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Preparation and C_3H_8/Gas Separation Properties of a Synthesized Single Layer PDMS Membrane

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In this paper, a new polydimethylsiloxane (PDMS) membrane was synthesized and its ability for separation of heavier gases from lighter ones was examined. Sorption, diffusion, and permeation of H_2, N_2, O_2, CH_4, CO_2, and C_3H_8 in the synthesized membrane were investigated as a function of pressure at 35°C. PDMS was confirmed to be more permeable to more condensable gases such as C_3H_8. This result was attributed to very high solubility of larger gas molecules in hydrocarbon−based PDMS in spite of their low diffusion coefficients relative to small molecules. The synthesized membrane showed much better gas permeation performance than others reported in the literature. Increasing upstream pressure increased solubility, permeability and diffusion coefficients of C_3H_8, while these values decreased slightly or stayed constant for other gases. Local effective diffusion coefficient of C_3H_8 and CO_2 increased with increasing penetrant concentration which indicated plasticization effect of these gases over the range of penetrant concentration studied. C_3H_8/gas solubility, diffusivity and overall selectivities also increased with increasing feed pressure. Ideal selectivity values of 4, 13, 18, 20, and 36 for C_3H_8 over CO_2, CH_4, H_2, O_2 and N_2, respectively, at upstream pressure of 7 atm, confirmed the outstanding separation performance of the synthesized mebrane.

Keywords diffusivity; permeability; polydimethylsiloxane (PDMS); selectivity; solubility

INTRODUCTION

Polyvbmeric membranes are the most common membranes used in gas separation processes. Gas transport through a non-porous polymeric membrane is known to follow the solution-diffusion mechanism (1). According to this three-step mechanism, the gas first sorbs into the membrane on the high-pressure side, then diffuses across the membrane under a partial pressure driving force and finally desorbs from the low pressure side of the membrane. Therefore, gas permeability in the membrane is dependent both on the solubility of the gas in the polymer as well as its diffusion coefficient in the polymer. Gas solubility in polymers typically increases with an increase in gas condensability, in the absence of specific interactions between the gas molecules and the polymer chains (2). On the other hand, gas diffusion coefficients decrease with an increase in the penetrant size (2). This is due to the fact that larger molecules interact with more segments of the polymer chains and this favors the passage of smaller molecules such as H_2 over larger ones such as C_3H_8. Thus, differences in molecular size and/or gas condensability can result in different gas permeation rates through a polymer. Differential permeation rates result in an increase in concentration of the faster permeating species on downstream side of the membrane as compared with its concentration in the feed stream, thus performing an effective separation of the gases in the mixture. This phenomenon is the underlying principle of membrane-based gas separation.

In glassy, rigid polymers, such as polysulphone (PS), permeant diffusion coefficient is more important than its solubility coefficient. Therefore, these polymers preferentially permeate the smaller, less condensable gases, H_2 and CH_4 over the larger, more condensable gases, C_3H_8 and CO_2. On the other hand, in rubbery polymers such as PDMS, permeant solubility coefficients are the most important. Thus, these polymers preferentially permeate the larger, more condensable gases over the smaller, less condensable gases (3). PDMS is the most commonly used rubbery membrane material for separation of higher hydrocarbons from permanent gases (4). Many studies have been carried out on the transport properties of pure and mixed gas mixtures of O_2, N_2, H_2, CO, CO_2, CH_4, C_2-C_4 olefins and paraffins using PDMS membranes (5 – 19).

Most researchers studied pure and mixed gas permeation through PDMS membranes and did not consider interaction of gas molecules with the polymer matrix (5,13–19). Shah et al. (6) measured solubility of CH_4, C_3H_8 and CO_2 in five silicone polymers including PDMS at 10, 35 and 55°C. Fleming and Koros (7) investigated sorption and desorption of CO_2 in silicone rubber as a function of

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pressure (0 – 900 psia) at 35°C. Merkel et al. (8,9) and Prabhakar et al. (11) focused on hydrocarbon and perfluorocarbons sorption in PDMS membranes. They also reported sorption and permeation of permanent gases (H_2, O_2 and O_2) in PDMS membranes. Raharjo et al. (10) 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°C. Kamiya et al. (12) 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°C by measuring the sorption of the gases and the concomitant dilation of the polymers.

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 (5 – 12). The synthesized PDMS membrane indicated better performance than other compared membranes. The solubility, permeability, and diffusivity coefficients were correlated with pressure at constant temperature (35°C). A strong correlation of these coefficients with critical properties of gases was also identified. The 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 the separation of organic vapors from permanent gases. Unlike conventional glassy polymers used for the 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 the 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:

$$P = \frac{Nl}{p_2 - p_1} \tag{1}$$

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 diffusion (20):

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

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:

$$P = \frac{1}{p_2 - p_1}\int_{C_1}^{C_2} D_{eff}\, dC \tag{3}$$

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,

$$P = \frac{C_2 - C_1}{p_2 - p_1} D_{eff} \tag{4}$$

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

$$P = SD \tag{5}$$

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

$$S = \frac{C}{p} \tag{6}$$

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 permeabilities (2):

$$\alpha_{A/B} = \frac{P_A}{P_B} \tag{7}$$

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

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

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 (2). 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 the Lennard Jones force constant, increases (2). 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 the penetrant size increases and, therefore, diffusivity selectivity increases as the relative size difference between two penetrants increases, with the smaller penetrant having higher diffusivity (2). Thus, a tradeoff often exists between solubility selectivity and diffusivity selectivity, with the overall selectivity depending on the relative magnitudes of these two terms.

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) readable to ±1 μm and found to be approximately 100 μm. The synthesized membranes were housed in the gas permeation module. Sorption experiments were conducted with thicker films (about 300 μm) of PDMS to monitor gas solubility more precisely. Crosslinking was achieved employing the same components and conditions as those used above. The crosslink density of the PDMS films used in the sorption and gas permeation experiments was estimated to be 1.5×10^{-3} mol/cm^3.

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 approximately 0.0024 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 m, 0.06 m, and 0.09 m, respectively.

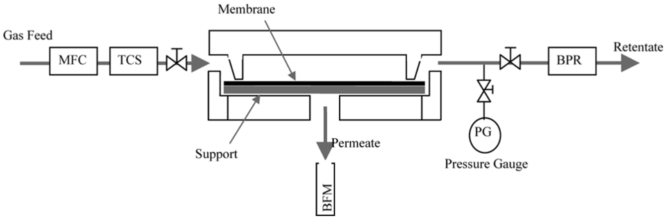


FIG. 1. Schematic view of the gas permeation module.

H_2, N_2, O_2, CO_2, and CH_4 gases with purity of 99.5% supplied by Technical Gas Services, Inc., and C_3H_8 gas with purity of 99.9% supplied by Air Products and Chemicals, Inc. were used as feed gases. The feed flow rate was controlled by Dwyer mass flow controllers (MFC), model GFC 2111 (0 − 15000 normal mL/min range). The gas temperature was set at 308 K (35°C) using a P&ID temperature control system (TCS) model. The constant transmembrane pressure was controlled by a back pressure regulator (BPR), model 26.60 SCFBXE262C086. The 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, the gas permeability was calculated using the following equation:

$$P = \frac{22,414}{A} \frac{l}{p_2 - p_1} \frac{p_1}{RT} \frac{dV}{dt} \tag{9}$$

where A is the membrane area (cm^2), R is the universal gas constant [6236.56 cm$^3 \cdot$ cmHg/(mol $\cdot$ 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 Fig. 2. Gas sorption apparatus consisted of a stainless module of known volume. The module was connected to vacuum pump and TCS by stainless steel valves. The gas pressure in this

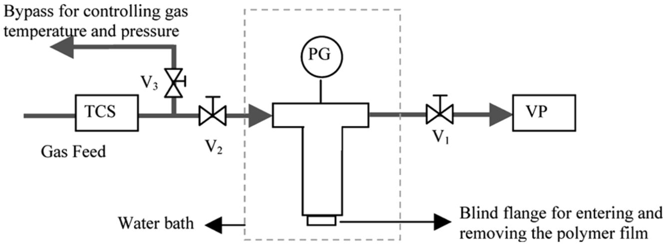


FIG. 2. Schematic view of the gas sorption module.

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, the temperature set−point of TCS and water bath was scheduled at 35°C. When gas temperature and pressure reached 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 (308 K) and known chamber volume (290 cm^3). Gas sorption into the polymer started exactly after opening V_2 and the pressure in the module decreased. When the system reached equilibrium (sorption and desorption of gas molecules became equal) the pressure reduction stopped. The difference between the 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 relation (6):

$$C = \frac{22,414}{RT}(p_i - p_f)\frac{V_m}{V_p} \tag{10}$$

where C is the uniform concentration of the dissolved penetrant at equilibrium state [cm^3(STP)/cm^3 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 [cm^3], respectively and 22,414 is the number of cm^3(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 H_2, O_2, N_2, CH_4, CO_2, and C_3H_8 in the synthesized PDMS membrane at 35°C are presented in Fig. 3. According to this figure, the sorption of gases in the synthesized PDMS membrane is higher than other membranes reported in the literature. However, for C_3H_8/gas separation application, the ratio of C_3H_8 the sorption to sorption of other gases in the membrane is more important and which will be discussed later.

The isotherms for all penetrants are linear (H_2, O_2, N_2 and CH_4) or nearly linear (CO_2 and C_3H_8), which is consistent with previously reported gas and vapor sorption isotherms in PDMS (6 − 11) and in rubbery polymers in general (19,21).

As observed in Figs. 3a–d, the isotherms for the diatomic gases (H_2, O_2 and N_2) and CH_4 are linear and obey Henry's law. 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 by (2):

$$C = k_d p \tag{11}$$

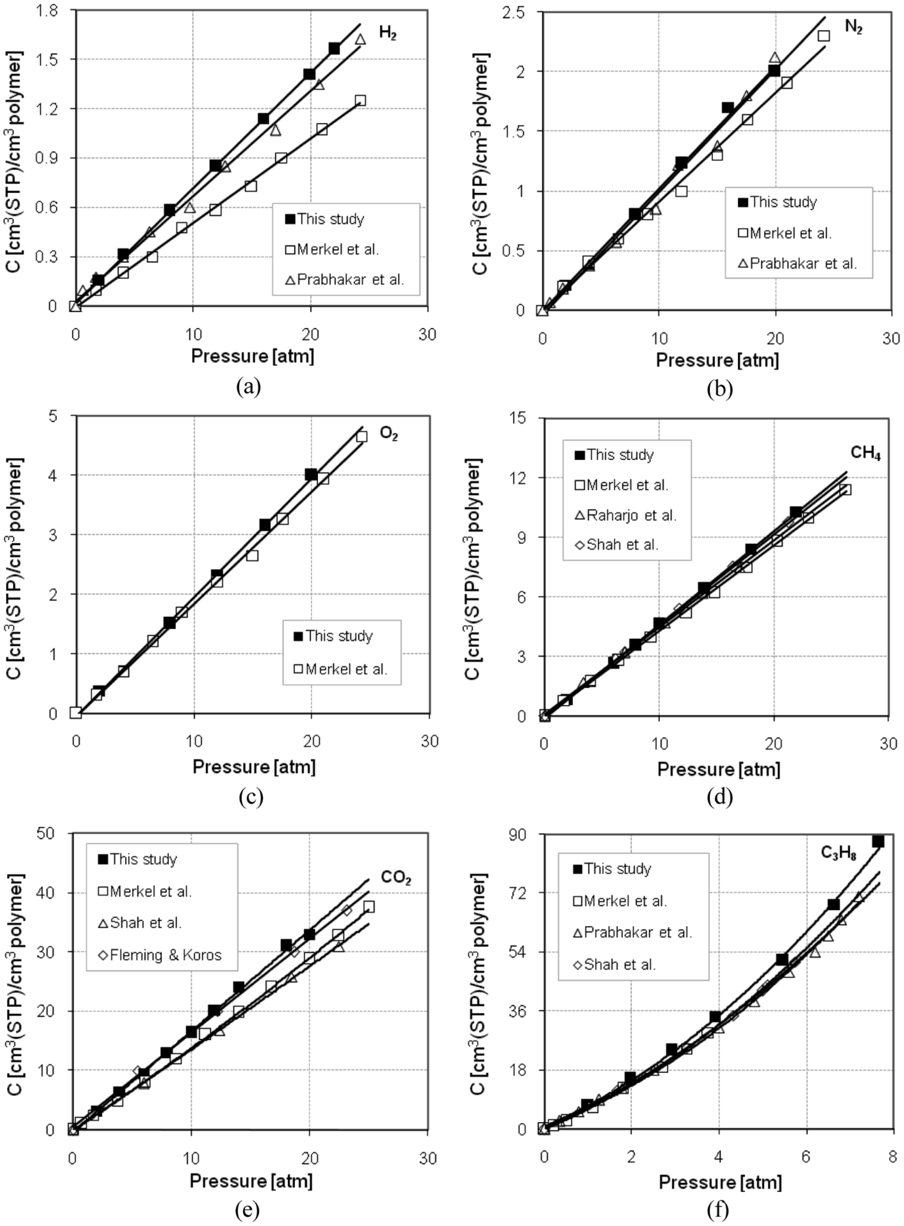
where C [cm^3(STP) of penetrant sorbed per cm^3 of polymer] is the equilibrium penetrant concentration in the polymer at pressure p (atm) and k_d [cm^3(STP)/(cm^3 atm)] is the Henry's law constant.

Since 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 the sorption ratio of the gases in the PDMS and some liquids. From Figs. 3 a and 3b, the ratio of N_2 to H_2 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. The value of this ratio in a wide variety of liquids lies between 1.2 and 2.2 (11). For example, the N_2/H_2 sorption ratio is 1.4 in CS_2, around 1.7 in alcohols and in the range of 1.9 − 2.2 in hydrocarbon liquids at 25°C and 1 atm (11). Thus, the N_2/H_2 sorption ratio of this study lies in the same range as that reported the literature.

CO_2 sorption isotherms in PDMS at 35°C (Fig. 3e), 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) (7). 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 [cm^3(STP)/cm^3 polymer atm] for CO_2 below 300 psia which is in good agreement with that obtained in our experiments (1.795 below 22 atm) (7).

C_3H_8 sorption isotherm (Fig. 3f) is convex to the pressure axis which is consistent with the behavior of highly sorbing penetrants in rubbery polymers (6 − 11). The concentration of C_3H_8 in the PDMS is 113.7, 93.3, 48.5, 20.8, and 5.7 times higher than that of H_2, N_2, O_2, CH_4, and CO_2 at 4 atm. The convex curvature of the C_3H_8 sorption isotherms is due to the high levels of sorbed penetrants at high pressures and is similar to that reported for vapor/polymer systems (21 − 27).

From the sorption isotherms, the solubility of each penetrant was calculated using Eq. (6). The values are presented as a function of pressure in Fig. 4. As shown,



(a) (b) (c) (d) (e) (f)

FIG. 3. Sorption isotherms for gases in the synthesized PDMS membrane at 35°C, data obtained in this study are compared with Merkel et al. (8), Prabhakar et al. (11), Shah et al. (6), Raharjo et al. (10) and Fleming and Koros (7) results.

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, the solubility coefficient of all gases can be well represented by the following linear equation:

$$S = S^{\infty} + np \tag{12}$$

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

$$S^{\infty} = \lim_{p \to 0}(C/p) \tag{13}$$

In Eq. (12), n characterizes the pressure dependence of solubility. S^{∞} and n values of gases are presented in Table 1.

For the relatively low–sorbing penetrants as H_2, O_2, N_2 and CH_4, the pressure dependence of solubility, n, is almost zero. Hence, as realized 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 (5,8).

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

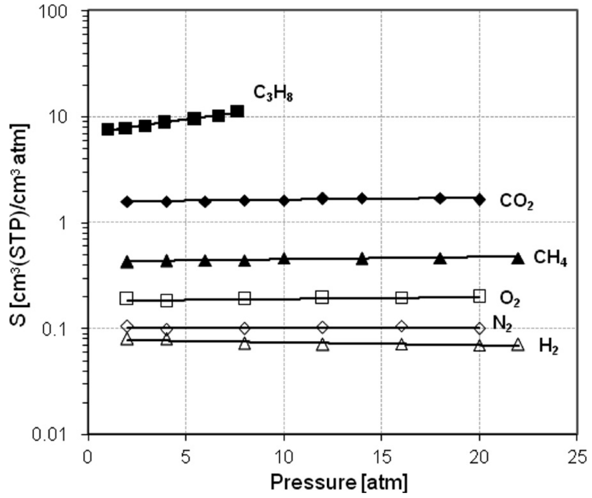


FIG. 4. Penetrant solubility in the synthesized PDMS membrane as a function of pressure at 35°C.

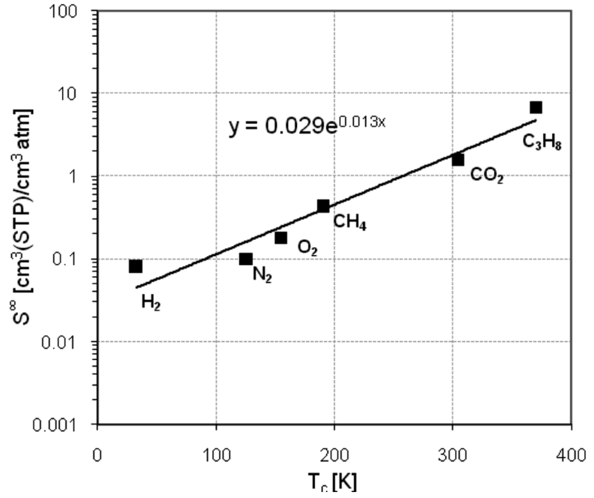


FIG. 5. Infinite dilution solubility as a function of penetrants' critical temperature at 35°C.

a typical behavior for many organic vapors in rubbery polymers (2,8).

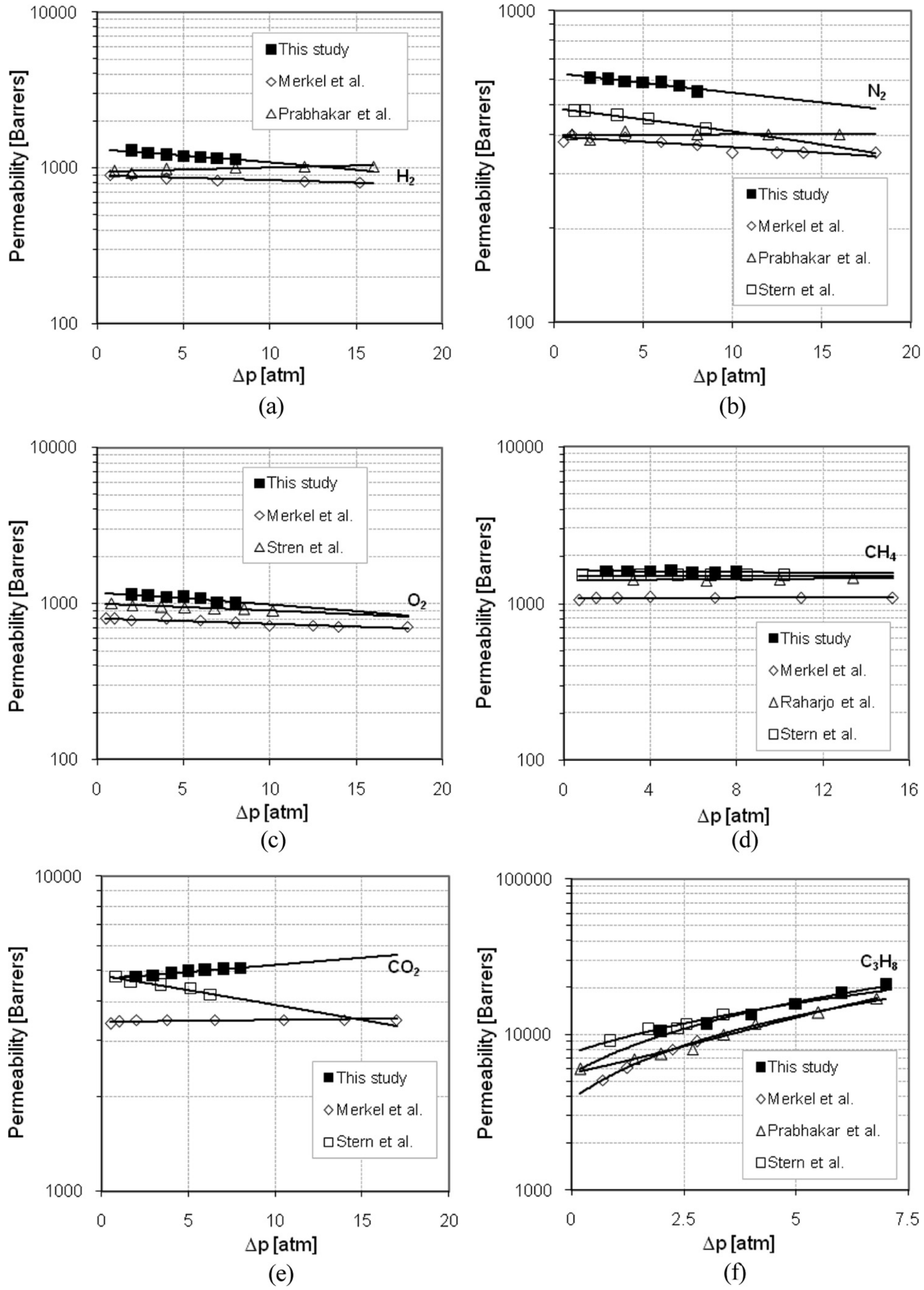
In the absence of specific interactions between the penetrant molecules and the polymer matrix, gas solubility coefficients are usually scaled with measures of penetrant condensability such as critical temperature, T_c (2,8,11). In order to compare the solubilities of the penetrants on a consistent basis, the solubility coefficient in the limit of zero pressure, S^{∞}, is utilized. Figure 5 presents S^{∞} as a function of the penetrants critical temperature. Previous results indicated that the logarithm of gas solubility in polymers often increases linearly with the penetrants' critical temperature. This trend is confirmed in Fig. 5. The 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 (8).

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 Fig. 6. This figure indicates that, the permanent gas and hydrocarbon permeability values are improved compared with previously reported values (5,6,8,10,11). All researchers found out that, N_2, O_2, H_2, and CH_4 exhibit constant or decreasing permeabilities at all upstream pressures tested (Figs. 6a–d), while permeabilities of CO_2 and C3H8 increase with increasing upstream pressure. Stern et al. showed that CO_2 behaves such a permanent gas and its permeability decreases with pressure. However, in this study as well as in Merkel et al. work, this result was rejected. As can be seen in Fig. 6e, 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 1). Merkel et al. (8), Prabhakar et al. (11) and Stern et al. (5) 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. 6f). In the present work P_0 was evaluated to be 5546 Barrer.

TABLE 1
Penetrants critical temperature [K] and volume [cm^3/mol], infinite dilution gas solubility S^{∞} [cm^3(STP)/cm^{3}atm], n [cm^3(STP)/cm^{3}atm^2], Infinite dilution gas permeability (P_0), m [Barrer/atm], Infinite dilution gas diffusivity ($\overline{D}_0$) and q [cm^2/atm s]

Penetrant	T_c	V_c	S^{∞}	$n \times 10^3$	P_0	m	$\overline{D}_0 \times 10^6$	$q \times 10^6$
H_2	33.2	64.3	0.0794	−0.50	1313	−23.15	100	−0.70
O_2	154.6	73.4	0.1828	0.90	1173	−18.70	50	−0.50
N_2	126.2	89.8	0.1013	0.06	626.7	−8.408	50	−0.40
CO_2	304.1	93.9	1.5821	6.40	4691	51.96	20	0.04
CH_4	190.5	99.2	0.4288	2.10	1629	−6.831	30	−0.20
C_3H_8	369.8	203.0	6.8093	542.51	5546	2108	9.0	1.00



(a) (b) (c) (d) (e) (f)

FIG. 6. Penetrants permeability through the synthesized PDMS membrane at 35°C, data obtained in this study are compared with Merkel et al. (8), Prabhakar et al. (11), Shah et al. (6), Raharjo et al. (10) and Stern et al. (5) results.

As shown in Fig. 6. permeability coefficients of the penetrants increase in the following order:

$$N_2 < O_2 < H_2 < CH_4 < CO_2 < C_3H_8$$

The "solubility coefficients of theses penetrants also increase as above with an exception of H_2 which is the smallest penetrant considered in this study. Based on the 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 inter–segmental 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 7 presents the permeability coefficients of the 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 (8,21).

Generally, as critical temperature increases, a penetrant becomes more soluble in the polymer and therefore more permeable (Eq. (5)). The results in Fig. 6 follow this trend with the exception of H_2, 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.

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

$$P = P_0 + m\Delta p \tag{14}$$

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 are recorded in Table 1. 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 (3,8,10).

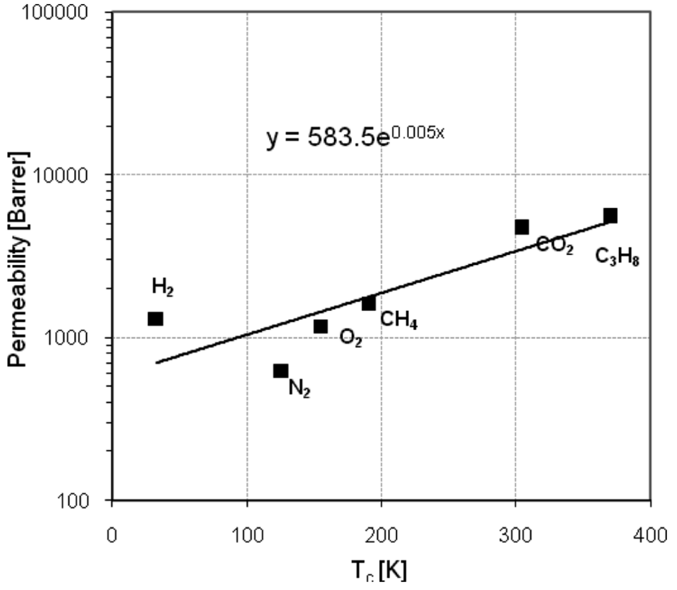


FIG. 7. Penetrants permeability through the synthesized PDMS membrane as a function of gas critical temperature. Experimental conditions: Upstream pressure = 1 atm ($\Delta p = 0$), Temperature = 35°C.

As upstream pressure and, therefore, penetrant concentration in a polymer increases, the 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 (8,25).

Hence, the permeability coefficients of low−sorbing penetrants, such as H_2, which do not plasticize the 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 1. 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.

Diffusivity

Concentration−averaged diffusion coefficient, $\overline{D}$, was estimated from the permeability and sorption data using the rearranged form of Eq. (4). The results are reported as a function of pressure difference across the PDMS membrane at 35°C in Fig. 8. For all penetrants, the pressure dependence of diffusion coefficient can be well described by the following linear equation:

$$\overline{D} = \overline{D}_0 + q\Delta p \tag{15}$$

where $\overline{D}_0$ is the diffusion coefficient at $\Delta p = 0$ and q is a parameter that characterizes the pressure dependence of diffusion coefficient. Values of $\overline{D}_0$, q are reported in Table 1. 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, the solubility of these gases is independent of upstream pressure. Hence, the permeability coefficient of light gases decreases slightly as the pressure increases. In contrast, more soluble penetrants (CO_2 and C_3H_8) exhibit an increase in both solubility and diffusivity coefficients with increasing penetrant pressure. Based on the data presented in Table 1, n and q are positive for these gases. Therefore, permeability of heavy gases in PDMS increases with pressure.

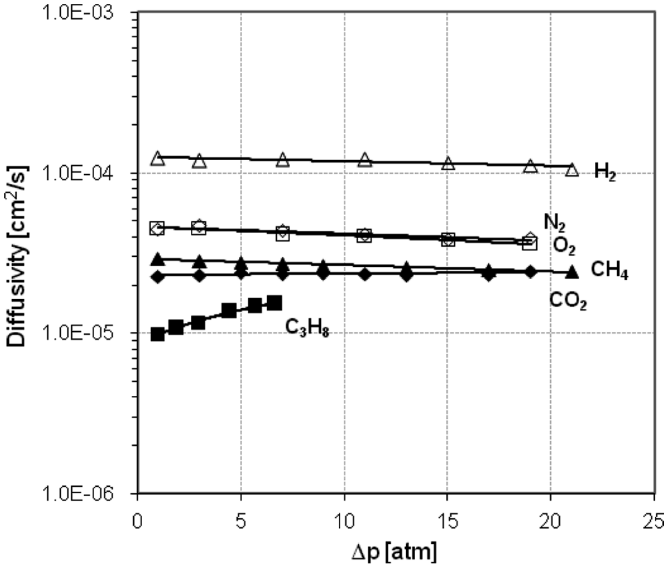


FIG. 8. Concentration–averaged diffusion coefficients of gases, $\overline{D}$, in the synthesized PDMS membrane as a function of transmembrane pressure difference at 35°C.

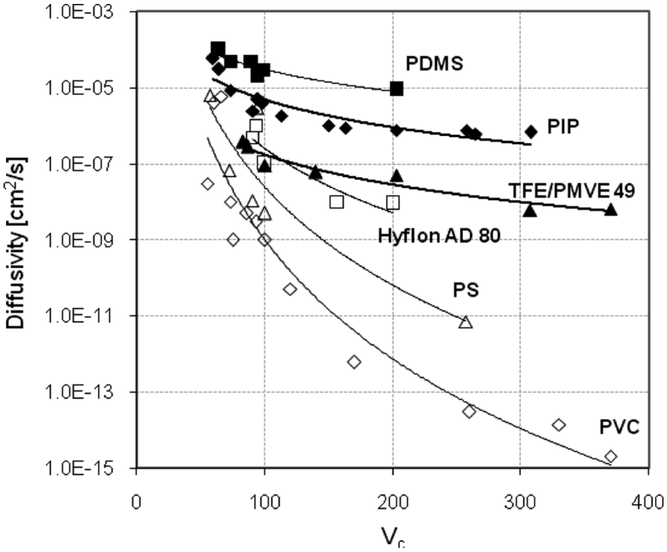


FIG. 9. Comparison of the variation of infinite dilution diffusion coefficients with penetrant critical volume in the synthesized PDMS membrane with that in rubbery polymers PIP (35) and TFE/PMVE 49 (36) and glassy polymers PVC (8), PS (37) and Hyflon AD 80 (37). The trendlines in the figure satisfy 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.

At low penetrant pressure, the diffusion coefficient increases in the following order:

$$C_3H_8 < CO_2 < CH_4 < O_2 \approx N_2 < H_2$$

This is almost the order of decreasing penetrants size and is typical behavior for both rubbery and glassy polymers (6 – 11,28 – 34). Figure 9 compares $\overline{D}_0$ values of gases in the synthesized rubbery PDMS membrane, polyisoprene (PIP) (35) and poly(tetrafluoroethylene–co-perfluoromethyl vinyl ether) or TFE/PMVE 49 (36) with those in glassy polyvinyl chloride (PVC) (8), polysulfone (PS) (37) and Poly(2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole-*co*-tetrafluoroethylene) commercially known Hyflon AD 80 (37) as a function of the critical volume of the gases. As can be seen, the diffusion coefficients in PDMS and PIP, like other rubbery polymers, are a relatively weak function of the penetrant size. For the entire range of penetrant sizes considered, the diffusion coefficients varied by less than two orders of magnitude. The 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 ($T_g \approx -120$°C). As a result, PDMS has a very weak ability to sieve penetrant molecules based on their sizes.

The local effective diffusion coefficient, D_{eff}, is a measure of the ability of the penetrant to migrate through a polymer at a particular penetrant concentration (8). Taking the derivative of Eq. (4) with respect to p_2, holding p_1 constant, yields the following equation for D_{eff}:

$$D_{eff}(C_2) = \left[P + \Delta P \frac{dP}{d\Delta P}\right]_{p_2} \left(\frac{dp}{dC}\right)_{p_2} \qquad (16)$$

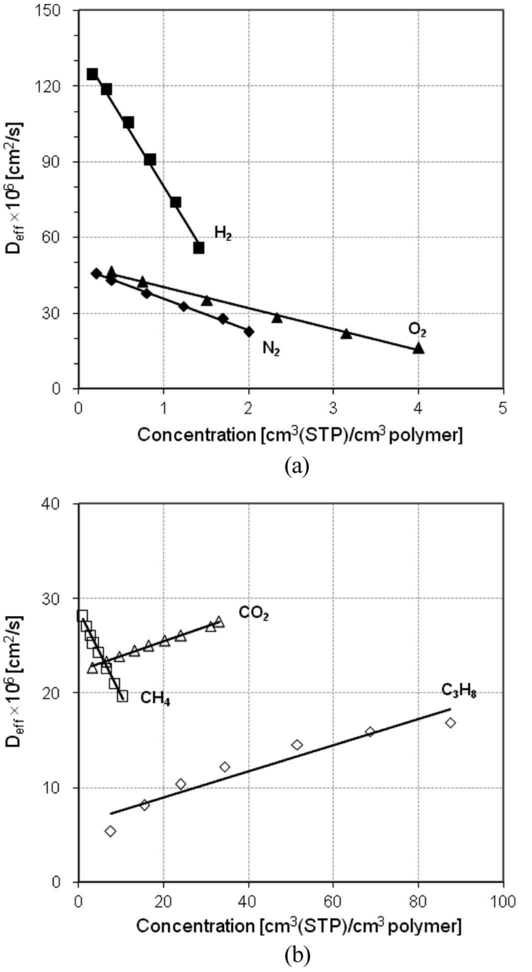
The derivatives in this equation can be evaluated utilizing Eqs. (12) and (14). This results in the following expression for the local effective diffusion coefficient:

$$D_{eff}(C_2) = \frac{P_0 + 2m(p_2 - p_1)}{S^{\infty} + 2np_2} \qquad (17)$$

Figures 10*a* and *b* presents D_{ef} as a function of penetrant concentration in the PDMS membrane. According to these figures, it was found out that C_3H_8 and CO_2 cause plasticization of the membrane over the range of the penetrant concentrations studied.

Ideal Selectivity

Selectivity of the synthesized PDMS membrane is expressed as the product of solubility selectivity and diffusivity selectivity. Solubility selectivity, diffusivity selectivity, and the overall selectivity of the PDMS membrane for C_3H_8 relative to other gases at $\Delta p = 0$, are presented in Table 2. C_3H_8 is significantly more condensable than other gases. Hence, C_3H_8/gas solubility selectivity is larger



(a)

(b)

FIG. 10. 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.

than 1. As mentioned earlier, C_3H_8 sorption isotherm is convex to the pressure axis due to the high levels of sorbed penetrants at high pressures. Hence, increasing rate of C_3H_8 solubility is much greater than those of other gases and C_3H_8/gas solubility selectivity increases as upstream pressure increases (Fig. 11).

TABLE 2
C_3H_8/gas solubility, diffusivity and overall ideal selectivity values at $\Delta p = 0$

Penetrant	S_{C3H8}/S_{gas}	D_{C3H8}/D_{gas}	P_{C3H8}/P_{gas}
H_2	85.75	0.09	4.22
O_2	37.25	0.18	4.72
N_2	67.21	0.18	8.84
CO_2	4.30	0.45	1.18
CH_4	15.87	0.30	3.40

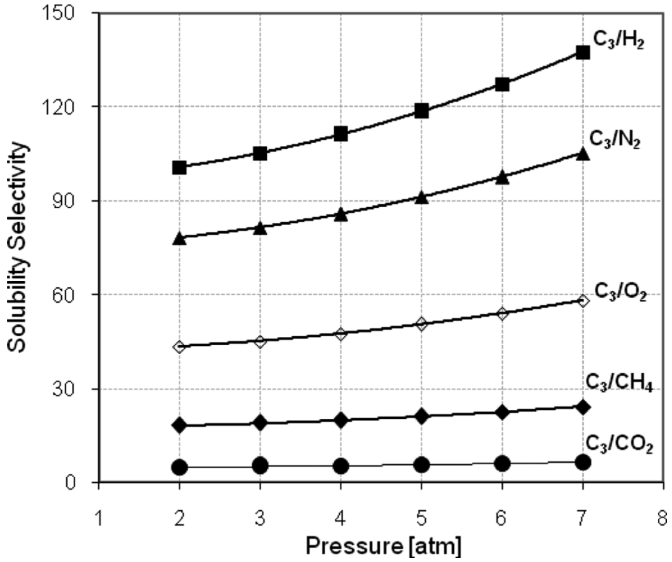


FIG. 11. C_3H_8/gas solubility selectivity of the synthesized PDMS membrane as a function of upstream pressure at 35°C.

C_3H_8/gas diffusivity selectivity values are smaller than 1 but, similar to solubility selectivity, they increase as the upstream pressure increases (Fig. 12). It means that, the 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 those of H_2, CO_2, and CH_4.

The overall selectivity values, $\alpha_{A/B}$, of the synthesized composite PDMS membrane for C_3H_8 over CO_2, CH_4, O_2, N_2, and H_2 (calculated using Eq. (7)) as a function of upstream pressure are presented in Fig. 13. The increasing

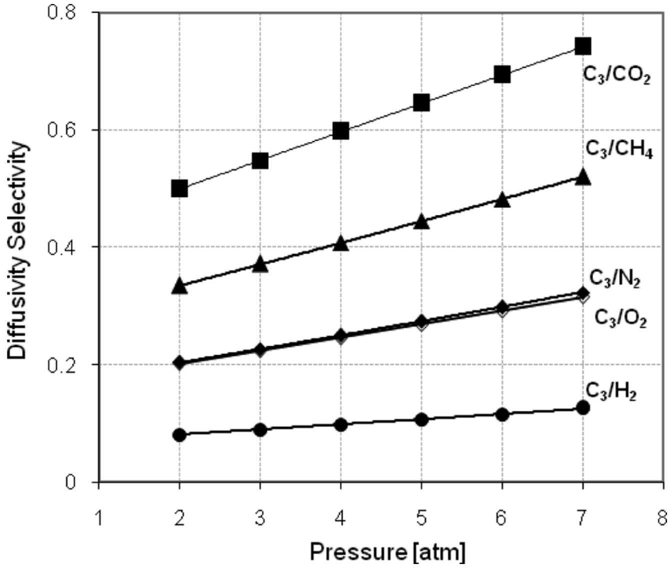


FIG. 12. C_3H_8/gas diffusivity selectivity of the synthesized PDMS membrane as a function of upstream pressure at 35°C.

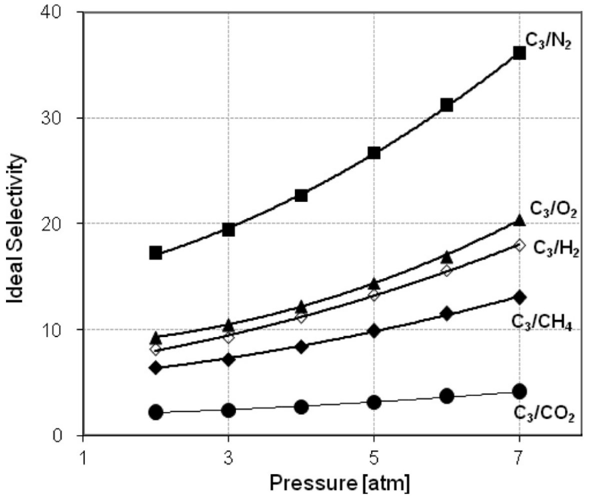


FIG. 13. C_3H_8/gas overall selectivity of the synthesized PDMS membrane as a function of upstream pressure at 35°C.

rate of ideal selectivity with pressure is observed to be completely dependent on the difference between the condensabilities or critical volumes of C_3H_8 and other gases. At $p = 7$ atm, the synthesized composite PDMS membrane is approximately 4, 13, 18, 20, and 36 times more permeable to C_3H_8 than CO_2, CH_4, H_2, O_2, and N_2, 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. As mentioned earlier, in all polymer materials, the diffusion coefficient decreases with increasing molecular size. However, the solubility increases with increasing molecular size. Thus, these polymers preferentially permeate the larger, more condensable gases, C_3H_8, over the smaller, less condensable gases, CO_2, CH_4, H_2, O_2, and N_2.

As a result it can be concluded that the synthesized composite PDMS membrane is an appropriate choice for separation of liquefied petroleum gases (LPG) from natural gas.

CONCLUSION

Sorption, diffusion, and permeation of C_3H_8, CO_2, CH_4, N_2, O_2, and H_2 in a synthesized PDMS membrane were studied. The solubility coefficient of C_3H_8 was significantly higher than those of other gases due to the more condensable nature of C_3H_8 regarding its critical properties. However, the diffusion coefficient of C_3H_8 in the PDMS membrane was lower than those of other gases, due to the fact that larger molecules interact with more segments of the polymer chains than smaller molecules, favoring the passage of smaller molecules such as H_2 over larger ones such as C_3H_8. In the synthesized PDMS membrane, like other rubbery membranes, the diffusion coefficients of penetrants varied less than their solubility coefficients. Consequently, the relative permeability of penetrants through PDMS was mainly determined by their relative solubility. The pressure dependence of permeability, solubility and diffusivity coefficients was well described by empirical linear equations. The solubility and diffusivity of C_3H_8 increased with increasing upstream pressure while for other gases, these values remained constant or decreased slightly. Hence, both C_3H_8/gas solubility and diffusivity selectivities increased as upstream pressure increased. High C_3H_8 permeability at upstream pressure of 8 atm (26493 Barrer) accompanied by high C_3H_8/gas ideal selectivities of (9, 30, and 82 over H_2, O_2, and N_2, respectively), confirmed acceptable performance of the synthesized composite PDMS membrane for the separation of organic vapors from supercritical gases. Application of this membrane for the separation of LPG from natural gas is under investigation.

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