 and C_3H_8 increase with increasing upstream pressure [Fig. 10(e,f)]. As shown in Figure 10(e), like other large gas molecules such as C_3H_8 , CO_2 permeability increases with increasing upstream pressure which is in concordance with what its critical temperature suggests (Table I). Merkel et al.⁶, Prabhakar et al.⁹ and Stern et al.³ reported infinite dilution C_3H_8 permeability ($P_0 = P_{\text{at}\Delta p=0}$) values of 3786, 5658, and 7547 Barrer, respectively at 35°C [Fig. 10(f)]. In the present work P_0 was evaluated to be 5546 Barrer.

As shown in Figures 9 and 10, permeability coefficients of the penetrants increase in the following order:

$$\text{N}_2 < \text{O}_2 < \text{H}_2 < \text{CH}_4 < \text{CO}_2 < \text{C}_3\text{H}_8$$

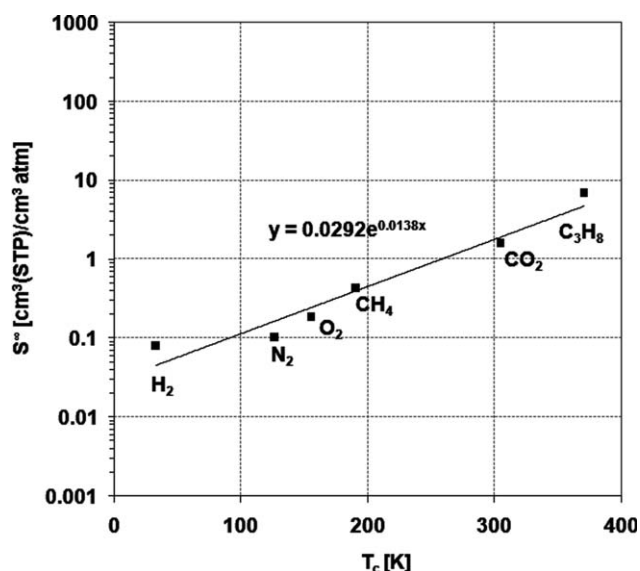


Figure 8 Infinite dilution solubility as a function of penetrants' critical temperature at 35°C.

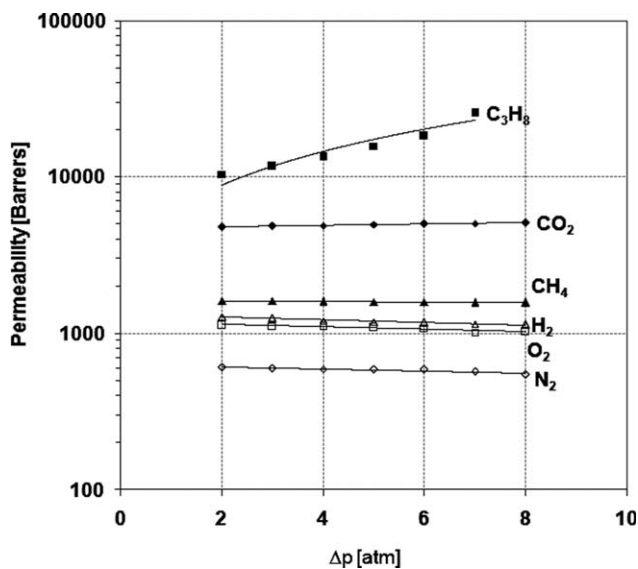


Figure 9 Penetrants permeability through the synthesized PDMS membranes as a function of transmembrane pressure difference at 35°C.

Solubility coefficients of these penetrants also increase as aforementioned with an exception of H₂, which is the smallest penetrant considered in this study. Based on solution-diffusion mechanism [eq. (5)], permeability is the product of diffusivity, D , and solubility, S , of the gas in the membrane material. Rubbery membranes have weak molecular sieve ability due to their weak intermolecular forces, resulting in broad distribution of intersegmental gap sizes responsible for gas diffusion. Diffusion coefficients of penetrants often change less than their solubility coefficients, so that more soluble penetrants are more permeable. Consequently, the relative permeability of penetrants through the PDMS membrane is mainly determined by their relative solubility.

Figure 11 presents the permeability coefficients of studied gases at 35°C and $\Delta p = 0$ in PDMS as a function of the gas critical temperature. Frequently, in a solubility selective polymer such as PDMS, there is a strong correlation between the logarithm of gas permeability and critical temperature.^{6,22}

Generally, as critical temperature increases, penetrant becomes more soluble in the polymer and therefore more permeable [eq. (5)]. The results in Figure 11 follow this trend with the exception of H₂, as noticed before. This is often the case, as the extremely small molecular size of hydrogen results in a very high diffusion coefficient, and consequently, a higher permeability coefficient than expected based on its critical temperature.

The ideal selectivity values, $\alpha_{A/B}$, of the PDMS membrane for C₃H₈ over CO₂, CH₄, H₂, O₂, and N₂ [calculated using eq. (7)] as a function of upstream pressure are presented in Figure 12. The increasing

rate of ideal selectivity with pressure is observed to be completely dependent on the difference between C₃H₈ and other gases condensabilities or critical volumes. At $\Delta p = 7$ atm, the synthesized PDMS membrane is approximately 4, 13, 18, 20, and 36 times more permeable to C₃H₈ than CO₂, CH₄, H₂, O₂, and N₂, respectively.

Based on eq. (8), the membrane selectivity depends on the relative diffusion coefficients (D_A , D_B) of the two gases (A and B) in the polymer and on the relative solubilities (S_A , S_B) of the gases in the polymer. In all polymer materials, the diffusion coefficient decreases with increasing molecular size because large molecules interact with more segments of the polymer chains than do small molecules, favoring the passage of smaller molecules such as H₂ over larger ones such as C₃H₈. However, the solubility increases with increasing condensability and therefore, increases with increasing molecular size (Solubility section). Thus, these polymers preferentially permeate the larger, more condensable gases, C₃H₈ and CO₂, over the smaller, less condensable gases, N₂, O₂, H₂, and CH₄.

For all penetrants, the permeability is a linear function of Δp and can be represented as follows:

$$P = P_0 + m\Delta p \quad (24)$$

where P_0 is the permeability coefficient at $\Delta p = 0$, the slope, m , characterizes the pressure dependence of permeability with Δp . P_0 and m values for six gases examined in this study as well as ideal selectivity of C₃H₈ over other gases ($P_{C_3H_8}/P_{gas}$) at $\Delta p = 0$ and $\Delta p = 7$ atm are recorded in Table V. The value of m is determined principally by the interplay between three factors: plasticization, hydrostatic pressure, and penetrant solubility. Plasticization refers to an increase in penetrant diffusivity resulting from increased polymer local segmental motion caused by the presence of penetrant molecules in the polymer matrix.^{6,8,34}

As upstream pressure, and therefore, penetrant concentration in a polymer increases, tendency to plasticize the polymer matrix increases, particularly for strongly sorbing penetrants. On the other hand, high upstream pressure acting on the polymer film can slightly compress the polymer matrix, thereby reducing the amount of free volume available for penetrant transport and reducing the penetrant diffusion coefficient. In addition to these dual effects, which affect the penetrant diffusion coefficient, the penetrant solubility in rubbery polymers frequently increases with pressure, especially for organic vapor penetrants, leading to a corresponding increase in permeability.^{6,26}

Hence, the permeability coefficients of low-sorbing penetrants, such as H₂, which do not plasticize the

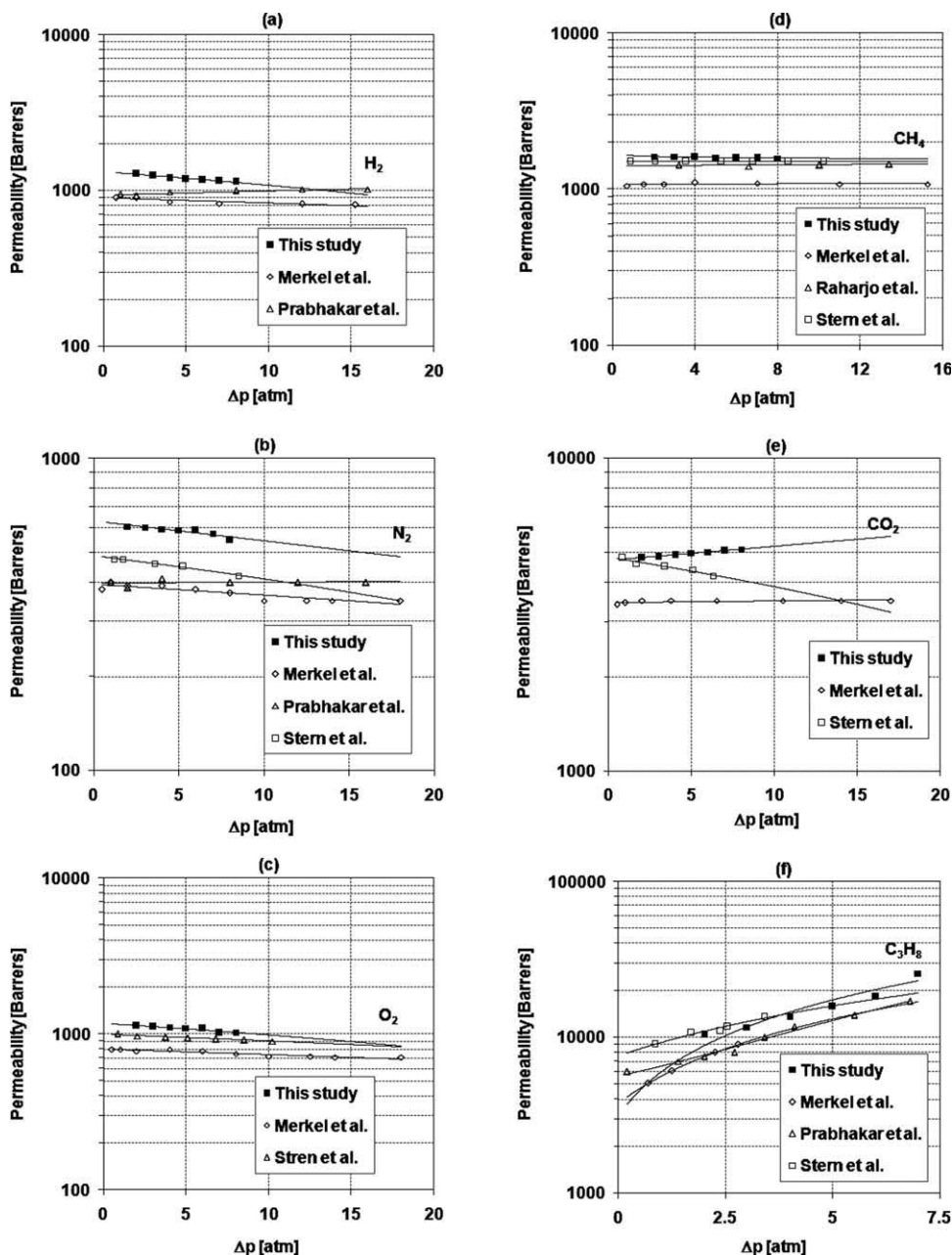


Figure 10 Penetrants permeability through the synthesized PDMS membrane at 35°C, data obtained in this study are compared with Merkel et al.,⁶ Prabhakar et al.,⁹ Shah et al.,⁴ Raharjo et al.,⁸ and Stern et al.³ results.

PDMS membrane, and as indicated before, have essentially pressure independent solubility coefficients, decrease very slightly with increasing pressure. This was confirmed by negative values of m in Table V. In contrast, the permeability coefficients of more soluble penetrants, such as C_3H_8 , which induce significant plasticization and have solubility coefficients that also increase significantly with pressure, increase with increasing pressure. For these penetrants m is positive.

According to the data presented in Table V, C_3H_8 /gas ideal selectivities at $\Delta p = 7$ atm are almost four times greater than that at $\Delta p = 0$. As mentioned

before, permeability of more soluble penetrants increases with the pressure whereas that of less soluble penetrants stays constant or even decreases with pressure, which results in higher selectivities at higher pressures. Thus, higher feed pressures are recommended to achieve better gas separation performance.

Diffusivity

Concentration-averaged diffusion coefficient, \bar{D} , was estimated from the permeability and sorption data using the rearranged form of eq. (4). The results are

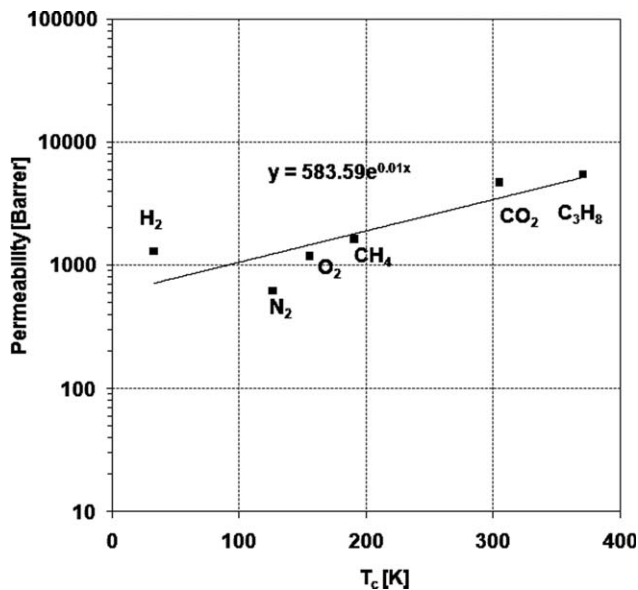


Figure 11 Penetrants permeability through the synthesized PDMS membrane as a function of gas critical temperature. Experimental conditions: Upstream pressure = 1 atm ($\Delta p = 0$), Temperature = 35°C.

reported as a function of pressure difference across the PDMS membrane at 35°C in Figure 13. For all penetrants, the pressure dependence of diffusion coefficient can be well described by the following linear equation:

$$\bar{D} = \bar{D}_0 + q\Delta p \quad (25)$$

where \bar{D}_0 is the diffusion coefficient at $\Delta p = 0$ and q is a parameter that characterizes the pressure dependence of diffusion coefficient. Values of \bar{D}_0 , q , and diffusivity selectivity at $\Delta p = 0$ and $\Delta p = 7$ atm for all penetrants are reported in Table VI. For the least soluble penetrants (H_2 , O_2 , N_2 , and CH_4), diffusivity decreases slightly with increasing pressure due to hydrostatic compression effects and q is consequently negative. As discussed earlier, solubility of these gases is independent of upstream pressure. Hence, permeability coefficient of light gases decreases slightly as pressure increases. In contrast, more soluble penetrants (CO_2 and C_3H_8) exhibit an

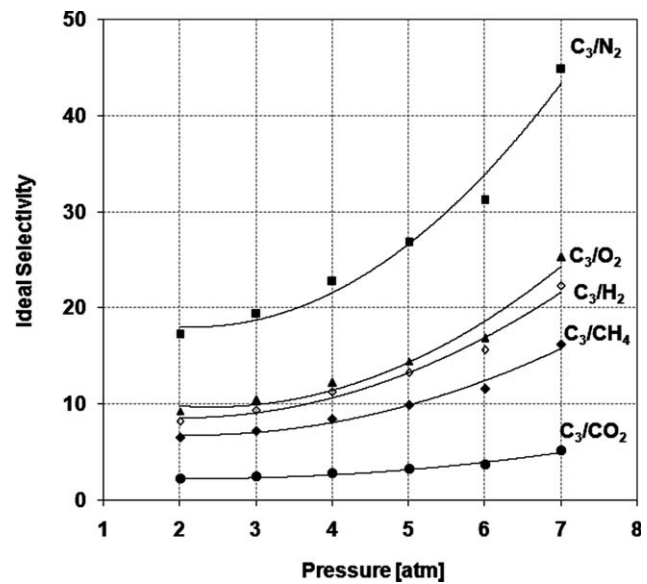


Figure 12 C_3H_8 /gas ideal selectivity in the synthesized PDMS membrane as a function of upstream pressure at 35°C.

increase in both solubility and diffusivity coefficients with increasing penetrant pressure. Based on the data presented in Tables IV and VI, n and q are positive for these gases. Therefore, permeability of heavy gases in PDMS increases with pressure.

C_3H_8 /gas diffusivity selectivity values are smaller than 1 and increase as penetrant pressure increases. It means that, diffusion coefficient of C_3H_8 is lower than those of other lighter gases. However, increasing rate of C_3H_8 diffusivity is greater than that of H_2 , N_2 , O_2 , CO_2 , and CH_4 . At low penetrant pressure, the diffusion coefficient increases in the following order:



This is almost the order of decreasing penetrants size and is typical behavior for both rubbery and glassy polymers.^{4-9,35-41} Figure 14 compares \bar{D}_0 values of gases in the synthesized rubbery PDMS membrane, polyisoprene (PIP)⁴², and poly(tetrafluoroethylene-*co*-perfluoromethyl vinyl ether) or TFE/PMVE

TABLE V
Infinite Dilution Gas Permeability (P_0), m (Barrer/atm) and Ideal Selectivity of C_3H_8 to Other Gases at $\Delta p = 0$ and $\Delta p = 7$ atm, at 35°C

Penetrant	P_0 (Barrer)	m (Barrer/atm)	Ideal selectivity ($P_{C_3H_8}/P_{gas}$)	
			$\Delta p = 0$ atm	$\Delta p = 7$ atm
H_2	1313 ± 35	-23.15 ± 4.4	4.22 ± 0.28	17.94 ± 0.9
O_2	1173 ± 20	-18.70 ± 2.5	4.72 ± 0.26	20.38 ± 1.2
N_2	626.7 ± 10	-8.408 ± 1.2	8.84 ± 0.47	36.06 ± 1.9
CO_2	4691 ± 200	51.96 ± 5.0	1.18 ± 0.1	4.09 ± 0.3
CH_4	1629 ± 40	-6.831 ± 1.0	3.40 ± 0.21	13.05 ± 0.8
C_3H_8	5546 ± 200	2108 ± 20	1.00 ± 0.0	1.00 ± 0.0

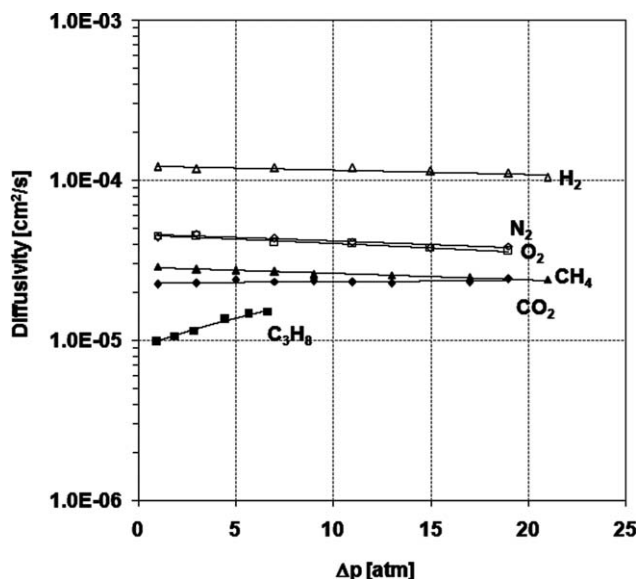


Figure 13 Concentration-averaged diffusion coefficients of gases, \bar{D} , in the synthesized PDMS membrane as a function of transmembrane pressure difference at 35°C.

^{49,43} with those in glassy polyvinyl chloride (PVC),⁹ polysulfone (PS)⁴⁴, and poly(2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole-*co*-tetrafluoroethylene) commercially known Hyflon AD 80⁴⁴ as a function of gases critical volume. As can be seen, diffusion coefficients in PDMS and PIP, like other rubbery polymers, are relatively weak function of penetrant size. For the entire range of penetrant sizes considered, the diffusion coefficients varied by less than two orders of magnitude. Diffusion coefficients in PDMS are larger than those in amorphous rubber, PIP, and amorphous random copolymer rubber TFE/PMVE 49. In fact, PDMS has the lowest diffusivity selectivity compared with any other rubbery polymers. It has a very flexible polymer backbone as indicated by its extremely low glass transition temperature ($T_g \approx -120^\circ\text{C}$). As a result, PDMS has a very weak ability to sieve penetrant molecules based on their sizes.

While for the strongly size-sieving glassy polymers, PVC and PS, diffusion coefficients varied by more than 8 and 6 orders of magnitude, respectively,

over a similar range of penetrant sizes (64–203 cm^3/mol).^{6,42–44} Size-sieving ability of Hyflon AD 80 seems to be much weaker than those of PVC and PS.

Therefore, to achieve high diffusivity selectivity, glassy polymers are clearly more useful than rubbery polymers. Hence, glassy polymeric membranes have been commercialized for the separation of gas pairs such as O_2/N_2 , H_2/CH_4 , and CO_2/CH_4 .

On the other hand, there are classes of separations for which strongly size-sieving polymers (i.e., those with very high diffusivity selectivity such as PVC and PS) are not appropriate. The separation of organic vapors and other condensable gases from supercritical gases,^{22,26,38,40,45–48} removal of volatile organic compounds (e.g., vinyl chloride monomer, propylene, ethylene, gasoline, and Freon) from mixtures with air or nitrogen,^{48–49} removal of higher hydrocarbons from refinery hydrogen purge streams or from methane in natural gas^{2,45} are applications of considerable industrial importance and can be performed economically using membranes. In these classes of separations, membranes with high organic vapor/supercritical gas selectivity and high organic vapor flux, i.e., rubbery polymers particularly PDMS, are required.

Variation of diffusion coefficient with critical volume (a measure of penetrant size) is usually described by the following equation:

$$D = \frac{\tau}{V_c^\eta} \quad (26)$$

where τ and η are adjustable parameters. η provides a measure of the reduction rate of diffusion coefficient with increasing penetrant size; the higher the value of η , the greater the diffusivity selectivity of the polymer. Polymers with larger values of η exhibit diffusion coefficients that depend more strongly on penetrant size compared with polymers with smaller values of η . Based on the data in Figure 14, the values of η are 10.5, 8.4, 5.7, 2.6, 2.4, and 2.0 for PVC, PS, Hyflon AD 80, TFE/PMVE 49, PIP and PDMS, respectively.^{6,42–44} For a variety of low

TABLE VI
Infinite Dilution Penetrants' Diffusion Coefficients (\bar{D}_0), q ($\text{cm}^2/\text{atm s}$) and Diffusivity Selectivity of C_3H_8 to Other Gases at $\Delta p = 0$ and $\Delta p = 7$ atm, at 35°C

Penetrant	$\bar{D}_0 \times 10^6$ (cm^2/s)	$q \times 10^6$ ($\text{cm}^2/\text{atm s}$)	Diffusivity selectivity ($\bar{D}_{\text{C}_3\text{H}_8}/\bar{D}_{\text{gas}}$)	
			$\Delta p = 0$ atm	$\Delta p = 7$ atm
H_2	100 ± 5	-0.70 ± 0.02	0.09 ± 0.008	0.12 ± 0.01
O_2	50 ± 3	-0.5 ± 0.01	0.18 ± 0.017	0.37 ± 0.03
N_2	50 ± 3	-0.40 ± 0.01	0.18 ± 0.017	0.34 ± 0.03
CO_2	20 ± 1	0.04 ± 0.001	0.45 ± 0.04	0.65 ± 0.06
CH_4	30 ± 1	-0.20 ± 0.008	0.30 ± 0.02	0.56 ± 0.04
C_3H_8	9.0 ± 0.4	1.00 ± 0.05	1.00 ± 0.0	1.00 ± 0.0

molar mass organic liquids, such as hexane and benzene, the value of η is equal to 0.45.⁶ This result demonstrates that the relative ability of PDMS to separate molecules based on their sizes is closer to that of organic liquids than that of glassy polymers such as PVC, PS, and Hyflon AD 80.

The local effective diffusion coefficient, D_{eff} , is a measure of the ability of penetrant to migrate through a polymer at a particular penetrant concentration.⁶ Taking the derivative of eq. (4) with respect to p_2 , holding p_1 constant, yields the following equation for D_{eff} :

$$D_{\text{eff}}(C_2) = \left[P + \Delta P \frac{dP}{d\Delta P} \right]_{p_2} \left(\frac{dp}{dC} \right)_{p_2} \quad (27)$$

The derivatives in this equation can be evaluated utilizing eqs. (21) and (24). This results in the following expression for the local effective diffusion coefficient:

$$D_{\text{eff}}(C_2) = \frac{P_0 + 2m(p_2 - p_1)}{S^\infty + 2np_2} \quad (28)$$

Figure 15 (a,b) presents D_{eff} as a function of penetrant concentration in the PDMS membrane. According to these figures, it was found out that C_3H_8 and

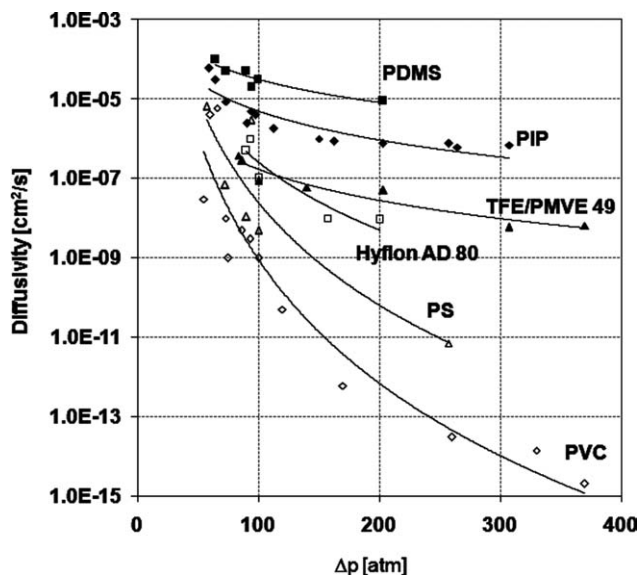


Figure 14 Comparison of the variation of infinite dilution diffusion coefficients with penetrant critical volume in the synthesized PDMS membrane with that in rubbery polymers PIP⁴² and TFE/PMVE 49⁴³ and glassy polymers PVC, PS⁴⁴, and Hyflon AD 80.⁴⁴ The trendlines in the figure satisfy the equation $D = \tau V_C^{-\eta}$ where η is a measure of the size sieving ability or the size selectivity of the polymer to penetrants. The best-fit values of η in the plot are as the following: PDMS, 2.0; PIP, 2.4; TFE/PMVE 49, 2.6; PVC, 10.5; PS, 8.4, and Hyflon AD 80, 5.7.

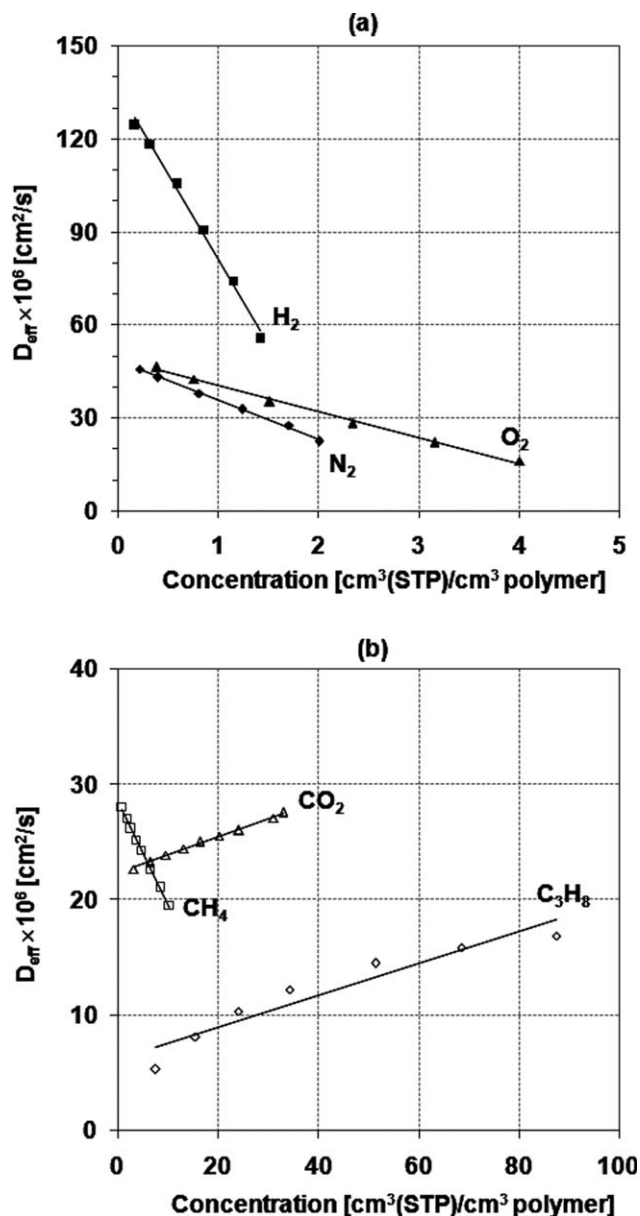


Figure 15 Local effective diffusion coefficients as a function of penetrants' concentration in the synthesized PDMS membrane at 35°C. (a) H_2 , O_2 , and N_2 ; (b) CH_4 , CO_2 , and C_3H_8 .

CO_2 cause plasticization of the membrane over the range of penetrant concentrations studied.

CONCLUSIONS

Solubility of H_2 and N_2 is lower than that of more condensable gases, C_3H_8 and CO_2 , due to less favorable polymer- H_2 and N_2 interactions (higher χ values) as well as less condensability of these gases. CH_4 and O_2 have lower χ values than C_3H_8 . However, more condensable nature of C_3H_8 than CH_4 and O_2 leads to higher solubility coefficients. FH theory was applied to describe C_3H_8 sorption in the

synthesized PDMS membrane. Comparing sorption isotherms obtained using two methods of correlating χ parameter, concentration-averaged χ parameter and Henry's law, it was realized that concentration dependent correlation of χ parameter derived in this study results in sorption isotherms, which are in excellent agreement with the experimental data. The pressure dependence of the permeability, solubility, and diffusivity coefficients was well described by empirical linear equations. Solubility and diffusivity of C_3H_8 increased with increasing upstream pressure. For other gases, these values were constant or decreased slightly with increasing pressure. Hence, both C_3H_8 /gas solubility and diffusivity selectivities increased as pressure increased. Plasticization effect of C_3H_8 and CO_2 was recognized by plotting local effective diffusion coefficient versus the range of penetrant concentrations studied. C_3H_8 ideal selectivities of 17.94, 20.38, and 36.06 over H_2 , O_2 , and N_2 , respectively, at $\Delta p = 7$ atm, confirmed acceptable performance of the synthesized PDMS membrane for separation of organic vapors from supercritical gases.

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